HIGH-PERFORMANCE CU/MGO CATALYSTS FOR SELECTIVELY CONVERTING BENZYL ALCOHOL TO BENZALDEHYDE WITHOUT THE USE OF AN O2 OR H2 ACCEPTOR

D. Subramanyam, Research Scholar, Sri Satya Sai University of Technology & Medical Sciences, Sehore, Madhya Pradesh, India

Dr. N.P. Rathore, Professor, Department of Chemistry, Sri Satya Sai University of Technology & Medical Sciences, Sehore, Madhya Pradesh, India

ABSTRACT:
A series of Cu/MgO catalysts with Cu loadings of 1, 3, 5, and 7% have been prepared with the goal of creating an effective catalyst for the selective dehydrogenation of benzyl alcohol into benzaldehyde in the absence of O2 and H2 acceptor. The 5% Cu/MgO catalyst in the gas phase demonstrated a remarkable performance with 98% conversion and 97% selectivity, and to support the performance, the catalysts have been characterised by various techniques like BET surface.

INTRODUCTION:
The use of molecular oxygen as an oxidant in liquid and gas phase operations is actively being researched in these One of the key processes is the selective oxidation of alcohols to aldehydes, particularly the conversion of benzyl alcohol to benzaldehyde, which has numerous applications in the food, pharmaceutical, cosmetic, and perfume industries. Traditionally, benzaldehyde is made in industrial processes by hydrolyzing benzyl chloride and oxidising toluene, or by stoichiometric oxidation of manganese and chromium salts. [1] These oxidants are toxic and generate a lot of hazardous waste, which has negative effects on the environmentand environmentally alarming times. [2,3] Overoxidation, explosion, and flammability are some of the unavoidable issues in the presence of oxygen, though. When O2 is used in the dehydrogenation processes, H2O is produced as a by-product, which frequently renders the catalyst inactive and necessitates laborious product purification. Instead, the creation of a catalyst that can function even in the absence of an oxidant and an H2 acceptor is particularly intriguing from a practical and environmental standpoint because I it prevents the formation of H2O, (ii) it generates stoichiometric amounts of H2, a promising feedstock for energy production, and (iii) it enhances selectivity by suppressing the overoxidation products.

Non-oxidative or oxidant-free dehydrogenation of alcohols has some advantages in real-world applications, although the conversion of benzyl alcohol to benzaldehyde is thermodynamically limited. According to recent studies, thermodynamic restrictions can be overcome by removing H2 from the system with an inert gas flow. [4–7] The information about gas-phase non-oxidative benzyl alcohol dehydrogenation processes is scarce despite the non-oxidative dehydrogenation processes' economic and environmental advantages. [8] According to reports, MgO and HT-supported Ag, Au, and Cu catalysts are very efficient at dehydrating alcohols without the use of oxidants. [4–6] In our earlier publications, hydrogenation, dehydrogenation, and coupling of these two reactions were carried out in the gas phase without the use of oxidants using Cu/MgO catalysts. [9–14] The effectiveness of Cu/MgO catalysts for the selective dehydrogenation of benzyl alcohol to benzaldehyde in the gas phase without the presence of an oxidant or an H2 acceptor has been outlined in this article.

EXPERIMENTAL:
Preparation of catalysts
Mg(NO3)26H2O (M/s Alfa Aesar, USA, 99% pure) and K2CO3 (M/s SD Fine Chem Ltd, India, assay, 99.5%) were used as the precursor and precipitating agent, respectively, in the precipitation method to create the MgO support. In a typical precipitation procedure, homogeneous aqueous solutions of Mg(NO3)26H2O and K2CO3 were made by adding separately 10 times their volume of

deionized water, and the solutions were then slowly mixed at a constant pH of 9 while being vigorously stirred at room temperature. The resulting precipitate was thoroughly washed in large quantities of deionized water before being dried at 393 K for 12 hours and calcined at 723 K for 6 hours in air. $Cu(NO_3)_2 3H_2O$ (M/s Sigma-Aldrich, USA, 99.9%) aqueous solution was used as a precursor to impregnate the calcined MgO to create Cu/MgO catalysts with 1, 3, 5, and 7% Cu loading (by weight).

The samples were then dried at 393 K for 12 hours, calcined at 723 K for 6 hours in air, and designated as 1Cu/MgO, 3Cu/MgO, 5Cu/MgO, and 7Cu/MgO (the prefixed number indicates the percentage of Cu loading (by weight) on the MgO support). The excess water was then removed using evaporation.

CHARACTERIZATION OF CATALYSTS:

N_2 gas adsorption at 77 K was used to calculate the BET surface area using a SMART SORB 92/93 (M/s SMART Instruments, India) in a dynamic environment. The Ultima IV diffractometer (M/s Rigaku Corporation, Japan) with a nickel-filtered Cu Ka radiation, operated at 40 kV and 20 mA in the 2y range of 2 to 801 having a scan speed of 21 min1 was used for the X-ray diffraction analysis. A Kratos analytical spectrophotometer was used to analyse the catalyst using X-ray photoelectron spectroscopy (XPS) using monochromated excited radiation of Mg Ka (1253.6 eV).

Around 109 mbar of residual pressure existed in the analysis chamber. Concerning the C 1s peak of the adventitious carbon, charging effects were taken into account when measuring binding energy (BE) (284.6 eV). TEM images were captured using a Philips Tecnai F12 FEI transmission electron microscope (TEM) that runs at 80–100 kV. On a homemade apparatus, temperature-programmed reduction (TPR), temperature-programmed CO_2 desorption, and N_2O pulse chemisorption experiments were conducted. The samples were pre-treated at 473 K for 1 h in an argon gas flow before the TPR experiments. After the pre-treatment was finished, the sample was exposed to a gas mixture composed of 5% H_2 in argon gas at a flow rate of 30 ml min1. A thermal conductivity detector was used to track the consumption of hydrogen. A well-known CO_2-TPD technique was used to measure the fundamental site distribution and a 10%. He and CO_2 gas mixture. In a typical experiment, 50 mg of the catalyst sample was pre-treated in flowing helium gas for 1 hour at 773 K, then cooled to 373 K. At this temperature, the pre-treated catalyst was exposed to a mixture of 10% CO_2 in helium gas with a flow rate of 20 ml min1, and it was then purged with helium gas at 373 K for 1 hour to remove the physiosorbed CO_2. The amount of CO_2 that was chemisorbed and desorbed in flowing helium gas at a flow rate of 20 ml. On a homemade pulse reactor, experiments with N_2O pulse chemisorption were conducted. The catalyst sample was typically reduced for two hours at 523 K by flowing H_2 gas, then cooled to 363 K. Then, until there was no change in the concentration of N_2O at the outlet, N_2O was pulsed-injected using a 6% N_2O-He gas mixture at regular intervals. ICP-OES (IRIS intrepid II, M/s Thermo Fisher Scientific) with a 2000 W RF generator operating at 27.12 MHz was used to estimate the potassium content. Catalyst samples were examined using potassium standards (10 ppm) that were commercially available.

CATALYTIC ACTIVITY TESTS:

The catalytic experiments are conducted in a fixed bed reactor with a 14 mm id and 400 mm length under a flow of N_2. The catalyst is loaded and reduced in an H_2 flow for three hours at a temperature of 553, G. The reaction temperature was set after the catalyst was reduced, and the reactant (benzyl alcohol) was fed at a flow rate of 1 ml/hr while N_2 gas flowed at a rate of 900 ml/hr. Every hour, the product was periodically collected in an ice cold trap for analysis by a GC 17A (M/s Shimadzu) outfitted with an OV-1 capillary column (30 m L 0.5 mm id 3 mm ft) and a FID detector. The 1Cu/MgO catalyst's XRD pattern shows Cu_2O and Cu0, suggesting that any copper species present are either in the amorphous phase or below the XRD detection limit. The 3Cu/MgO catalyst's XRD pattern showed a new diffraction peak at 2y = 50.51. This diffraction peak got stronger as the Cu

loading got higher. According to JCPDS card No. 4-0836, it is undoubtedly the second-highest diffraction peak characteristic of Cu0. In fact, the XRD patterns of Cu/MgO catalysts lack the 100% intense diffraction peak that should be present at 2y = 43.31 for metallic copper (JCPDS card No. 4-0836). This specific Cu0 characteristic peak could be combined with the MgO support's incredibly strong diffraction peak (2y = 42.91). The calcined CuO/MgO catalysts were examined by H2-TPR to assess the reduction behaviour of CuO, and the resulting reduction profiles are shown in Fig. 2. A single symmetric reduction peak can be seen in the Cu/MgO reduction profiles.

Table 1 Physico-chemical characteristics of Cu/MgO catalysts

Catalyst	$S_{BET}{}^a$ (m² g⁻¹)	$S_{Cu}{}^b$ (m² g⁻¹)	$P_{Cu}{}^c$ (nm)	$D_{Cu}{}^d$ (%)
MgO	40	—	—	—
1Cu/MgO	39	0.37	18.1	5.9
3Cu/MgO	37	0.97	20.8	5.0
5Cu/MgO	36	1.45	23.1	4.5
7Cu/MgO	32	1.73	27.2	3.8

BET surface area determined from N2 gas absorption. b Cu metal surface area obtained from N2O pulse chemisorption. c Cu particle size determined from N2O pulse chemisorption. d Cu metal dispersion obtained from N2O pulse chemisorption.
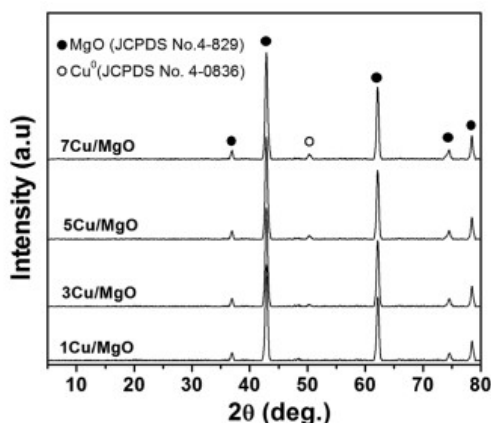

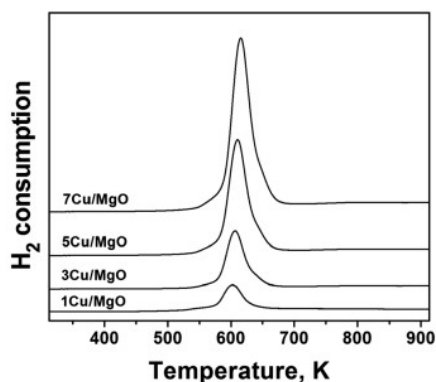*Fig. 1 XRD patterns of reduced Cu/MgO catalysts.*

Fig. 2 TPR of calcined CuO/MgO catalysts

This demonstrates how the CuO species in the CuO/MgO catalyst are completely reduced into Cu0 (CuO + H2 - Cu + H2O) in a single step. The reduction profiles show that the Cu loading and the amount of H2 used are strikingly balanced. On the MgO support, there is a slight shift in temperature maxima from 600 to 615 K towards higher temperatures, indicating the attainment of bulk CuO with increased Cu loading. [15]
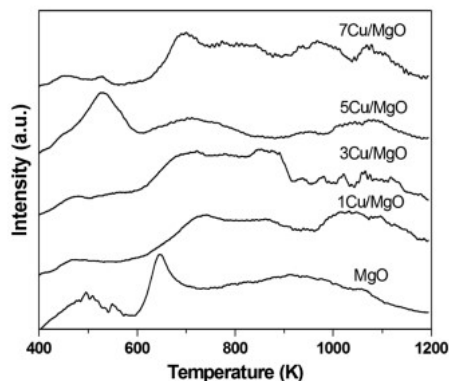
Fig. 3 CO2 TPD of Cu/MgO catalysts.

A study on temperature-programmed CO2 desorption was conducted to confirm the fundamental properties of Cu/MgO catalysts, and the resulting patterns are shown in Fig. 3. There are three different types of basic sites, such as moderate, strong, and very strong, according to the CO2 TPD pattern of the MgO support.

All Cu/MgO catalysts, except the 5Cu/MgO catalyst, exhibit the same type of basic sites. The majority of the basic sites in the 5Cu/MgO catalyst are weak by nature.
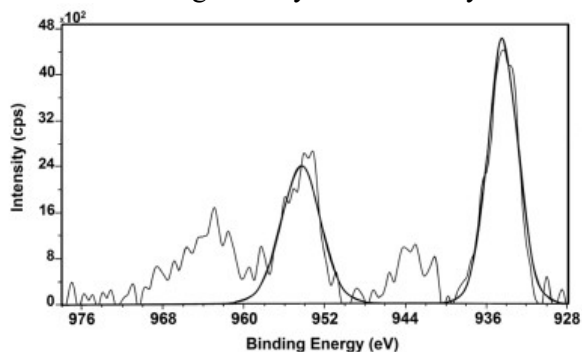

Fig. 4 XPS spectra of the reduced 5Cu/MgO catalyst.

Fig. 4 shows the X-ray photoelectron spectrum of the reduced 5Cu/MgO catalyst. There are two distinct peaks at binding energies of 934.7 and 954.4 eV for Cu 2p3/2 and Cu 2p1/2, respectively.

The Cu 2p3/2 main peak that should have appeared at about 936 eV is missing and may have been combined with the 934.4 eV peak, but there is a small peak at about 944 eV that may be the Cu 2p3/2 satellite peak of the 5Cu/MgO catalyst. If so, the 5Cu/MgO catalyst might contain a trace amount of Cu2+. The presence of either Cu1+ or Cu0 in the catalyst is shown by the appearance of the Cu 2p3/2 main peak at the binding energy of 934.3 eV.
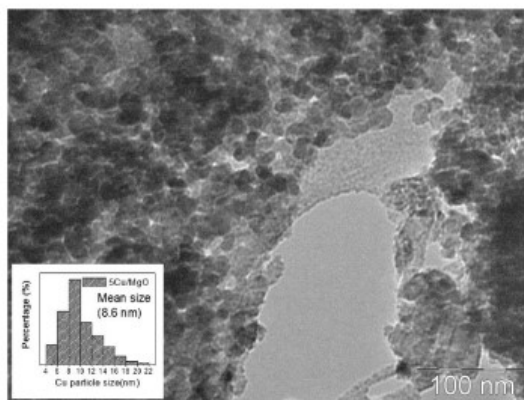

Fig. 5 TEM image of the 5Cu/MgO catalyst

It is challenging to distinguish between Cu1+ and Cu0 by XPS alone due to the close binding energies of the Cu 2p3/2 main peak of both Cu1+ and Cu0 (E1 eV). By using XPS to analyse CuO/SiO2 catalysts that had been calcined and reduced at various temperatures, Chang et al. found that the binding energies of the Cu 2p3/2 main peak are 936.4 eV for Cu2+ and 934.3 eV for Cu1+ or Cu0. The 5Cu/MgO catalyst's XPS results and the data from the published literature are in agreement. [15] The Cu0 metallic nanoparticles are evenly distributed on the surface of the MgO support, as seen in Fig. 5. The majority of the Cu atoms in the 5Cu/MgO catalyst have a size of 8.6 nm. The Cu metal particles are populated between 4 and 22 nm, according to the histogram shown in Fig. 5's inset. The 5Cu/MgO catalyst's average particle size, which was determined by N2O pulse chemisorption, is 23.1 nm (Table 1), which is higher than average in comparison. This inconsistent result could be the result of experimental error or different techniques being used. Due to benzaldehyde's importance in industry, it is attempted to selectively dehydrate benzyl alcohol to benzaldehyde in the gas phase without using either an oxidant or a hydrogen acceptor. It is discovered that Cu/MgO catalysts can more effectively catalyse the dehydrogenation of benzyl alcohol into benzaldehyde with a very small amount of toluene. No other by-products are detected besides toluene.

The reviewed literature reveals that the dehydrogenation of benzyl alcohol, particularly in the enhancement of conversion, depends critically on the use of molecular oxygen as an oxidant.According to reports, benzyl alcohol is converted on the BaPb0.6Bi0.4O3 perovskite catalyst by about 50% in the presence of oxygen, compared to only 25% in the absence of oxygen, meaning that the conversion is almost doubling in the presence of oxygen.[8] According to Tang et al.[16], the conversion of benzyl alcohol over the Cu-Mn/Al2O3 catalyst is about 90% with 499% selectivity to benzaldehyde.
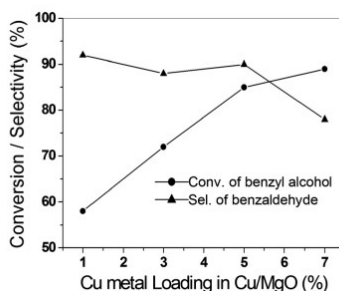

Fig. 6 Catalytic activity versus Cu metal loading

Jia et al.[17] also reported that over the Ag/HMS catalyst, benzyl alcohol conversion is almost 100% with 96% selectivity of benzaldehyde. Similar kinds of high conversions and selectivities have been reported for Au-Cu/SiO2 catalysts, but molecular oxygen was always used as the oxidant in these studies. A recent study found that a hexagonal mesoporous K-Cu-TiO2 catalyst had excellent catalytic activity for the low-temperature gas-phase oxidation of benzyl alcohol to benzaldehyde (483 K). 19The drawbacks of this catalyst, in addition to utilising molecular oxygen, include its high temperature sensitivity and the formation of byproducts at 520 K.[17] Even in the absence of an oxidant or a reductant, this catalyst's efficiency from the perspective of activity is comparable to that of the best catalysts previously reported. In the presence of molecular oxygen, it appears that some catalysts are very effective at oxidising alcohols to aldehydes, but others are not effective when there is no oxidation. For instance, in the absence of oxygen, the gas phase oxidation of benzyl alcohol to benzaldehyde over Ag/SiO2 promoted by alkaline earth metals showed very poor activity. The yield of benzaldehyde is greater than 60% when benzyl alcohol, N2, and O2 are used; however, when the flow of O2 is stopped, the yield of benzaldehyde is negligible. [20] There are other sources for catalytic studies of this nature.[17,21] Cu/MgO catalysts were found to be effective, and the reaction parameters were then optimised. The dehydrogenation of benzyl alcohol to benzaldehyde was carried out on all four catalysts (1Cu/MgO, 3Cu/MgO, 5Cu/MgO, and 7Cu/MgO catalysts) in the gas phase at 533 K

in the inert atmosphere using nitrogen gas. The results are shown in Fig. 6, which show that the increase in conversion of benzyl alcohol with increase in Cu loading from 1 to 5% is due to increase in However, the marginal increase in conversion from 5 to 7% Cu loading suggests that high metal content may result in the agglomeration of Cu metal particles, and selectivity to benzaldehyde was also significantly reduced. It can be determined that the active sites involved in the hydrogenolysis and dehydrogenation of benzyl alcohol are distinct from one another. The 5Cu/MgO catalyst from the Cu/MgO catalyst series showed the highest activity with a benzyl alcohol conversion rate of 86% and a benzaldehyde selectivity of 90%.The outcomes show that the Cu loading has a significant impact on the MgO support. Over the 5Cu/MgO catalyst, it appears that there is an impressive balance between the conversion of benzyl alcohol and selectivity to benzaldehyde. Consequently, 5Cu/MgO is the series' best catalyst. Figure 7 shows the TOF of the Cu/MgO catalysts and the yield of benzaldehyde with respect to Cu metal loading in Cu/MgO catalysts, demonstrating that the two parameters have a more-or-less similar trend. With an increase in Cu metal loading up to 5%, there was a gradual increase in the TOF and the yield. But above 5% Cu loading, the yield slightly increases rather than plateaus, which may be because the particle size and dispersion are similar (Table 1). After realising the best catalyst (5Cu/MgO) of the Cu/MgO catalyst series, other reaction parameters were optimized.
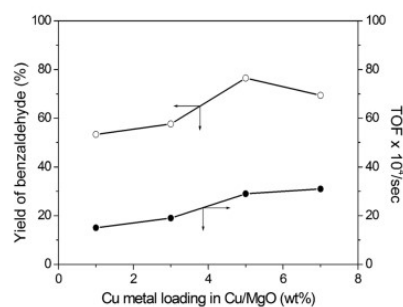

Fig. 7 The yield of benzaldehyde and its TOF against Cu metal loading.

Initially, to verify the nature of reaction, an experiment was conducted without the catalyst using quartz pieces as inert medium in the reactor, and no products were detected. A homogeneous surface/volume effect was thus disregarded. Later, to verify the formation of hydrogen along with benzaldehyde, an in situ activity measurement was conducted using a glass microreactor interfaced with a TCD equipped GC, as described elsewhere[22]. The outcomes show that benzyl alcohol over the 5Cu/MgO catalyst produces hydrogen even in the absence of oxygen. KF titration was used to confirm that H2O was produced during the hydrogenolysis of benzyl alcohol to toluene. Since 5Cu/MgO is the most effective catalyst in the Cu/MgO catalyst series, the effect of reaction temperature on this catalyst's catalytic activity is investigated. The findings are shown in Fig. 8. A time-onstream study was conducted at 573 K for 10 hours in order to understand the life of the 5Cu/MgO catalyst. The results are shown in Fig. 8, which shows that there is no appreciable activity loss.
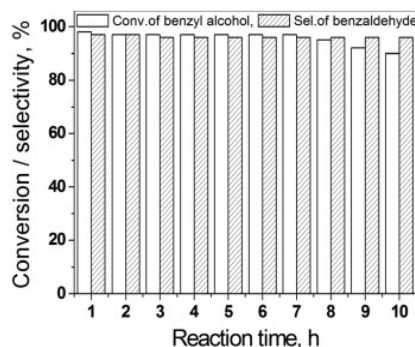

Fig. 8 The catalytic activity against time-on-stream.

According to a wealth of literature, catalysts' acid-base properties are crucial to the dehydrogenation of alcohols. [23,24] Dehydrogenation of alcohols is significantly aided by the addition of bases as co-catalysts or by the creation of basic sites in the catalyst. According to reports, Pd supported on simple supports like MgO or hydrotalcite is very effective at dehydrating alcohols, in contrast to the same Pd supported on alumina, silica, and zeolite B, which is ineffective. [25] Since Cu/MgO is an effective catalyst, it makes sense that the MgO support has the fundamental sites needed for the adsorption of alcohols and the abstraction of hydrogen from benzyl alcohol, as depicted in Scheme 1. According to reports, the basic sites can engage in nucleophilic activity and remove a proton from alcohol to create an intermediate that is negatively charged. 6,[26–28] Benzaldehyde is created as a result of the removal of b-H from the alkoxide.

The oxidation reactions of p-methyl alcohol, p-methoxy benzyl alcohol, m-methoxy benzyl alcohol, and m-phenoxy benzyl alcohol were further investigated to assess the scope of the reaction (Table 2). As mentioned above, all of the substrates consistently underwent selective dehydrogenation to produce high yields of the corresponding aldehydes.

CONCLUSION:

it has been shown that Cu/MgO catalysts performed admirably in the gas-phase dehydrogenation of benzyl alcohol to benzaldehyde without the use of either an oxidant or a hydrogen acceptor. With 98% conversion and 97% selectivity, the 5Cu/MgO catalyst has proven to be one of the best in its class.

REFERENCES :

[1] G. Centi, F. Cavani and, F. Trifiro, Selective oxidation by heterogeneous catalysis, Kluwer Academic/Plenum Publishers, New York, 2001.

[2] T. Mallat and A. Baiker, Chem. Rev., 2004, 104, 3037.

[3] R. A. Sheldon, I. Arends, G. J. Ten Brink and A. Dijksman, Acc. Chem. Res., 2002, 35, 774.

[4] T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa and K. Kaneda, Angew. Chem., Int. Ed., 2008, 47, 138.

[5] W. Fang, Q. Zhang, J. Chen, W. Deng and Y. Wang, Chem. Commun., 2010, 46, 1547.

[6] W. Fang, J. Chen, Q. Zhang, W. Deng and Y. Wang, Chem.–Eur. J., 2011, 17, 1247.

[7] T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa and K. Kaneda, Chem. Commun., 2008, 4804.

[8] R. Sumathi, K. Johnson, B. Viswanathan and T. K. Varadarajan, Appl. Catal., A, 1998, 172, 15.

[9] B. M. Nagaraja, V. Siva Kumar, V. Shasikala, A. H. Padmasri, B. Sreedhar, B. David Raju and K. S. Rama Rao, Catal. Commun., 2003, 4, 287.

[10] B. M. Nagaraja, A. H. Padmasri, B. David Raju and K. S. Rama Rao, J. Mol. Catal. A: Chem., 2007, 265, 90.

[11] B. M. Nagaraja, V. Siva Kumar, V. Shashikala, A. H. Padmasri, S. Sreevardhan Reddy, B. David Raju and K. S. Rama Rao, J. Mol. Catal. A: Chem., 2004, 223, 339.

[12] B. M. Nagaraja, A. H. Padmasri, P. Seetharamulu, K. Hari Prasad Reddy, B. David Raju and K. S. Rama Rao, J. Mol. Catal. A: Chem., 2007, 278, 29.

[13] K. Hari Prasad Reddy, R. Rahul, S. Sree Vardhan Reddy, B. David Raju and K. S. Rama Rao, Catal. Commun., 2009, 10, 879.

[14] K. Hari Prasad Reddy, N. Anand, V. Venkateswarlu, K. S. Rama Rao and B. David Raju, J. Mol. Catal. A: Chem., 2012, 355, 180.

[15] F.-W. Chang, H.-C. Yang, L. S. Roselin and W.-Y. Kuo, Appl. Catal., A, 2006, 304, 30.

[16] Q. Tang, X. Gong, Peizheng Zhao, Y. Chen and Y. Yang, Appl. Catal., A, 2010, 389, 101.

[17] L. Jia, S. Zhang, F. Gu, Y. Ping, X. Guo, Z. Zhong and F. Su, Microporous Mesoporous Mater., 2012, 149, 158.

[18] C. D. Pina, E. Falletta and M. Rossi, J. Catal., 2008, 260, 384.

[19] J. Fan, Y. Dai, Y. Li, N. Zheng, J. Guo, X. Yan and G. D. Stucky, J. Am. Chem. Soc., 2009, 131, 15568.

[20] Y.-S. Sawayama, H. Shibahara, Y. Ichihashi, S. Nishiyama and S. Tsuruya, Ind. Eng. Chem. Res., 2006, 45, 8837.

[21] Y. Li, D. Nakashima, Y. Ichihashi, S. Nishiyama and S. Tsuruya, Ind. Eng. Chem. Res., 2004, 43, 6021.

[22] A. Venugopal and M. S. Scurrell, Appl. Catal., A, 2003, 245, 137.

[23] J. I. Di Cosio, V. K. Diez, M. Xu, E. Iglesia and C. R. Apesteguia, J. Catal., 1998, 178, 499.

[24] G. Colon, J. A. Navio, R. Monaci and I. Ferino, Phys. Chem. Chem. Phys., 2000, 2, 4453.

[25] U. R. Pillai and E. S. Demessie, Green Chem., 2004, 6, 161. 26 T. Ishida, M. Nagaoka, T. Akita and M. Haruta, Chem.–Eur. J., 2008, 14, 8456.

[27] K.-I. Shimizu, K. Sugino, K. Sawabe and A. Satsuma, Chem.–Eur. J., 2009, 15, 2341

[28] R. Shi, F. Wang, Tana, Y. Li, X. Huang and W. Shen, Green Chem., 2010, 12, 108.

[29] B. H. Gross, R. C. Mebane and D. L. Armstrong, Appl. Catal., A, 2001, 219, 281.

[30] M. M. Aghayan, R. Boukherroub and M. Rahimifard, Tetrahedron Lett., 2009, 50, 5930.