



Journal of Nanoscience and Nanotechnology Vol. 15, 5816–5822, 2015 www.aspbs.com/jnn

Selective Oxidation of *n*-Hexane by Cu (II) Nanoclusters Supported on Nanocrystalline Zirconia Catalyst

Shankha Shubhra Acharyya, Shilpi Ghosh, Shubhadeep Adak, Raghuvir Singh, Sandeep Saran, and Rajaram Bal*

Catalyst Conversion and Process Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, India

Cu (II) nanoclusters supported on nanocrystalline zirconia catalyst (with size ~15 nm), was prepared by using cationic surfactant cetyltrimethylammonium in a hydrothermal synthesis method. The catalyst was characterized by XRD, XPS, TGA, SEM, TEM, FTIR and ICP-AES. The catalyst was found to be efficient in selective oxidation of *n*-hexane to 2-hexanol. An *n*-hexane conversion of 55%, with a 2-hexanol selectivity of 70% was achieved over this catalyst in liquid phase, without the use of any solvent. The catalyst can be reused several times without any significant activity loss.

Keywords: Selective Oxidation, Liquid Phase, *n*-Hexane, Cu (II) Nanoclusters, Nanocrystalline Zirconia, Heterogeneous Catalysis.

Delivered by Ingenta to: West Virginia University/ Health Sci Ctr Llb

1. INTRODUCTION

At the nano scale, materials exhibit fascinating optical, electronic, and magnetic properties that are often radically different from their bulk counterparts. So, controllable synthesis of metal nanoparticls and their catalytic performances has drawn a tremendous amount of attention over the past two decades.¹⁻⁵ Zirconium oxides have always been a very important ceramic material due to its broad range of applications for catalysis,^{6–8} oxygen sensors,^{9,10} fuel cells,^{11,12} biological materials,^{13,14} automobile parts etc. Copper catalysts (nanoparticles) are widely employed commercially for the dehydrogenation of cyclohexanol to cyclohexanone,15 oxidation of cyclohexane,16 the synthesis of methanol,17 the direct decomposition of NO to N2,18-20 CO oxidation etc.21 In addition, they can also be used in hydrogen fuel cells to generate energy for vehicles.²²⁻²⁴ The catalytic properties of the active copper phase can be greatly influenced by the nature of the supported oxide and the dispersion of the active component.²⁵ However, the nature of the active species of these catalysts is still the subject of extensive investigation by many researchers. Cu/ZrO2 nanoparticles catalyst showed interesting catalytic behavior for CO and CO₂ hydrogenation.²⁶ The catalyst can also be used for the upgradation of bio-oil e.g., hydrogenation of levulinic acid to γ -valerolactone.²⁷ Furthermore, Cu/ZrO₂ catalyst

exhibits mechanical stability, with moderately high specific surface and good semiconducting properties.²⁸ Cu/ZrO₂ bimetallic catalyst can be synthesized in various methods like impregnation method,^{29,30} co-precipitation method,³¹ sol–gel process,^{32,33} etc. Herein, we report cationic surfactant CTAB-mediated synthesis of Cu(II) nanoclusters supported on nanocrystalline zirconia catalyst (with size ~15 nm) in hydrothermal route. Although there are several reports on the preparation of Cu/ZrO₂ catalysts, with Cu²⁺ as an active component, there is no report on cationic surfactant CTAB mediated hydrothermal preparation of Cu/ZrO₂ catalyts with ~15 nm particles size and its catalytic use in *n*-hexane oxidation reaction.

The selective transformation of inert C—H bonds of alkanes into useful functional groups has attracted much attention because alkanes are less expensive and more readily available than the current petrochemical feedstocks.^{34,35} However, selective catalytic oxidation of sp³ hybridized carbons, within hydrocarbons, to alcohols, aldehydes, or ketones remains a challenging topic in contemporary chemical research,^{36,37} because desired products sequentially convert to CO₂ and the position of oxygen attachment is dictated solely by C—H bond energies.³⁸ *n*-Hexane is one of the hydrocarbons from which a number of useful oxygenates can be prepared. Several researchers reported oxidations of *n*-hexane with different oxidants;^{39–41} and the production of specific oxygenate selectively with high yield is highly demanding.

^{*}Author to whom correspondence should be addressed.

^{1533-4880/2015/15/5816/007}

Acharyya et al.

Herein, we report a *n*-hexane conversion of 55% with 2-hexanol selectivity of 70% over our so prepared Cu/ZrO₂ nanoparticles catalyst at room temperature with H_2O_2 as oxidant at liquid phase without using any solvent.

2. EXPERIMENTAL DETAILS

2.1. Materials

Zirconium (IV) oxychloride octahydrate [ZrO₂Cl₂ \cdot 8H₂O], copper (II) nitrate trihydrate [Cu (NO₃)₂ \cdot 3H₂O], cetrimoniumbromide, ammonia solution (25%), hydrazine (80% aqueous solution), *n*-hexane and hydrogen peroxide were purchased from Sigma Aldrich. All chemicals were used as received without further purification.

2.2. Catalyst Preparation

The catalyst was prepared followed by our own preparation method.⁴² In a typical experiment, 1.5 g of $Cu(NO_3)_2$. 3H₂O and 26 g ZrOCl₂ · 8H₂O were dissolved (taking 4% Cu loading on ZrO₂ by weight) in 34 g deionized water at RT to give a clear blue solution. The pH of solutions was measured by pH Meter Eutec (Code: 08001-07), which was standardized for pH measurement prior to use. The pH of the medium was made 9, by gradual addition of NH₄OH solution dropwise; the colour of the solution became forest green gradually. Then 1.7 g of CTAB was dissolved in water by intensive stirring for 2 h. A solution of hydrazine monohydrate (80% aqueous solution) was added drop wise (0.6 g) to the well stirred mixture at RT by simultaneous, vigorous agitation. All the reagents were used maintaining the ratio: Cu: CTAB: hydrazine: $H_2O = 1:0.75:1:300$. The mixture was stirred vigorously for 30 min and subsequently sealed in a Teflon lined stainless-steel autoclave (250 mL capacity). The autoclave was heated to and maintained at 180 °C for 24 h and then allowed to cool to RT. The sky-blue fluffy solid products (precipitates) were collected by centrifugation at 5000 rpm and washed with water and ethanol several times prior to drying in air at 60 °C for 6 h. The resulting dry powder was transferred to a quartz reactor inside a tubular resistance furnace for calcination. The calcination was operated at 800 °C under O₂ atmosphere at ramp of 1 °C min⁻¹. The obtained oxides were stored for further characterization.

2.3. Catalyst Characterization Techniques 2.3.1. X-Ray Power Diffraction (XRD)

Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K_{α} radiation source. Diffraction patterns in the 2°–80° region were recorded at a rate of 0.5 degrees (2q) per minute.

2.3.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy images were taken on a FEI Quanta 200 F, using tungsten filament doped with

J. Nanosci. Nanotechnol. 15, 5816-5822, 2015

lanthanumhexaboride (LaB_6) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer.

2.3.3. Transmission Electron Microscopy (TEM)

TEM images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid.

2.3.4. X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were recorded on a Thermo Scientific K-Alpha X-Ray photoelectron spectrometer and binding energies $(\pm 0.1 \text{ eV})$ were determined with respect to the position C 1s peak at 284.8 eV.

2.3.5. Inductively Coupled Atomic Absorption Spectroscopy (ICP-AES)

Chemical analyses of the metallic constituents were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer; model: PS 3000 uv, (DRE), Leeman Labs, Inc. (USA) 1058-17

cientific Publishers

2.3.6. Thermogravimetric Analyses (TGA)

The uncalcined catalyst were carried out in a Pyris Diamond, Perkin Elmer Instruments, and Technology by SII [(SEIKO Instruments INC), USA] instrument-balance by heating 2.15 mg samples at 5 °C min⁻¹ in flowing air.

2.3.7. Fourier Transform Infra-Red Spectroscopy (FT-IR)

The FTIR spectra were recorded on a Thermo Nicolet 8700 (USA) instrument with the operating conditions: resolution: 4 cm^{-1} , scan: 36, operating temperature: 23-25 °C and the frequency range: 4000–400 cm⁻¹. Spectra in the lattice vibrations range were recorded for wafers of sample mixed with KBr.

2.4. Liquid Phase Catalytic Reaction

The catalytic reactions were carried out batchwise in a 25 ml round bottomed flask with continuous stirring (1100 rpm). In a typical run, 50 mg of the catalyst was dispersed in a solution (total volume = 2 ml) containing 1 g of *n*-hexane, 0.8 g of H₂O₂ (50% aqueous solution). Aliquots were periodically collected every 1 h, centrifuged to remove the solid particles and analyzed by GC (GC, Agilent 7890) using a capillary column, HP5 (5% phenylmethylsiloxane (30 m length, 0.28 mm id, 0.25 μ m film thickness), equipped with FID detector. The identities of the products were established by GC, compared with the authentic products and GC-MS (Hewlett Packard). The total conversion and product distribution (estimated in moles) were evaluated with a calibration curve (obtained by injecting known amounts of authenticated standard compounds), the individual yields being calculated and normalized with respect to the GC response factors.

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization

XRD pattern of the prepared and used Cu/ZrO₂ catalyst samples are shown in Figure 1. The appearance of the indexed diffraction lines at $2\theta = 30.16^{\circ}$, 34.45° , 35.3° and 50.37° indicate the presence of the crystalline phases of tetragonal ZrO₂ in the sample.³⁰ The particle size evaluated from the Scherrer equation using the peak at 2θ value of 50.37° having the maximum intensity, and it was found to be 16.8 nm, which beared consistency with the HRTEM results (Fig. 5). In addition to the characteristic peaks of tetragonal zirconia, XRD peaks due to the crystalline CuO phase were also noticed with 2θ value of 35.5° and 38.7° which probably the active phase, supported on nanocrystalline zirconia.³⁰ We also noticed that, with the increment in Cu loading three distinct peaks of Cu(II) gradually increased (Fig. 1). Furthermore, no significant change in the XRD pattern of the spent catalyst (only negligible decrement in intensity) was observed (Fig. 1(d)); which ascertained the fact that, there was no phase change during catalysis.

The catalyst surface compositions as well as the oxidation state were investigated by XPS. Figures 2(a) and (b)



Figure 1. XRD diagram of Cu/ZrO₂ catalyst with Cu loading (a) 2.6%, (b) 3.6%, (c) 9.8% and (d) spent Cu/ZrO₂ catalyst (after 5 reuse).

show Cu2p and Zr3d XPS spectra of the Cu/ZrO₂ catalyst respectively. The binding energy of the Cu2p_{3/2} peak at 934.2 and the characteristic shakeup feature at a binding energy of 944 eV are indicative for Cu²⁺ species.³⁰ Zr $3d_{5/2}$ and Zr $3d_{3/2}$ binding energy values are in the range of 181.8 and 184.5 eV, respectively. This provides an evidence for the presence of Zirconium oxide in 4+ oxidation state.³⁰

A representative SEM (Fig. 3) image has been plotted to show the morphology of the catalyst. SEM images revealed that the sample is composed of almost homogeneously distributed uniform nanoparticles with size 10–20 nm. SEM-EDX diagram has been plotted (Fig. 3(c)) as an evidence of the presence of Cu, Zr and O in the sample. We also noticed that there was no morphological change of the catalyst even after 5 recycles from its corresponding SEM image (Fig. 3(d)). SEM images of the Cu/ZrO₂ catalyst prepared using acidic pH (pH = 1.0) (Fig. 4) has been plotted to compare the morphological difference with the former catalyst; formation of larger particle with non-uniform particles was noticed. More interestingly, no peak due to the presence of Cu was detected in the SEM-EDAX diagram (Fig. 4(d)). This observation actually states the necessity of basic medium for the synthesis of the uniform Cu/ZrO₂ nanoparticles catalyst.

Transmission Electron Microscopy (TEM) images of the catalyst (Fig. 5) revealed the formation of uniform particle size with an average size of ~10 nm. From the HRTEM diagram (Fig. 4(c), inset), two different patches with corresponding to two different interplanar spacings, d = 0.29 nm and d = 0.23 nm are noticed; these may be attributed due to the presence of tetragonal zirconia with (111) plane [JCPDS. 17-923] and CuO with (111) plane [JCPDS. 89-2530]. Furthermore, the TEM diagram of the spent catalyst (Fig. 4(d)) was almost same with that of the fresh one (Figs. 4(a)–(c)), indicating the fact that, the catalyst was devoid of any severe structural change during catalysis (Table I).

It is worth mentioning that, the embedment of the CTAB molecules on the uncalcined catalyst can be analyzed by the FTIR analysis (Fig. 6). A comparison of the FTIR-spectra of dried uncalcined sample, with that of pure CTAB was analyzed, which not only confirmed the presence, but also revealed the nature of interaction of CTA- molecules with the Cu-Zr surface. The peaks of the sample at 809, 1062 cm⁻¹ can be assigned to the C—N⁺ stretching modes of CTAB molecules.43 The peak at 1378 and at 1462 cm⁻¹ were assigned to symmetric mode of vibration of the head groups of the methylene moiety $(N^+ - CH_3)$ and CH_2 scissoring mode respectively.⁴³ The frequencies above 1600 cm⁻¹ to 3000 cm⁻¹ can be attributed due to CH2 symmetric antisymmetric vibrations region. It is to be noted that, the shift of vibrations to lower frequency suggested that, alkyl chains experienced

J. Nanosci. Nanotechnol. 15, 5816-5822, 2015



Figure 2. XPS diagram: (a) Cu2p and (b) Zr3d core level spectra.



Figure 3. (a)–(b): SEM images at different magnifications (c) SEM-EDAX of the CuO/ZrO₂ catalyst and (d) SEM of the spent CuO/ZrO₂ catalyst (after 5 recycles).



Figure 4. (a)–(c): SEM images and (d) SEM-EDAX diagram of the catalyst prepared at pH = 1.

J. Nanosci. Nanotechnol. 15, 5816-5822, 2015



a more hydrophobic environment in Cu-Zr blocks upon the surface of which the CTAB moieties were supposed to be bounded.⁴³ These typical frequencies were absent when the material was calcined at 750 °C in presence of oxygen (fresh catalyst) in the case of the prepared catalyst, which indicated that, the embedded CTAB moieties have been completely removed from the catalyst surface during calcination. The IR spectra of the calcined sample showed a strong absorption at 470 cm⁻¹ due to the Zr–O vibration, which was expected to be generated after calcination.⁴⁴ Furthermore, the absorption bands at 350, 485 and 590 cm⁻¹ indicated the formation of tetragonal zirconia, which further supported the XRD data.

The embedment of CTAB molecules on the pre-calcined catalyst surface was further confirmed from TGA analysis. TGA analysis (Fig. 7) was operated to understand the various decomposition regimes. The TGA diagram showed



Figure 5. TEM images of (a)–(c) fresh and (d) spent (after 5 recycle) Cu/ZrO₂ catalyst.

	Catalyst	Cu loading(%)	$C_H(\%)^b$	$S_{ m P}(\%)^c$					
Entry				1-ol	2-ol	2-one	3-ol	Others	\mathbf{E}_{o}^{d}
1	СиО ^{сом}	>99	3	_	10	15	22	53	0.3
2	Cu ₂ O ^{COM}	>99	3.5	_	8	12	28	52	0.28
3	ZrO_2^{COM}	-	6	_	12	17	28.5	42.5	0.7
4^e	Cu/ZrO ₂ ^{PM}	15	4.5	_	12.5	22	24	41.5	0.6
5^{f}	Cu/ZrO_2^{NP}	3.6	55	1	70	20	5	4	38.5
6 ^g	Cu/ZrO_2^{NP}	3.6	48	0.05	65	22	8	4.95	31.2
7	$Cu/ZrO_2^{NP1.6}$	2.6	18	_	72	15	6	7	12.9
8	Cu/ZrO ₂ ^{NP9.8}	9.8	57	0.08	55	12	10	23	31.3
10	No Catalyst	-	_	_	_	_	_	_	_
11^{h}	Cu/ZrO ₂ ^{NP}	3.6	62	_	45	18	25	12	9.3
12^{i}	Cu/ZrO_2^{NP}	3.6	67	_	32	28	22	18	21.4
13	Cu/ZrO_2^{NP}	3.6	_	-	-	-	-	_	-

Table I.	Reaction	conditions	of	catalytic	oxidation	of	<i>n</i> -hexane ^{<i>a</i>} .
				~			

Notes: ^aTypical reaction conditions: substrate (*n*-hexane) = 1 g, catalyst = 0.05 g, *n*-hexane: H_2O_2 (molar ratio) = 1:1, reaction temperature = RT, time = 6 h. ${}^{b}C_{H}$ = Conversion of *n*-hexane based upon the FID-GC using chloroform as external standard = [Moles of *n*-hexane reacted/initial moles of *n*-hexane used] × 100; ${}^{c}S_{P}$ = Selectivity to 2-hexanol = [Moles of products produced/moles of *n*-hexane reacted] × 100; ${}^{d}E_{o}$ = H_2O_2 efficiency = [Moles of 2-hexanol formed/total moles of H_2O_2 added] × 100; ${}^{e}Cu/ZrO_2$ catalyst prepared by physical mixing (PM) of CuO and ZrO₂; ${}^{f}Cu(II)$ nanoclusters supported on nanocrystalline ZrO₂ fresh catalyst; ${}^{g}Cu(II)$ nanoclusters supported on nanocrystalline ZrO₂ spent (after 5 recycle) catalyst; ${}^{h}n$ -hexane: H_2O_2 (molar ratio) = 1:3 and i reaction temperature = 50 °C.

that the weight loss has three regimes, first being the loss of water followed by the decomposition of reactants to form NO_x and organic phases at 150 to 250 °C and finally the combustion of CTAB between 250°–350 °C. A further small mass loss is noticed between 400°–550 °C due to the elimination of remaining carbon and organic compounds. Further weight loss was not observed when the temperature was further increased from 780°–900 °C, indicating the generation of the Cu/ZrO₂ catalyst (zirconia at its tetragonal phase) in that temperature range. The total mass loss is 21.2% upto 800 °C.

3.2. Activity of the Catalyst

Table I shows the activities of the Cu/ZrO_2 nanoparticles catalyst in the direct oxidation of *n*-hexane in liquid phase

 $\left(\begin{array}{c} \text{(III)}\\ \text{(III$

Figure 6. FTIR images of (a) pure CTAB, (b) uncalcined Cu/ZrO₂ catalyst, (c) calcined Cu/ZrO₂ catalyst and (d) Cu/ZrO₂ catalyst after 5 reuse.

by using H₂O₂ as oxidant. Blank experiment was performed without the catalyst and it was found that there was no conversion of the reactant. Commercial CuO, Cu₂O, ZrO_2 did not show any activity for *n*-hexane oxidation (Table I, Entry 1-3). Commercial CuO, mixed with commercial zirconia by physical mixing (Table I, Entry 4) and was introduced as a catalyst in the oxidation reaction; but still, no improvement in the catalytic activity was noticed. Introducing the prepared Cu/ZrO₂ nanoparticles catalyst (Cu/ZrO₂^{NP}), significant increment in the catalytic activity was noticed (Table I, entry 5). Room temperature (35 °C) as well as low concentration of oxidant rendered the production of 2-hexanol. Increment of either of these parameters lead to the decrement in the selectivity of 2-hexanol, although conversion of *n*-hexane increased. Six hour reaction time was proved to be the optimum one. It was also noticed that, with time, the conversion of *n*-hexane increased, but the selectivity to the desired



Figure 7. TGA of the uncalcined Cu/ZrO₂ catalyst.

J. Nanosci. Nanotechnol. 15, 5816-5822, 2015



Figure 8. Effect of time on *n*-hexane oxidation. $[\blacksquare]$ Conversion of *n*-hexane; $[\bullet]$ Selectivity to 2-hexanol; $[\blacktriangle]$ yield of to 2-hexanol. Reaction Condition: *n*-hexane = 1 g; Catalyst = 0.05 g; *n*-hexane: H₂O₂ mole ratio = 1:1; temperature = RT (35 °C).

product was considerably less due to the formation of other oxygenates with time (Fig. 8). Moreover, higher loading of copper also affects the reaction. Higher loading of copper indicates the increment of active copper sites on the catalyst, which renders the conversion of the reactant; but selectivity to 2-hexanol decreases considerably (Table I, Entry 8).

The oxidation path probably follows participation of free radicals in the presence of the oxidant H_2O_{29} over transition metals.⁴⁵ Addition of small quantities of hydroquinone, a free-radical scavenger, greatly hinders the oxidation (Table I, Entry 13), and thereby confirms the involvement of free radicals in the oxidation reaction.

3.3. Reusability Test

At the end of the reaction, the catalyst was filtered in the hot condition and the resulting filtrate was independently analyzed by ICP-AES for free or dissolved metal ions. Only trace amounts of Cu^{2+} (<3 ppb) were detected; which indicated the fact that, the catalyst is almost devoid of leaching properties; this may be attributed by the fact that, Cu^{2+} remains strongly anchored upon ZrO_2 support,

Table II. The reusability of Cu/ZrO₂ catalyst.^a

Recycling	C^b_{μ}			%Cu Loading			
no.	(%)	1-ol	2-ol	2-one	3-ol	Others	(ICP-AES)
1	55	1	70	20	5	4	3.6
2	54	1	70	20	5.5	3.5	3.6
3	52.5	1	68.5	20	6	4.5	3.6
4	50	0.08	68	21.5	6	4.4	3.6
5	49.5	0.07	66.5	21	7	5.4	3.6
6	48	0.05	65	22	8	4.95	3.6

Notes: ^{*a*}Typical reaction conditions: substrate (*N*-hexane) = 1 g, catalyst = 0.05 g, *n*-hexane: H_2O_2 (molar ratio) = 1:1, reaction temperature = RT, time = 6 h. ^{*b*}C_{*H*} = Conversion of *n*-hexane; ^{*c*}S_{*P*} = Selectivity to products.

J. Nanosci. Nanotechnol. 15, 5816-5822, 2015

Table III. The comparative studies on the selective oxidation of n-hexane.

			~ .		
Entry	Catalyst	Oxidant	Reaction conditions	Yield of 2-Hexanol	References
1	MnAlPO-18	O ₂	100 °C,	0.7	Nature 398, 227 (1999).
			1.5 MPa		
			Pressure		
2	Vanadium phosphorus oxide	H_2O_2	65 °C	-	New J. Chem. 27, 525 (2003).
3	Polyoxometalate	H_2O_2	69 °C	18.5	Nature Chem. 2, 478 (2010)
4	Cu-ZrO ₂	H_2O_2	RT	38.5	Our work (2014)

possessing highly stable tetragonal phase.²² Recycling and reusability of the catalyst was examined by introducing the used catalyst subsequently 5 times to carry out the catalytic oxidation (Table II). The reusability of the catalyst was studied without regeneration of the catalyst in the same experimental condition. Before each recycle, the catalyst was recovered easily from the reaction mixture (after 6 h) by centrifugation, repeatedly washed with ethanol and acetone and kept for drying at 120 °C for overnight. The catalyst showed $\sim 65\%$ selectivity even after 5 successive runs and the catalyst was proved to be truly of heterogeneous nature.

ered by Ingenta to: West Virginia University/ Health Sci Ctr Llb

4. CONCLUSION

In conclusion, we have successfully prepared Cu (II) nanoclusters supported on nanocrystalline ZrO_2 by hydrothermal synthesis method in presence of surfactant cetyltrimethylammonium bromide and found that the catalyst can convert *n*-hexane to 2-hexanol without using any solvent. The catalyst was thoroughly characterized by XRD, XPS, SEM, TEM, FTIR, TGA and ICP-AES. A *n*-hexane conversion of 55% with 2-hexanol selectivity of was achieved over this catalyst. The catalyst did not change any significant activity even after 5 reuses, showing the true heterogeneity of the catalyst.

Acknowledgments: Shankha Shubhra Acharyya thanks CSIR and Shilpi Ghosh thanks UGC, New Delhi, India, for their respective fellowships. Rajaram Bal thanks CSIR, New Delhi for the financial support in the form of 12 FYP Project (CSC-0125).The Director, CSIR-IIP is acknowledged for his help and encouragement. The authors thank Analytical Section Division, IIP for the analytical services.

References and Notes

- M. Manikandan, T. Tanabe, P. Li, S. Ueda, G. V. Ramesh, R. Kodiyath, J. Wang, T. Hara, A. Dakshanamoorthy, S. Ishihara, K. Ariga, J. Ye, N. Umezawa, and H. Abe, *ACS Appl. Mater. Interfaces* 6, 3790 (2014).
- M. Boronat, A. Leyva-Pérez, and A. Corma, Acc. Chem. Res. 47, 834 (2014).

- 3. N. A. Fadil, G. Saravanan, G. V. Ramesh, F. Matsumoto, H. Yoshikawa, S. Ueda, T. Tanabe, T. Hara, S. Ishihara, H. Murakami, K. Ariga, and H. Abe, Chem. Commun. 50, 6451 (2014).
- 4. J. Lee, K. Han, and D. Jang, Appl. Catal. A Gen. 469, 380 (2014). 5. M. Jafarpour, M. Ghahramaninezhad, and A. Razaeifard, RSC Adv. 4, 1601 (2014).
- 6. J. Goscianska, M. Ziolek, E. Gibson, and M. Daturi, Catal. Today 152, 33 (2010).
- 7. D. A. Ward and E. I. Ko, Ind. Eng. Chem. Res. 34, 421 (1995).
- 8. Y. W. Li, D. H. He, Z. X. Cheng, C. L. Su, J. R. Li, and M. Zhu, J. Mol. Catal. A: Chem. 175, 267 (2001).
- 9. G. Korotcenkov, S. D. Han, and J. R. Stetter, Chem. Rev. 109, 1402 (2009).
- 10. E. C. Subbarao and H. S. Maiti, Adv. Ceram. 24, 731 (1988).
- 11. S. P. S. Badwal, F. T. Ciacchi, V. Zelizko, and K. Giampietro, Ionics 9. 315 (2003).
- 12. E. C. Sbuarao and H. S. Maiti, Solid State Ionics 11, 317 (1984).
- 13. P. F. Manicone, P. R. Iommetti, and L. Raffaelli, J. Dent. 35, 819 (2007).
- 14. Y. Q. Wang and G. Sayre, Surf. Coat. Technol. 203, 2186 (2009).
- 15. V. Z. Fridman and A. A. Davydov, J. Catal. 195, 20 (2000).
- 16. B. Sarkar, P. Prajapati, R. Tiwari, R. Tiwari, S. Ghosh, S. S. Acharyya, C. Pendem, R. K. Singha, L. N. S. Konathala, J. Kumar, T. Sasaki, and R. Bal, Green Chem. 14, 2600 (2012).
- 17. T. W. Kim, M. W. Song, H. L. Koh, and K. L. Kim, Appl. Catal. A 210. 35 (2002).
- 18. G. Centi and S. Perathoner, Appl. Catal. A 132, 179 (1995)
- 19. A. Dandekar and M. A. Vannice, Appl. Catal. B 22, 179 (1999).
- 20. M. Matsuoka, W. Ju, K. Takahashi, H. Yamashita, and M. Anpo, J. Phys. Chem. B 104, 4911 (2000).
- 21. A. Martinez-Arias, M. Fernandez-Garcia, O. Galvez, J. M. Coronado, J. A. Anderson, J. C. Conesa, J. Soria, and G. Munuera, J. Catal. 195, 207 (2000).
- 22. K. J. Choi and M. A. Vannice, J. Catal. 131, 22 (1999). 185 On: Tue
- 24. D. L. Trimm and Z. I. Onsan, Catal. Rev. 43, 31 (2001).

- 25. A. Dandekar and M. A. Vannice, J. Catal. 178, 621 (1998).
- 26. Y. Sun and P. A. Sermon, J. Chem. Soc. Chem. Commun. 1242 (1993).
- 27. A. M. Hegne and C. V. Rode, Green Chem. 14, 1064 (2012).
- 28. Z. Y Ma, C. Yang, W. Wei, W. H. Li, and Y. H. Sun, J. Mol. Catal. A: Chem. 231, 75 (2005).
- 29. Y. Okamoto, T. Kubota, H. Gotoh, Y. Ohto, H. Aritani, T. Tanaka, and S. Yoshida, J. Chem. Soc. Faraday Trans. 94, 3743 (1998).
- 30. K. V. R. Chary, G. Vidya Sagar, C. S. Srikanth, and V. V. Rao, J. Phys. Chem. B 111, 543 (2007).
- 31. G. Wu, Y. Sun, Y. W. Li, H. Jiao, H. W. Xiang, and Y. Xu, J. Mol. Str. Theochem. 626, 287 (2003).
- 32. Y. Sun and P. A. Sermon, J. Chem. Soc. Chem. Commun. 1242 (1993).
- 33. Y. Sun and P. A. Sermon, Catal. Lett. 29, 361 (1994).
- 34. C. Jia, T. Kitamura, and Y. Fujiwara, Acc. Chem. Res. 34, 633 (2011).
- 35. J. A. Labinger and J. E. Bercaw, Nature 417, 507 (2002).
- 36. R. A. Sheldon and J. K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York (1981).
- 37. Y. Wang, H. Li, J. Yao, X. Wang, and M. Antonietti, Chem. Sci. 2. 446 (2011).
- 38. J. A. Labinger, J. Mol. Catal. A: Chem. 220, 27 (2004).
- 39. J. M. Thomas, R. Raja, G. Sankar, and R. G. Bell, Nature 398, 227 (1999).
- 40. B. Z. Zhan, B. Modén, J. Dakka, J. G. Santiesteban, and E. Iglesia, J. Catal. 245, 316 (2007).
- 41. K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara, and N. Mizuno, Nature Chem. 2, 478 (2010).
- 42. S. S. Acharyya, S. Ghosh, R. Tiwari, B. Sarkar, R. K. Singha, C. Pendem, T. Sasaki, and R. Bal, Green Chem. 16, 2500 (2014)
- 43. W. Cheng, S. Dong, and E. Wang, Langmuir 19, 9434 (2003).
- 44. L. A. Pérez-Maqueda and E. Matijević, J. Mater. Res. 12, 3286 (1997)
- 23. J. Szanyi and D. W. Goodman, Catal. Lett. 21, 165 (1993). Start Star Heterogeneous Catalysis Academic, London (1967), p. 383.

Received: 3 May 2014. Accepted: 2 June 2014.