9th INTERNATIONAL SYMPOSIUM ON GROUP FIVE ELEMENTS

BOOK OF ABSTRACTS

22 – 24 Nov 2017
New Delhi, India

9th International Symposium on Group Five Elements

22 – 24 November, 2017

New Delhi, India

Organized by

Department of Chemical Engineering
Indian Institute of Technology, Kanpur

Preface

The Symposia on Group Five Elements has a rich history, which dates back to a symposium held in Hawaii in 1989 devoted to compounds of Niobium. This symposium was followed by conferences held in 1993 and 1995 in Tokyo, Japan, with a “hope that material presented in this issue will stimulate the further development of niobium catalysis science and its industrial application”. For the 3rd International Symposium of Group Five Elements at Rio de Janeiro in 1999, the scope of the meetings was expanded to include the other group five elements Vanadium and Tantalum and the name was changed from International Symposium on Niobium Compounds to International Symposium on Group Five Elements. Subsequently, International Symposia were held every three years at other locations around the world.

For the 9th International Symposium in New Delhi, we continue with highlighting the application of Group Five Elements, Vanadium, Niobium and Tantalum, as functional materials. A significant number of contributions in this symposium deal with the structure-performance relationships of heterogeneous and homogeneous catalysts containing these materials. Presentations dealing with electro-catalysis, photocatalysis, organo-metallic compounds, specialized steel making and other applications and properties of Group Five elements find a prominent place. A session on electronic structure calculations was relevant since it reflected the growing involvement of the scientific community in this area.

It was a pleasure and honour to receive overwhelming support from the Keynote Speakers and delegates. Not all of the presentations could be accommodated. However, we look forward to their support in the future.

Financial assistantship from the Government of India and Indian Industries went a long way towards meeting our goals. Without their support it would have been difficult to conduct the Symposium and the exchange of ideas of the scientific community would have been limited. Special mention goes to the Science and Engineering Research Board (SERB) of Department of Science and Technology, Council of Scientific & Industrial Research (CSIR), PID Eng & Tech and SABIC.

Prof. C. Venkatesan provided immense support into the conduct of the symposium and Dr. K. Routray assisted tremendously in garnering funds from the Industry. The cooperation and assistance of the Department of Chemical Engineering, Indian Institute of Technology at Kanpur and its administration was extremely helpful in fulfilling our dreams of holding the 9th International Symposium on Group Five Elements.

Sincerely,

Raj Ganesh S. Pala, Brishti Mitra, Raju Kumar Gupta,

Aditya Shankar Sandupatla, Sudhir Charan Nayak and Goutam Deo

Head’s message

It is with great pleasure and excitement that I extend my heartiest welcome, on behalf of the Department of Chemical Engineering, IIT Kanpur, to the delegates of the 9th International Symposium on Group Five Elements, to be held from the 22nd to 24th November, 2017. The local organizing committee, which includes faculty colleagues and those who have had previous associations with the Department of Chemical Engineering of IIT Kanpur, has put in a lot of effort in organizing the symposium.

The Department of Chemical Engineering at IIT Kanpur is ranked among the nation’s best schools in the discipline and is endowed with a distinguished faculty who have earned many national and international honours. The research efforts of this department are directed towards diversified fields ranging from fundamentals of chemical engineering like separation science or reaction engineering to the multidisciplinary efforts required in nano- and micro- technologies. Included in these fields is the application of Group Five Elements as heterogeneous catalysts, electro-catalysts, photo-catalysts and computational catalysis. I sincerely hope that the efforts of the local organizing committee will make the symposium something to remember for the years to come.

I am confident that the delegates will strive together to provide an excellent forum for the exchange of ideas. Once again, my best wishes to all the participants for a rich and rewarding experience at the 9th International Symposium on Group Five Elements.

Prof. V. Shankar

Head, Department of Chemical Engineering

Indian Institute of Technology Kanpur

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Technical Program

22nd November

Registration	08:00 – 09:00	
Opening Ceremony	09:00 – 09:15	
Session 1		**Chair: Jih-Mirn Jehng** (National Chung Hsing University)
Keynote 1	09:15 – 10:00	M. Zu, J.-K. Lai, U. Tumuluri, M.E. Ford, Z. Wu and **Israel E. Wachs** *“Reaction Mechanism, Surface Intermediates and Kinetics for SCR of NOx with NH_3 by Titania-Supported Vanadium Oxide Catalysts”*
OR 1	10:00 – 10:25	**V. Narayana Kalevaru**, Naresh Dhachapally and Andreas Martin *“Highly active and selective metal vanadate catalysts for the ammoxidation of 2-methylpyrazine”*
OR 2	10:25 – 10:50	**M. Olga Guerrero-Pérez**, A.J. McCue and J.A. Anderson *“Rapid scan operando reveals propane (am)oxidation mechanisms over Vanadium based catalysts”*
Tea/Coffee	10:50 – 11:20	
Session 2		**Chair: Jih-Mirn Jehng** (National Chung Hsing University)
OR 3	11:20 – 11:45	**Maciej Trejda**, Dorota Kryszak, Natalia Benedyczak and Maria Ziolek *“Ca/MCF materials – the impact of niobium on the basicity”*
OR 4	11:45 – 12:10	**Natalia Candu,** Simona M. Coman and Vasile I. Parvulescu *“Nb-BEA zeolites for one-pot conversion of glucose to HMF”*
OR 5	12:10 – 12:35	**Anna Wojtaszek-Gurdak**, J. Latańska, M. Zagaja and Maria Ziolek *“New modification routes of layered MWW zeolites by including niobium and amine species”*
Lunch	12:35 – 14:00	
Session 3		**Chair: M. Olga Guerrero-Pérez** (Universidad de Málaga)
Keynote 2	14:00 – 14:45	**Debbie C. Crans**, M. Selman and Jean-Simon Diallo *“Vanadium compounds in oncolytic virotherapy”*
OR 6	14:45 – 15:10	**Palyam Subramanyam**, M. Deepa and Ch. Subrahmanyam “*Mo-doped $BiVO_4$ incorporated rGO as an Efficient Photoanode for Photoelectrochemical Water Splitting*”
OR 7	15:10 – 15:35	**Ankit Tyagi** and Raju Kumar Gupta *“Nickel Vanadium layered double hydroxides nanostructures for high-performance supercapacitor applications”*
Tea/Coffee	15:35 – 16:00	
Session 4		**Chair: M. Olga Guerrero-Pérez** (Universidad de Málaga)
OR 8	16:00 – 16:25	K.B. Renjani, S. Mahendran and **P. Selvam** *“Synthesis, Characterization and Catalytic Properties of Ordered Mesoporous Niobosilicates”*
OR 9	16:25 – 16:50	A. Feliczak-Guzik, A. Wawrzyńczak and **Izabela Nowak** *“Niobium-containing mesoporous materials as catalysts for phenol transformations”*
OR 10	16:50 – 17:15	Sarthani Ammaji, Sk. Hussain, Vijay Kumar Velisoju and **Komandur V.R. Chary** *“Vapour phase conversion of glycerol to acrolein over Nb_2O5/SBA-15 catalyst: A value addition process”*

23rd November

Session 5		**Chair: Raju Kumar Gupta** (IIT Kanpur)
Keynote 3	09:15 – 10:00	**Wataru Ueda** *"New porous complex metal oxides of group V and VI elements"*
OR 11	10:00 – 10:25	J.J. Ternero-Hidalgo, **M. Olga Guerrero-Pérez**, J. Rodríguez-Mirasol and T. Cordero *"Group V elements based nanofiber catalysts prepared in one step by electrospinning for partial oxidation reaction"*
OR 12	10:25 – 10:50	**V. Vijay Kumar**, P. Ganga Bhavani, K. Manasa, K.V.R. Chary and A. Venugopal "Role of group V elements on the hydrogenation activity of Ni/TiO_2 catalyst for the vapour phase conversion of levulinic acid to γ-valerolactone"
Tea/Coffee	10:50 – 11:20	
Session 6		**Chair: Raju Kumar Gupta** (IIT Kanpur)
OR 13	11:20 – 11:45	**Tomohiro Higashi**, Yutaka Sasaki, Atsushi Ohnishi, Tsutomu Minegishi, Takashi Hisatomi, Masao Katayama, Hiroshi Nishiyama, Taro Yamada and Kazunari Domen *"Sunlight-Driven Water Splitting by Ta_3N_5 Thin-Film Photoanode and $BaTaO_2N$ Particulate Photoanode"*
OR 14	11:45 – 12:10	**Loveleen K. Brar** and O. P. Pandey *"Effect of size vs. phase purity on the electro catalytic and photo catalytic performance of nano Tantalum Carbide"*
OR 15	12:10 – 12:35	P. Krishna Kumari, B. Srinivasa Rao and **N. Lingaiah** *"Selective conversion of fructose and 5-hydroxymethylfurfural to 5-ethoxymethylfurfural over Ta containing heteropoly tungustate catalysts"*
Lunch	12:35 – 14:00	
Session 7		**Chair: Vishal Agarwal** (IIT Kanpur)
Keynote 4	14:00 – 14:45	**Monica Calatayud** *"Describing reducibility of metal oxides from ab initio calculations"*
OR 16	14:45 – 15:10	Koshal Kishor, Sulay Saha, Sri Sivakumar and **Raj Ganesh S. Pala** *"Activating RuO_2 for Electrochemical Chlorine Evolution Selective Reaction through Dopants of Group V Elements"*
OR 17	15:10 – 15:35	**Aditya Shankar Sandupatla**, Sudhir C. Nayak, Chalumuri Sivananda and Goutam Deo *"Experimental and Density Functional Theory Insights into the Role of Support in ODH of Propane Over Supported Vanadia Catalysts"*
Session 8		**Chair: Vishal Agarwal** (IIT Kanpur)
POSTER SESSION	16:00 – 18:00	P1 to P16
+Tea		

24th November

Session 9		**Chair: Raj Ganesh S. Pala** (IIT Kanpur)
Keynote 5	09:00 – 09:45	**Miguel A. Banares** *“Tackling active sites in supported vanadium oxide catalysts: which one is "operando" (working)?”*
OR 18	09:45 – 10:10	**E.V. Kondratenko**, V.Yu. Bychkov, V.N. Korchak, D. Linke, U. Rodemerck, S. Sokolov, M. Stoyanova and Yu. P. Tyulenin *“Effect of support and VOx species on activity, selectivity and stability in non-oxidative alkane dehydrogenation”*
OR 19	10:10 – 10:35	B. Hari Babu, P. Rajitha, P. S. Sai Prasad and **N. Lingaiah** *“Synthesis, characterization and catalytic evaluation of V_2O5 supported on La_2O3 modified Al_2O_3 catalysts for ammoxidation of 2-chlorotoluene”*
Tea/Coffee	10:35 – 11:00	
Session 10		**Chair: Raj Ganesh S. Pala** (IIT Kanpur)
OR 20	11:00 – 11:25	**Łukasz Wolski**, Lukasz Wolski, Izabela Sobczak, and Maria Ziolek *“Nb_2O_5 and $ZnNb_2O_6$ modified with gold – surface and catalytic properties”*
OR 21	11:25 – 11:50	**Rahul Ranjan**, Aditya Kumar Parmar, Ashish Garg and Raju Kumar Gupta *“Ta doped compact TiO_2 and interface modification for improved performance in perovskite solar cells”*
OR 22	11:50 – 12:15	Ashwini Nalge, Akshay Shingweker, Nitin Amte, Sirshendu Chattopadhyay and Deepak Gupta *“Experience of Niobium and Vanadium micro alloying at Essar Steel India Ltd”*
	12:15 – 12:45	**Israel E. Wachs** *“Personal musing on Group Five Elements – Past, present and the future”*
	12:45 – 13:00	Concluding remarks
Lunch	13:00 – 14:30	Lunch

Keynote Lectures

Reaction Mechanism, Surface Intermediates and Kinetics for SCR of NO_x with NH_3 by Titania-Supported Vanadium Oxide Catalysts

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Introduction

Selective Catalytic Reduction (SCR) of NO_x with NH_3 by supported vanadium oxide catalysts is the only technology for reducing acidic NO_x emissions from power plants. Rational design of improved catalysts, however, is still hampered by lack of consensus about reaction pathways, role of surface intermediates and kinetics of this critical technology.

Experimental

The SCR fundamentals were addressed and finally resolved by applying multiple time-resolved *in situ* spectroscopies (UV-vis, Raman and temperature programmed surface reaction (TPSR)) and isotopically labelled molecules ($^{18}O_2$, $H_2{}^{18}O$, $^{15}N^{18}O$, and ND_3).

Results and discussion

This unique series of experiments directly revealed that the SCR reaction occurs at the surface $V^{5+}O_4$ active sites (Mars-van Krevelen mechanism) that are maintained in the oxidized state by gas phase molecular O_2 and the rate-determining-step involves reduction of the surface $V^{5+}O_4$ sites by reaction between an NO-NH_3 complex with the N-H bond breaking being the slow step.

Both surface $NH_{3,ads}$ species on Lewis acid sites and surface $NH_4{}^+{}_{,ads}$ species on Brønsted acid sites were found to participate in the SCR reaction. The less reactive surface $NH_4{}^+{}_{,ads}$ species are the most abundant intermediates while the more reactive $NH_{3,ads}$ species are less abundant. Furthermore, in the presence of moisture and elevated temperatures, the surface $NH_{3,ads}$ species are transformed to surface $NH_4{}^+{}_{,ads}$ species making the surface $NH_4{}^+{}_{,ads}$ species the most abundant reaction intermediates during industrial SCR conditions.

Conclusions

The molecular level details of SCR of NO with NH_3 by supported vanadia catalysts have finally been elucidated with the application of time-resolved *in situ* spectroscopies (UV-vis, Raman and TPSR) and isotopically labelled molecules.

Acknowledgements

The authors acknowledge financial support from the Center for Understanding & Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by DOE, Office of Science, and Office of Basic Energy Sciences under grant DE-SC0012577. Part of the work was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Vanadium compounds in oncolytic virotherapy

Debbie C. Crans[1], Mohammed Selman[2] and Jean-Simon Diallo[2]

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Introduction

Oncolytic viruses are an emerging class of anticancer bio-therapeutics that induce antitumor immunity through selective replication in tumor cells.[1,2] The efficacy of oncolytic viruses as single agents can however be improved and we have developed a strategy that boosts the therapeutic efficacy of oncolytic viruses by combining their activity with immuno-modulating, small molecule protein tyrosine phosphatase inhibitors. Since vanadium are potent phosphatase inhibitors,[3,4] and their inhibition is attributed to the favorable five-coordinate geometry of phosphate ester hydrolysis transition states much of the research carried out in this area can be used in studies with oncolytic viruses.

Results and Discussion

Five coordinate geometries for transition metal ions such as vanadium, however, are often found to be in an intermediate form between square planar geometry and trigonal bipyramidal geometry.[3,4] A number of vanadium compounds have been used as inhibitors, and detailed interaction of vanadate with phosphatases have described crystallographically.[3,4] Recent data mining studies led to a better understanding of the key aspects of inhibition of phosphatases and future inhibitor development. We found that vanadium-based phosphatase inhibitors could enhance oncolytic viruses infection *in vitro* and *ex vivo,* in resistant tumor cell lines. Furthermore, vanadium compounds increased anti-tumor efficacy in combination with oncolytic viruses in several syngeneic tumor models, leading to systemic and durable responses, even in models otherwise refractory to oncolytic viruses and drug alone.

Conclusions

We introduce a strategy that boost the therapeutic efficacy of oncolytic viruses by combining their activity with immuno-modulating small molecules protein tyrosine phosphatase inhibitors. Overall, we present studies on the novel ability of vanadium-based compounds to simultaneously maximize viral oncolysis and systemic anticancer immunity, offering new avenues for the development of improved immunotherapy strategies.

Acknowledgments: JSD thanks the Canadian Institutes of Health Research, Terry Fox Research Institute and Canadian Cancer Society for funding.

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New porous complex metal oxides of group V and VI elements

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Introduction

Multi-elemental metal oxides with crystal structure complexity become increasingly important because new extraordinal catalytic functions can be resulted from the complex structure. Four examples of the unit synthesis of new porous crystalline complex metal oxides using group V and VI elements are presented.

Results and discussion

1. $Mo_3VO_{11.2}$ crystal with tunable pore by redox

Polyoxometalates (POMs) are utilized as building blocks for construction of microporous complex metal oxides. Assembling of MoV-POMs provides pentagonal units of $[Mo_6O_{21}]$ and VO lincker and then forms orthorhombic $Mo_3VO_{11.2}$ oxide and trigonal $Mo_3VO_{11.2}$ oxide under hydrothermal conditions[1]. This unit-networking shown in Figure 1 accompanies with the microporous heptagonal channels in $Mo_3VO_{11.2}$ oxide. The micropore aperture is tunable by redox treatment.

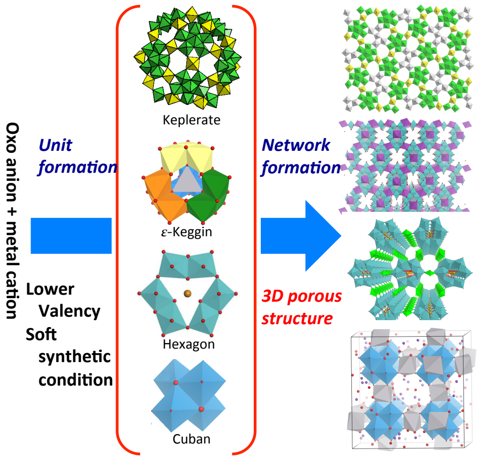

Figure 1 Unit synthesis

2. Crystalline $Bi_2(VMo_{9.5}V_{2.5}O_{40})$ with FAU type pore

All inorganic Mo-POM-based 3D crystals with intrinsic microporosity have been synthesized for the first time[2]. Assembling of ε-Keggin Mo-POMs with bismuth ions as the linker produces cubic NH_4-$Bi_2(VMo_{9.5}V_{2.5}O_{40})$ under a hydrothermal condition. In this structure ε-Keggin type $VMo_{9.5}V_{2.5}O_{40}$ are connected with Bi^{3+} linkers with three oxygen atoms of hexagons of ε-Keggin cluster to form 3D framework. The formation of the framework gives cages and channels(Figure 1).

3. $Co_m\{[SeW_6O_{21}]^{2-}\}_n$ with porous soft-framework structure

One dimensional anionic tungstosellenate molecular wire building block, $\{[SeW_6O_{21}]^{2-}\}_n$, is formed by linear connection of hexagonal tungstosellenate POM units and lincked with the Co^{II} ion to form a crystalline microporous materials[3]. This material enables water adsorption/desorption in the pore with structure flexibility, so that the material is all-inorganic soft-framework complex metal oxides.

4. $M_2\{(VO)_3[W_4O_{16}^{-}]\}$ with A zeolite-type pore

A crystalline transition metal oxide based on vanadium and tungsten was synthesized. In this material, $[W_4O_{16}]$ building blocks are orderly connected with VO_5 linkers to form a microporous framework with a pore diameter of 0.4 nm. The micropore is fully opened, which is accessible to small molecules.

References

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Describing reducibility of metal oxides from ab initio calculations

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Abstract

Reducibility is a concept widely used by chemists to indicate the ability of a compound to withdraw electrons, and is intimately related to redox reactivity. The family of metal oxides shows very different redox behavior from very irreducible (MgO, SiO_2) to very reducible (WO_3, CrO_3) systems. In this talk I will present the common descriptors used to characterize reducible materials from ab initio DFT calculations: band gap, oxygen vacancy formation energy, electron affinity and electron localization. A selection of bulk oxides in which the cation is in the highest oxidation state (MgO, Y_2O_3, TiO_2, m-ZrO_2, m-HfO_2, CeO_2, V_2O_5, Nb_2O_5, Ta_2O_5, WO_3, CrO_3, Al_2O_3, β-Ga_2O_3, SiO_2, SnO_2 and ZnO) has been studied as regards these descriptors. We find that there is no single criterion for characterizing the reducibility. Moreover, other effects like morphology and relaxation can play an important role in the stabilization of the reduced systems. I will present some examples in particular V_2O_5, Nb_2O_5 and Ta_2O_5.

Computational details

State of the art periodic DFT has been used as implemented in VASP. The valence electrons are represented by plane waves and the core electrons are frozen following the PAW procedure. PBE+U functional together with B3LYP calculations are used. The bulk structures are calculated as stoichiometric unit cells and reduced (by formation of an O-vacancy)

Results and discussion

The reducibility of a set of metal oxides has been studied as regards descriptors involving morphology (atom coordination and environment), electronic structure (band gap, vertical affinity, electron localization) and energetics (oxygen vacancy formation energy). Some general trends arise although each descriptor used leads to a different ranking in reducibility. Thus, irreducible systems (Al_2O_3, MgO, SiO_2) show a large band gap, large VEA, and need larger energies to remove an oxygen from the lattice; in addition, after O removal the electrons left localize in the vacancy site. On the contrary, reducible systems (CrO_3, WO_3, V_2O_5) show low band gap and VEA, low energy to form an O vacancy and the electrons left reduce the cationic sites, leading in many cases to spin polarized ground states. The ordering depends on the descriptor used, see Figure 1. Intermediate or ambivalent cases are found for ZrO_2, HfO_2, ZnO, Y_2O_3, β-Ga_2O_3, Nb_2O_5, Ta_2O_5 and SnO_2. The ability of the lattice to relax may affect the energetics and ease the formation of oxygen vacancies, increasing the reducibility of the systems.

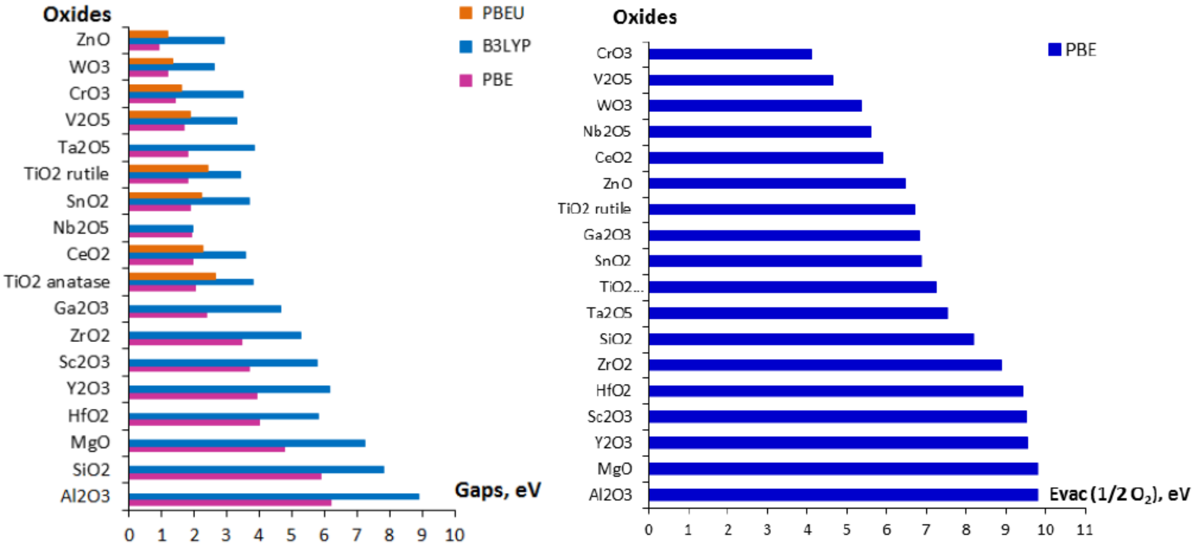

Fig 1. Ranking of selected bulk metal oxides as regards band gap (left) and oxygen formation energy (right). Reducibility decreases from top (very reducible) to bottom (poorly reducible) systems.

Conclusions

The reducible character of a series of metal oxides with the metal in its higher oxidation state has been analyzed as regards geometric parameters (crystalline phase, atomic coordination, reconstruction) and chemical descriptors (metal oxidation state, band gap, vertical electron affinity, oxygen vacancy formation energy, electron localization). Although all the descriptors do not lead to the same ordering, some general trends arise, and the role of relaxation is found to play a key role in stabilizing reduced systems.

Acknowledgements

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Tackling active sites in supported vanadium oxide catalysts: which one is "operando" (working)?

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Introduction

Through the years, many discussions have addressed the role of the vanadyl bond on oxidative dehydrogenation catalysis. It has been proposed as the key site by some authors but experimental evidences rule out its role. Vanadyl bond is particularly active in Raman and in this contribution, we will present a study on the role of additives, support, coverage, hydration and reaction conditions on the states of supported vanadium and its relevance for catalytic reaction and reducibility. We will cover the evolution of in situ studies to operando ones and how they engage with complementary methodologies, bringing examples for alkane selective (amm)oxidations and for NOx remediation.

This presentation summarizes the experience of the author to tackle which oxygen site is the relevant one for oxidative conversion of alkanes and for reducibility and shows the importance of collaborative research in Catalysis Science.

Experimental

Supported oxide catalysts have been prepared as described elsewhere (see e.g., [1-3]). The catalysts were characterized by Raman spectroscopy either during TPR/TPR experiments or as operando Raman-GC analyses (see e.g., [4,5]). A fundamental rationale is also provided by the use of computational chemistry (see e.g., [6,7].

Results and Discussion

The data presented show the effect of support, coverage, additives and reaction on the structure and reactivity of supported vanadia. This is complemented with computational calculations.

Conclusions

The terminal vanadyl bond is not the critical site for oxidative conversion of alkanes, at least for oxidative dehydrogenation reaction and for reducibility. The bridging oxygens appear to be directly involved in the reaction.

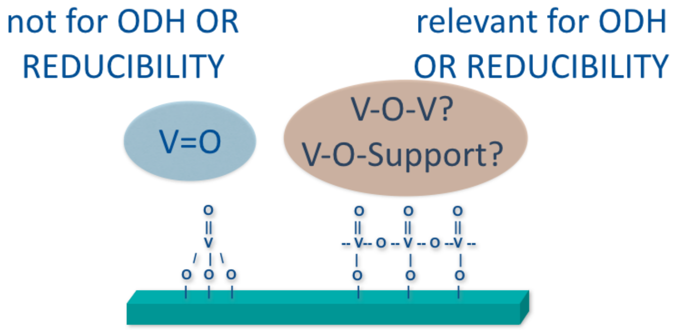

Fig 1. Illustration of the possible active oxygen sites.

Acknowledgements
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Oral Presentations

Highly active and selective metal vanadate catalysts for the ammoxidation of 2-methylpyrazine

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Introduction

Ammoxidation of various hydrocarbons to produce a variety of industrial important nitriles has been the subject matter of great interest in recent times. The desired nitriles are very useful organic intermediates to prepare a good number of value added fine chemicals. Ammoxidation of 2-methylpyrazine (MP) to 2-cyanopyrazine (CP), in particular, is of special importance due to unique application of CP as an efficient anti-tubercular drug. Vanadium containing catalysts are generally applied for different ammoxidation reactions in general; however we found that the metal vanadates are more promising catalysts for the title reaction. In this contribution, we describe the application of different metal vanadates as highly efficient catalyst compositions for the ammoxidation of MP with a special emphasis devoted to enhance the yield of CP.

Experimental

Various metal vanadate (MVO_x, M=Al, Fe, Cr, La, Bi) catalysts were prepared by citric acid decomposition method [1]. The catalysts were characterised by various techniques such as N_2-adsorption, XRD, FTIR, XPS etc. Catalytic tests were carried out in a fixed bed reactor at ambient pressure and at 360 to 420°C. The products analysis was made off-line by GC equipped with FID and methaniser.

Results and discussion

Among different metal vanadates investigated, $LaVO_x$ displayed the superior performance followed by $NbVO_x$ catalyst. Besides the target product (CP), formation of some by-products such as pyrazine (Py), pyrazinamide (PyA), CO_x were also observed. After suitable optimisation, $La_{0.1}V_{0.9}O_x$ solid exhibited a MP conversion of ca. 100% with a CP yield of ≥85% along with acceptably good long-term stability (Fig. 1). In addition, the space-time-yields (STY) of CP were also observed to be enhanced significantly. The nature of metal cation and the M/V ratios were found to be crucial for improved performance. Tuning the surface composition of metal vanadates using different cations led to the development of a new class of highly active and selective catalysts for the ammoxidation of MP. For instance, an enrichment of V in the near-surface-region is beneficial for improved selectivity of CP [2].

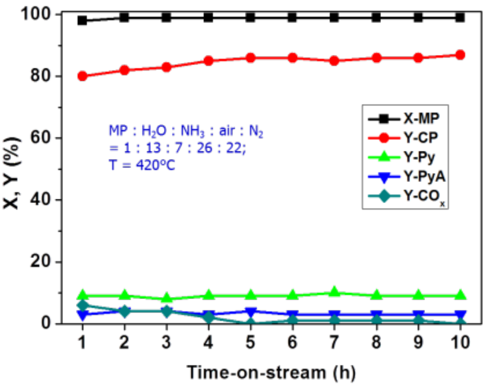

Fig. 1. Long-term stability of $La_{0.1}V_{0.9}O_x$ solid

Conclusions

Results revealed that the nature of metal cation in metal vanadate has shown strong influence on the catalytic performance. Among all, $La_{0.1}V_{0.9}O_x$ exhibited the best performance (X-MP: 100% & Y-CP: >85%. Amazingly high STY (500 to ~900 $g_{CP}/kg_{cat}/h$) could also be successfully achieved over this catalyst.

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Rapid scan operando reveals propane (am)oxidation mechanisms over Vanadium based catalysts

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Introduction

Rapid-scan operando has been shown to be a powerful tool to study the mechanisms of reactions performed over heterogeneous catalysts [1] as it combines rapid scan for IR spectroscopy monitoring in the millisecond time frame and operando methodology.

Experimental

The experimental details of the experimental procedure of the rapid scan operando system can be found elsewhere [1]. Alumina supported V and Sb-V-O catalysts were prepared following the procedure described [2].

Results and discussion

Alumina supported VOx and SbVOx catalysts were tested during propane oxidation and ammoxidation reactions. The experimental procedure permits species which are formed on the catalysts surface to be monitored at the millisecond range during the first minutes of each reaction. In the case of propane dehydrogenation, oxygenates are detected by DRIFTS, as has been described before, with bands near 1555 and 1460 cm^{-1}, which some authors have described as intermediates [3]. The results here show that these oxygenates (probably carboxylate species) are formed during the initial stages of the reaction but are still detected after propane is removed from the feed. That is, there concentration does not respond to a change in the feed indicating that they are not key intermediates but rather act as spectator species. In the case of ammoxidation reaction over a SbVO catalysts, is was possible to follow the reaction by pulsing 1 uL propane into a NH_3-O_2 flow. When only ammonia and oxygen were fed, N_2O was detected in the spectra and by mass spectrometry. When propane was introduced the ammonia was no longer oxidized to NOx, but instead, propylene was detected. Once that propylene was formed, acrylonitrile was also detected by mass spectrometry, along with a band near 2200 cm^{-1} characteristic of nitrile, indicating that the acrylonitrile forms directly by the formation of a nitrile from the intermediate propylene, while the intensity of bands due to carboxylate type species remained at constant intensity.

Conclusions

Rapid scan operando has been shown to be a powerful technique allowing the partial oxidation reactions at the millisecond scale to be monitored, and allowing aspects of the mechanism of the propane ammoxidation reaction over a SbVO catalyst to be assessed by distinguishing between spectators, secondary products, and intermediates.

Acknowledgements

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Ca/MCF materials – the impact of niobium on the basicity

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Introduction

Catalysts having basic properties are of great importance for fine-chemical industry and they are involved in different processes. In this study we applied siliceous MCF solid also doped with Nb as a support for Ca species in order to obtain basic catalysts.

Experimental

MCF materials were prepared using similar procedure like described in [1]. For niobium containing samples, ammonium niobate(V) oxalate was used (Si/Nb molar ratio 30). Calcium species were incorporated by impregnation with aqueous solution of calcium acetate monohydrate and calcined at 973 K for 5h. Materials obtained were characterized by XRD, N_2 adsorption/desorption, XPS, TEM, CO_2 thermoprogrammed desorption, FTIR and UV-Vis. Cyclisation and dehydration of 2,5-hexanedione were examined at 623 K. The activity of materials obtained was evaluated in transesterification of ethyl butyrate with methanol at 333 K.

Results and discussion

Three series of catalysts were prepared: i) CaO on MCF; ii) CaO on NbMCF and iii) CaO on Nb/MCF. N_2 adsorption measurements and TEM images confirmed typical structure of MCF. Catalysts obtained were tested in transesterification process of ethyl butyrate with methanol (Fig. 1). The best performance showed CaNb/MCF material which allowed obtaining 74 % of conversion after 8 h of reaction. A high activity of this sample was in line with the results of cyclisation and dehydration of 2,5-hexanedione. This process allowed to point out on a high basicity demonstrated by the formation of 3-methyl-2-cyclopentenone. Moreover, this was a sole material showing $Ca(OH)_2$ crystal phase in XRD patterns. Contrary, Ca/NbMCF showed the lowest activity in transesterification process instead of basic character indicated in 2,5-hexanedione reaction. This feature could be explained by the lowest window diameter (9nm) measured for this material (ca. 14 nm for other two samples). All materials were characterized in details and several parameters having an impact on catalytic performance were examined and they will be discussed.

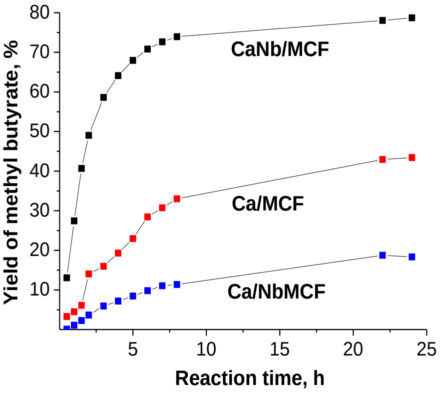

Fig 1. Results of ethyl butyrate transesterification with methanol

Conclusions

CaNb/MCF sample obtained within this study appeared to be a promising basic catalyst in transesterification process of ethyl butyrate with methanol.

Acknowledgements

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Nb-BEA zeolites for one-pot conversion of glucose to HMF

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Introduction

To date only scarcely examples of Nb based zeolites catalytic systems have been reported. [1]. Taking into account our interest in Nb-based catalysts synthesis and in biomass valorisation [2], here we present the production of highly dispersed Nb species (0.02-0.05moles%) into the BEA zeolite matrix.

Experimental

Nb-Beta zeolites were prepared through the two-step post synthesis methodology, involving a dealumination of H-Beta zeolite followed by its impregnation with Nb etoxide. The obtained catalysts were exhaustively characterized using different techniques as XRD, adsorption-desorption of liquid nitrogen at -196 °C, DRIFT, TG-DTA), XPS, ICP-OES, and NH_3-TPD. Activity tests in batch mode were carried out for the glucose dehydration by using water or biphasic solvent (aqueous solution of NaCl and MIBK), at 180°C, for 12-24 h.

Results and discussion

Characterisation results of the prepared Nb-BEA zeolites demonstrate the presence of residual framework Al-acid sites, extra-framework isolated Nb(V)O-H species and Nb_2O_5 pore-encapsulated clusters. As expected no insertion of Nb into the tetrahedral positions occupied by aluminium took place. However, the presence of these species highly increases the Lewis/Brønsted acid sites concentration with moderate strengths but also stabilise the zeolite, most probably through the framework polarisation. This acidity in association to the mesoporous texture generates an efficient environment for the dehydration of glucose to HMF. On this basis, these catalysts in a biphasic water/MIBK solvent, at 180°C and after 12h, MHF allow selectivities of 81% for a conversion of glucose of 44% (Figure 1).

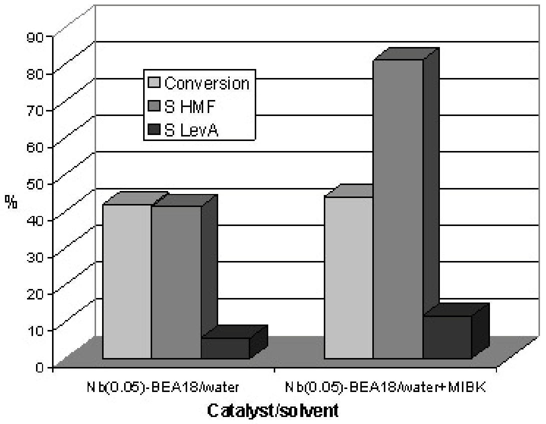

Fig 1. Catalytic performances of Nb(0.05)-Beta18 catalyst in water and water/MIBK biphasic solvent

Conclusions

Nb-BEA zeolites prepared through the post-synthetic methodology contain highly dispersed Nb-species, water resistant and highly catalytically active for the direct synthesis of HMF from glucose.

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New modification routes of layered MWW zeolites by including niobium and amine species

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Introduction

MWW zeolites are very attractive materials mainly because of the large range of possible structural, textural and compositional modifications which allows the design and formation of new catalysts with unique properties. In this work we focused on post synthesis modification of MWW zeolites by pillaring with niobium silicate towards a new type of MCM-36 and also with amino-group to generate basic centres.

Experimental

The MCM-22 and MCM-56 zeolites were synthesized according to procedures described in literature [1] and [2] respectively. They were modified by swelling and pillaring with niobium silicate as new pillaring agent to get NbMCM-36. Basicity of obtained MWW zeolites was generated by grafting of 3-aminopropyl-trimethoxysilane (APTMS). The catalysts prepared were characterized by different techniques (XRD, XPS, UV-Vis TGA/DTA). FTIR study with pyridine adsorption was performed to investigate the zeolites surface properties. The catalytic activity was tested in dehydratation of 2-propanol and oxidation of cyclohexene with H_2O_2.

Results and discussion

All synthesized zeolites showed well defined crystal structures typical of the MWW zeolites. In the XRD patterns of both NbMCM-36 and MCM-36 zeolites obtained from MCM-22 and MCM-56 XRD reflections typical of MWW structure were present. The use of niobium silicate as a pillaring agent gave a new type of MCM-36 zeolite. The UV-Vis and XPS spectroscopy confirmed that all Nb was at +5 oxidation state in tetrahedral coordination. No band characteristic of niobium oxide was detected. This can suggest that all niobium was introduced into pillars of MCM-36 zeolites. Different characterisation techniques and test reactions applied in this study confirmed strong acid character of all zeolites prepared. The presence of Brønsted (BAS) and Lewis (LAS) acid sites were detected after pyridine adsorption in all materials. To evaluate the catalytic activity of MWW zeolites prepared liquid phase oxidation of cyclohexene with hydrogen peroxide was performed. Obtained zeolites showed high activity and selectivity to epoxide, especially in the case of NbMCM-36 (~30%). As concerns generation of basicity, DTA/TG analysis confirmed APTMS anchoring. The lowest number of APTMS molecules were in AP/MCM-22. Niobium enhanced APTMS stability. The MWW zeolites after modification with amino-group were active catalysts in dehydratation of 2-propanol. The impact of APTMS and Nb on structural/textural parameters as well as on catalytic activity of MWW zeolites will be discussed in details.

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OR-6

Mo-doped $BiVO_4$ incorporated rGO as an Efficient Photoanode for Photoelectrochemical Water Splitting

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Introduction

Photoelectrochemical (PEC) water splitting is of great interest, where semiconductors use light energy to dissociate water molecules into hydrogen and oxygen. $BiVO_4$ is one of the interesting candidates for PEC water splitting owing to its suitable band gap. However various modifications are needed to improve the efficiency. In this work, molybdenum (Mo)-$BiVO_4$@RGO nanocomposite photoanode was prepared, characterized and employed as a catalyst for water splitting.

Experimental

rGO was prepared by a modified Hummer's method, whereas, Mo-$BiVO_4$ was prepared a precipitation followed by calcination method. Various physico-chemical techniques were used to ensure the formation of the catalyst materials.

Results and discussion

The PEC activity of the modified BiVO4 was evaluated for water oxidation under solar light irradiation. Typical i-v data (Fig.1a) indicated that $BiVO_4$ has no photoactivity under dark conditions and the visible light activity of $BiVO_4$ increases with Mo-loading. Significantly, a 4-fold improvement in PEC activity was observed with Mo-$BiVO_4$@RGO compared to $BiVO_4$, whereas under the same conditions, Mo-$BiVO_4$ showed nearly 2-fold increment in the performance (Fig. 1a). Interestingly, Mo-$BiVO_4$@RGO also showed a constant transient photocurrent response, as shown in Fig. 1b. The better performance of Mo-$BiVO_4$@RGO in PEC water splitting is attributed to the longer electron lifetime due to minimization of the exciton recombination and a facile electron injection into RGO.

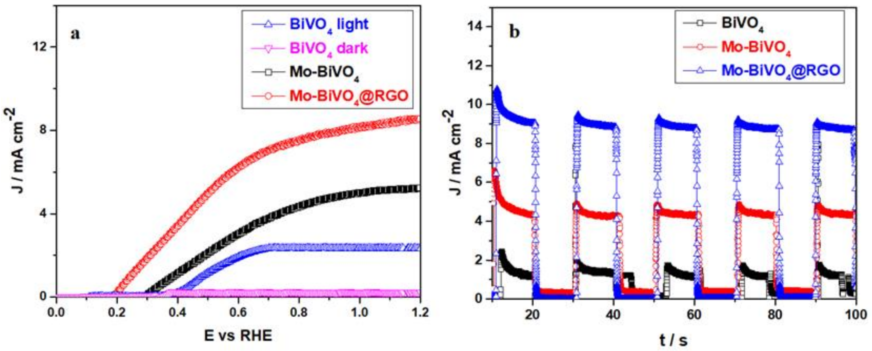

Fig 1. (a) linear sweep voltammetry (LSV) plots and (b) I-t curves of electrodes.

Conclusions

Mo-$BiVO_4$@RGO appears to be a promising photoanode for PE water splitting. The best activity of Mo-$BiVO_4$ is due to the reduced charge recombination.

Acknowledgement

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Nickel Vanadium layered double hydroxides nanostructures for high-performance supercapacitor applications

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Introduction

In recent times, demand for portable electronic devices like mobile phones, cameras and laptops etc. is increasing day by day. Energy storage devices such as batteries and supercapacitors have significant importance because of their high energy density and high power density, respectively.[1] Supercapacitor is gaining great amount of attention because it uses less toxic material, offers high power density, excellent electrochemical stability, wide range of operating temperatures and durability. A facile fabrication of low cost, efficient, stable, eco-friendly and earth-abundant electrode materials for supercapacitors is critical.[2] Layered double hydroxide (LDH) is new class of material having general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}^{n-}.mH_2O]^{x-}$ (where, M^{2+} and M^{3+} are the bivalent and trivalent metal cations and A^{n-} is the charge balancing anion of valence n; $x=\left(\frac{M^{3+}}{M^{2+}+M^{3+}}\right)$), has showed enormous supercapacitive performance.[3]

Experimental

In this work, an ionic lamellar, two-dimensional (2D) nickel-vanadium layered double hydroxide (NV LDH) nanosheets over Ni foam have been synthesized via facile, cost effective and potentially scalable hydrothermal method. The as-prepared 2D NV LDH nanosheets on nickel foam (NF/NV LDH) was used as supercapacitor electrode. The electrochemical characterization techniques such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to characterize the material for its electrochemical properties, while SEM, TEM, XRD, BET, and XPS etc. techniques have been used for their morphological, structural and physical characterization.

Results and discussion

High specific capacitance of ~950 F g^{-1} at the current density of 1 A g^{-1} was observed in three-electrode system using 2 M KOH as electrolyte, which remained ~500 F g^{-1} at increased current density of 10 A g^{-1}.

Conclusion

This work demonstrates great potential for NV LDH nanosheets as electrode material for supercapacitor applications.

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Synthesis, Characterization and Catalytic Properties of Ordered Mesoporous Niobosilicates

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Introduction

The development of heterogeneous catalytic systems for the oxidation of organic compounds is a highly attractive. For example, oxidation of cyclohexene is a very important reaction as the oxidation products, viz., cyclohexanol and cyclohexanone, are precursors for the production of adipic acid and caprolactam which in-turn are key intermediates in the manufacture of nylon-6 and nylon-66 [1,2]. In this context, niobosilicates have been found to be attractive and efficient and long-lived catalysts for a single-step synthesis of one of the precursors of nylon-6,6-cyclohexene epoxide [3-5]. In this work, an attempt has been made to prepare mesoporous niobosilicates, designated as NbMCM-41.

Experimental

NbMCM-41 was prepared according to the reported procedure for the preparation of MCM-41 [2] with the addition of niobium oxalate in 0.1M oxalic acid. The *p*H of the gel was adjusted to 11 and the mixture was subjected to hydrothermal treatment at 100°C for 24 h. After crystallization, the product was filtered, washed, dried and calcined at 550°C for 1 h in flowing nitrogen followed by 5 h in air at a heating rate of 1°C per min. The resulting materials was designated as NbMCM-41.

Results and discussion

NbMCM-41 of two different Si/Nb ratios of 32 and 64 were prepared successfully synthesized and characterized systematically using various analytical, spectroscopic and imaging methods. Both the catalysts, viz., NbMCM-41(32) and NbMCM-41(64) displayed well-ordered framework with typical mesoporous 2D-hexagonal structure and very high surface area and good thermal stability. The nitrogen sorption isotherms of the catalysts exhibit reversible type IV isotherms with sharp inflection and the H1-type hysteresis loop. This reflects the mesoporosity of the prepared catalysts and uniformity of the pores.

Conclusion

The niobium incorporated catalysts show higher acidity than the pristine samples, and that NbMCM-41(32) showed excellent catalytic activity for cyclohexene oxidation than the corresponding NbMCM-41 (64).

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Niobium-containing mesoporous materials as catalysts for phenol transformations

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Introduction

Catalytic reactions for organic synthesis have recently been the subject of many scientific reports. The choice of a proper catalyst and appropriate reaction conditions are very important in the phenol hydroxylation (using H_2O_2 as an oxidant), i.e. OHx and hydrodeoxygenation, i.e. HDO reactions. In this study, catalysts based on niobosilicate matrix was prepared and characterized with a goal to effective utilizing in organic synthesis of dihydroxybenzenes (OHx reaction) and benzene (HDO reaction) from phenol. The incorporation of various organic groups into the mesoporous materials provides enormous possibilities to tune their physico-chemical properties [1], thus this strategy was also utilized.

Experimental

A direct synthesis route was used to prepare functionalized materials, ordered mesoporous niobosilicates (Nb-PMS) and organoniobosilicates (Nb-PMO). The new materials exhibited high surface area and quite uniform mesopores of width ca. 4-12 nm.

Results and discussion

The catalysts showed high activity and selectivity on phenol hydroxylation, which was then pursued under various parameters in attempts to find the optimal reaction conditions. The OHx reaction was conducted at temperatures of 50–90 °C and a H_2O_2 concentration of 25% mol in relation to phenol. It should be pointed out that catalysts based on Nb-PMO with ethyl bridging groups reached conversion of 95% with a selectivity to hydrochinone of ~`70%.

By the insertion of Nb within the mesoporous framework, a bifunctional catalyst with strong hydrogenation and acid properties was obtained. A high selectivity towards benzene was observed with Nb-PMO. Also some selectivity towards methylcyclopentane, indicating contributions of acidic surface chemistry, was detected.

Conclusions

The results show that a proper reaction temperature and H_2 pressure/hydrogen peroxide concentration are necessary to control the phenol transformations over Nb-containing mesoporous materials.

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Vapour phase conversion of glycerol to acrolein over Nb_2O_5/SBA-15 catalyst

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Introduction

The increasing production of biodiesel has resulted in a price decline of crude glycerol. This makes glycerol as an attractive compound for the synthesis of fine and crude chemicals [1,2]. Catalytic conversion of glycerol to acrolein, an important intermediate, could be one of the important routes for using glycerol resources. In this work, we have synthesised SBA-15 supported Nb_2O_5 catalysts with different niobium loadings and tested them for the vapour phase conversion of glycerol to acrolein.

Experimental

SBA-15 was prepared by the procedure described in the literature. The Nb supported SBA-15 catalysts were prepared by wet impregnation method. The physico-chemical properties of the catalysts were characterized by various spectroscopic and adsorption techniques. The catalysts were tested in a down flow fixed- bed quartz reactor and the products were analysed using gas chromatography equipped with an FID.

Results and discussion

The surface area and acidity of the catalysts were determined and these results are compared with the results obtained from the vapour phase conversion of glycerol to acrolein in Table 1. The results revealed a higher acrolein yield over the 30wt%Nb/SBA-15 catalyst compared with the other Nb loading catalysts. The high activity of 30wt%Nb/SBA-15 is attributed to the presence of more number of acid sites on the catalyst surface. A decrease in the activity at higher Nb loadings is due to the formation of micro crystalline Nb_2O_5 species on SBA-15. Furthermore, the influence of reaction parameters and stability studies show that 30wt%Nb/SBA-15 is a promising catalyst for the vapour phase glycerol conversion to acrolein.

Table 1 Activity comparison with physico-chemical characteristics of the catalysts

Nb loaded SBA-15 (wt.%)	Surface area (m^2/g)	Total acidity (μmol/g)	Acrolein yield (%)
0.0	700	-	-
10.0	526	281.5	22.4
20.0	368	352.1	33.6
30.0	321	373.8	51.0
40.0	233	342.1	33.7
50.0	218	290.1	29.4

Conclusions

Nb catalysts supported on SBA-15 was explored in the vapour phase dehydration of glycerol to acrolein. A 30wt% Nb supported on SBA-15 catalyst has shown superior performance towards the formation of acrolein, glycerol which is attributed to the presence of higher acidic sites on the catalyst surface.

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Group V elements based nanofiber catalysts prepared in one step by electrospinning for partial oxidation reaction

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Introduction

V-containing catalysts are one of the most studied heterogeneous catalytic systems for selective oxidation processes. The activity and selectivity of these catalysts can be modified by the addition of other elements as a promoter such as Nb, Mo, Sb, etc. [1]. For instance, there are several selective oxidation reactions in which Nb is used as promoting agent in vanadium-based catalysts [2]. On the other hand, the use of a catalyst with fibrous structure of very low diameter for fixed bed reactors has several advantages, such as low resistance to internal diffusion and pressure drop [3]. In this work, it is proposed the preparation of V and Nb containing fiber catalysts by using the electrospinning technique, and their use in the propane oxydehydrogenation (ODH) reaction.

Experimental

Zirconia nanofibers doped with vanadium and/or niobium has been prepared by the electrospinning method, incorporating the vanadium and/or niobium precursors during the synthesis of the fibers. Then, the electrospun fibers were calcined at 500ºC. The mass concentration of V+Nb in each sample was 5%. The resulting nanofibers were characterized and evaluated for the propane ODH reaction.

Results and discussion

TEM images showed that all the samples present fibrous shape. N_2 adsorption–desorption isotherms at −196 ºC indicated that a high porosity is developed when V and/or Nb are incorporated during the synthesis of the fiber, being the BET area values of the doped samples (~60 m^2/g) higher than the one of the bare ZrO_2 support (26 m^2/g). XPS, XRD and Raman results confirmed the presence of well-dispersed Vanadium and Niobium species on the surface of tetragonal zirconia. The catalytic results showed that the V-containing sample were the most active, whereas the presence of Nb produces an increase of the selectivity to propylene and a decrease in the conversion during the propane ODH.

Conclusions

Group V based supported catalysts on zirconia nanofibers have been prepared in only one step by electrospinning, a very simple and low-cost synthesis method, resulting in promising catalysts for partial oxidation reactions.

Acknowledgements

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Role of group V elements on the hydrogenation activity of Ni/TiO_2 catalyst for the vapour phase conversion of levulinic acid to γ-valerolactone

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Introduction

The conversion of levulinic acid (LA) to fuels and fuel additives is an attractive process in bio-refinery. One such conversion is its hydrogenation to γ-valerolactone (GVL) [1]. Previous investigations were carried out in liquid phase at high pressures; however, currently vapour phase conversion of LA at atmospheric pressures is being pursued [2]. Here we report the vapour phase conversion of LA to GVL at ambient H_2 pressure over V, Nb and Ta modified Ni/TiO_2 catalysts.

Experimental

All the catalysts were prepared by wet impregnation method [3]. The surface and bulk properties of the catalysts were investigated by powder XRD, N_2-sorption, CO-pulse chemisorption, N_2O titration, XPS, TEM and pyridine adsorbed DRIFTS analysis. The activity testing of the catalyst was carried out in a fixed-bed quartz reactor in down flow mode at 275°C, atmospheric H_2 pressure and a GHSV of 9.74 mL g_{cat}^{-1} s^{-1}.

Results and Discussion

Some of the physicochemical properties of the catalysts are listed in Table 1. Interestingly, a relatively higher Ni surface area is observed for Nb promoted Ni/TiO_2 catalyst. The vapour phase conversion of LA to GVL revealed a higher $Rate_{GVL}$ over the Nb promoted Ni/TiO_2 catalyst. In contrast, the V and Ta promoted Ni/TiO_2 catalysts demonstrated lower $Rate_{GVL}$ at the cost of angelica lactones (α and β) formation, which are intermediates in the conversion of LA to GVL.

Table 1. Physicochemical properties and activity data of the catalysts

10wt% Ni supported on	Surface Area (m^2/g)	CO-uptake (μmol/gcat)	S_{Ni} (m^2/gNi)	$Rate_{GVL}$ (μmol $gcat^{-1}s^{-1}$)
2wt%V/TiO_2	46.3	29.6	11.6	0.33
2wt%Nb/TiO_2	43.8	42.2	16.5	1.21
2wt%Ta/TiO_2	40.9	30.8	12.0	0.54

Conclusions

The vapour conversion of levulinic acid to γ-valerolactone is investigated at atmospheric H_2 pressure over V, Nb and Ta modified Ni/TiO_2 catalysts. The Nb promoted Ni/TiO_2 catalyst showed higher activity towards GVL compared to other V and Ta promoted catalysts.

Acknowledgements
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Sunlight-Driven Water Splitting by Ta_3N_5 Thin-Film Photoanode and $BaTaO_2N$ Particulate Photoanode

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Introduction

Ta_3N_5 and $BaTaO_2N$ (BTON) with absorption edge wavelength at 600 nm or longer have received considerable attention in terms of having suitable bandgap positions for the photoelectrochemical (PEC) water splitting reaction.[1] In the present work, we focused on the surface modifications of the Ta_3N_5 and the BTON photoanodes as a means of enhancing the photocurrents at the onset potentials for PEC oxygen evolution. Overall water splitting using the PEC cells composed of Ta_3N_5 and BTON photoanodes and $La_5Ti_2(Cu,Ag)S_5O_7$ (LTCA) photocathodes will be demonstrated.

Experimental

Ta_3N_5 thin-film photoanodes were prepared by a sequential sputtering and nitridation process.[2] BTON photoanodes were prepared using powder materials through the particle-transfer method.[3,4] The PEC measurements were carried out using Ag/AgCl reference electrode and a Pt wire counter electrode in Ar gas atmosphere. The amounts of evolved gases were quantified with a gas chromatograph.

Results and discussion

The $NiFeO_x$-loaded T_3N_5 photoanode ($NiFeO_x/Ta_3N_5$) showed a lower onset potential than that of the NiO_x-loaded Ta_3N_5 photoanode for the PEC oxygen evolution reaction. The enhanced photocurrent for the $NiFeO_x/Ta_3N_5$ is attributable to the lower overpotential resulting from the $NiFeO_x$ catalyst. The PEC cell containing a Ta_3N_5/LTCA photoelectrodes exhibited a stoichiometric H_2 and O_2 generation (Figure 1).

The BTON photoanode sequentially modified with Ir and Co (Ir/Co/BTON) produced a significantly higher photocurrent at the onset potential compared to the Co-loaded BTON photoanode. The PEC cell containing a BTON/LTCA photoelectrodes showed the overall water splitting with the solar-to-hydrogen energy conversion efficiency of about 0.2%.

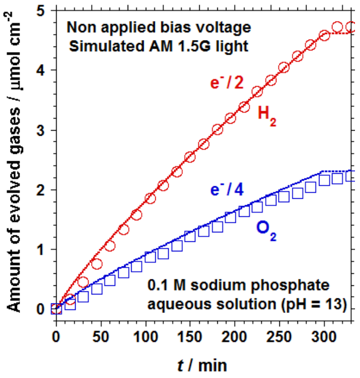

Figure 1. H_2 and O_2 generation over time using the PEC cell containing a Ta_3N_5/LTCA photoelectrodes under AM 1.5G.

Conclusions

Surface modifications of Ta_3N_5 and BTON photoanodes could significantly enhance the photocurrents at the onset potentials. The PEC cells consisting of Ta_3N_5/LTCA and BTON/LTCA photoelectrodes generated H_2 and O_2 without external bias voltage.

Acknowledgements.

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Effect of size vs. phase purity on the electro catalytic and photo catalytic performance of nano Tantalum Carbide

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Introduction

Clean energy as well as environment is the way to future. Pollution free fuels and clean energy storage methods are need of the hour. Hydrogen is emerging as a key fuel in this category. Transition metal carbides (TMCs) are primary candidates for the replacement of noble metals as electro catalysts for hydrogen evolution reaction (HER) in fuel cells as well as hydrogen production. Using solar energy for removal of organic pollutants is gaining favour. In recent years TMCs have shown significant photo catalytic activity for degradation of organic compounds. The electro catalytic as well as photo catalytic activity are significantly affected by the size as well as the phase purity of the TMCs. In this work well characterized, nanosized TaC powders been used to understand the effect of size as compared to phase purity on the electro catalytic as well as the photo catalytic performance of the powders. The nano-TaC used was synthesized from Tantalum Ethoxide (Ta-E) at low temperature (800 °C) [1].

Experimental

Two samples A and B were used for the present work. Sample A has a mixed phase of TaC, Ta_2C and Ta_4O, size: 21 nm, BET surface area: 159 m^2/g. Sample B has a mixed phase of TaC and Ta_2C, size: 45 nm, BET surface area: 45 m^2/g. The electrochemical characterization was done using as 3 electrode cell with 0.5 mol/lt H_2SO_4 solution, RHE standard electrode and graphite rod as the counter electrode. The sample was deposited on the glassy electrode. LSV was used to determine the current density, Tafel slope as well as the over potential values. For the photo catalytic characterization the Methylene Blue (MB) dye degradation under visible light has been studied.

Results and discussion

For the electrochemical reactions it is observed that sample A gives higher current density (1 mA/cm^2) as well as lower Tafel slope (154 mv/dec) indicating an enhanced electro catalytic activity as compared to sample B (0.185 mA/cm^2, 261 mV/dec). For the MB degradation experiments Sample gives 58% degradation in 420 minutes whereas sample B can only achieve 55% degradation in 480 minutes.

Conclusions

Together these results indicate that size and the specific surface area plays a more vital role in determining the catalytic properties of the TaC powders.

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Selective conversion of fructose and 5-hydroxymethylfurfural to 5-ethoxymethylfurfural over Ta containing heteropoly tungustate catalysts

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Introduction: Currently the growing paucity of energy sources and increasing intensification of global warming has motivated the world to search for alternative precursors of energy. The renewable biomass is the only sustainable source for the production of fuels and chemicals [1]. Although various chemicals produced from biomass, 5-ethoxy methyl furfural (EMF) has been considered as excellent fuel additive. It has high energy density as diesel and enhances the fuel properties [2]. In the present study, tantalum containing heteropoly tungstate supported on tin oxide catalyst is studied for the preparation of EMF from fructose and 5-HMF.

Experimental: Ta exchanged TPA (TaTPA) supported on SnO_2 catalysts were prepared. The physicochemical properties of all these catalysts were derived from XRD, FT-IR, Laser Raman spectroscopy, Py-IR and NH_3-TPD. In a typical reaction, 0.126 g of HMF, 2 g of ethanol and 0.08 g of catalyst were charged in a 15 mL sealed tube and the reactions were carried at 120 °C for 45 min. The products were analysed by gas chromatography.

Results and discussion: XRD patterns of the catalysts are shown in Fig 1. These patterns suggest the presence of tetragonal structure of SnO_2. The less intense peaks related to Keggin ion of TaTPA were seen for the catalysts with above 20 wt% of TaTPA on SnO_2. Fig 2 indicating the total amount of acid sites determined by NH_3-TPD and the acidity was found to increase with an increase in TaTPA content on the support. The catalytic activity of TaTPA catalysts were shown in Fig 3, HMF conversion and EMF yield were increased with an increase in TaTPA loading up to 30 wt%. When further increase in TaTPA loading EMF yield decreased due to the ethanolysis of EMF to ethyl levulinate (EL). As shown in Fig 4 this catalyst also showed best activity towards the conversion of fructose to EMF.

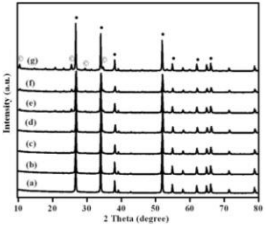

Fig.1

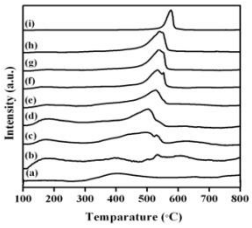

Fig.2

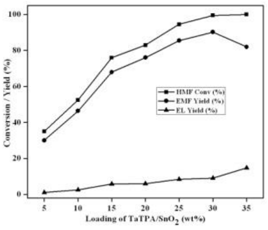

Fig.3

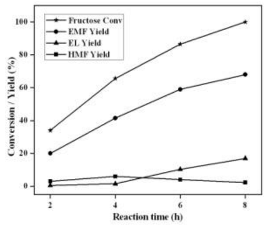

Fig.4

Conclusions: Ta exchanged TPA supported on SnO_2 catalysts were prepared with retention of Keggin ion structure. Etherification of HMF depends on the total acidity of the catalysts which related to the content of TaTPA on support.

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Activating RuO_2 for Electrochemical Chlorine Evolution Selective Reaction through Dopants of Group V Elements

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Introduction:

The electrochemical Cl_2 production is an important industrial process as it is used in variety of other processes such as waste-water treatment, insecticide and pesticide production etc. However, electrochemical chlorine evolution reaction (CER) occurs with parallel oxygen evolution reaction (OER) as their thermodynamic redox potentials are 1.36 V and 1.23 V, respectively [1]. This observation necessitates the design of electrocatalysts which are selective to CER. Industrially, Ru-based electrocatalysts are used for both CER [1] and OER [2, 3]. For enhancing the CER selectivity, we explored the utility of group-V element (V, Nb and Ta) doped RuO_2 electrocatalysts.

Results and discussion:

All the doped electrocatalysts were synthesized using a two-step procedure as follows (1) group-V elements were co-electrodeposited with Ru in electrochemically reducing condition in their metallic state and (2) then the electrodes are annealed to their oxide state. Experimental results yield Nb-doped RuO_2 electrocatalyst to be more CER selective in comparison V-doped and Ta-doped doped RuO_2 electrocatalysts while Ta-doped electrocatalysts show better OER selectivity in an electrolyte solution of (0.5 M + 1 M HCl). Apart from the selectivity, group-V doped RuO_2 electrocatalyst yields increased combined activity of OER and CER in comparison to undoped RuO_2. Density functional theory based computational studies indicate that a charge transfer mechanism of $M_{group\text{-}V} + Ru \rightarrow M_{group\text{-}V}^{\delta-} + Ru^{\delta+}$ ($M_{group\text{-}V}$ = V, Nb, Ta in RuO_2) to be active within RuO_2 structure which is said to be responsible for reduced OER and CER overpotentials. The oxidation state of Ru in RuO_2 has found to be increased while going down of periodic table (V to Ta) with dopants. Also, the dopants are found to get activated in RuO_2 structure and act as an active sites for OER and CER though rutile structures of VO_2, NbO_2 and TbO_2 are not active towards both of the reaction as indicated by computational studies. Both OER and CER are found to follow coupled-electron pathway similar to Eley-Rideal mechanism [4]. The iso-valent nature of the dopants (V, Nb and Ta) in RuO_2 also restrict the probability of increase in kinetics of parallel OER mechanistic pathway comprising lattice oxygen vacancy formation [5].

Conclusions:

The present study identifies Nb-doped RuO_2 as superior electrocatalyst among group-V doped electrocatalysts. Further, our study provides a new insight in activating RuO_2 electrocatalysts towards CER while suppressing OER.

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Experimental and Density Functional Theory Insights into the Role of Support in ODH of Propane Over Supported Vanadia Catalysts

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Introduction

Oxidative dehydrogenation (ODH) of propane to propylene over vanadia catalysts using O_2 is known to depend on the support [1]. Here we first experimentally reconfirm the effect of the support and then theoretically attempt to understand the role of support. While doing so we try to identify suitable catalyst descriptors.

Experimental and Theory

Vanadia catalysts supported over silica, alumina, titania and zirconia were prepared by the incipient wetness impregnation method. The reaction was carried out at atmospheric pressure in an isothermal fixed-bed reactor. Catalysts were modelled and optimized using Vienna Ab Initio Simulation Package (VASP) [2].

Results and Discussion

Reactivity data showed that the activity of vanadia on different supports varied as: $V/TiO_2 > V/ZrO_2 > V/Al_2O_3 > V/SiO_2$ (Table 1). Structural optimization of monomeric VO_4 species by Density Functional Theory (DFT) revealed that $O{=}VO_2(OH)$ is likely to form on supports due to geometric constraint. As shown in Table 1 no correlation between the reactivity data, structural parameters and O=V vibrational frequency was observed. Charge analysis and calculation of transition state of the rate determining step which involves the activation of the secondary C-H bond of propane [2] are currently underway. The correlation of these parameters with the reaction data will also be carried out with an aim to find a suitable descriptor.

Table 1. Experimental and DFT data for vanadia supported on different oxides

Vanadia supported on	Experimental		Theoretical	
	Rate at 380°C mol C_3H_6 $(g.sec)^{-1}$	O=V Raman shift (cm^{-1})	O=V stretch by DFT (cm^{1})	O=V bond length (pm)
SiO_2	0.00	1037	1067	161.4
Al_2O_3	$2.28*10^{-5}$	1025	-	162.4
ZrO_2	$2.93*10^{-4}$	1028	-	-
TiO_2	$7.23*10^{-4}$	1025	1052	161.6

Conclusions

There seems to be no correlation between the reactivity data and O=V stretching frequency or O=V bond length. Support might influence the electronic structure of the surface vanadia species which could be evident by charge analysis and transition state calculations.

Acknowledgements

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Effect of support and VO_x species on activity, selectivity and stability in non-oxidative alkane dehydrogenation

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Introduction

Catalytic dehydrogenation (DH) of C_3-C_4 alkanes provides an on-purpose production of the corresponding olefins. In view of toxicity and high costs of commercially applied catalysts on the basis of CrO_x and Pt respectively, there is a need for alternatives free of such drawbacks.[1] VO_x-based catalysts can be considered as such candidate.[2] The purpose of the current work was to identify physico chemical properties of such catalysts responsible for their activity, coke formation, and onstream stability in propane and isobutane DH. To this end, we prepared and investigated catalysts with differently structured VO_x species on various supports.

Experimental

SiO_2 (MCM-41), SiO_2-Al_2O_3 (1-70 wt.% SiO_2) and Al_2O_3 were used as supports. Supported catalysts were prepared by grafting $VO(acac)_2$ from a toluene solution onto the supports and characterized by UV-vis, XRD, H_2-TPR, and NH_3-TPD. Catalytic tests were carried out at 550°C using i-$C_4H_{10}/N_2=4/6$ or i-$C_3H_8/N_2=4/6$ feeds. A thermobalance SETSYS (Setaram) was applied for monitoring coke formation.

Results and discussion

VO_x/Al_2O_3-SiO_2 showed high activity and selectivity in both propane and isobutane DH. SiO_2 content in SiO_2-Al_2O_3 was established to be an important factor determining DH performance of VO_x species. The content affects the structure of such species. A correlation between turn-over frequency of propene or isobutene formation and the degree of polymerization of VO_x was established. This correlation suggests that isolated species possess higher intrinsic activity than their oligomerized counterparts. Further results also pointed out that VO_x species were significantly more active for coke formation than support acid sites. Moreover, no correlation between catalyst acidity and the rate constant of coking could be drawn, while such constant increases with the degree of polymerization of VO_x species

Conclusions

We have elucidated fundamental factors affecting performance of VO_x-based catalysts in DH of propane and isobutane. The kind of VO_x species was established to determine their intrinsic activity for both olefin and coke formation. This result suggests that an ideal catalyst should possess isolated VO_x species. Moreover, their Lewis acidity should be strong enough to activate C-H bond of alkanes but not too strong to catalyze cracking and skeletal isomerization in case of isobutane DH.

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Synthesis, characterization and catalytic evaluation of V_2O_5 supported on La_2O_3 modified Al_2O_3 catalysts for ammoxidation of 2-chlorotoluene

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Introduction

One-step formation of carbonitriles (R–CN) by oxidation of simple olefins or methyl aromatic compounds using molecular oxygen in the presence of ammonia is generally referred to ammoxidation [1,2]. Ammoxidation is an important reaction in industry. In an ideal case, the only byproduct found in the ammoxidation is water, which makes the ammoxidation a green and sustainable reaction. Halogen substituted benzonitriles have wide range of applications in fine chemical sector and therefore preparation of these compounds by ammoxidation process is of particular interest. Vanadia based catalysts are well known and widely employed as catalysts for ammoxidation reaction [2,3]. Supporting vanadia on an appropriate support leads to increase in catalytic activity. The nature of the support plays a vital role. In the present investigation, V_2O_5 supported on Al_2O_3 modified with La_2O_3 catalysts are prepared and studied for their activity for ammoxidation of 2-chlorotoluene (2-CT) to 2-chlorobenzonitrile (2-CBN).

Experimental

A series of V_2O_5 supported on La_2O_3 modified Al_2O_3 catalysts were prepared in two steps by wet impregnation method and evaluated for their activity in ammoxidation of 2-CT to 2-CBN in a fixed bed reactor at atmospheric pressure. The catalysts were characterized by BET, XRD, TPR, UV-DRS and NH_3-TPD.

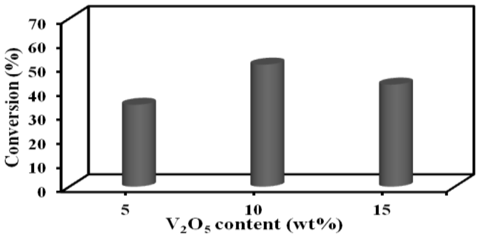

Fig.1. Effect of V_2O_5 loading on catalytic activity during ammoxidation of 2-chlorotoluene

Results and discussion

Characterization results revealed that the vanadium is existed mainly as isolated monomeric and polymeric vanadium species with tetrahedral coordination and these species were in highly dispersed state and/or strong interaction with La_2O_3/Al_2O_3 support up to 10 wt% V_2O_5 loading and bulk-like V_2O_5 crystallites formed at 15 wt% of V_2O_5. All the catalysts in the present study, irrespective of V_2O_5 loading selectively yielded the desired 2-CBN. The 10 wt% V_2O_5 dispersed on 5 wt% La_2O_3/Al_2O_3 catalyst is found to be the best catalyst composition compared to other catalysts. The reaction parameters were optimized and the results were explained based on the characteristics of the catalysts.

Conclusions

V_2O_5 supported on La_2O_3/Al_2O_3 catalysts were active and selective for ammoxidation reaction. Well dispersed tetrahedrally coordinated isolated monomeric and polymeric vanadia species were responsible for high ammoxidation activity. The presence of metal vanadate species are responsible for high selectivity to 2-CBN.

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Nb_2O_5 and $ZnNb_2O_6$ modified with gold – surface and catalytic properties

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Introduction

Metal oxide support can change the electronic structure of gold particles by strong gold-support interaction and thus also the electron transfer from the support to gold [1]. The aim of this study was to use gold catalysts supported on niobium(V) oxide and mixed niobium-zinc oxide in methanol oxidation and to characterize step by step changes on the surface of catalysts resulting from activation of the catalyst and methanol oxidation.

Experimental

Mesoporous Nb_2O_5 and $ZnNb_2O_6$ were prepared by solvent evaporation method. The oxides were modified by gold grafting and characterized by XRD, N_2 ads./des., XPS, SEM-EDX, TEM, FTIR and UV-Vis. Methanol oxidation with oxygen was performed on these catalysts in the temperature range of 373 – 573 K. The catalysts were analyzed after activation in argon flow and after the catalytic reaction by XPS.

Results and discussion

The interaction between gold and the supports (Nb_2O_5 and $ZnNb_2O_6$) was studied and the changes in the state of the catalyst components resulting from activation of the catalysts and their use in methanol oxidation were observed. The most important finding from this work was the identification of changes in the surface composition of gold catalysts dependent on the nature of the support and the treatment conditions (thermal activation in inert gas and methanol oxidation with oxygen). These changes covered cyclic dehydroxylation / rehydroxylation of the supports, formation of oxygen defects and their filling with water, atomic oxygen chemisorption, reduction and oxidation of niobium cations and gold species. A special focus was on the changes in gold species caused by the oxidation reaction. Chemisorption of oxygen on metallic or negatively charged gold particles determined selective or total methanol oxidation. The interaction between atomic oxygen chemisorbed on metallic gold (the main gold species after activation of the catalysts) and methoxy species chemisorbed on the support led to the products of selective oxidation. During methanol oxidation, surface hydroxyls were rebuilt and metallic gold become surrounded by negative charge ($(Au^0)^{\delta-}$). Oxygen chemisorbed on such gold particles was active in total oxidation of methanol. This effect was more pronounced on Au-$ZnNb_2O_6$ and therefore this catalyst was proposed as attractive candidate for low temperature total oxidation of VOCs. The role of niobium in the electron transfer from the support to metallic gold particles and from $(Au^0)^{\delta-}$ to the reagents was evidenced.

Conclusions

Methanol conversion and selectivity in its oxidation depended on the surface properties of the catalysts and the presence of hydroxyls, metallic and negatively charged gold nanoparticles as well as small amounts of cationic gold species.

Acknowledgements

We are grateful to the National Science Center in Poland for support (project no. 2016/21/N/ST5/00533).

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Ta doped compact TiO_2 and interface modification for improved performance in perovskite solar cells

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Introduction

Perovskite solar cells have become an attractive light-absorber system with a rapid improvement of cell efficiencies from less than 4% in 2009 to a certified 22.1% in 2016. The low conductivity of TiO_2 poses obstacle in its efficiency enhancement. In this work, we have carried out tantalum (Ta) doping in compact TiO_2 layer in order to improve the conductivity of TiO_2. Further, investigation of interfacial engineering at TiO_2/perovskite junction has been carried out using different anchoring agents.

Experimental

Tantalum (V) ethoxide was mixed in titanium precursor solution in 1.0, 3.0 and 5.0 mol%. The solution was spin coated on ozonized substrate immediately at 3000 rpm for 1 min and annealed at 500℃ for 30 min in muffle furnace. For linker deposition, 2 mM solution of different anchor agents in ethanol or water was prepared and the prepared TiO_2 coated substrates were dipped in a solution of anchor agents for 6 h.

Results and discussion

Ta doping in TiO_2 was confirmed through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The improvement in the conductivity of TiO_2 upon Ta doping is accompanied by suppression of anatase to rutile phase transformation of TiO_2, as anatase is a more desirable phase due to its higher conductivity. Further, Ta doping of 3.0% led to a 40% improvement in the overall efficiency as compared with undoped TiO_2. Results from impedance spectra indicate that there is a decrease in charge transfer resistance with Ta-doping.

Conclusions

Doping of Ta was successfully done in compact TiO_2 layer using sol-gel method and increment in the conductivity of TiO_2 was observed. Ta doping not only increased the conductivity of TiO_2 but also supresses anatase to rutile phase transformation. Efficiency of ~9 % was obtained for the perovskite solar cell devices using Ta doped compact TiO_2.

Acknowledgements

Authors wish to acknowledge Department of Science and Technology (DST), India for financial support.

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Experience of Niobium and Vanadium micro alloying at Essar Steel India Ltd

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Abstract

Niobium and Vanadium which represent Group Five elements are extensively used in steel industry for producing high strength steels. Addition of these elements in steel is in the form of ferro-alloys. They are normally used in very small quantities (<0.10 weight %) in high strength low alloy steels and hence called as micro-alloys. Micro-alloy in steel contributes to excellent combination of strength, toughness and weldability due to their inherent characteristics of grain refinement and precipitation strengthening. Essar Steel always has focused on high strength value added grades and has approximately 25% of product mix using these elements. These elements find application in steels for automotive, line-pipe for oil and gas transportation, ship building and construction etc. This paper highlights micro-alloy design considerations for few high strength steels recently developed in Essar Steel India Ltd. It also briefly touches upon the practical aspects of steelmaking, casting and rolling of steels containing micro-alloys.

Keywords: Micro-alloy, Grain refinement, Precipitation strengthening, High strength steel

Poster Presentations

POSTER SESSION	**23rd November 16:00 – 18:00**
P 1	A. Srivani and **N. Lingaiah** *“Vanadium incorporated heteropoly tungstate: A selective catalyst for oxidative amination of 2-cyclohexenones with anilines to N- aryl anilines”*
P 2	Aditya Shankar Sandupatla, **Chalumuri Sivananda**, Sudhir C. Nayak and Goutam Deo *“Oxidative Dehydrogenation of Propane Using CO_2 Over Supported Chromia, Vanadia and Vanadia-Chromia Catalysts”*
P3	Yu-Sheng Lai and **Jih-Mirn Jehng** *“The hydrogen evolving efficiency over the synthesized $(NH_4)_2V_6O_{16}$ by the hydrothermal process”*
P 4	Debaprasad Shee, Brishti Mitra and **Goutam Deo** *“In situ DRIFTS studies of alkane adsorption on vanadia supported titania-doped catalysts”*
P5	J.-K. Lai, M. Zu, M.E. Ford and **Israel E. Wachs** *“Tungsten Oxide Promotion of SCR of NO_x with NH_3 by Titania-Supported Vanadium Oxide Catalysts”*
P6	**V. Veeramani**, P. Muthuraja and P. Manisankar *“V_2O_5 catalyst one-pot multicomponent synthesis of 5-hydroxy-3-methyl 4,5-dihydro-1H-4-pyrazol-4-ylpropan-2-one”*
P7	**Maciej Trejda**, Dorota Kryszak and Maria Ziolek *“Insight into the interaction of calcium species with mesoporous silica and niobiosilica”*
P8	Katarzyna Stawicka, Piotr Decyk, **Anna Wojtaszek-Gurdak** and Maria Ziolek *“Comparative study of basic oxygen formed on MCF impregnated with niobium and cerium species – NO as a probe molecule”*
P9	I. Sobczak, M. Wlodarczyk, **Lukasz Wolski**, M. Ziolek, V. Calvino-Casilda and R. Martin-Aranda *“Modification of APTMS-Nb/MCF basicity by gold and copper dopants”*
P10	**Aayush Gupta**, Rameez Ahmad Mir and O.P. Pandey *“Synthesis and photo-catalytic behaviour of NbB/C nanocomposite”*
P11	O. Yalcin and **Israel E. Wachs** *“Niobium Oxide Promotion of Iron Oxide-Based Catalysts for the High Temperature Water-Gas Shift (HT-WGS) Reaction”*
P12	Agata Wawrzyńczak and **Izabela Nowak** *“Mesoporous silicas with different arrangements of pores and containing Nb species as catalyst in the oxidation of selected alcohols”*
P13	Agnieszka Feliczak-Guzik, Myroslav Sprynskyy, **Izabela Nowak** and Boguslaw Buszewski *“Catalytic activities of Nb-containing hierarchical zeolites in the isomerization of trioses”*
P14	**Perumal Muthuraja**, S. Prakash, V. Veeramani and P. Manisankar *“Environmentally Benign niobium chloride catalyst one-pot multicomponent synthesis of spiro[indoline-3,4’-pyrano[2,3-c]pyrazole]”*
P15	Agata Smuszkiewicz, **Jesus López-Sanz**, Izabela Sobczak, Rosa M. Martín-Aranda, Maria Ziolek and Elena Pérez-Mayoral *“Tantalum vs Niobium MCF nanocatalysts in the green synthesis of chromenes derivatives”*
P16	**Deepak Raikwar**, Meghana Munagala, Saptarshi Majumdar and Debaprasad Shee *“Hydrodeoxygenation of Lignin derived Guaiacol over Mo, W and Ta Modified Supported Nickel Catalysts”*

Vanadium incorporated heteropoly tungstate: A selective catalyst for oxidative amination of 2-cyclohexenones with anilines to N- aryl anilines

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Introduction

The selective formation of carbon–nitrogen bond is a fundamental transformation in organic synthesis [1]. In recent years, the direct amination of C-H bond is a powerful alternative synthetic route for aryl amines under oxidative conditions and great progress has been made in the intra and intermolecular amination of C-H bonds. Keggin type heteropoly acids have been employed as promising catalysts for various oxidation and acid-catalyzed reactions [2]. 12-Tungstophosphoric acid (TPA), a highly acidic heteropoly acid, is modified with incorporation of V to shift its acid-dominated properties to a redox nature. In the present work supported vanadium incorporated heteropoly tungstate (TPAV) is explored as heterogeneous catalyst for the synthesis of diphenylamine from reaction of 2-cyclohexenone with aniline under mild reaction conditions.

Experimental

Vanadium incorporated tungstophosphoric acid [$H_{3+x}PW_{12-x}V_xO_{40}$ (x=1, 2, 3)] were prepared according to the reported procedure [3]. The supported $TPAV_1$ catalysts were prepared by impregnation method. The required quantity of $TPAV_1$ was dissolved in minimum amount of water and this solution was added to support with constant stirring. The excess water was removed on hot plate and the catalyst masses were dried in hot air oven at 120 °C for 12 h and finally calcined at 300°C for 2h.

Results and discussion

Laser Raman spectra of the catalysts are shown in Fig. 1. The characteristic Raman bands for Keggin ion are observed for the modified catalysts. The catalysts were tested for amnation reaction. Bulk $TPAV_1$ catalyst showed high activity for oxidative amination reaction and it is highly soluble in polar solvents. This catalyst can be made into heterogeneous by supporting on supports such as SiO_2, ZrO_2 and Nb_2O_5. The $TPAV_1$ supported on SiO_2, ZrO_2 and Nb_2O_5 showed good activity for oxidative amination reaction. The highest conversion for oxidative amination of 2-cyclohexenone with aniline was obtained for $TPAV_1$ supported on silica catalyst compared to other supported catalysts as shown in Table 1.

Table 1. Comparison of different catalysts for oxidative amination reaction

Catalyst	Conversion
$20TPA/SiO_2$	14.5
$20TPAV_1/SiO_2$	94.6
$20TPAV_1/Nb_2O_5$	56.7
$20TPAV_1/ZrO_2$	13.3

Reaction conditions: Aniline: 1 mmol; 2-Cyclohexenone: 1 mmol; TBHP in decane: 3 mmol; Catalyst weight: 100 mg; DMSO (solvent): 2 ml; Reaction temperature: 90 °C;

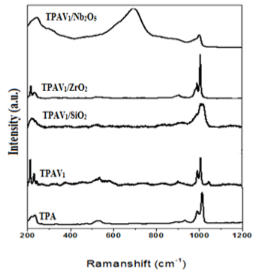

Fig. 1. Laser Raman spectra of the catalysts

Conclusions

Presence of vanadium in the primary structure of heteropoly tungstate enhances the catalytic activity and selectivity due to controllable acidity and redox nature.

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P-2

Oxidative Dehydrogenation of Propane Using CO_2 Over Supported Chromia, Vanadia and Vanadia-Chromia Catalysts

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Introduction

Use of CO_2 in place of O_2 for the oxidative dehydrogenation (ODH) of propane has been recently reported to enhance selectivity and lower coke formation [1]. In the present study we examine the ODH using O_2 and CO_2 using supported vanadia (V), chromia (Cr) and vanadia-chromia (V-Cr) catalysts.

Experimental

The alumina supported metal oxide catalysts were prepared by the incipient wetness impregnation method similar to those used previously [2]. The gases were analysed using a gas chromatograph equipped with flame ionization detector. The catalysts will also characterized using techniques commonly used for supported metal oxides, such as Raman, FITR and DR-UV-vis under ambient and *in situ* conditions.

Results and discussion

ODH of propane to propylene using O_2 was significantly influenced by using vanadia-chromia catalyst as shown in Figure 1. The trend in catalytic activity is V-Cr > V > Cr. However, for CO_2-ODH the trend in catalytic activity is V-Cr ~Cr > V. Studies related to effect of support, V/Cr ratio and detailed characterization of the catalysts are currently underway.

Conclusions

We observed that CO_2-ODH is possible over supported metal oxide catalysts. However, CO_2-ODH requires higher operating temperatures than O_2-ODH. A distinct promotional effect of using chromia with vanadia was observed in case of O_2-ODH, while the same was not observed in case of CO_2-ODH.

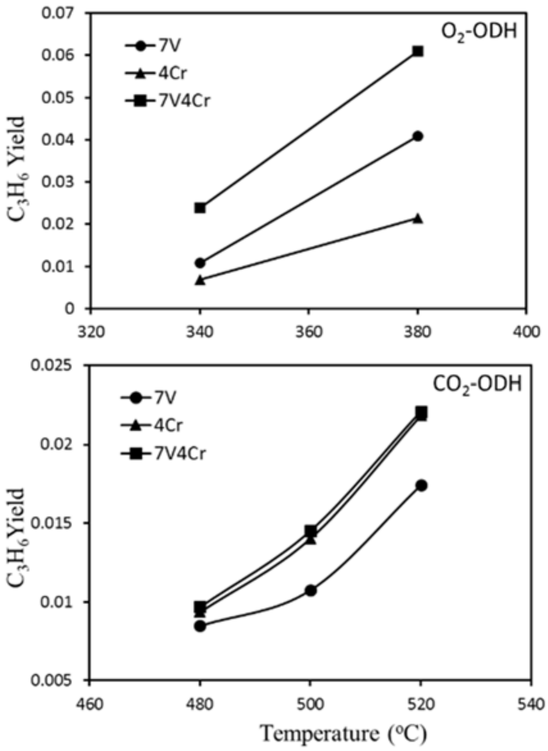

Figure 1. Propene yield at different temperatures

Acknowledgements

A. S. Sandupatla acknowledges the National Post-Doctoral Fellowship (PDF/2016/001459) granted by Science and Engineering Research Board (SERB), Government of India.

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The hydrogen evolving efficiency over the syntheized $(NH_4)_2V_6O_{16}$ by the hydrothermal process

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Introduction

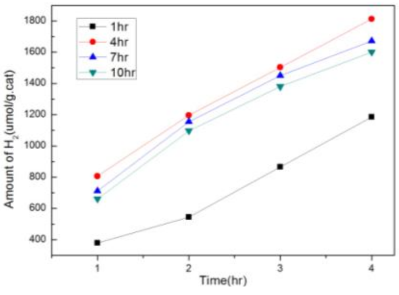
In past decade, semiconductor photocatalysis has extensively interested because of its special photocatalytic and electrochemical properties to decompose water by solar energy and an oxide semiconductor to generate clean-energy hydrogen. However, ammonium vanadium oxide have not been investigated in photocatalytic application. In this study, ammonia hydroxide has been used to control the solution pH, and synthesized the $(NH_4)_2V_6O_{16}$ crystalline phase by hydrothermal method. The formation of $(NH_4)_2V_6O_{16}$ can be optimized by pH value and hydrothermal treatment time.

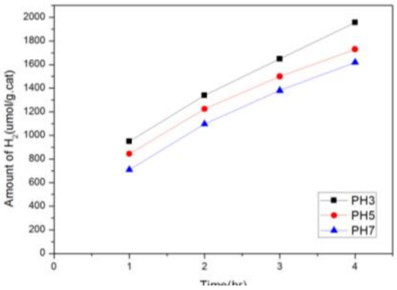
Experimental section

The $(NH_4)_2V_6O_{16}$ powders were firstly prepared by hydrothermal process from NH_4VO_3 (Ammonium metavanadate). The NH_4VO_3 was dissolved in 70 ml distilled water. Then adjust the pH value to 3, 5 and 7, separately, by adding the proper amount of ammonium hydroxide. After continuous stirring for 1 hr, the solution was transferred into a Teflon-lined stainless steel autoclave. Hydrothermal treatment was performed for 1 hr, 4 hrs, 7 hrs, 10 hrs at 200 ℃. After completing the hydrothermal process, the powder was centrifuged, washed with distilled water and ethanol several times. The powder was dried under 60 ◦C in vacuum oven for 1 hr.

Results and discussion

Photocatalytic reactions were carried out in a closed gas circulation system. A 0.15 g powder sample was suspended in 300 ml distilled water contain 100 ml ethanol using quartz reactor. A 300W Xe lamp was placed in center of reactor. The evolved gases were analyzed with a TCD gas chromatograph (China chromatography, GC9800). Figure1 (a) and (b) shows the results of the hydrogen evolving reaction as a funciton of time.





Conclusions

In this study, the optimum conditions to synthesis pure $(NH_4)_2V_6O_{16}$ are at pH3, hydrothermal temperature is 200 ℃, hydrothermal treatment time is 4hr. The accumulative concentration of hydrogen is 1957μ mol/g・cat.

Acknowledgements
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In situ DRIFTS studies of alkane adsorption on vanadia supported titania-doped catalysts

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Introduction

The low surface area and anatase to rutile phase transformation of the TiO_2 support at relatively low temperatures are serious drawbacks for the use of supported vanadia catalyst for high temperature reactions [1, 2]. These drawbacks can be overcome by doping TiO_2 with another metal oxide (Al_2O_3, SiO_2, WO_3) that exhibits high surface area and good thermal stability. The present study deals with the diffuse reflectance FTIR spectroscopy (DRIFTS) study of ethane and propane adsorption on these support modified catalysts.

Experimental

The TiO_2-SiO_2, TiO_2-Al_2O_3 and TiO_2-WO_3 supports containing 90 wt % TiO_2 were synthesized by the sol-gel method. Supported vanadia catalysts containing 2% vanadia were synthesized using these supports by the incipient wetness impregnation method. The catalysts were characterized by various techniques and specifically by DRIFTS during which the adsorption of ethane and propane was examined.

Results and discussion

The DRIFTS spectra reveal that during adsorption of alkanes primarily ethoxide or isopropoxide, acetaldehyde or acetone, formate or acetate and cyclic anhydride are formed. Unstable alkoxides species are observed only for the $90TiO_2$-Al_2O_3 supported vanadia catalyst. This catalyst is also the most active. The identification of alkoxides suggests that abstraction of hydrogen and the formation of alkoxides species is the initial step for alkane adsorption. Dehydrogenation of the alkoxide species results in the formation of olefins during the ODH reaction. The alkoxide species further oxidize to form the corresponding aldehyde or ketone, which is readily converted to formate and acetate at high temperatures. The acetate and formate are the precursors for CO and CO_2 formation. In addition to these surface species, adsorbed olefins/aldehyde or ketone associated with conjugated C=O and C=C double bond are also observed.

Conclusions

The DRIFT studies of ethane and propane adsorption over mixed oxide supported vanadia catalysts reveal various surface oxygenate species. Formation of ethoxide and isopropoxide at relatively low adsorption temperature suggest that ethane and propane are adsorbed through the formation of an alkoxide species, which further oxidizes to other surface oxygenated species. The formation of cyclic anhydride, a precursor for CO + CO_2, is suppressed by the presence of surface vanadia species.

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Tungsten Oxide Promotion of SCR of NO_x with NH_3 by Titania-Supported Vanadium Oxide Catalysts

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Introduction

The Selective Catalytic Reduction (SCR) of NO_x with NH_3 by titania-supported vanadium oxide catalysts is promoted by the tungsten oxide promoter. The tungsten oxide promotion mechanisms, however, are not fully understood.

Experimental

The catalysts were synthesized by incipient-wetness impregnation of aqueous ammonium metavanadate and ammonium metatungstate solutions onto a TiO_2 support (Evonik (Degussa), P-25, ~60m^2/g, ~80% anatase). The catalysts were dried at 110^{o}C and then calcined at 500^{o}C to form the oxide forms. The catalysts were also hydrothermally aged to examine the effect of tungsten oxide on the thermal stability of the titania-supported vanadium oxide catalysts. The catalysts were characterized with both *in situ* Raman spectroscopy and BET surface area measurements, and tested for steady-state SCR activity.

Results and discussion

In situ Raman spectroscopy revealed that the supported vanadium and tungsten oxide phases were present as mono-oxo surface VO_4 and WO_5 species on the TiO_2 support and that the surface VO_4 species polymerized in the presence of surface WO_5. Although the surface WO_5 sites were not active for SCR, the formation of high local concentrations of polymeric surface VO_4 sites in the presence of surface WO_5 sites correlates with the enhanced SCR activity that increased with surface WO_5 coverage.

The surface tungsten oxide promoter also has a dramatic effect on the hydrothermal stability of the titania-supported vanadium oxide catalysts. Without promotion of surface WO_5, the BET surface area of the titania-supported vanadium oxide catalysts collapsed and TiO_2 (anatase) transformed to TiO_2 (rutile). Addition of low amounts of tungsten oxide to the catalyst (~1% WO_3) retarded these structural changes, but addition of high concentrations of tungsten oxide to the catalyst (~8% WO_3) completely prevented the loss in BET and transformation of TiO_2 (anatase) to TiO_2 (rutile). The absence of low BET surface areas and transformation of TiO_2 (anatase) to TiO_2 (rutile) resulted in highly active SCR catalysts.

Conclusions

The molecular level promotion mechanisms of tungsten oxide upon titania-supported vanadium oxide SCR catalysts have finally been elucidated.

Acknowledgements

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V_2O_5 catalyst one-pot multicomponent synthesis of 5-hydroxy-3- methyl 4,5-dihydro-1H-4-pyrazol-4-ylpropan-2-one

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Introduction

The synthetic strategy employed for the synthesis of 4- alkyl-1*H*-pyrazoles includes condensation of hydrazines with 1,3-dicarbonyl compounds and b-oxodithioesters, [2+3] cycloaddition of 1,3-dipolar diazo compounds with alkenes and alkynes, reactions of hydrazones with nitro olefins. In recent years several Michael addition strategies have been proposed.[1-2]

Experimental

A reactant mixture of the 4-benzyloxy-3-methoxybenzaldehyde (1.0 mmol), 4-bromoacetophenone (1 mmol), 3-methyl-1H-pyrazol-5(4H) one was stirred in presence of V_2O_5 at room temperature. Solid products were formed and all the compounds were purified from column chromatography using silica gel 60-120 mesh and checked by thin layer chromatography

Results and discussion

We have synthesized a set of multi-substituted 5-hydroxy-3-methyl 4,5-dihydro-1H- 4-pyrazol-4-ylpropan-2-one from of 4-bromoacetophenone, 4-benzyloxy-3- methoxybenzaldehyde and 3-methyl-1H-pyrazol-5(4H)one in the presence of vanadium oxide as catalyst in one-pot four component method at room temperature. The present synthetic protocol provides several advantages like simplicity of operation, wide range of products, excellent yields, short reaction times, low temperature and easy work up which resulted in higher atom economy. The synthesized compounds were confirmed by FT-IR, 1D and 2D NMR spectroscopic techniques maybe wrapped around Tables and Figures

Conclusions

In summary, we have developed novel series of 5-hydroxy-3-methyl 4,5-dihydro-1H- 4-pyrazol-4-ylpropan-2-on derivatives using V_2O_5 catalyst. This procedure is solvent less condition, high yields, easy method and the eco-friendliness.

Acknowledgements

Authors are thanks to Madurai Kamarajar University for facility of NMR instrumentation.

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Insight into the interaction of calcium species with mesoporous silica and niobiosilica

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Introduction

Market demand and legislation are the driving force behind development of fuels alternative to fossil ones. Although they can be obtained using the homogeneous basic catalysts such as sodium or potassium hydroxide, the heterogenization of catalytic systems is desirable and welcome. In this work we examine the solid materials of SBA-15 type also containing niobium and having a relatively high content of calcium (up to 40 wt%) and stable mesoporous structure.

Experimental

SBA-15 and NbSBA-15 materials were prepared via standard hydrothermal synthesis previously described in [1]. Calcium species were incorporated by impregnation with aqueous solution of calcium acetate monohydrate or calcium nitrate tetrahydrate. The amount of Ca in final materials was 20 wt% and 40 wt%. Sample were calcined at 973 K for 5h. Materials obtained were characterized using: XRD, N_2 adsorption/desorption, XRF, FTIR and UV-Vis. The basicity of materials was tested in cyclisation and dehydration of 2,5-hexanedione at 623 K.

Results and discussion

XRD and N_2 adsorption/desorption measurements confirmed typical mesoporous structure of starting materials, i.e. SBA-15 and NbSBA-15 (2 wt% of Nb). The impregnation of mesoporous supports with calcium salts resulted in a decrease in surface area and pore volume in the final material. These changes depended on the kind of calcium salts and were smaller for calcium acetate monohydrate. Nevertheless when calcium nitrate tetrahydrate (40 wt% of Ca) was used for SBA-15 modification the mesoporous structure was not observed anymore. This was not the case of NbSBA-15 support, which structure was preserved after calcium incorporation. The UV-Vis measurements indicated that niobium species were present on NbSBA-15 surface as tetra- and penta-coordinated niobium species. The intensity of bands related to over-mentioned species increases after Ca incorporation suggesting the possible interaction of calcium with niobium species. Moreover, the FTIR measurements pointed on the participation of silanol/metal hydroxyl groups in the interaction with calcium species.

Conclusions

The impregnation of SBA-15 with calcium salts strongly influenced the textural parameters of mesoporous support. The calcium acetate led to smaller textural changes, whereas calcium nitrate (40 wt% of Ca) caused the destruction of SBA-15 structure. The incorporation of niobium into SBA-15 during the synthesis of mesoporous solid allowed preservation of the structure of the support.

Acknowledgements

We are grateful to the National Science Center in Poland for support (project no. 2014/15/B/ST5/00167).

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P-8

Comparative study of basic oxygen formed on MCF impregnated with niobium and cerium species – NO as a probe molecule

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Introduction

This contribution is focused on the properties of oxygens coming from cerium and niobium oxides loaded on the mesoporous cellular foam MCF. The choice of metal oxides was dictated by the differences in their properties. Oxygen ions in CeO_2 are mobile compared with the Ce cations that determine basic/redox properties of ceria [1], whereas niobium(V) oxide is known as acidic metal oxide. NO was adsorbed for estimation of basicity of oxygen ions in metal oxides.

Experimental

MCF was modified by impregnation with cerium and niobium sources separately (10 and 13,6 wt % of metal loading, respectively) towards Ce/MCF and Nb/MCF or both metal species in one pot (CeNb/MCF). The samples were characterized by XRD, N_2 ads./des., UV-Vis, XPS. FTIR and EPR studies were performed after NO adsorption.

Results and discussion

Two metal oxides loaded on MCF material were located in different positions of the mesoporous structure. Niobium was included into the silica matrix, whereas cerium was placed as crystalline CeO_2 in the cells of MCF. The location and chemical properties of both types of metal oxides influenced the properties of oxygen ions. Basicity of theses ions was estimated by NO adsorption followed by FTIR and EPR study. After NO adsorption on Nb/MCF activated in the vacuum cell, two kinds of species were detected; NO chemisorbed on niobium cations (Lewis acid sites giving a broad band between 1800-1900 cm^{-1}) which was a consequence of Nb inclusion into the silica skeleton, as discussed in [2], and nitrate species (1500-1700 cm^{-1} range) characteristic of samples containing negatively charged oxygens (Fig.1). Cerium modified MCF showed properties typical of CeO_2, i.e. NO was chemisorbed in oxygen defect holes (concluded from EPR) and formed NO_2 (IR band at ca 1600 cm^{-1}) and nitrite species (1300–1200 cm^{-1}). Nitrate species were generated by heating at 473 K. Interestingly, all above mentioned species were observed on CeNb/MCF material. The properties of oxygen will be discussed in detail.

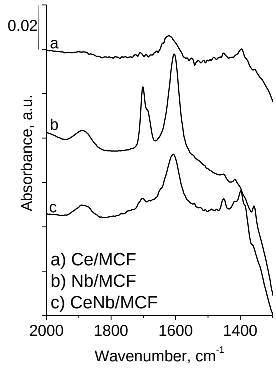

Fig 1. FTIR spectra after NO adsorption at RT.

Conclusions

NO adsorption followed by FTIR and EPR study appeared to be a useful tool for differentiation of acidic- basic properties of different metal oxides. The fundamental differences in these properties between cerium and niobium oxides were proved.

Acknowledgements
We are grateful to the National Science Center in Poland for support (project no. 2014/15/B/ST5/00167).

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Modification of APTMS-Nb/MCF basicity by gold and copper dopants

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Introduction

Our recent papers [e.g. 1] showed that Nb modified mesoporous silicas used as supports for APTMS were attractive in Knoevenagel condensations. In this work we considered the role of additional dopants, Au and Cu, on surface properties and catalytic activity.

Experimental

MCF material was impregnated with niobium source (1 wt.%). Both, MCF and Nb/MCF, were functionalized by APTMS (3-aminopropyl-trimethoxysilane) and next gold precursor (APTMS-Au/MCF and APTMS-Au-Nb/MCF) or gold and copper sources (APTMS-AuCu-Nb/MCF) were added. The materials obtained were fully characterized (XRD, N_2 ads./des., XPS, TEM, FTIR and UV-Vis) and tested in Knoevenagel condensation between ethyl cyanoacetate and benzaldehyde, or 2-nitrobenzaldehyde, or 2,4-dichlorobenzaldehyde.

Results and discussion

Dispersion of gold was influenced by the presence of Nb and Cu and changed in the following order: APTMS-Au/MCF > APTMS-Au-Nb/MCF > APTMS-AuCu-Nb/MCF. In the first material gold was present exclusively as metallic particles surrounded by negative charge $(Au^0)^{\delta-}$, whereas a part of negative charge was abstracted by niobium species in the other samples and pure metallic gold dominated in these materials. This behaviour had an impact on catalytic activity in Knoevenagel condensation of 2-nitrobenzaldehyde, or 2,4-dichlorobenzaldehyde but not in the reaction with benzaldehyde. The electron transfer between gold and niobium and/or copper enhanced the activity in the condensation with 2-nitrobenzaldehyde, while the negatively charged gold nanoparticles were promoters in the reaction with 2,4-dichlorobenzene. The detailed characterization of the catalysts allowed us to propose the reaction pathways and relationship between the surface properties and interaction with reagents. These issues will be discussed in the presentation.

Conclusions

Modification of APTMS-Nb/MCF with gold or gold and copper led to the increase in activity in the condensation between ethyl cyanoacetate and 2-nitrobenzaldehyde. Gold dopant in APTMS-Au/MCF enhanced activity in the reaction with 2,4-dichlorobenzene.

Acknowledgements
We are grateful to the National Science Center in Poland for support (project no. 2014/15/B/ST5/00167).

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Synthesis and photo-catalytic behavior of NbB/C nanocomposite

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Keyword: NbC, nanocomposite, photodegradation

Introduction

Research owing to a better harvesting of solar energy in photocatalyst for environmental remediation requires more efforts due to growing pollution issues. Morphology, particle size, electron-hole recombination and vacancies are considered as key parameters for photocatalytic degradation of organic pollutants. Apart from mechanical applications, transition metal carbides have shown photocatalytic activity for the degradation of various organic compounds. In the present work, NbC/C nanocomposite has been synthesized at low temperature as photo-catalyst to study the degradation behavior of methylene blue (MB) dye.

Experimental

Niobium pentoxide (Nb_2O_5, 1.329g), Mg metal powder (2g) and smoked cigarette filters (CGF, 2g) were taken as niobium source, reducing agent and carbon source respectively and charged to specially designed autoclave. The mixture of reactants was heated to desired temperatures (600, 700 and 800°C) at the rate of 5°C/min for different holding times [1]. The as-synthesized black powder was leached with diluted HCl (1:1) and washed several times with distilled H_2O to achieve a neutral solution which is followed by the drying at 120 °C. As synthesized samples were characterized by XRD, TEM, RAMAN, UV-visible, PL spectroscopy, BET and photodegradation.

Results and discussion

The reaction parameters to synthesize NbC were varied to get a variation of carbon content in the lattice of NbC_x. Further, as synthesized nanocomposite samples were used for the degradation of MB dye under solar irradiations. A comparative study of photocatalytic behavior of synthesized samples has been done as an effect of synthesis conditions. CGFs provided the optimized parameters at 800°C for 20h. Such higher temperature and prolonged holding might be associated to the solid state reaction among the reactants. With the help of UV-Vis., photo-luminescence and XPS spectroscopy, sub-stoichiometric carbon content induces vacancies inducing multiple oxidation states of Nb which facilitate the delayed electron-hole recombination process. Due to which degradation of organic MB dye has been observed under solar irradiations. For photo-degradation studies, different reaction parameters have been optimized by CGFs samples and the best conditions were implemented on all the samples. Among all the recorded observations, 1mg/L and 60mg/L were optimized concentration of dye solution and photo-catalyst, respectively. With the increase in the content of lower oxides of Nb in the sample, the photo-catalytic activity is decreased, which may be associated to the presence of different oxidation states of Nb and various organic functional groups.

Conclusions

A single phase NbC sample (20B800) has successfully obtained at 800°C with 20h holding time and this sample has shown better degradation as compared to other studied samples which might be associated to the higher specific surface area and other structural features.

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Niobium Oxide Promotion of Iron Oxide-Based Catalysts for the High Temperature Water-Gas Shift (HT-WGS) Reaction

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Introduction

The Iron Oxide-based catalysts for the High Temperature Water-Gas Shift (HT-WGS) reaction is currently promoted by chromium oxide, but the carcinogenic properties of hexavalent chromium has motivated research for Cr-free catalysts.

Experimental

The catalysts were synthesized by co-precipitation of aqueous Fe-nitrate, Cu-nitrate and Nb-oxalate, initial drying at room temperature, further drying at 110°C and calcination in air at 500°C. The catalysts were characterized with *in situ* Raman spectroscopy during reaction, High Sensitivity Low Energy Ion Scattering (HS-LEIS) and *in situ* BET surface area, and tested for steady-state HT-WGS activity.

Results and discussion

In situ Raman spectroscopy revealed that a partial solid solution of $Fe_{2-x-y}Nb_xCu_yO_3$ (hematite) was present after calcination. HS-LEIS surface analysis with depth profiling indicated that the oxidized Cu and Nb possessed comparable concentrations in the outermost surface layer and in the bulk lattice (no surface enrichment). The Nb promoter significantly increased the catalyst BET surface area (by ~3x).

During the HT-WGS reaction, the bulk mixed oxide hematite catalyst transformed to bulk Fe_3O_4 (magnetite) and Nb_2O_5 nanoparticles. Although it is known from prior studies that the Cu oxide is reduced to metallic Cu nanoparticles, the metallic Cu is not Raman active. HS-LEIS surface analysis with depth profiling revealed that the outermost surface layer (~0.3nm) was enriched with Nb. The intensity of the HS-LEIS signal for Cu markedly decreased due to sintering of the metallic Cu nanoparticles. The Nb promoter still imparted the catalyst during HT-WGS with a higher BET surface area, but the increase was only ~30%.

The Nb promoted supported Cu/iron oxide (magnetite) catalyst, however, exhibited poorer performance for the HT-WGS reaction in spite of its higher BET surface area. There are two possible scenarios for the poorer catalytic performance: (1) some NbOx covers the surface of the metallic Cu particles decreasing CO adsorption or (2) NbOx interferes with migration of active FeOx to the surface of the metallic nanoparticles.

Conclusions

Although Nb promotion of supported Cu/iron oxide increases the BET surface area of Cr-free HT-WGS catalysts, it does not enhance the catalyst performance.

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Mesoporous silicas with different arrangements of pores and containing Nb species as catalyst in the oxidation of selected alcohols

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Introduction

Selective oxidation of alcohols plays an important role in the organic synthesis. Products of the oxidation of primary alcohols are valuable intermediates for the pharmaceutical, fine chemical and agrochemical industry [1]. Catalytic oxidation, where inexpensive and environment-friendly oxidants may be used, is extremely appreciated. Hydrogen peroxide, along with molecular oxygen, seem to be the most ecological oxidants, since they produce only water as a by-product. Mesoporous silicas with their high surface area and ordered arrangement of channels come across as promising supports for oxidation catalysts. In addition, Nb-containing mesoporous molecular sieves have been reported as effective catalysts in many catalytic reactions, among others: liquid and gas phase oxidation, epoxidation, hydrocracking, ethanol dehydration and dehydrogenation or gas phase Beckmann rearrangement [2].

Experimental

Presented studies were focused on the assessment of catalytic activity of mesoporous silicas possessing diverse arrangement of channels and containing Nb species in the oxidation of alcohols with H_2O_2 in moderate temperatures. Thorough characterization of the catalysts' texture and structure was performed by the means of low-temperature nitrogen sorption measurements, as well as XRD and TEM/SEM analysis.

Results and discussion

The influence of the mesoporous matrix structure could be evaluated, since materials with hexagonally or regularly organized mesopores (SBA-15, SBA-16, MCM-41, MCM-48, KIT-5 and KIT-6) were selected as supports for niobium-based catalysts. Moreover, several types of alcohols were chosen for catalytic tests, among others: cyclohexanol, benzyl alcohol, menthol, propan-1-ol, propan-2-ol and 1,2-propanediol. This diversity permitted the differentiation in the catalytic activity of the tested materials with respect both to the catalysts' supports the and chemical structure of the reagents. Furthermore, several reaction conditions were tested (e.g. substrate to oxidant ratios) and different types of solvents were taken under consideration. Attempts to reduce the reaction time by using microwave irradiation were also made.

Conclusions

The oxidation of alcohols is an important reaction in the production of chemicals. Since oxidation processes have long been performed with highly toxic oxidants, the environmental and economic benefits of using H_2O_2, the moderate reaction temperatures and Nb-containing mesoporous silicas as catalysts seem to be worth mentioning.

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Catalytic activities of Nb-containing hierarchical zeolites in the isomerization of trioses

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Introduction

Hierarchical zeolites are a promising class of compounds exhibiting characteristics typical for microporous molecular sieves and mesoporous materials. In contrary to microporous zeolites, application of hierarchical zeolites as catalysts may increase catalytic activity and decrease tendency of the catalyst for deactivation [1-3].

This work focuses on the synthesis of hierarchical zeolites containing niobium and their use as catalysts in the isomerization of dihydroxyacetone (DHA) to lactic acid or alkyl lactates. Lactic acid (LA) is an α-hydroxy carboxylic acid with a chiral center at its second carbon and is widely used in many catalytic productions of green solvents, fuel precursors or fine-chemicals [4].

Experimental

Nb-hierarchical zeolites were used in the reaction of dihydroxyacetone isomerization (DHA) to alkyl lactates and lactic acid: 0.045 DHA, 10 ml of solvent (methanol, ethanol or water) and 0.05 of catalyst were placed in a vessel inside the catalytic reactor. The reaction was carried out at 80°C for 1h using microwave radiation of heating.

Results and discussion

The main obtained reaction products were: lactic acid, alkyl lactates (methyl lactate – ML, ethyl lactate – EL), or pyruvic aldehyde (PAL). Conversion of DHA over synthesized niobium catalysts was 100% and reaches 95-97% yield of conversion to alkyl lactates and lactic acid. The time required to complete the DHA isomerization does not exceed 1 h.

Conclusions

The use of hierarchical zeolites containing niobium allows to carry out a reaction of DHA isomerization with very good selectivity and yield to the desired reaction products: alkyl lactates and lactic acid.

Acknowledgements

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Environmentally Benign niobium chloride catalyst one-pot multicomponent synthesis of spiro[indoline-3,4’-pyrano[2,3- c]pyrazole

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Introduction

In recent days researchers are giving much importance in the synthesis of compounds with spiropyrrolidinyl-oxindole derivatives because of the presence of bioactive moieties.[1-2] Even though an attempt has been made to use 4-DMAP, as a catalyst for the synthesis of spiro[indoline-3,4’-pyrano[2,3-c]pyrazole, search for novel catalyst and methodology that can lead to newer derivatives with better yield under mild conditions continues.

Experimental

Mixture of ethylacetoacetate 1 (1 mmol), 4-methoxyphenylhydrazine 2 (1 mmol), 5-bromoisatin 3 (1 mmol), ethyl cyanoacetate 4 (1 mmol) and niobium chloride 5% (by weight) in EtOH (10 mL) was stirred at room temperature for 3 h. The completion of the reaction is confirmed by using TLC.

Results and discussion

We have synthesized various spiro[indoline-3,4’-pyrano[2,3-c]pyrazole] derivatives from 5-bromo isatin and various phenyl hydrazine derivatives, ethylacetoacetate and /2-bromoacetonitrile/malononitrile/2-hydroxy-1,4-naphthaquionone. Spiro[indoline- 3,4’-pyrano[2,3-c]pyrazole] was synthesized from an equivmolar mixture of 5-bromo satins, bromo acetonitrile, 4-methoxyphenylhydrazine and ethyl acetoacetate by adopting one-pot four-component reaction method **.**

Conclusions

We reported novel and convenient one-pot synthesis of multi-substituted spiro[indoline-3,4’-pyrano[2,3-c]pyrazole] derivatives using four-component reactions. The four component reactions proceeded smoothly and resulted in good to excellent yields. Our one-pot method offers several advantages, including short reaction time, simple experimental procedure and no toxic byproducts. The products are new heterocyclic molecules containing nitrogen, oxygen and two carboxyl groups and they may have potent biological activities.

Acknowledgements
Authors are thanks to Madurai Kamarajar University for facility of NMR instrumentation.

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Tantalum *vs* Niobium MCF nanocatalysts in the green synthesis of chromenes derivatives

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Introduction

In the last decades the development of Nb-containing molecular sieves has underwent a significant progress [1]. Such materials have widely been investigated because of their catalytic properties in the synthesis of valuable products. Our research groups have recently contributed to this reporting new family of bifunctional Nb/MCF silicas for the preparation of relevant heterocyclic systems [2]. However, analogous Ta nanocatalysts have barely been explored. In this sense, we communicate herein a comparative study of the catalytic application of alkali metal modified Nb and Ta/MCF mesoporous silicas for the multicomponent synthesis of 2-amino-4*H*-chromenes, heterocyclic scaffolds of importance because of their therapeutic uses.

Experimental

The synthesis of alkaline metal modified T/MCF (T = Nb or Ta) was performed according to the procedure reported in Refs 2b using Nb or Ta ethoxides as metal sources. The materials were characterized by N_2 adsorption/desorption, XRF, FTIR, UV–vis and test reactions. These catalysts were tested in the reaction between 2-hidroxibenzaldehyde and ethyl cyanoacetate, at 303K, under solvent-free conditions.

Results and discussion

The texture of modified T/MCF significantly changes after modification with alkaline metals towards lower S_{BET} and pore volumes than the unmodified ones. UV-vis spectra for Nb/MCF samples indicated a tetrahedral coordination for Nb, whereas spectra for Ta/MCF series showed a band (257-268 nm), which was shifted depending on the alkaline metal-Ta interactions. Both supports, Nb or Ta/MCF silicas were inactive in the reaction studied. However, modified Ta/MCF led to the corresponding chromenes with increased yields than the Nb/MCF counterparts but maintaining the selectivity toward the most stable isomer (*anty*/*syn* ratio 3:2).

Conclusions

Ta/MCF silicas modified with alkaline metals showed an enhanced catalytic performance than the Nb ones. Our experimental observations suggest a compromise between the metal center and the alkaline cation sizes for the most active catalysts in each series – (Li)Ta/MCF and (Na)Nb/MCF.

Acknowledgements

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Hydrodeoxygenation of Lignin derived Guaiacol over Mo, W and Ta Modified Supported Nickel Catalysts

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Introduction

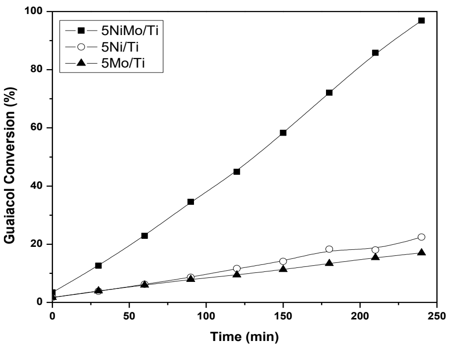
The declining of fossil fuels reserve stimulates the research for the production of energy and chemicals in sustainable manner. Only lignocellulosic biomass has the potential to deliver various forms of energy and chemicals. Lignocellulosic biomass is comprised of cellulose (40-45%), hemicellulose (25-35%) and lignin (15-30%) [1]. The cellulose and hemicellulose have been investigated extensively to produce various valuable chemicals. The complex bio-polymer lignin can be a potential resource for valuable chemicals such as aromatics. Depolymerization of lignin and subsequent processing can produce valuable chemicals [1]. In the present investigation, hydrodeoxygenation (HDO) of lignin derived monomer guaiacol was studied over Mo, W and Ta modified supported nickel catalysts.

Experimental

Several Mo, W and Ta modified nickel catalysts supported on titania (TiO_2, Degussa P25) and alumina (γ-Al_2O_3) were prepared by incipient wetness impregnation method. All the catalysts were characterized by BET, XRD, TPR, TPD, pyridine IR. The HDO of guaiacol was performed in a high pressure and temperature batch reactor.

Results and discussion

Detailed characterization studies revealed presence of dispersed and bulk metal (or oxides) depending on the loading of respective metal oxide. The major products identified were phenol, cresol, anisole, catechol and cyclohexane. Among the modified catalysts, Mo modified nickel catalyst supported on titania showed superior activity and the trend in activity was Mo>W>Ta. The conversion of guaiacol over pure supported nickel and molybdena catalysts was much lower than NiMo catalysts. The increase in combined loading of metals increases the HDO activity. However, the relative increment in HDO activity for higher metals loading NiMo/TiO_2 catalysts (above monolayer coverage) was lower in comparison to low (below monolayer coverage) metal oxides loading. The variation in NiMo ratio and process parameters affects the product distribution. The HDO of guaiacol over bulk metal oxides was also performed and was found not active for HDO reaction.



Conclusions

The Mo modified nickel catalyst showed highest activity. The dispersed metals (or oxide) appears to be more active than respective bulk oxide. The Ni/Mo ratio affects the product distribution.

Acknowledgements
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Author Index

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