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JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Contents

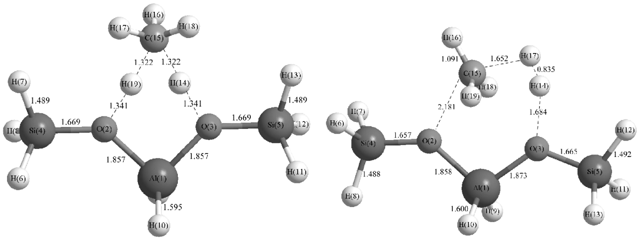
Articles

Xiaobo Zheng, Paul Blowers

Journal of Molecular Catalysis A: Chemical 246 (2006) 1

A computational study of methane catalytic reactions on zeolites

In this work, zeolite catalyzed methane hydrogen exchange and dehydrogenation reactions are investigated using Density Functional Theory and ab initio methods. Applying the cluster approach method, the activation barriers for each reaction are calculated and the reaction rate constants are estimated using Transition State Theory. Additionally, zeolite acidity effects on activation barriers are discussed. We find good agreement with experimental results and can also extrapolate the results to other zeolites using the zeolite acidity effect.

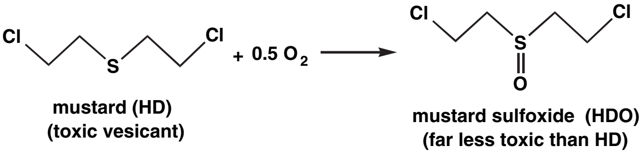


Nelya M. Okun, James C. Tarr, Daniel A. Hilleshiem, Lei Zhang, Kenneth I. Hardcastle, Craig L. Hill

Journal of Molecular Catalysis A: Chemical 246 (2006) 11

Highly reactive catalysts for aerobic thioether oxidation

The Fe-substituted ployoxometalate/hydrogen dinitrate system

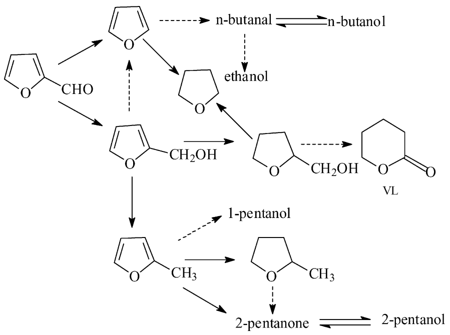


Hong-Yan Zheng, Yu-Lei Zhu, Bo-Tao Teng, Zong-Qing Bai, Cheng-Hua Zhang, Hong-Wei Xiang, Yong-Wang Li

Journal of Molecular Catalysis A: Chemical 246 (2006) 18

Towards understanding the reaction pathway in vapour phase hydrogenation of furfural to 2-methylfuran

Based on the results of this work and other literature, a new reaction pathway for furfural hydrogenation is proposed. This work has unified some conflicting mechanisms and discussed the origin of some interesting products, which is important to understand the mechanism and reaction pathway of furfural hydrogenation, and to provide an instruction for the design of new catalytic formulations.



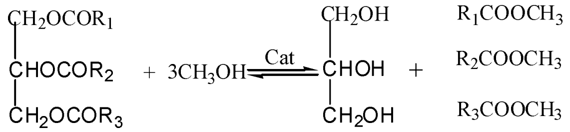
doi:10.1016/S1381-1169(05)00831-9

Wenlei Xie, Hong Peng, Ligong Chen

Journal of Molecular Catalysis A: Chemical 246 (2006) 24

Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil

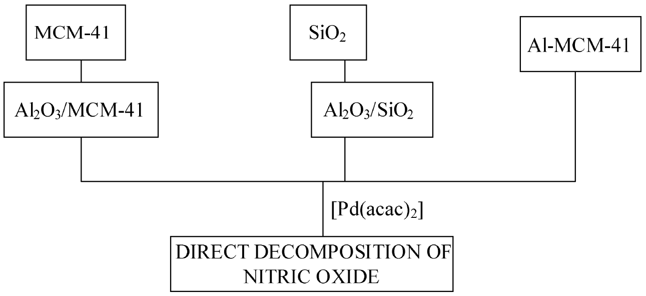
Biodiesel can be produced by methanolysis of soybean oil to methyl esters using calcined Mg–Al hydrotalcite as a solid base catalyst in a heterogeneous manner.



Julia María Díaz Cónsul, Carlos Alexandre Peralta, Edilson Valmir Benvenutti, Juan A.C. Ruiz, Heloise O. Pastore, Ione Maluf Baibich

Journal of Molecular Catalysis A: Chemical 246 (2006) 33

Direct decomposition of nitric oxide on alumina-modified amorphous and mesoporous silica-supported palladium catalysts

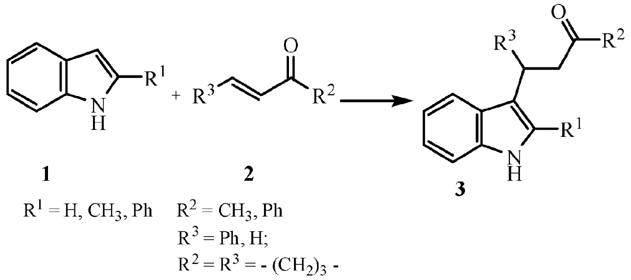


Rachid Tahir, Klaus Banert, Abderrahim Solhy, Saïd Sebti

Journal of Molecular Catalysis A: Chemical 246 (2006) 39

Zinc bromide supported on hydroxyapatite as a new and efficient solid catalyst for Michael addition of indoles to electron-deficient olefins

The synthesis of 3-substituted indoles was carried out in presence of zinc bromide supported on hydroxyapatite. The substitution on the indole nucleus occurred exclusively at the 3-position and *N*-alkylation products have not been observed. The results obtained in this reaction demonstrate the potential application of hydroxyapatite as inorganic macroligand for Lewis acid catalyst.

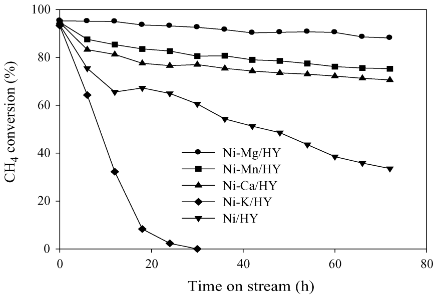


Heondo Jeong, Kweon Ill Kim, Dongsik Kim, In Kyu Song

Journal of Molecular Catalysis A: Chemical 246 (2006) 43

Effect of promoters in the methane reforming with carbon dioxide to synthesis gas over Ni/HY catalysts

Methane reforming with carbon dioxide to synthesis gas was investigated over a series of Ni/HY catalysts promoted by Mg, Mn, K, and Ca. Among the catalysts tested, the Ni-Mg/HY catalyst showed the highest carbon resistance and the most stable catalytic performance.

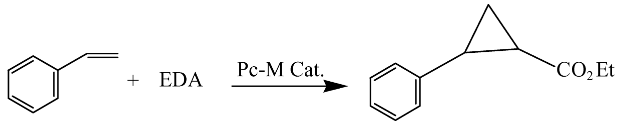


Hui-Hua Liu, Yi Wang, Yuan-Jie Shu, Xiang-Ge Zhou, Jiang Wu, Sheng-Yong Yan

Journal of Molecular Catalysis A: Chemical 246 (2006) 49

Cyclopropanation of alkenes catalyzed by metallophthalocyanines

Metallophthalocyanines bearing substituents especially electron-withdrawing substituents are found to be efficient catalysts for cyclopropanation of alkenes with EDA. The influences of reaction conditions have been studied, leading to the highest yield of 91% for styrene by using fluoro-substituted ruthenium–phthalocyanine complex.

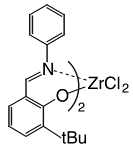


Dongbing Liu, Shibo Wang, Hongtao Wang, Wei Chen

Journal of Molecular Catalysis A: Chemical 246 (2006) 53

Trialkylaluminums: Efficient cocatalysts for bis(phenoxy-imine)zirconium complexes in ethylene polymerization

Trialkylaluminums such as triethylaluminum (Et_3Al), trihexylaluminum (He_3Al), or trimethylaluminum (Me_3Al) could be efficient cocatalysts to activate bis(phenoxy-imine)Zr complexes, for highly active ethylene polymerization.



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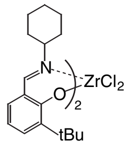


2

Gábor Rangits, László Kollár

Journal of Molecular Catalysis A: Chemical 246 (2006) 59

Palladium catalysed hydroethoxycarbonylation in imidazolium-based ionic liquids

Imidazolium-based ionic liquids with $[PF_6]^-$, $[BF_4]^-$ and $[GaCl_4]^-$ counterions have been synthesised and used in palladium catalysed hydroethoxycarbonylation of styrene.

$PhCH{=}CH_2$

[R—MIM][X] ↓ CO, EtOH

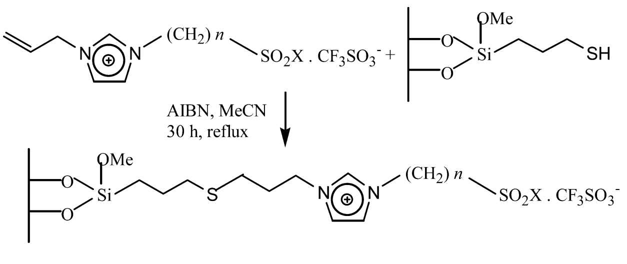
$PhCH(COOEt)CH_3$
+
$PhCH_2CH_2COOEt$

Kun Qiao, Hisahiro Hagiwara, Chiaki Yokoyama

Journal of Molecular Catalysis A: Chemical 246 (2006) 65

Acidic ionic liquid modified silica gel as novel solid catalysts for esterification and nitration reactions

Covalent bond immobilized ionic liquids are prepared via radical chain transfer reaction of 1-allylimidazolium based ionic liquids on modified silica gel and proved to be recyclable heterogeneous acidic catalysts for esterification and nitration reaction.



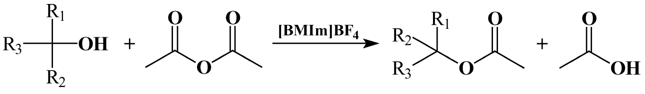
3a. $n = 3$, X = OH, **3b**. $n = 4$, X = OH
4a. $n = 3$, X = Cl, **4b**. $n = 4$, X = Cl

Zhiying Duan, Yanlong Gu, Youquan Deng

Journal of Molecular Catalysis A: Chemical 246 (2006) 70

Neutral ionic liquid $[BMIm]BF_4$ promoted highly selective esterification of tertiary alcohols by acetic anhydride

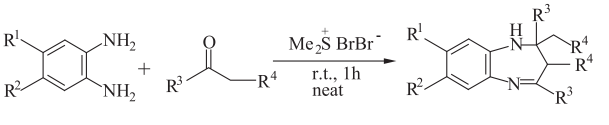
Esterification of *tert*-butanol by acetic anhydride, a typical acid–base catalytic reaction, was conducted with excellent selectivity and high yield in a neutral ionic liquid $[BMIm]BF_4$ (1-butyl-3-methylimidazolium tetrafluoroborate). Many other tertiary alcohols could also be successfully converted to the corresponding esters in $[BMIm]BF_4$. Separation of product and recovery and reuse of ionic liquid are all convenient in this system. Here, the need for catalysts is avoided through the use of catalytically active ionic liquids as solvents.



Biswanath Das, R. Ramu, B. Ravikanth, V. Saidi Reddy

Journal of Molecular Catalysis A: Chemical 246 (2006) 76

(Bromodimethyl) sulfonium bromide: An efficient catalyst for solvent-free synthesis of 1,5-benzodiazepines



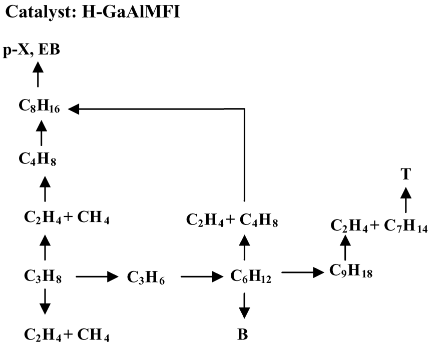
1 **2** **3**

T.V. Choudhary, A. Kinage, S. Banerjee, V.R. Choudhary

Journal of Molecular Catalysis A: Chemical 246 (2006) 79

Influence of space velocity on product selectivity and distribution of aromatics in propane aromatization over H-GaAlMFI zeolite

Aromatization of propane has been investigated over H-GaAlMFI zeolite at different space velocities (1500–49,000 cm3/g/h) in the temperature range of 450–600 °C. A simplified reaction pathway for the propane aromatization reaction over H-GaAlMFI was proposed based on the observed product distribution.

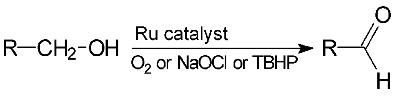


A. Kückritz, M. Sebek, A. Dittmar, J. Radnik, A. Brückner, U. Bentrup, M.-M. Pohl, H. Hugl, W. Mägerlein

Journal of Molecular Catalysis A: Chemical 246 (2006) 85

Ru-catalyzed oxidation of primary alcohols

Primary alcohols were transfered into the corresponding aldehydes by catalytic oxidation with heterogeneous ruthenium catalysts, such as Ru(III) and Ru(0) species deposited on titania and zirconia supports by wet chemical and plasmachemical methods. Molecular oxygen, bleach and *tert*-butyl hydroperoxide were used as oxidants. The dispersion of the catalytically active centres influenced significantly the catalytic activity in the oxidation with molecular oxygen.

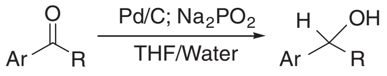


Amadeu F. Brigas, Custódia S.C. Fonseca, Robert A.W. Johnstone

Journal of Molecular Catalysis A: Chemical 246 (2006) 100

Metal-assisted reactions, Part 31 [1]: Adsorption isotherms and selective catalytic transfer reduction of aldehydes and ketones

Carbonyl group in aromatic aldehydes and ketones was reduced using Pd/C as a catalyst and sodium phosphinate as a hydrogen donor in THF/water solvent system (see Scheme 1). The adsorption isotherms measured provide fundamental information on the competitive adsorption of aldehydes and solvent molecules at sites on the catalyst surface. These results allowed discovering an excellent solvent system for these reductions.



A. Fuerte, A. Corma, M. Iglesias, E. Morales, F. Sánchez

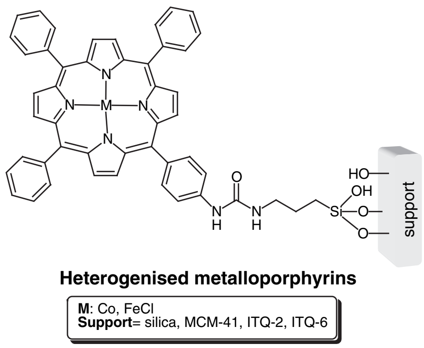
Journal of Molecular Catalysis A: Chemical 246 (2006) 109

Approaches to the synthesis of heterogenised metalloporphyrins

Application of new materials as electrocatalysts for oxygen reduction

A new general method to heterogenise porphyrins and different metalloporphyrins (Co, Fe) on inorganic supports, such as silica, mesoporous MCM-41 and delaminated zeolites ITQ-2 and ITQ-6, yields stable materials, which act as active catalysts for the electrochemical oxygen reduction, without catalyst desorption from the electrode or deactivation.

Pictogram

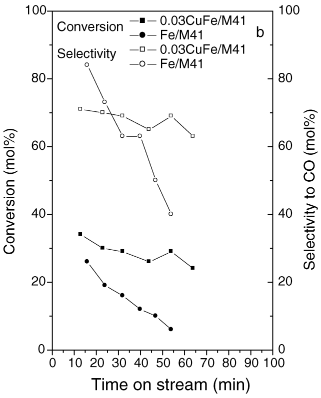


Tanya Tsoncheva, Sami Areva, Momtchil Dimitrov, Daniela Paneva, Ivan Mitov, Mika Linden, Christo Minchev

Journal of Molecular Catalysis A: Chemical 246 (2006) 118

MCM-41 silica modified with copper and iron oxides as catalysts for methanol decomposition

Addition of very small amounts of Cu to Fe supported on MCM-41 materials (0.03CuFe/M41) leads not only to substantial increase and stabilization of the catalytic activity in methanol decomposition, but also to a decrease in the methane selectivity. The formation of iron and copper complex catalytic active center, including Fe(III) and Cu(II) species in various ratio is assumed.

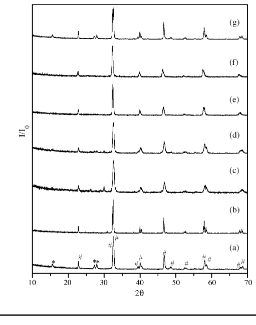


M.R. Pai, B.N. Wani, B. Sreedhar, S. Singh, N.M Gupta

Journal of Molecular Catalysis A: Chemical 246 (2006) 128

Catalytic and redox properties of nano-sized $La_{0.8}Sr_{0.2}Mn_{1-x}Fe_xO_{3-\delta}$ mixed oxides synthesized by different routes

The $La_{0.8}Sr_{0.2}Mn_{1-x}Fe_xO_{3-\delta}$ (LSMF) samples of perovskite-type structure, with the value of x ranging from 0 to 1.0 were synthesized by using two different methods, viz. nitrate and solid-state routes, and by calcining at different temperatures. Efforts were directed to identify the microstructural and morphological properties responsible to the substitution-induced modification in catalytic behavior of these materials. The XRD studies showed that the incorporation of iron resulted in single-phase samples of orthorhombic symmetry instead of the rhombohedral symmetry of the parent perovskite LSM phase. The Mössbauer spectra revealed that iron existed in trivalent state but in three distinctive coordinative environments. At one of these sites iron was found to be paramagnetic in nature and the concentration of these species decreased with the increasing iron content. On the other hand, XPS results revealed that the valence state of 'B' site cations Fe and Mn was different at the surface of the sample as compared to the bulk. No significant segregation of an individual metal was noticed at the surface layer. At the same time, the particles of Fe-containing samples were smaller in size as compared to LSM and it was found to have a direct impact on the lowered reduction temperature and the enhanced catalytic activity of LSMF samples. The results of our study reveal that in addition to the oxygen ion vacancies generated in the lattice due to multiple oxidation states of 'B' site cations, the subtle changes in particle morphology may also play an important role in deciding the catalytic behavior of the LSMF perovskites.

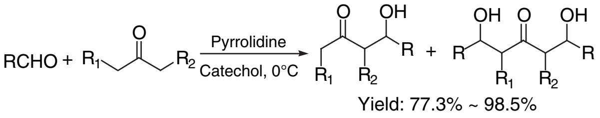


Changyun Ji, Yungui Peng, Chengzhi Huang, Ning Wang, Zhen Luo, Yaozhong Jiang

Journal of Molecular Catalysis A: Chemical 246 (2006) 136

An efficient method for direct aldol reactions catalyzed by pyrrolidine/catechol

The combination of pyrrolidine and catechol are very efficient for catalyzing the direct aldol reaction to proceeding under mild conditions with high yield in short time.

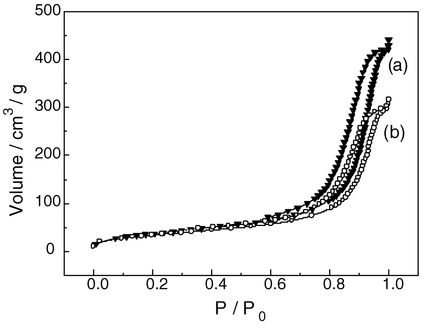


Lei Zhao, Jixiang Chen, Jiyan Zhang

Journal of Molecular Catalysis A: Chemical 246 (2006) 140

Deactivation of Ni/K_2O-La_2O_3-SiO_2 catalyst in hydrogenation of *m*-dinitrobenzene to *m*-phenylenediamine

Deactivation of Ni/K_2O-La_2O_3-SiO_2 catalyst in hydrogenation of *m*-dinitrobenzene to *m*-phenylenediamine was systematically investigated by means of N_2 adsorption–desorption, XRD, TGA/DTA, SEM and AAS. The main reasons for the catalyst deactivation were the surface coverage and the pore blockage with bulky molecular species.

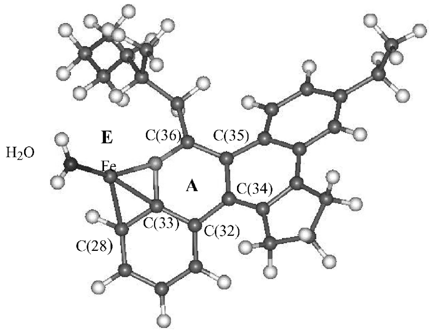


Sergio Rosales, Iván Machín, Morella Sánchez, Guaicaipuro Rivas, Fernando Ruette

Journal of Molecular Catalysis A: Chemical 246 (2006) 146

Theoretical modeling of molecular interactions of iron with asphaltenes from heavy crude oil

Adsorption mode of Fe on site E of asphaltene fragment F1. Final location of water molecule and Fe after interaction with H_2O–[F1–Fe]0. Note that Fe was initially on site A.

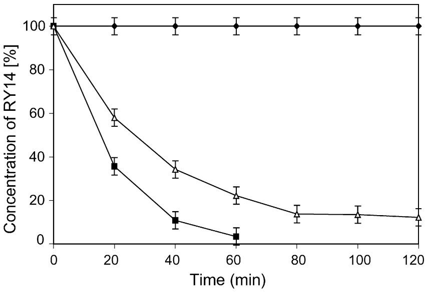


M. Muruganandham, N. Shobana, M. Swaminathan

Journal of Molecular Catalysis A: Chemical 246 (2006) 154

Optimization of solar photocatalytic degradation conditions of Reactive Yellow 14 azo dye in aqueous TiO_2

The photocatalytic degradation of Reactive Yellow 14 azo dye has been carried out using solar light. The effects of various experimental parameters on decolourisation and degradation have been investigated to find out optimum conditions. The decolourisation and degradation kinetics follow the Langmuir kinetic model. The effect of electron acceptors and dye assisting chemicals on photooxidation was investigated and a plausible mechanism was proposed.

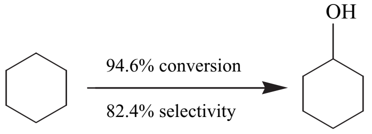


Wenhua Yao, Yongjuan Chen, Liang Min, Hua Fang, Zhiyin Yan, Honglin Wang, Jiaqiang Wang

Journal of Molecular Catalysis A: Chemical 246 (2006) 162

Liquid oxidation of cyclohexane to cyclohexanol over cerium-doped MCM-41

Ce-MCM-41 presented high substrate conversion and good product (cyclohexanol) selectivity for the oxidation of the cyclohexane under relatively mild reaction conditions in acetic acid using aqueous hydrogen peroxide as oxidant without adding any initiator. The catalyst can be reused once without losing the activity.



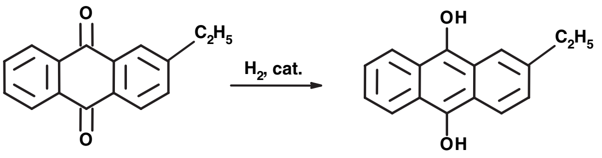
Reagents and conditions: substrate / oxidant =0.77;
Ce-MCM-41catalyst

Alicja Drelinkiewicz, Anna Waksmundzka-Góra

Journal of Molecular Catalysis A: Chemical 246 (2006) 167

Investigation of 2-ethylanthraquinone degradation on palladium catalysts

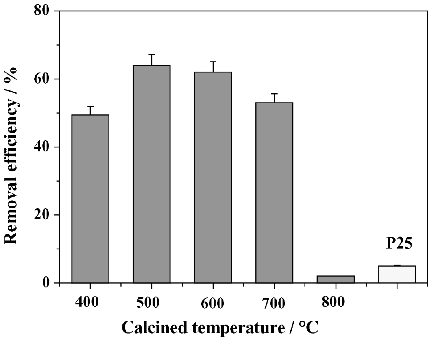
A role of the type of catalyst (Pd/Al_2O_3, Pd/SiO_2, Pd/C) in degradation process during the catalytic hydrogenation of 2-ethylanthraquinone (eAQ) is examined. Degradation of eAQ in the catalytic experiments has been discussed on the basis of reaction pattern for the reduction of C–O in anthraquinone by standard procedures (Zn, Sn, $NaBH_4$). By-products formed by tautomerization of hydroquinones (OXO-isomers), hydrogenolytic cleavage of C–O (2-ethylanthrone and derivatives, 2-ethylanthracene) and intermediate product (2-ethyl-9,10-dihydroxy-9,10-dihydroanthraquinone), precursor of 2-ethylanthrone are identified. Much higher reactivity in the whole degradation process and especially in the formation of intermediate product exhibits Pd/Al_2O_3.



Jiaguo Yu, Minghua Zhou, Bei Cheng, Xiujian Zhao

Journal of Molecular Catalysis A: Chemical 246 (2006) 176

Preparation, characterization and photocatalytic activity of in situ N,S-codoped TiO_2 powders

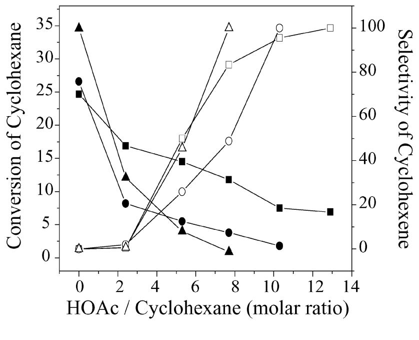


Yu Jun Zhu, Jing Li, Xiao Fan Xie, Xiang Guang Yang, Yue Wu

Journal of Molecular Catalysis A: Chemical 246 (2006) 185

Effect of different $VOPO_4$ phase catalysts on oxidative dehydrogenation of cyclohexane to cyclohexene in acetic acid

α_I-$VOPO_4$, α_{II}-$VOPO_4$ and β-$VOPO_4$ have been investigated as catalysts for the gas phase oxidative dehydrogenation of cyclohexane to cyclohexene with the addition of acetic acid (HOAc) in the feeds. α_I-$VOPO_4$ phase catalyst gives better catalytic performances than α_{II}-$VOPO_4$ and β-$VOPO_4$ in presence of acetic acid due to its higher acidity.

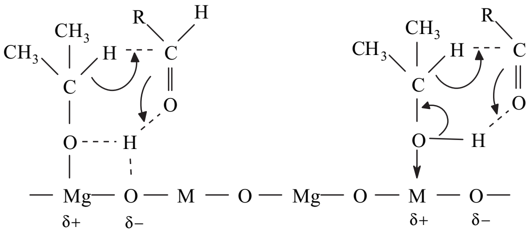


Conversion: ■ α_I-$VOPO_4$, ● α_{II}-$VOPO_4$, ▲ β-$VOPO_4$
Selectivity: □ α_I-$VOPO_4$, ○ α_{II}-$VOPO_4$, Δ β-$VOPO_4$

José R. Ruiz, César Jiménez-Sanchidrián, Julia M. Hidalgo, José M. Marinas

Journal of Molecular Catalysis A: Chemical 246 (2006) 190

Reduction of ketones and aldehydes to alcohols with magnesium–aluminium mixed oxide and 2-propanol

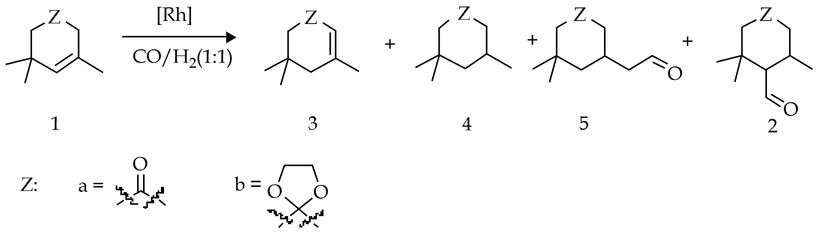


Stefano Paganelli, Federica Battois, Mauro Marchetti, Raffaello Lazzaroni, Roberta Settambolo, Silvia Rocchiccioli

Journal of Molecular Catalysis A: Chemical 246 (2006) 195

Rhodium catalyzed hydroformylation of β-isophorone: An unexpected result

β-Isophorone (**1**) hydroformylation should, in principle, afford aldehyde **2**, a valuable intermediate for the synthesis of the floral woody fragrance δ-Damascone, as the only oxo-product. Surprisingly, when the hydroformylation is carried out in the presence of rhodium carbonyl complexes at 80–120 °C and 100–150 atm of syngas (CO/H_2 = 1) the main oxo-product obtained is the acetaldehyde derivative **5**, while **2** is formed in a smaller amount.

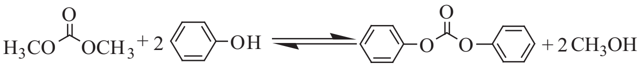


Zhiping Du, Wukui Kang, Tong Cheng, Jie Yao, Gongying Wang

Journal of Molecular Catalysis A: Chemical 246 (2006) 200

Novel catalytic systems containing *n*-BuSn(O)OH for the transesterification of dimethyl carbonate and phenol

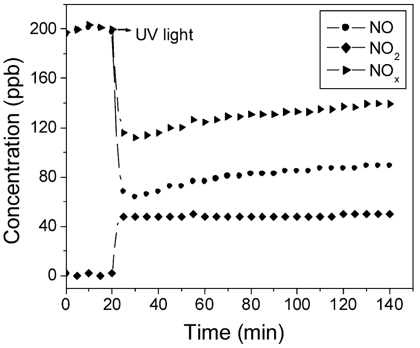
n-BuSn(O)OH and Cu_2O/CuX (X = Cl, Br, I) constituted a highly efficient catalytic system for the transesterification of DMC and phenol. Cu_2O and CuX were demonstrated to be excellent promoters, and the stronger was the anion electronegativity in the promoter, the weaker was its promoting catalysis.



Huogen Yu, S.C. Lee, Jiaguo Yu, C.H. Ao

Journal of Molecular Catalysis A: Chemical 246 (2006) 206

Photocatalytic activity of dispersed TiO_2 particles deposited on glass fibers

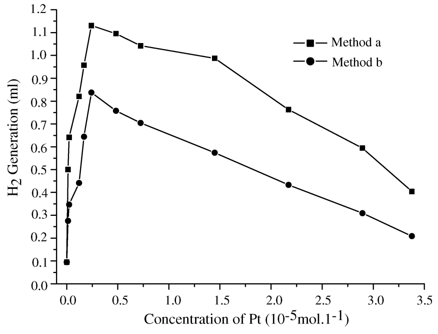


Yuexiang Li, Chunxia Ren, Shaoqin Peng, Gongxuan Lu, Shuben Li

Journal of Molecular Catalysis A: Chemical 246 (2006) 212

Effect of preparation method of colloidal platinum on performance of 12-tungstosilicate for photocatalytic hydrogen generation

Colloidal platinum nanoparticles for hydrogen evolution were prepared using 12-tungstosilicate as photocatalyst by two methods in which photolysis and reduction reaction took place at different time (method 'a') and at the same time (method 'b'), respectively. The rate of the photocatalytic H_2 depends on the number of Pt particles. For method 'b', the keggin structure of 12-tungstosilicate is destroyed.

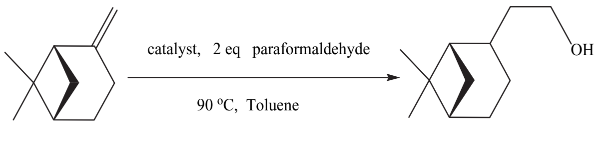


M. Selvaraj, S. Kawi

Journal of Molecular Catalysis A: Chemical 246 (2006) 218

Highly selective synthesis of nopol over mesoporous and microporous solid acid catalysts

A novel mesoporous Zn-Al-MCM-41 is found to be a highly active and recyclable heterogeneous catalyst suitable for the selective synthesis of nopol by Prins condensation of β-pinene and paraformaldehyde in toluene having much higher acidity and activity than other catalysts, such as Al-MCM-41, USY, Hβ, H-ZSM-5 and H-mordenite.

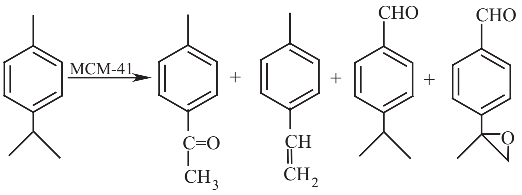


S. Vetrivel, A. Pandurangan

Journal of Molecular Catalysis A: Chemical 246 (2006) 223

Aerial oxidation of *p*-isopropyltoluene over manganese containing mesoporous MCM-41 and Al-MCM-41 molecular sieves

The vapour phase oxidation of *p*-isopropyltoluene with air was carried out over manganese oxide impregnated MCM-41 and Al-MCM-41 gave 4-methylacetophenone, 4-isopropylbenzaldehyde, 1,2-epoxyisopropylbenzaldehyde and 4-methylstyrene as the major products. The structure of MCM-41 catalysts was confirmed by low-angle XRD. The presence of Mn^{2+} in the impregnated catalysts was evident through DRS and ESR studies. The *p*-isopropyltoluene conversion and products selectivity was found to be higher over Mn-MCM-41. The activities of catalysts follow the order Mn-MCM-41 < Mn-AlMCM-41 (99) < Mn-AlMCM-41 (158).

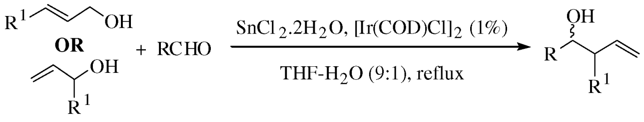


Moloy Banerjee, Sujit Roy

Journal of Molecular Catalysis A: Chemical 246 (2006) 231

Highly efficient Barbier allylation from allyl alcohol using iridium(I)/tin(II): Unusual and indirect roles of allyl alcohol and tin

Facile one-carbon homologation of allyl alcohol to homoallyl alcohol using Ir^{I}–$SnCl_2$ as reagent is described, which might involve the intermediacy of a π-allyl-iridium intermediate.

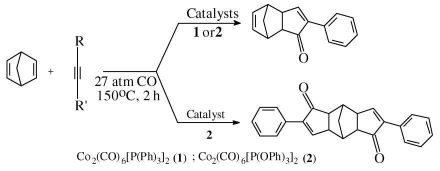


José Luis Arias, Armando Cabrera, Pankaj Sharma, Noe Rosas, Rafael Sampere

Journal of Molecular Catalysis A: Chemical 246 (2006) 237

Stable catalyst for intermolecular Pauson–Khand reaction

Detailed accounts of intermolecular Pauson–Khand reaction catalyzed by two stable $Co_2(CO)_6[P(Ph)_3]_2$ (**1**) and $Co_2(CO)_6[P(OPh)_3]_2$ (**2**) complexes, have been described. The results indicate that these complexes are attractive alternatives to $Co_2(CO)_8$ as catalyst and in addition, complex **2** is an alternative catalyst for double cyclocarbonylation reaction.



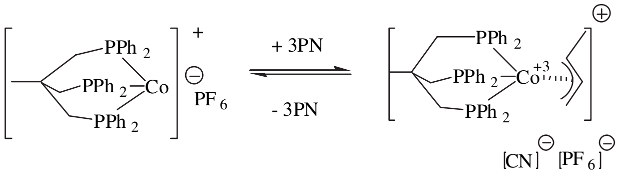
a) R = H; R' = Ph b) R = H; R' = butyl
c) R = methyl; R' = propyl d) R = R' = Ph

Vincent Lecocq, Catherine C. Santini, Yves Chauvin, Jean-Marie Basset, Jean-Christophe Galland

Journal of Molecular Catalysis A: Chemical 246 (2006) 242

Reactivity of 2-methyl-3-butenenitrile in the presence of catalytic amounts of various cobalt complexes in ionic liquid

2M3BN in the presence of catalytic amount of several cobalt complexes was mainly isomerized into 2M2BN due to a easier activation of C–H bond instead of C–CN bond. With 3PN, the first example of a reversible cleavage of the C–CN with complex derived from Co^+ was evidenced.

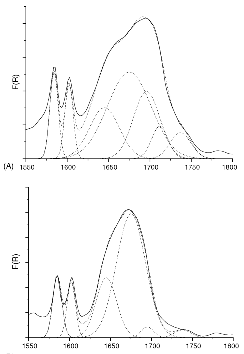


A.G. Potapov, G.D. Bukatov, V.A. Zakharov

Journal of Molecular Catalysis A: Chemical 246 (2006) 248

DRIFT study of internal donors in supported Ziegler–Natta catalysts

DRIFT spectra of carbonyl groups in supported titanium–magnesium ($TiCl_4$/ID/$MgCl_2$) catalysts suggest that internal donors (ethyl benzoate and di-*n*-butyl phtalate) form several different types of surface complexes. The possible nature of these complexes as related to the different Mg ions, to the mode of donor coordination and to the effects of $TiCl_4$ are discussed.



DRIFT spectra of the the EB/$MgCl_2$ sample (A) and $TiCl_4$/EB/$MgCl_2$ catalyst (B) demonstrating effect of $TiCl_4$ on the distribution of EB over $MgCl_2$ surface.

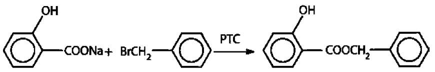
Hung-Ming Yang, Ching Ching Li

Journal of Molecular Catalysis A: Chemical 246 (2006) 255

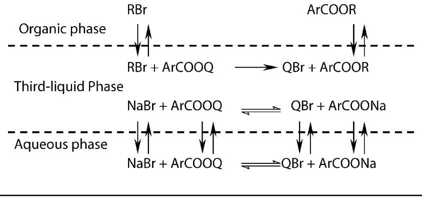
Kinetics for synthesizing benzyl salicylate by third-liquid phase-transfer catalysis

Third-liquid phase-transfer catalyzed esterification of sodium salicylate to synthesize benzyl salicylate:

Reaction mechanism:



Aqueous reactant: sodium salicylate (ArCOONa)
Organic reactant: benzyl bromide (RBr)
Phase-transfer catalyst: tetra-*n*-butylphosphonium bromide, etc. (QBr)
Product: benzyl salicylate (ArCOOR)

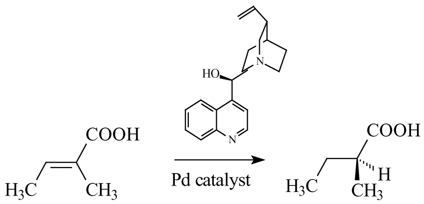


M. Casagrande, S. Franceschini, M. Lenarda, O. Piccolo, A. Vaccari

Journal of Molecular Catalysis A: Chemical 246 (2006) 263

Cinchonidine doped Pd catalysts in the enantioselective hydrogenation of (*E*)-2-methyl-2-butenoic acid

Commercial Pd (5 wt.%) catalysts doped with cinchonidine (CD) were investigated in the enantioselective hydrogenation of (*E*)-2-methyl-2-butenoic acid ($P = 4.0$ MPa of H_2, $T = 298$ K) with the aim of determining how the enantioselectivity and TON may be affected by specifications of the catalytic system (support acidity, surface area, metal dispersion and particle size). A significant importance seems to be the size of the Pd clusters, influencing the total or partial covering of the catalytic surface by the modifier. Furthermore the acidity of the support favours the adsorption of CD, and the stronger this interaction is the more stable the anchoring of the modifier is during the reaction.

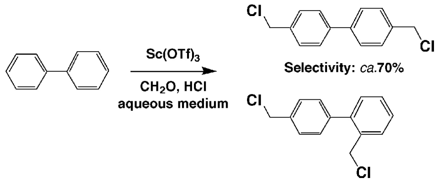


Tohru Kishida, Takayoshi Yamauchi, Kenichi Komura, Yoshihiro Kubota, Yoshihiro Sugi

Journal of Molecular Catalysis A: Chemical 246 (2006) 268

The chloromethylation of biphenyls catalyzed by group 3 and 4 metal triflates

Group 3 and 4 metal triflates, such as $Sc(OTf)_3$ are active for the chloromethylation of biphenyl in aqueous medium. The selectivity for 4,4′-bis(chloromethyl)biphenyl is ca. 70%.



Biswanath Das, Katta Venkateswarlu, Anjoy Majhi, Majjigapu Ravinder Reddy, Kuravallapalli Nagabhushana Reddy, Yerra Koteswara Rao, Krishnan Ravikumar, Balasubramanian Sridhar

Journal of Molecular Catalysis A: Chemical 246 (2006) 276

Highly efficient, mild and chemo- and stereoselective synthesis of enaminones and enamino esters using silica supported perchloric acid under solvent-free conditions