ELSEVIER

Journal of Molecular Catalysis A: Chemical 237 (2005) v–xiv

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Contents

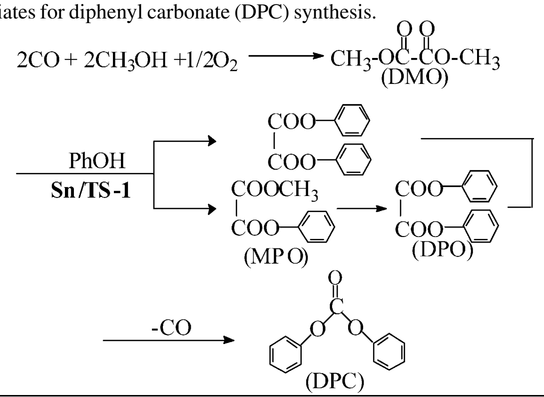
Articles

Xinbin Ma, Jinlong Gong, Shengping Wang, Fei He, Hongli Guo, Xia Yang, Genhui Xu

Journal of Molecular Catalysis A: Chemical 237 (2005) 1

Characterization and reactivity of stannum modified titanium silicalite TS-1 catalysts for transesterification of dimethyl oxalate with phenol

Stannum modified titanium silicalite TS-1 has proved to be an effective catalyst for the transesterification of dimethyl oxalate with phenol to produce methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO), the important intermediates for diphenyl carbonate (DPC) synthesis.



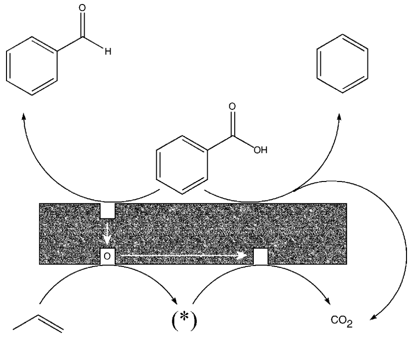
F. Dury, S. Meixner, D. Clément, E.M. Gaigneaux

Journal of Molecular Catalysis A: Chemical 237 (2005) 9

Coupling the deoxygenation of benzoic acid with the oxidation of propylene on a Co molybdate catalyst

The deoxygenation of benzoic acid is successfully coupled with the oxidation of propylene on a Co molybdate catalyst.

This system allows to correlate in real time the oxidation performances of the catalyst with the presence of the oxygen vacancies at their surface. The work shows that the oxidation of propylene occurs in such way that it leaves single oxygen vacancies at the surface.



Stanislaw Krompiec, Mariola Pigulla, Michal Krompiec, Bogdan Marciniec, Dariusz Chadyniak

Journal of Molecular Catalysis A: Chemical 237 (2005) 17

Highly selective isomerization of *N*-allylamines catalyzed by ruthenium and rhodium complexes

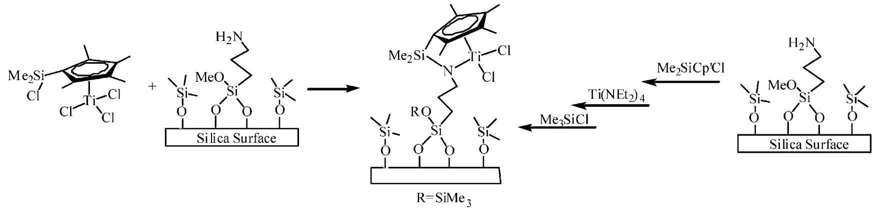
Synthesis of enamines *via* isomerization of *N*-allylamines ($R_1R_2NCH_2CH{=}CH_2$ and $PhMeNCH_2CH{=}CHSiMe_3$) catalyzed by $[RhH(CO)(PPh_3)_3]$ or $[RuClH(CO)(PPh_3)_3]$ is described. In the case of the ruthenium complex, double bond migration was successful only for allylamines with bulky groups at the nitrogen atom. A strong *E*-selectivity (resulting from specific coordination effects, as demonstrated by theoretical calculations) in the isomerization of allylamines was observed.

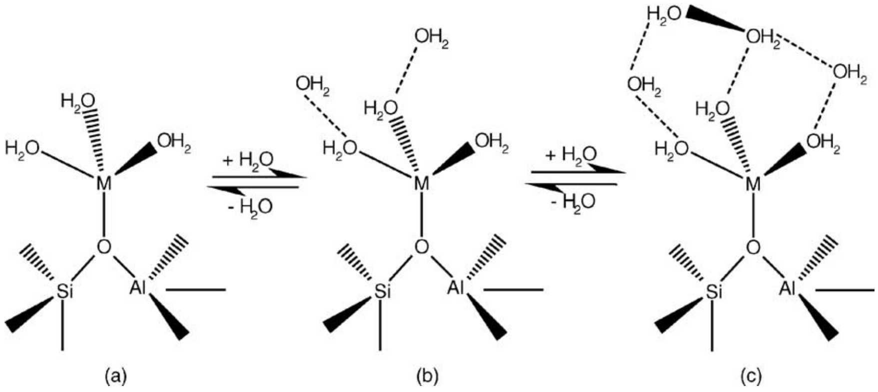
$$R^1R^2NCH_2CH{=}CHR^3 \xrightarrow{[Ru]\text{ or }[Rh]} R^1R^2NCH{=}CHCH_2R^3$$

R^1, R^2, R^3 = Me, Me, H; Me_3Si, Me_3Si, H; Ph, Me, $SiMe_3$; ...

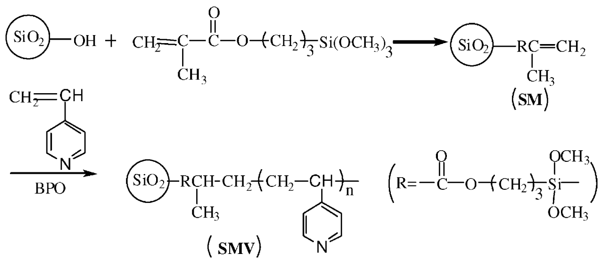
doi:10.1016/S1381-1169(05)00386-9

Constrained geometry-inspired catalysts (CGCs) are assembled on porous silica using two metallation protocols. The speciation of the surface moieties, catalyst loading, and catalytic activity in ethylene polymerization are probed.

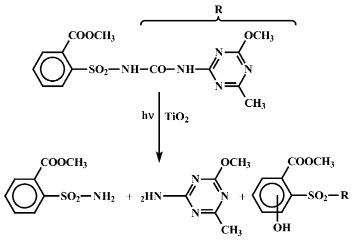




Monomeric silica (SM) and silica-poly[3-(trimethoxysilyl)propyl methacrylate-co-4-vinylpyridine] inorganic–organic hybrid (SMV) have been synthesized, and by loading zirconocene catalyst on the carrier, novel zirconocene supported catalyst has been made and tested for ethylene polymerization. Ethylene polymerization data demonstrate that the SMV supported catalyst has higher activity than the SM supported one.



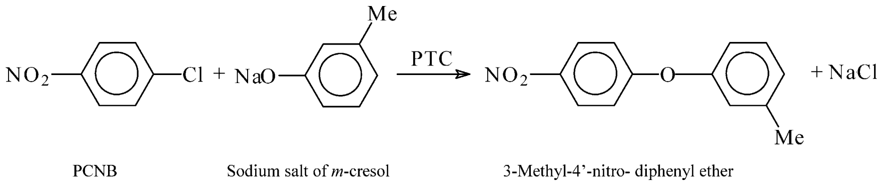
The photocatalytic degradation of metsulfuron methyl on TiO_2 in aqueous solutions leads to the occurance of several processes involving hydroxyl radicals: hydroxylation of the aromatic part, demethylation on the methoxy group and the cleavage of the sulfonyl urea bridge. The processes were shown to be efficient in pure water as well as in natural waters from the rivers Allier (Clermont-Ferrand, France) and Rio Mondego (Coimbra, Portugal).



Ganapati D. Yadav, Suraj A. Purandare

Journal of Molecular Catalysis A: Chemical 237 (2005) 60

Novelties of selective synthesis of 3-methyl-4′-nitro-diphenyl ether under solid–liquid phase transfer catalysis

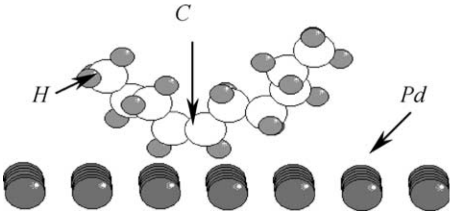


María B. Fernández, Gabriela M. Tonetto, Guillermo H. Crapiste, María L. Ferreira, Daniel E. Damiani

Journal of Molecular Catalysis A: Chemical 237 (2005) 67

Hydrogenation of edible oil over Pd catalysts: A combined theoretical and experimental study

Three Pd planes and *cis*-4-decene (Figure) were modeled in order to study the *cis*/*trans* isomerization and full hydrogenation of oleic acid. Two different reaction pathways were studied: Horiuti–Polanyi and adsorbed monoyne-mediated mechanism. The systems were studied out using molecular mechanics and Extended Hückel calculations.
The studies demonstrated that both mechanisms are possible on the Pd planes, but the monoyne-mediated mechanism is always energetically more exothermic.

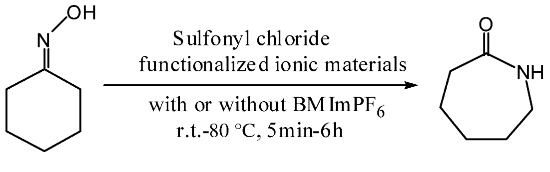


Zhengyin Du, Zuopeng Li, Yanlong Gu, Juan Zhang, Youquan Deng

Journal of Molecular Catalysis A: Chemical 237 (2005) 80

FTIR study on deactivation of sulfonyl chloride functionalized ionic materials as dual catalysts and media for Beckmann rearrangement of cyclohexanone oxime

Several novel sulfonyl chloride functionalized ionic materials were used as media and catalysts for Beckmann rearrangement of cyclohexanone oxime and satisfactory results were achieved under mild conditions. The effects of all parameters were discussed. Moreover the deactivation of ionic liquid catalytic system during the recycle was investigated by using FTIR spectroscopy and mass balance calculation. The trapping of acidic ionic material with basic product is proved to be mainly responsible for the difficulties encountered in the reuse of this type of material. A possible mechanism was conjectured.

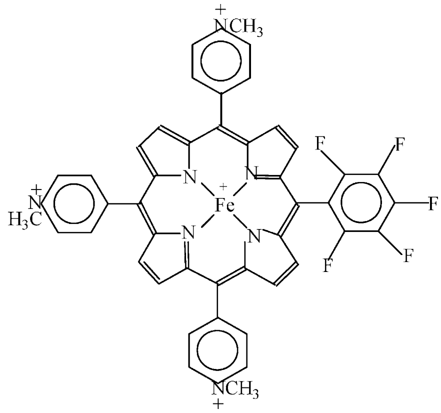


Fabiana C. Skrobot, Ieda L.V. Rosa, Ana Paula A. Marques, Patrícia R. Martins, J. Rocha, Anabela A. Valente, Yassuko Iamamoto

Journal of Molecular Catalysis A: Chemical 237 (2005) 86

Asymmetric cationic methyl pyridyl and pentafluorophenyl porphyrin encapsulated in zeolites: A cytochrome P-450 model

Adamantane oxidation at room temperature and atmosferic pressure by iron(III)tris(4-*N*-methyl-pyridyl)-mono(pentafluorophenyl)-porphyrin complex encapsulated ([Fe{T(4-*N*-MePy)MFPP}]Cl_4-NaY) and impregnated ([Fe{T(4-*N*-MePy)MFPP}]Cl_4-NaY_{imp}) in the NaY framework gives rise to 1-adamantanol as the main product as expected for a P-450 model. The activity of the [Fe{T(4-*N*-MePy)MFPP}]Cl_4-NaY and [Fe{T(4-*N*-MePy)MFPP}]Cl_4-NaY_{imp} is considerably higher than that of bulk [Fe{T(4-*N*-MePy)MFPP}]Cl_4. The presence of a fluoro-phenyl group promotes selective oxidation of cyclohexane.

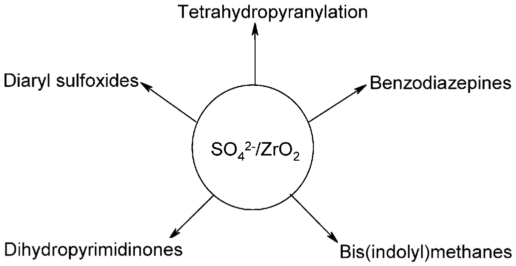


Benjaram M. Reddy, Pavani M. Sreekanth, Pandian Lakshmanan

Journal of Molecular Catalysis A: Chemical 237 (2005) 93

Sulfated zirconia as an efficient catalyst for organic synthesis and transformation reactions

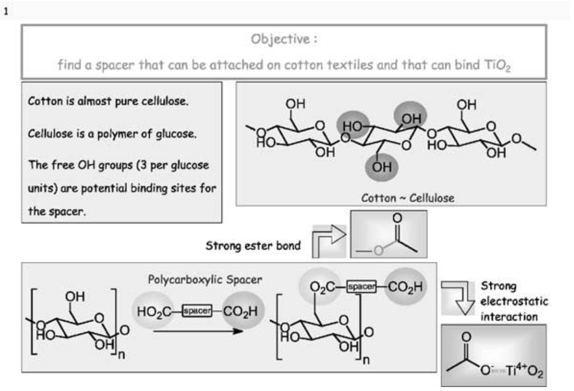
Sulfated zirconia as an efficient catalyst for organic synthesis and transformation reactions. The efficacy of sulfated zirconia catalyst was investigated towards various acid-catalyzed organic syntheses and transformation reactions in the liquid phase. The SO_4^{2-}/ZrO_2 efficiently catalyzes the synthesis of 1,5-benzodiazepines, bis(indolyl)methanes, diaryl sulfoxides 3,4-dihydropyrimidinones and tetrahydropyranylation of alcohols and phenols.



K.T. Meilert, D. Laub, J. Kiwi

Journal of Molecular Catalysis A: Chemical 237 (2005) 101

Photocatalytic self-cleaning of modified cotton textiles by TiO_2 clusters attached by chemical spacers



find a spacer that can be attached on cotton textiles and that can bind TiO_2

Cotton is almost pure cellulose.

Cellulose is a polymer of glucose.

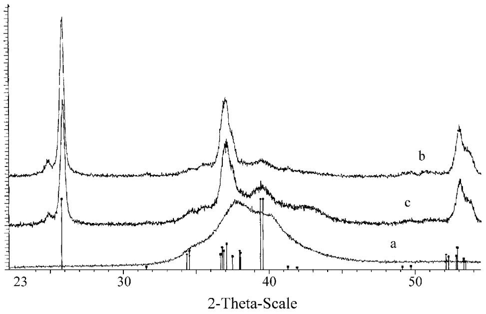
The free OH groups (3 per glucose units) are potential binding sites for the spacer.

Anne-Félicie Lamic, Thi Lan Huong Pham, Claude Potvin, Jean-Marie Manoli, Gérald Djéga-Mariadassou

Journal of Molecular Catalysis A: Chemical 237 (2005) 109

Kinetics of bifunctional isomerization over carbides (Mo, W)

The kinetics of isomerization of *n*-heptane was studied over transition metal oxides and carbides. The global consumption of *n*-heptane is a first order reaction to the reactant and the global kinetics of the reaction only occurs on acidic sites.

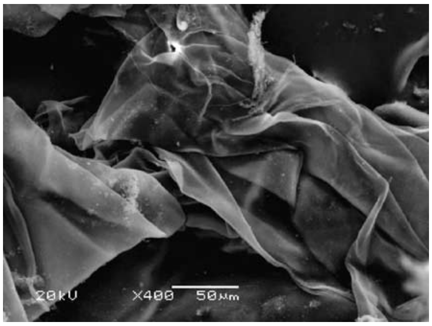


Alexandre G.S. Prado, Elaine A. Faria, Jurandir R. SouzaDe, Jocilene D. Torres

Journal of Molecular Catalysis A: Chemical 237 (2005) 115

Ammonium complex of niobium as a precursor for the hydrothermal preparation of cellulose acetate/Nb_2O_5 photocatalyst

Hydrothermal reaction by using ammonium niobium oxalate as a precursor was performed to prepare cellulose acetate/Nb_2O_5 catalysts. These materials presented homogeneous dispersion of niobium on cellulose acetate surface with Bronsted and Lewis acid sites based on SEM/EDS microscopy and infrared spectroscopy. These catalysts were applied as photocatalyst to degrade indigo carmine dye in water.



Yuanchen Cui, Lei Zhang

Journal of Molecular Catalysis A: Chemical 237 (2005) 120

Polyvinyl chloride–polyethylene–polyamine supported palladium complexes as high efficient and recyclable catalysts for Heck reaction

Polyvinyl chloride–polyethylene–polyamine supported palladium complexes are efficient catalysts for Heck reaction of acrylic acid with aryl iodides in air at the low temperature (50°C) using 0.125mol% of the catalysts. Effect of amount of the catalyst indicates that the Heck reaction acrylic acid with iodobenzene can be carried out with tiny amount of the catalyst (0.02%) at 90°C. The complexes have high thermal stability and can be easily separated and recovered from the reaction mixture by filtration and reused many times.

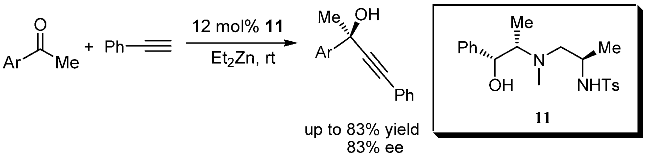
$X = I, Br$ $R_1 = H, CH_3, CH_3O, Cl, NO_2$ $R_2 = CO_2H, Ph$

Jincheng Mao, Boshun Wan, Fan Wu, Shiwei Lu

Journal of Molecular Catalysis A: Chemical 237 (2005) 126

Sulfamide-amine alcohol catalyzed enantioselective alkynylation of aromatic ketones

Readily available sulfamide-amine alcohol **11** was found to be effective in catalyzing the enantioselective phenylacetylene addition to aromatic ketones without using another central metal, providing the chiral tertiary propargylic alcohols in good yields (up to 83%) and enantioselectivities (up to 83% e.e.).

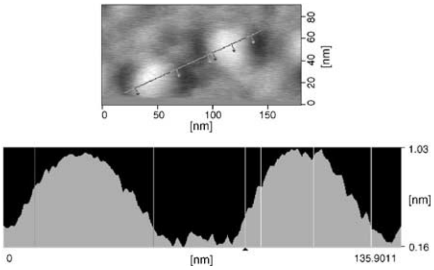


Min Chen, Hao Zheng, Chunmiao Shi, Renxian Zhou, Xiaoming Zheng

Journal of Molecular Catalysis A: Chemical 237 (2005) 132

Synthesis of nanoparticle Ce–Mg–O mixed oxide as efficient support for methane oxidation

A new material of Ce–Mg–O nanoparticle, which can be applied as catalyst support for methane combustion reaction, has been successfully synthesized and characterized by XRD, AFM, Raman and temperature-programmed reduction (TPR). The design of adding alkaline-earth metals into CeO_2, the typical structure of Mg^{2+} enters the lattice of CeO_2 to form a solid solution, whose activity for methane combustion is reasonable. The Ce–Mg–O new material supported iron catalysts are very active for methane comustion (the methane conversion reaches 90% at 560°C). The effect of nanoparticle size and good capability of oxygen storage are also key factors affecting catalyst activity.

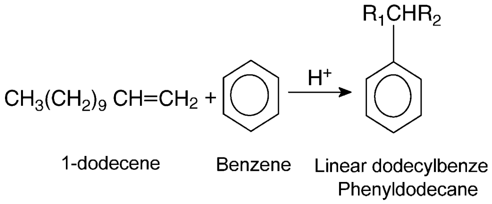


Dhanashri P. Sawant, S.B. Halligudi

Journal of Molecular Catalysis A: Chemical 237 (2005) 137

Alkylation of benzene with α-olefins over zirconia supported 12-silicotungstic acid

Liquid phase alkylation of Benzene to LAB (linear alkyl benzene) with α-olefins has been investigated with 12-silicotungstic acid supported on zirconia (STA/ZrO_2) as the catalyst. Among the catalysts, 15wt.% STA/ZrO_2 calcined at 750°C was found to be most active than others in the alkylation reaction.

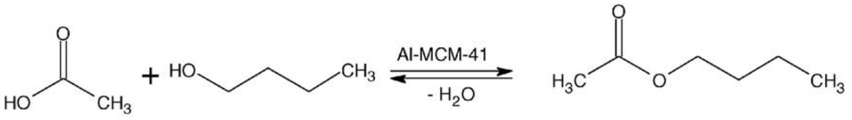


B. Rabindran Jermy, A. Pandurangan

Journal of Molecular Catalysis A: Chemical 237 (2005) 146

A highly efficient catalyst for the esterification of acetic acid using *n*-butyl alcohol

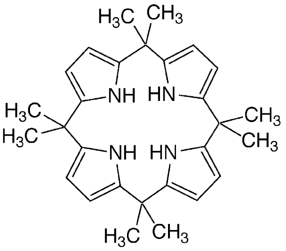
The catalytic activity of the Al-MCM-41 material was tested in the esterification of acetic acid using *n*-butyl alcohol. This work has provided an alternative usage of Al-MCM-41 catalyst with very high Si/Al ratios. The hydrophobic property of the catalyst tends to have greater influence in spite of autogeneous pressure. Further the reaction is proposed to occur mainly within the pores of the catalyst. This observation indirectly proves planting of Brönsted acid sites insides the pore of the catalyst.



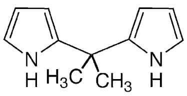
Motkuri Radha Kishan, Vippagunta Radha Rani, Shivanand Janardan Kulkarni, Kondapuram Vijaya Raghavan

Journal of Molecular Catalysis A: Chemical 237 (2005) 155

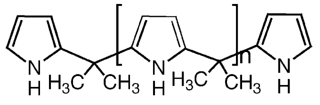
A new environmentally friendly method for the synthesis of calix(4)pyrroles over molecular sieve catalysts



1a



1b



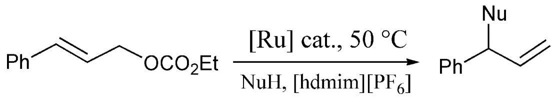
1c: n=1;**1d**: n=2

Claudie Hubert, Jean-Luc Renaud, Bernard Demerseman, Cédric Fischmeister, Christian Bruneau

Journal of Molecular Catalysis A: Chemical 237 (2005) 161

Ruthenium-catalyzed allylation reaction in ionic liquid

The ruthenium-catalyzed allylation of carbon nucleophiles and phenol has been performed in ionic liquid with high conversion and regioselectivity. The catalyst is safely immobilized in the ionic solvent, and thus, can be recycled without loss of catalytic activity and regioselectivity.

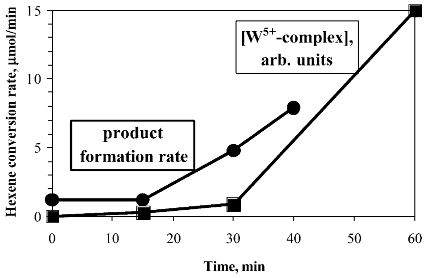


A.V. Kucherov, A.V. Vasnev, A.A. Greish, L.M. Kustov

Journal of Molecular Catalysis A: Chemical 237 (2005) 165

Catalytically active species in new metathesis systems [$W^{n+}(Mo^{n+})$–ionic liquid–olefin]: A quantitative ESR study

A quantitative approach is successfully used in the ESR study of catalysts for olefin metathesis [$W^{n+}(Mo^{n+})$–ionic liquid–olefin]. The key role of isolated complexes of W^{5+} and Mo^{5+} ions in catalysis is demonstrated. The kinetics of formation/accumulation of the isolated W^{5+} species at the initial step of W^{6+} reduction by an olefin agrees closely with the kinetics of metathesis.



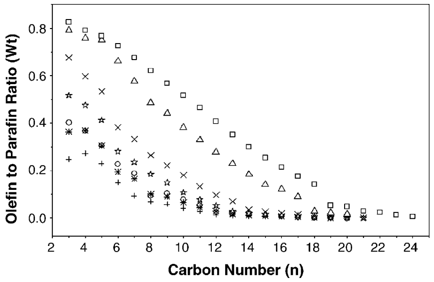
Yuhua Zhang, Haifeng Xiong, Kongyong Liew, Jinlin Li

Journal of Molecular Catalysis A: Chemical 237 (2005) 172

Effect of magnesia on alumina-supported cobalt Fischer–Tropsch synthesis catalysts

A series of magnesia-modified alumina-supported cobalt catalysts were prepared using the incipient wetness method. The effect of magnesia on Co/Al_2O_3 Fischer–Tropsch catalyst has been investigated. Small amounts of magnesia were found to improve the activity of cobalt catalyst for Fischer–Tropsch synthesis but larger amounts of magnesia decreased the activity.
The figure shows the effect of the magnesia content on the olefin to paraffin ratio. The ratio of olefin to paraffin decreases with increasing chain length for all catalysts, and a significant trend can be observed that the ratio of olefin to paraffin increases with increasing magnesia content.

(+) 15CoA; (○) 15Co03MA; (✱) 15Co08MA; (☆) 15Co2MA; (×) 15Co5MA; (△) 15Co9MA; (□) 15Co12MA.

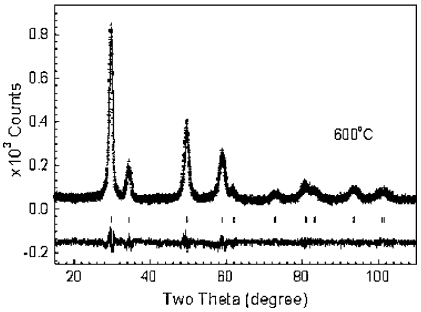


J.H. Zhang, Y.Q. Yang, J.M. Shen, J.A. Wang

Journal of Molecular Catalysis A: Chemical 237 (2005) 182

Mesostructured CeO_2 and Pd/CeO_2 nanophases: Templated synthesis, crystalline structure and catalytic properties

A ceria nanophase with lattice defects was prepared through a surfactant-templated route. A 100% NO conversion with a selectivity to 100% N_2 was achieved over the Pd/ceria catalyst at a reaction temperature of 300°C, which is much superior to the catalysts of Pt or Rh supported on TiO_2, Al_2O_3, $TiO_2–Al_2O_3$ and $ZrO_2–Al_2O_3$.

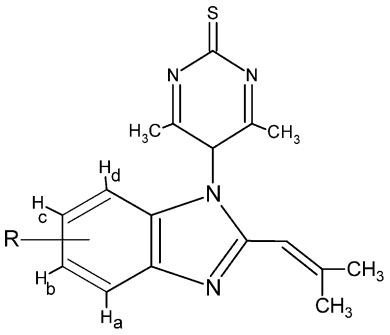


Pratibha Sharma, Ashok Kumar, Manisha Sharma

Journal of Molecular Catalysis A: Chemical 237 (2005) 191

Generation of 4,6-dimethyl-5-[2-(2-methylprop-1-enyl)-1*H*-benzimidazol-1-yl]pyrimidine-2(5*H*)-thiones under kinetically controlled phase transfer catalysis conditions

The insertion of dimethylvinylidene carbene into azo moiety was investigated in order to synthesize 4,6-dimethyl-5-[2-(2-methylprop-1-enyl)-1*H*-benzimidazol-1-yl] pyrimidine-2(5*H*)-thiones [7a–j] under kinetically controlled phase transfer catalysis conditions. The reaction follows the pseudo-first order rate law. Rational mechanism of the reaction is proposed according to the experimental evidence. Effects of stirring speed, amount of catalyst and effect of temperature on the reaction rate were investigated in detail.

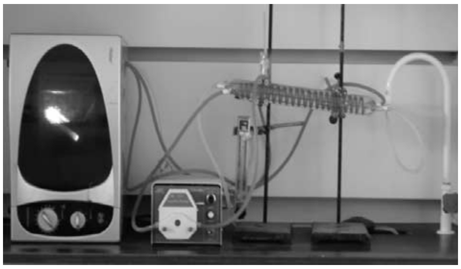


Xiwang Zhang, Yizhong Wang, Guoting Li

Journal of Molecular Catalysis A: Chemical 237 (2005) 199

Effect of operating parameters on microwave assisted photocatalytic degradation of azo dye X-3B with grain TiO_2 catalyst

The photocatalytic decomposition of azo dye X-3B was investigated in microwave assisted photocatalysis with microwave electrodeless lamp as light source (MWL/TiO_2). A novel grain TiO_2 (GT01) had been used as catalyst, which was easily separated from water. The effect of different operating parameters on photocatalytic oxidation was discussed. Moreover, influence of microwave irradiation on effect of operating parameters was investigated.

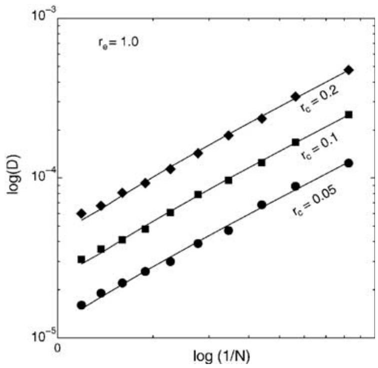


Juan R. Sánchez

Journal of Molecular Catalysis A: Chemical 237 (2005) 206

Metal surface adsorbed clusters: Structure and dynamics

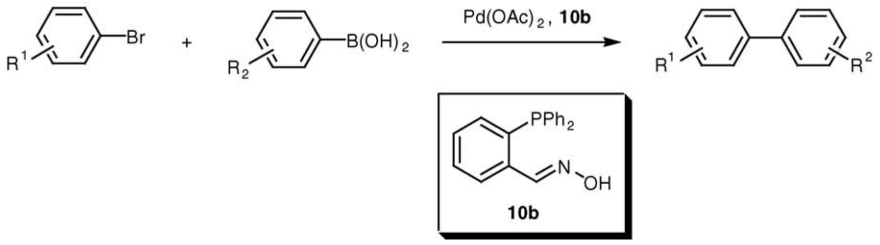
Extensive numerical simulation are reported for the structure and dynamics of large clusters on metal(100) surfaces. Different types of perimeter hopping processes makes center-of-mass of the cluster to follow a a random walk trajectory. A *diffusion coefficient D* for the whole cluster can be defined as limt→∞D(t), with $D(t)=\langle d^2\rangle/(4t)$ and d the displacement of the center-of-mass from its initial position. The dependence of the diffusion coefficient on those perimeter hopping processes can be analyzed in detail, since the relations between different rates for the processes are explicitly considered as parameters. The value of the diffusion coefficient D behaves as $D \sim N^{-\alpha}$, while different values for the exponent α have been proposed depending on which diffusion mechanism is considered to facilitate the movement of the cluster.



Lei Xu, Di Zhu, Fan Wu, Rongliang Wang, Boshun Wan

Journal of Molecular Catalysis A: Chemical 237 (2005) 210

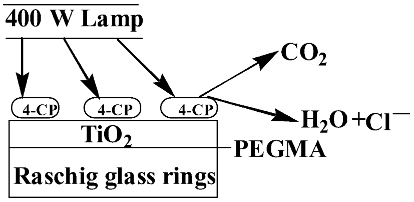
Highly efficient palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl bromides using 2-(diphenylphosphino) benzaldoxime ligand



P. Raja, M. Bensimon, A. Kulik, R. Foschia, D. Laub, P. Albers, R. Renganathan, J. Kiwi

Journal of Molecular Catalysis A: Chemical 237 (2005) 215

Dynamics and characterization of an innovative Raschig rings–TiO_2 composite photocatalyst



Yang Xuzhuang, Shen Yuenian, Yuan zhangfu, Zhu Huaiyong

Journal of Molecular Catalysis A: Chemical 237 (2005) 224

Ferric ions doped 5A molecular sieves for the oxidation of HCHO with low concentration in the air at moderate temperatures

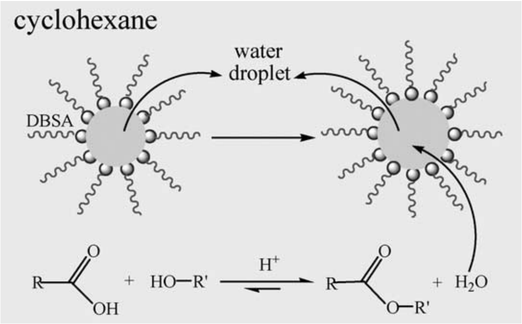
$$\mathrm{HCHO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{HCOOH}, \quad \mathrm{HCOOH} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O},$$

$$\mathrm{HCHO} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

Yuchun Han, Ying Chu

Journal of Molecular Catalysis A: Chemical 237 (2005) 232

The catalytic properties and mechanism of cyclohexane/DBSA/water microemulsion system for esterification

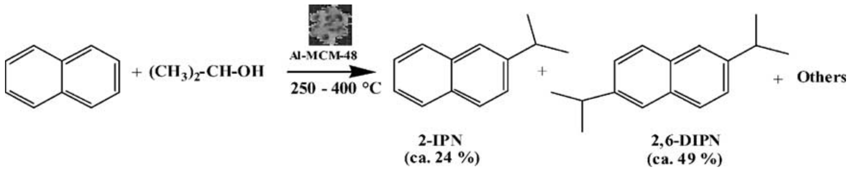


T. Krithiga, A. Vinu, K. Ariga, B. Arabindoo, M. Palanichamy, V. Murugesan

Journal of Molecular Catalysis A: Chemical 237 (2005) 238

Selective formation 2,6-diisopropyl naphthalene over mesoporous Al-MCM-48 catalysts

Vapour phase isopropylation of naphthalene (NAP) with isopropyl alcohol (IPA) was carried out over H-form of Al-MCM-48 catalysts with different n_{Si}/n_{Al} ratios. The feed molar ratio of 1:2:10 (NAP:IPA:CYH) and WHSV ($5.36h^{-1}$) were found to be the optimized conditions for good NAP conversion with selectivity of 2,6-diisopropylnaphthalene (2,6-DIPN). The effect of 2,6/2,7-DIPN ratio was also studied for catalysts with various n_{Si}/n_{Al} ratios and at different temperatures. Among the catalysts used in the present study, AlMCM-48 (25) showed a high NAP conversion and selectivity to 2,6-DIPN under the optimized reaction conditions.

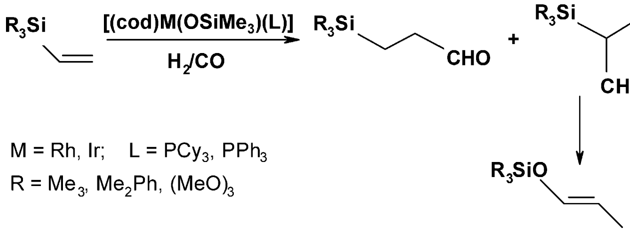


Ewa Mieczyńska, Anna M. Trzeciak, Józef J. Ziółkowski, Ireneusz Kownacki, Bogdan Marciniec

Journal of Molecular Catalysis A: Chemical 237 (2005) 246

Hydroformylation and related reactions of vinylsilanes catalyzed by siloxide complexes of rhodium(I) and iridium(I)

Rhodium(I) and iridium(I) siloxide complexes used as catalysts of hydroformylation of the vinylsilanes at 80°C and 10 atm of H_2/CO (H_2:CO=1) produced aldehydes (n + iso) as the main products with yields of up to 100%. In the presence of the iridium complexes some amounts of ethylsilanes, up to 40%, were obtained, besides aldehydes, as a result of hydrogenation of the substrates. In the presence of the rhodium complexes, isomerization of iso-aldehydes to 1-siloxypropenes was observed under the reaction conditions. Under 10 atm of H_2, the rhodium complexes appeared to be also very effective catalysts of vinylsilanes hydrogenation.



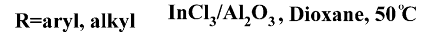
M = Rh, Ir; L = PCy_3, PPh_3
R = Me_3, Me_2Ph, $(MeO)_3$

Masoud Salavati-Niasari, Samansa Hydarzadeh

Journal of Molecular Catalysis A: Chemical 237 (2005) 254

An effective method for the selective synthesis of geminal diacetates (acylals) from aromatic aldehydes using alumina-supported $InCl_3$

Aliphatic and aromatic aldehydes can be converted to acylals in mild conditions by a treatment with acetic anhydride in the presence of $InCl_3/Al_2O_3$ (indium chloride loading = $1.2mmolg^{-1}$). For all reactions, $InCl_3/Al_2O_3$ is the best catalyst with reusable and highly activity.



$$\underset{R=aryl,\ alkyl}{RCHO + Ac_2O} \ \underset{InCl_3/Al_2O_3,\ Dioxane,\ 50^{\circ}C}{\overset{InCl_3/Al_2O_3,\ Acetic\ anhydride}{\rightleftarrows}} \ RCH(OAc)_2$$

Khadija Aboulaala, Catherine Goux-Henry, Denis Sinou, Mohamed Safi, Mohamed Soufiaoui

Journal of Molecular Catalysis A: Chemical 237 (2005) 259

Synthesis and evaluation of a range of enantiopure β-aminoalcohols derived from tartaric acid for asymmetric hydrogen transfer reduction of prochiral ketones

Several (2*R*,3*R*)-3-amino- and (alkylamino)-1,4-bis(benzyloxy)butan-2-ol have been prepared from readily available (+)-diethyl tartrate. These β-aminoalcohols in association with Ru(II) or Ir(I) complexes gave ee up to 80% in the hydrogen transfer reduction of various aryl alkyl ketones.