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Contents

Articles

Jie Chen, Yue-Sheng Li, Ji-Qian Wu, Ning-Hai Hu

Journal of Molecular Catalysis A: Chemical 232 (2005) 1

Synthesis and styrene polymerization behavior of new titanium complexes Cp*TiCl(OCHRCH₂. NAr)

A series of new titanium complexes Cp*TiCl(OCHRCH₂NAr) has been synthesized and characterized, and is shown to be high active catalysts for the syndiospecific polymerization of styrene.

$$\begin{array}{c|c}
R_1 & R_2 \\
\hline
R_1 & CI & Cp^*
\end{array}$$

$$\begin{array}{c|c}
R_1 & Cp^* \\
\hline
MAO$$
Syndiotactic

Jincheng Mao, Boshun Wan, Fan Wu, Rongliang Wang, Shiwei Lu

Journal of Molecular Catalysis A: Chemical 232 (2005) 9

Reversal of stereochemistry by adding Ti(OⁱPr)₄ in the enantioselective phenylacetylene addition to aldehydes using l-prolinol-backbone ligand

The readily synthesized chiral ligand 1 in combination with $\text{Ti}(Oi\text{Pr})_4$ provided the products with opposite absolute configuration in significant enantiomeric excesses and high yields. The ratio of $\text{Ti}(Oi\text{Pr})_4$ to the ligand had great influence on the enantiomeric excess of the product.

Carlo Carlini, Mario Marchionna, Marilena Noviello, Anna Maria Raspolli Galletti, Glauco Sbrana, Francesco Basile, Angelo Vaccari

Journal of Molecular Catalysis A: Chemical 232 (2005) 13

Guerbet condensation of methanol with *n*-propanol to isobutyl alcohol over heterogeneous bifunctional catalysts based on Mg-Al mixed oxides partially substituted by different metal components

The synthesis of isobutyl alcohol, via the Guerbet condensation of methanol with *n*-propanol, was studied. Bifunctional heterogeneous catalysts based on dehydrogenating/hydrogenating metals (Pd, Rh, Ni or Cu) and basic Mg/Al mixed oxides, obtained from hydrotalcite-type (HT) precursors, were investigated. Co-precipitated systems based on Cu/Mg/Al mixed oxides revealed the best performances, in terms of activity and selectivity.

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Dinesh Bilehal, Raviraj Kulkarni, Sharanappa Nandibewoor

Journal of Molecular Catalysis A: Chemical 232 (2005) 21

Comparative study of the chromium(III) catalysed oxidation of L-leucine and L-isoleucine by alkaline permanganate: A kinetic and mechanistic approach

The following general scheme is proposed for the chromium(III) catalysed oxidation of l-leucine and l-isoleucine (AA) by alkaline permanganate to explore the observed experimental results.

$$\begin{array}{lll} R-CH-COO^{-} + [Cr(OII)_{4}(II_{2}O)_{2}] & \stackrel{K}{=} & Complex (C) \ + \ H_{2}O \\ \\ Complex (C) \ + \ MnO_{4}^{-} & \stackrel{k}{=} & R-\mathring{C}H \ + \ MnO_{4}^{2} \ + [Cr(OH)_{4}(II_{2}O)_{2}]^{-} \ + \ CO_{2} \\ \\ R-\mathring{C}H \ + \ MnO_{4}^{-} \ + OH^{-} & \stackrel{k}{=} & R-CHO \ + \ MnO_{4}^{2} \ + \ NH_{3} \\ \\ NH_{3} & & \\ \end{array}$$

Where R= CH₂-CH Me₂ for L-leucine and R= -CH Me Et for L-Isoleucine

The above scheme leads to the following rate law:

Rate =
$$\frac{kK[MnO_4]^{-} [Cr(III)]_T [AA]_T}{\{1 + K [Cr(III)]_T \} \{1 + K[AA]_T\}}$$

Eleni Heracleous, Maria Machli, Angeliki A. Lemonidou, Iacovos A. Vasalos

Journal of Molecular Catalysis A: Chemical 232 (2005) 29

Oxidative dehydrogenation of ethane and propane over vanadia and molybdena supported catalysts

Vanadia and molybdena catalysts with monolayer coverage supported on alumina and titania were tested for the oxidative dehydrogenation of C_2 – C_3 alkanes to the corresponding alkenes. The support was found to have a great impact on the catalytic performance with titania exhibiting significantly higher reactivity with both alkanes.

$$C_nH_{2n} + O_2 \xrightarrow{k_1} C_nH_{2n-2} \xrightarrow{k_6} k_6$$

Christian Vogl, Eckhard Paetzold, Christine Fischer, Udo Kragl

Journal of Molecular Catalysis A: Chemical 232 (2005) 41

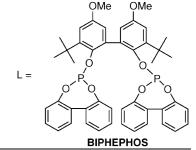
Highly selective hydroformylation of internal and terminal olefins to terminal aldehydes using a rhodium-BIPHEPHOS-catalyst system 2-Pentene was hydroformylated to 1-hexanal with a rhodium-phosphite-ligand-system with high conversion. The catalytic system with the ligand BIPHEPHOS is able to synthesize aldehydes easily from terminal olefins (C_5 – C_{12}) with high TONs and TOFs, and with lower activities from internal olefins, in both cases with high regioselectivities of linear:branched ratio up to 99:1. For 1-dodecene a TOF of $44,000h^{-1}$ was achieved.

$$Rh/L$$

$$R = C_2H_5 - C_9H_{19}$$

$$CO/H_2$$

$$Rh/L$$



Paramasivam Manisankar, Anandhan Gomathi

Journal of Molecular Catalysis A: Chemical 232 (2005) 45

Electrocatalysis of oxygen reduction at polypyrrole modified glassy carbon electrode in anthraquinone solutions

Anthraquinones catalyze the reduction of dioxygen to hydrogen peroxide via two-electron transfer at polypyrrole modified glassy carbon electrode. Mass specific activity of catalysts, diffusion coefficient of oxygen and heterogeneous rate constant for oxygen reduction were determined by voltammetric techniques.

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Hynek Balcar, Naděžda Žilková, Jan Sedláček, Jiří Zedník

Journal of Molecular Catalysis A: Chemical 232 (2005) 53

MCM-41 anchored Schrock catalyst Mo(=CHC Me₂Ph)(=N-2,6-i-Pr₂C₆H₃)[OCMe(CF₃)₂]₂-activity in 1-heptene metathesis and cross-metathesis reactions

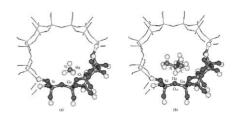
Hybrid catalyst for olefin metathesis was prepared by anchoring Schrock carbene complex on mesoporous molecular sieve MCM-41.

Nan Jiang, Shuping Yuan, Jianguo Wang, Zhangfeng Qin, Haijun Jiao, Yong-Wang Li

Journal of Molecular Catalysis A: Chemical 232 (2005) 59

An ONIOM study of amines adsorption in H-[Ga]MOR

The adsorption of amines (NH₃, MeNH₂, Me₂NH and Me₃N) in two stable bridging oxygen sites (O10H and O2H) in H-[Ga]MOR clusters is investigated by using the ONIOM2 method. All amines are protonated and the formed [HNR₃]⁺ are stabilized by the H-bonds between the negatively charged zeolite oxygen atoms and the hydrogen atoms of the NH and CH bonds in the adsorbates. On the basis of the calculated adsorption energies, it is concluded that the relative basicity of amines follows the order of Me₂NH>Me₃N>-MeNH₂>NH₃. Due to the effect of introduced methyl groups and their different basicity and structures, NH3 prefers to adsorb at the O2H Brønsted site (Fig. a), while Me2NH and Me3N prefer to adsorb at the O10H site (Fig. b), and $MeNH_2$ can be in equilibrium between O_2H and $O_{10}H. \label{eq:constraint}$



Zaihui Fu, Yan Yu, Dulin Yin, Youzhi Xu, Huiping Liu, Huiying Liao, Qiong Xu, Fuqiang Tan, Jing Wang

Journal of Molecular Catalysis A: Chemical 232 (2005) 69

Vapor-phase highly selective O-methylation of catechol with methanol over $ZnCl_2$ modified γ - Al_2O_3 catalysts

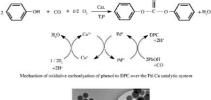
It is firstly discovered that $ZnCl_2$ modified γ - Al_2O_3 ($ZnCl_2/\gamma$ - Al_2O_3) solid Lewis acid catalyst, which is prepared by solid-state reaction, is very active and extremely selective for the preparation of guaiacol by the vapor phase O-methylation of catechol with methanol in a fixed-bed reactor at 553K.

Wei Xue, Jingchang Zhang, Yanji Wang, Qian Zhao, Xinqiang Zhao

Journal of Molecular Catalysis A: Chemical 232 (2005) 77

Effect of promoter copper on the oxidative carbonylation of phenol over the ultrafine embedded catalyst Pd-Cu-O/SiO₂

Effect of promoter copper on the oxidative carbonylation of phenol to diphenyl carbonate (DPC) over the ultrafine embedded catalyst PdCuO/SiO₂ was studied. The promoter copper can be divided into the heterogeneous Cu(II) contained in the catalyst and the homogeneous Cu²⁺ charged into the reactor directly. They influence the activity of the catalyst through different routes.





TEM image of the ultrafine embedded catalyst Pd-Cu-O/SiO,

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Praveen K. Tandon, Sumita Sahgal, Alok K. SinghGayatri, Manisha Purwar

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Oxidation of ketones by ceric perchlorate catalysed by iridium(III)

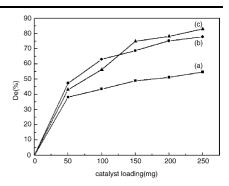
IrCl₃, a sluggish catalyst in alkaline media, surpasses catalytic efficiency of osmium and ruthenium in aqueous perchloric acid medium in the oxidation of aliphatic ketones by ceric perchlorate. Following rate law explains all findings –dCe(IV)dt=2kK₁K₂Ce^{IV}SIr^{III}H⁺1+K₁K₂Ce^{IV}S

Xinshu Niu, Honghua Li, Guoguang Liu

Journal of Molecular Catalysis A: Chemical 232 (2005) 89

Preparation, characterization and photocatalytic properties of REFeO₃ (RE = Sm, Eu, Gd)

Nanometer materials of rare earth mixed oxides $REFeO_3$ (RE=Sm, Eu, Gd) with the structure of perovskite-type were synthesized by the sol-gel method in the citric acid system and characterized by X-ray diffractometer and TEM. These mixed oxides showed high photocatalytic activities in the degradation of various water-soluble dyes.



Fatemeh Rajabi, Babak Karimi

Journal of Molecular Catalysis A: Chemical 232 (2005) 95

Efficient aerobic oxidation of alcohols using a novel combination *N*-hydroxy phthalimide (NHPI) and a recyclable heterogeneous cobalt complex

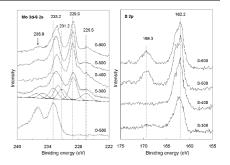
The catalyst can be recovered 5 times

Xueqin Wang, Umit S. Ozkan

Journal of Molecular Catalysis A: Chemical 232 (2005) 101

Effect of pre-treatment conditions on the performance of sulfided Ni–Mo/ γ -Al₂O₃ catalysts for hydrogenation of linear aldehydes

Both of sulfidation and post-sulfidation degassing temperatures can be effectively used to manipulate the surface density of anion vacancy, hydroxyl, and sulfhydryl sites over sulfided Ni–Mo/Al $_2$ O $_3$ catalysts. Sulfidation temperatures in excess of 500°C, lead to the formation of a sulfate phase.



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Babak Karimi, Maryam Khalkhali

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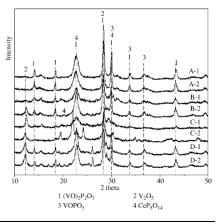
Solid silica-based sulfonic acid as an efficient and recoverable interphase catalyst for selective tetrahydropyranylation of alcohols and phenols Various types of alcohols and phenols are converted to the corresponding tetrahydropyranyl (THP) ether using a catalytic amount of solid silica-based sulfonic acid. The catalyst shows high thermal stability (up to 300°C) and can be recovered and reused for at least eight treaction cycles without loss of reactivity.

Ling Zeng, Huachang Jiang, Junfeng Niu

Journal of Molecular Catalysis A: Chemical 232 (2005) 119

The study of L-VPO catalysts prepared by microwave methods

The L-VPO catalyst with Ce and La prepared by microwave method, showed the best activity with the yield and selectivity of acrylic acid for partial oxidation propane.



Surya K. De, Richard A. Gibbs

Journal of Molecular Catalysis A: Chemical 232 (2005) 123

Vanadyl triflate as an efficient and recyclable catalyst for trimethylsilyl cyanide addition to carbonyl compounds

$$\begin{array}{c|c}
 & \text{a. TMSCN} \\
\hline
 & VO(\text{OTf})_2 \\
 & \text{b. 1 N HCl}
\end{array}$$

L. Lisi, G. Ruoppolo, M.P. Casaletto, P. Galli, M.A. Massucci, P. Patrono, F. Pinzari

Journal of Molecular Catalysis A: Chemical 232 (2005) 127

Vanadium-metal(IV)phosphates as catalysts for the oxidative dehydrogenation of ethane Cubic vanadium-exchanged Ti, Zr, and Sn-pyrophosphates were investigated as catalysts for the oxidative dehydrogenation of ethane. The catalytic activity is proportional to surface vanadium species, V/TiP catalyst providing the best performances due both to the good VO^{2+} exchange capacity and to the high stability. The very good ethylene selectivity, even at quite high conversion, was attributed to the great vanadium site isolation.

$$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$$

X Contents

Susana L.H. Rebelo, Mário M.Q. Simões, M. Graça P.M.S. Neves, Artur M.S. Silva, Pietro Tagliatesta, José A.S. Cavaleiro

Journal of Molecular Catalysis A: Chemical 232 (2005) 135

Oxidation of bicyclic arenes with hydrogen peroxide catalysed by Mn(III) porphyrins

Some Mn(III) porphyrin complexes were evaluated as catalysts in the oxidation of indane and tetralin with H_2O_2 in the presence of ammonium acetate. Catalysis by Mn(III)TDCPPCl gave rise mainly to monooxygenation products, but in over-oxidation conditions, hydroxy-keto compounds were selectively obtained. Catalysis by $Mn(III)TF_5PPCl$ leaded to dehydrogenated products and several studies to understand the reaction pathways were undertaken.

$$(CH_2)_n \xrightarrow{Mn(Porph)Cl} (CH_2)_n \xrightarrow{(CH_2)_n} (CH_2)_n OH$$

Piotr Roszkowski, Krystyna Wojtasiewicz, Andrzej Leniewski, Jan K. Maurin, Tadeusz Lis, Zbigniew Czarnocki

Journal of Molecular Catalysis A: Chemical 232 (2005) 143

Enantioselective synthesis of 1-substituted tetrahydro- β -carboline derivatives via the asymmetric transfer hydrogenation Several 1-substituted-3,4-dihydro- β -carboline derivatives were subjected to asymmetric transfer hydrogenation catalysed by chiral ruthenium complexes to give both enantiomers of 1,2,3,4-tetra-hydro- β -carbolines of high optical purity and in good yields. The absolute stereochemistry of 4c was established on the basis of X-ray analysis of its Moshers amide.

Quinten Knijnenburg, Andrew D. Horton, Harry van der Heijden, T. Martijn Kooistra, Dennis G.H. Hetterscheid, Jan M.M. Smits, Bas de Bruin, Peter H.M. Budzelaar, Anton W. Gal

Journal of Molecular Catalysis A: Chemical 232 (2005) 151

Olefin hydrogenation using diimine pyridine complexes of Co and Rh

Square-planar cobalt diimine pyridine complexes LCoR are active in the hydrogenation of monosubstituted and disubstituted olefins; sterically more hindered trisubstituted olefins do not react. Intermediate alkyl species of the hydrogenation cycle were detected. The mechanism was further investigated by EPR measurements and DFT calculations.

R. Bisignani, S. Franceschini, O. Piccolo, A. Vaccari

Journal of Molecular Catalysis A: Chemical 232 (2005) 161

The solvent effect in the enantioselective hydrogenation of (*E*)-2-methyl-2-butenoic acid with cinchonidine doped Pd/Al₂O₃

The hydrogenation of (*E*)-2-methyl-2-butenoic acid (tiglic acid), using a commercial 5wt% Pd/ Al₂O₃ (Engelhard) doped with cinchonidine (CD) was investigated in depth to evidence the nature of the interaction CD:acid and the specific role of the solvent polarity on the enantiomeric excess (e.e.). A linear correlation between the dielectric constant of the solvent (ε) and the e.e. was observed, with a decrease in e.e. by increasing ε . The highest enantiomeric excess (e.e.=48%) was obtained with *n*-hexane.

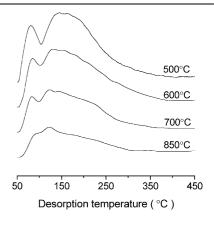
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Guojie Jin, Guanzhong Lu, Yanglong Guo, Yun Guo, Junsong Wang, Weiying Kong, Xiaohui Lin

Journal of Molecular Catalysis A: Chemical 232 (2005) 165

Effect of preparation condition on performance of Ag–MoO₃/ZrO₂ catalyst for direct epoxidation of propylene by molecular oxygen

The $Ag-MoO_3/ZrO_2$ catalyst for an epoxidation of propylene by molecular oxygen was prepared and characterized by N_2 adsorption, XRD, NH₃-TPD and CO_2 -TPD. For the $Ag-MoO_3/ZrO_2$ catalyst, the lower surface area, larger pore size, modest and weaker surface acidity–basicity and suitably larger particle size of Ag are in favor of the formation of propylene oxide, which can be controlled by optimizing the preparation conditions of the ZrO_2 support and catalyst.



Oxana A. Kholdeeva, Tatiana A. Trubitsina, Maria N. Timofeeva, Gennadii M. Maksimov, Raisa I. Maksimovskaya, Vladimir A. Rogov

Journal of Molecular Catalysis A: Chemical 232 (2005) 173

The role of protons in cyclohexene oxidation with H_2O_2 catalysed by Ti(IV)-monosubstituted Keggin polyoxometalate

Heteropolyacid $H_5PTiW_{11}O_{40}$ and its acid sodium salts $Na_{5-n}H_nPTiW_{11}O_{40}$ (n=2-4) catalyse efficiently cyclohexene oxidation by aqueous H_2O_2 in acetonitrile via heterolytic oxygen-transfer mechanism to yield *trans*-cyclohexane-1,2-diol. The diprotonated peroxotitanium species $[H_2PTi(O_2)W_{11}O_{39}]^{3-}$ is suggested as an active intermediate responsible for this reaction.

$$\begin{array}{c|c} & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

M.M. Diwakar, R.M. Deshpande, R.V. Chaudhari

Journal of Molecular Catalysis A: Chemical 232 (2005) 179

Hydroformylation of 1-hexene using Rh/TPPTS complex exchanged on anion exchange resin: kinetic studies

$$\begin{array}{c|c} & & & \\ \hline \\ L \\ H \\ \hline \\ CO \\ \\ L \\ \hline \\ R \\ \hline \\ Resin \\ \\ R \\ \hline \\ Resin \\ \\ Re$$

Ian D. Cunningham, Khatereh Fassihi

Journal of Molecular Catalysis A: Chemical 232 (2005) 187

Kinetics and mechanism of methyl acrylate homoand co-polymerisation catalysed by cyclopentadienyltitanium trichloride–MAO $CpTiCl_3$ -MAO catalysed polymerisation and co-polymerisation of methyl acrylate and styrene occurs via insertion of an O-complexed monomer into a η^3 enolate-Ti growing polymer chain. For the co-polymerisation a balance between the complexation ability of styrene and the insertion ability of methyl acrylate results in a 1:1 co-polymer.

$$\begin{array}{c} R \\ \bigcirc OMe \\ \hline T_1^{+} \bigcirc O \\ \hline C_p \end{array} \begin{array}{c} CO_2Me \\ \bigcirc OMe \\ \hline OMe \\ \bigcirc C_p \end{array} \begin{array}{c} R \\ \bigcirc OMe \\ \bigcirc OMe \\ \bigcirc C_p \end{array}$$