Catalytic Properties for Decomposition of *sec*-Butyl Alcohol Over ZnO@SiO₂ Nanocomposites Sol-Gel Catalysts

XIAOMEI ZHU, RU LI, NGOC LONG NGUYEN and BING SUN[*]

College of Environment Science and Engineering, Dalian Maritime University, Dalian, P.R. China

*Corresponding author: Tel/Fax: +86 411 84727679; E-mail: zxmhc7879@126.com

ZnO@SiO₂ catalysts of two different zinc oxide contents were prepared by the sol-gel technique and calcined at 653 and 953 K. ZnO/SiO₂ catalyst with 9 % zinc oxide content was prepared by impregnation method as compare. The samples prepared were then used as catalyst in the decomposition of *sec*-butyl alcohol. They were found to give the opposite selectivity for dehydrogenation or dehydration on the catalysts prepared *via* the different methods. Characterization of the catalysts by TEM, BET and XPS confirmed that the difference of selectivity for dehydrogenation or dehydration was no obvious relation with the crystal, size, surface area, pore volume and reaction temperature. Further studies indicate that the reason of the different surface properties is caused by different interactions between zinc oxide and the silica matrix.

Keywords: *sec*-Butyl alcohol, ZnO@SiO₂, Sol-gel catalysts.

INTRODUCTION

The sol-gel preparation of multicomponent materials composed of transition metal dispersed on a silica matrix has been the subject of considerable attention[1,2]. This interest has been spurred by the broad potential uses for these materials in applications ranging from catalysis, optics, electronics and chemical sensing[3-8]. The low synthesis temperatures often lead to the formation of oxides with amorphous or metastable phases, which are not produced by other synthesis routes[9]. Because of the molecular-level mixing, *i.e.*, the formation of M-O-M' bond[10,11], active species is effectively incorporated into the ionic oxide network and may lead to more stable catalysts by the sol-gel method than those prepared by conventional methods[12,13].

Zinc oxide has a broad range of applications, *e.g.*, in pigments, rubber additives, gas sensors and catalysts *etc*. Recently, some authors reported the effects of process variables on the microstructure and the growth of particles or propose dispersion of zinc oxide nanoparticles on support in order to avoid the tendency of nanopowders to aggregate and control the nanoparticle size distribution[14-17]. Some literatures report the structural properties and characterization of a fine dispersion of zinc oxide nanoparticles on the matrix[17,18]. For the surface properties and catalytic application of ZnO@SiO₂, little has been published compared with other metal oxide nanocomposites such as MgO-SiO₂[19] and CuO-SiO₂[20].

In the present work, zinc oxide nanoparticles on the silica matrix have obtained through the sol-gel and impregnation methods. The samples prepared are characterized by the XRD, BET, TEM and XPS techniques. Furthermore, the decomposition of *sec*-butyl alcohol has chosen as a probe reaction for investigating activity and selectivity toward dehydration or dehydrogenation to probe the surface properties of the samples prepared by the different methods.

EXPERIMENTAL

Preparation of catalyst: ZnO@SiO₂ nanocomposites studied in this work were prepared by a sol-gel method from Si(OC₂H₅)₄ (TEOS) and Zn(NO₃)₂·6 H₂O precursors according to reference[18]. The ZnO content was 9 and 16 % and the calcination temperature was 653 and 953 K, respectively. The ZnO@SiO₂ samples were prepared by mixing an alcoholic solution of TEOS and an aqueous solution of zinc nitrate. The molar ration TEOS/C₂H₅OH/H₂O was 1:4:10 and there was Zn(NO₃)₂·6 H₂O in the right amount to get the nominal ZnO content. After 1 h of stirring at room temperature, the clear sol was poured into a Teflon beaker and allowed to gel in air. After one week, the gel was dried in an oven by slowly raising the temperature to 363 K over a week. The samples were then powdered and heated to temperatures up to the setting temperature, in steps of 100 K maintaining the temperature at each step for 0.5 h. The sample of ZnO/SiO₂ used in this paper was obtained by the impregnation method as follow: the SiO₂ was

calcined at 723 K for 4 h and impregnated with zinc nitrate solution. The sample impregnated was then dried at 343 K for 12 h then heated up to 653 K in the same procedure with $ZnO@SiO_2$. All samples are donated $Z_x@S_y$ and Z_x/S_y, where "x" indicates the wt. % of ZnO and "y" the calcination temperature, '@' means the sample obtained from sol-gel method and '/' the impregnation way, respectively. "z" represents ZnO and "s" SiO_2. SiO_2 was prepared by the same procedure with $Z_x@S_y$ samples. ZnO was obtained by adding $(NH_4)_2CO_3$ solution into zinc nitrate solution and then calcination the deposition at 723 K for 2 h.

The catalysts were characterized using powder X-ray diffraction, transmission electron microscopy, BET and X-ray photoelectron spectroscopy.

Power X-ray diffraction pattern were collected on Rigaku D/max IIIA diffractometer with CuK$_\alpha$ radiation at 35 kV and 25 mA. BET specific surface areas of the samples were measured on a Micromeritics ASAP 2010 system under liquid-N_2 temperature using N_2 as the adsorbate. XPS were performed using ESCA LAB MK II (VG Co., England) with Al K$_\alpha$ (1486.6 eV) radiation. Charging effects were corrected by adjusting C1s peak to 284.6 eV. Spectra O1s were recorded and the samples were used as powders. TEM was carried out on a Hitachi H-8100 transmission electron microscope operating at 200 kV to observe the zinc oxide nanoparticles.

Catalytic activity measurements: Decomposition of *sec*-butyl alcohol was carried out in a fixed bed reactor system. The catalyst (0.46 g, 40-60 mesh) was held in place by a glass-wool in a stainless steel reactor vertically positioned in an electrical heater whose temperature was controlled to 553-653 K. *sec*-Butyl alcohol was directly introduced into the reactor using a LB PULSELESS pump (made in Shanghai, China) without any carrier gas. At selected intervals, a fixed volume of the reacted mixture was analyzed with on-line gas chromatograph using a flame ionization detector. The areas of the GC peaks were determined with a Shimadzu C-R6A Chromatopac.

RESULTS AND DISCUSSION

The XRD spectra of ZnO/SiO_2 and all the $ZnO@SiO_2$ samples do not display any diffraction peaks with only the amorphous pattern of vitreous silica, it indicates that the ZnO particles are very small or highly dispersed on the support. In the case of ZnO catalyst, the XRD pattern reveals that all peaks can be attributed to crystalline zinc oxide (Fig. 1).

Surface characterization (BET): Table-1 presents the surface characteristic of $ZnO@SiO_2$, Z_9/S_{653} catalysts and fresh SiO_2. Table-1 shows that all the catalysts have less surface area, pore volume, pore diameter and pore surface areas than the fresh SiO_2. For the $ZnO@SiO_2$ samples, the content of zinc oxide and calcination temperature influence the surface characteristics. The higher contents of zinc oxide and the higher calcination temperature are, the lower surface areas and the smaller volume, diameter, surface areas of pore are obtained. The phenomenon indicates that some small pores will be blocked and this blockage will become severe with zinc loading and calcination temperature by the sol-gel method. Furthermore, though the preparation method is different, Z_9/S_{653} and Z_9-S_{653} have the similar BET characteristic.
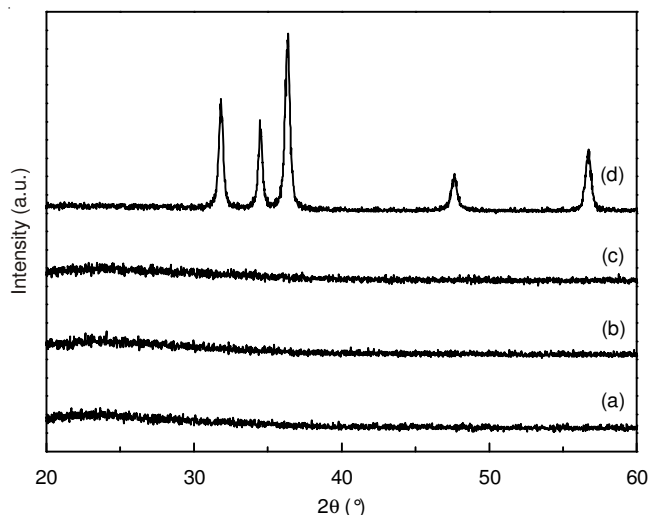

Fig. 1.   XRD patterns of the samples: (a) Z_9/S_{653}, (b) $Z_9@S_{673}$, (c) $Z_{16}@S_{953}$ and (d) ZnO

TABLE-1
BET CHARACTERIZATION OF $Z_x@S_y$, Z_x/S_y AND SiO_2 SAMPLES

Samples	Surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)
$Z_9@S_{653}$	453	0.167	2.1
$Z_{16}@S_{953}$	276	0.110	1.5
Z_9/S_{653}	438	0.165	2.3
S_{653}	808	0.368	2.7

Transmission electron microscopy: Transmission electron microscopy of catalysts are shown in Fig. 2. For Z_9/S_{653} sample, the zinc oxide nanoparticles are observed, but size is slightly bigger than that of $Z_9@S_{653}$. The reason is probably because that the zinc oxide particles are limited by the silica network and avoid the tendency to aggregate by the sol-gel method. The results indicates that ZnO nanocrystal influenced slightly by the differents preparation methods.
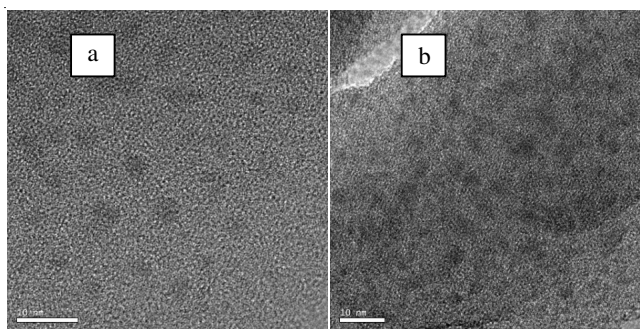

Fig. 2. TEM photo of the samples: (a) $Z_9@S_{653}$, (b) Z_9/S_{653}

X-ray photoelectron spectroscopy: The O 1s XPS binding energies are shown in Table-2. The O 1s peak at 530.3 eV is assigned to ZnO. The contributions at 533.4 eV is assigned to the matrix SiO_2, while the highest energy contribution for 534.8 eV is assigned to unreacted Si-OH on the SiO_2[21,22]. As for the fourth contribution to the O 1s peak at 532.2 eV, may be assigned to a combination of oxygen in Zn-O-Si linkages and the Z-OH linkages. The deduction is base on the results of Aronson *et al.*[23], who speculated similar binding energies for O 1s in Zn/Mn-MCM-41. Actually, formation of Si-O-Zn bonds

between zinc oxide particles and silica has been confirmed by Cannas *et al.*[18] and Khouchaf *et al.*[16]. As shown in Table-2, much Zn-OH except ZnO is observed on surface of ZnO sample. For Z$_9$/S$_{653}$ catalyst, Zn-O-Si, Zn-OH/Si-OH, SiO$_2$ and ZnO are all found. The ZnO and Si-OH are not observed for Z$_9$@S$_{653}$ sample.

TABLE-2
XPS BINDING ENERGIES FOR ZnO, Z$_9$/S$_{653}$ AND Z$_9$@S$_{653}$ SAMPLES

	Element orbital	Binding energy (eV)	Assignment
ZnO	O 1s	530.3	ZnO
		532.1	Zn-OH
Z$_9$/S$_{653}$	O 1s	530.4	ZnO
		532.2	Zn-O-Si, Zn-OH
		533.4	SiO$_2$
		534.8	Si-OH
Zn$_9$@S$_{653}$	O 1s	532.3	Zn-O-Si, Zn-OH
		533.9	SiO$_2$

Catalytic activity: The results for *sec*-butyl alcohol conversion and selectivity to dehydrogenation or dehydration are shown in Table-3. No decomposition products can be examined at 553 K when the SiO$_2$ is used as catalyst, even if the reaction temperature is elevated to 653 K, the silica also shows a poor conversion of *sec*-butyl alcohol. However, when ZnO is supported on silica (Z$_9$/S$_{653}$) by impregnation method, high reaction activity is observed and the conversion is increased with the reaction temperature, from 81.9 % for 553 K to 99 % for 653 K. For ZnO@SiO$_2$ catalysts prepared by sol-gel method, the conversion of *sec*-butyl alcohol improves with zinc oxide content and reaction temperature. As for products distribution, in contrast to ZnO@SiO$_2$ samples the Z$_9$/S$_{653}$ exhibits opposite selectivity for dehydration and dehydrogenation. High selectivity to butene (more than 90 %) is showed over ZnO@SiO$_2$ samples, but high selectivity toward product of dehydrogenation (methyl ethyl ketone, 90 %) on Z$_9$/S$_{653}$ sample is observed at all reaction temperature.

X-ray diffraction confirmed that zinc oxide particles on silica prepared by the both methods are amorphous. TEM pictures proved that zinc oxide nanoparticles homogeneously dispersed in a silica matrix and the particles size increased slightly with zinc oxide content and treatment. XPS results showed that more Si-OH bond and "free" zinc oxide are present on the surface of Z$_{10}$/SiO$_2$ and little on the ZnO@SiO$_2$ sol-gel catalysts. The results indicate that there will be more strong

interactions between zinc oxide and silica gel matrix by the sol-gel method than the impregnation method. According the reaction results, it is found that the more zinc oxide exits on the surface, the high selectivity for dehydrogenation observed. Obviously, the dehydrogenation reaction is probably due to this kind of zinc oxide. This phenomenon was very similar in decomposition of 2-propanol using ZnO/Al$_2$O$_3$ as catalyst and the kind of zinc oxide is called "free" zinc oxide[24]. So the high selectivity for dehydrogenation observed on Z$_9$/S$_{653}$ is because of much free zinc oxide present on the surface of the silica support. However, the sol-gel method make the zinc oxide and the silica molecular-level mixing and zinc oxide can be effectively incorporated into the silica network, hence increasing the chance of interactions between zinc oxide and Si-OH to form more Zn-O-Si bonds and leading to remain less zinc oxide on the surface of silica matrix. This may be the reason to produce the different selectivity for decomposition between Z$_9$/S$_{653}$ and Z$_9$@S$_{653}$ sol-gel catalysts.

Conclusion

ZnO@SiO$_2$ catalysts of two different zinc oxide contents were prepared by the sol-gel technique and calcined at 653 and 953 K. ZnO/SiO$_2$ catalyst with 9 % zinc oxide content was prepared by impregnation method as compare. The samples prepared were then used as catalysts in the decomposition of *sec*-butyl alcohol. The reaction results showed that the samples prepared by different methods were found to give the opposite selectivity for dehydrogenation or dehydration. Characterization of the catalysts by TEM, BET and XPS confirmed that the difference of selectivity for dehydrogenation or dehydration was no obvious relation with the crystal, size, surface area, pore volume and reaction temperature. Further studies indicated that the reason of the different surface properties is caused by different interactions between zinc oxide and the silica matrix. The high selectivity for dehydrogenation observed on the catalyst prepared by impregnation method was because of much free zinc oxide present on the surface of the silica support and the dehydration products were caused by the interactions between zinc oxide and Si-OH.

TABLE-3
DECOMPOSITION OF *sec*-BUTYL ALCOHOL OVER DIFFERENT CATALYSTS[a]

Samples	553 K			603 K			653 K		
	Selectivity (%)		Conv. (%)	Selectivity (%)		Conv. (%)	Selectivity (%)		Conv. (%)
	Butene	MEK		Butene	MEK		Butene	MEK	
Z$_9$@S$_{653}$	96.9	4.0	65.6	95.2	5.1	99.0	90.9	10.5	99.5
Z$_{16}$@S$_{953}$	94.9	6.0	37.5	88.6	11.6	97.2	80.9	22.6	99.9
S$_{953}$	0	0	0	66.9	38.0	0.4	49.6	52.3	3.0
Z$_9$/S$_{653}$	7.0	94.1	81.9	12.3	89.1	94.4	11.3	87.6	99.0
ZnO	4.0	96.0	69.3	–	–	–	–	–	–

[a]Reaction conditions: reaction time 10 min, GHSV = 1400 h^{-1}, no carrier gas. Before reaction the catalysts is pretreated by argon at 653 K for 30 min., MEK = methyl ethyl ketone, Conv. = Conversion of *sec*-butyl alcohol

REFERENCES

1. J.H. Hong, Y.F. Wang, G. He and J.X. Wang, *J. Non-Cryst. Solids*, **356**, 2778 (2010).
2. R. Anedda, C. Cannas, A. Musinu, G. Pinna, G. Piccaluga and M. Casu, *J. Nanopart. Res.*, **10**, 107 (2008).
3. Z. Yang, Z.Z. Ye, B.H. Zhao, X.L. Zong and P. Wang, *J. Sol-Gel Sci. Technol.*, **54**, 282 (2010).
4. K.J. Chen, F.Y. Hung, S.J. Chang, S.J. Young and Z.S. Hu, *Curr. Appl. Phys.*, **11**, 1243 (2011).
5. S.M. Hossein Hejazi, F. Majidi, M. Pirhadi Tavandashti and M. Ranjbar, *Mater. Sci. Semicond. Process.*, **13**, 267 (2010).
6. R. Longloilert, T. Chaisuwan, A. Luengnaruemitchai and S. Wongkasemjit, *J. Sol-Gel Sci. Technol.*, **61**, 133 (2012).
7. S. Esposito, M. Turco, G. Bagnasco, C. Cammarano and P. Pernice, *Appl. Catal. A Gen.*, **403**, 128 (2011).
8. A. Kaddouri, N. Dupont, P. Gélin and A. Auroux, *Catal. Commun.*, **15**, 32 (2011).
9. C.J. Brinker and G.W. Scherer, Sol-Gel Science, Academic Press, San Diego (1990).
10. K. Masuda, T. Sano, F. Mizukami and K. Kuno, *Appl. Catal. A*, **133**, 59 (1995).
11. N.E. Bogdanchikova, S. Fuentes, M. Avalos-Borja, M.H. Farias, A. Boronin and G. Diaz, *Appl. Catal. B*, **17**, 221 (1998).
12. J. Yan, A.M. Buckley and M. Greenblatt, *J. Non-Cryst. Solids*, **180**, 180 (1995).
13. M.G. Ferreira da Silva and J.M. Fernandez Navarro, *J. Non-Cryst. Solids*, **100**, 447 (1988).
14. Y. Han, X.Y. Kang, T.D. Wang, Y. Han, M.D. Tao and M.J. Tu, *Mater. Res. Bull.*, **32**, 1165 (1997).
15. E.A. Meulenkamp, *J. Phys. Chem. B*, **102**, 5566 (1998).
16. L. Khouchaf, M.H. Tuilier, M. Wark, J.J. Paillaud and M. Soulard, *J. Phys. IV*, **7**, C2-267 (1997).
17. S. Lu, L. Zhang and X. Yao, *Chin. Sci. Bull.*, **41**, 1923 (1996).
18. C. Cannas, M. Casu, A. Lai, A. Musinu and G. Piccaluga, *J. Mater. Chem.*, **9**, 1765 (1999).
19. T. López, R. Gomez, M.E. Llanos and E. López-Salinas, *Mater. Lett.*, **38**, 283 (1999).
20. G. Díaz, R. Pérez-Hernández, A. Gómez-Cortés, M. Benaissa, R. Mariscal and J.L.G. Fierro, *J. Catal.*, **187**, 1 (1999).
21. A.Y. Stakheev, E.S. Shpiro and J. Apijok, *J. Phys. Chem.*, **97**, 5668 (1993).
22. C.D. Wagner, D.A. Zatko and R.H. Raymond, *Anal. Chem.*, **52**, 1445 (1980).
23. B.J. Aronson, C.F. Blanford and A. Stein, *J. Phys. Chem. B*, **104**, 449 (2000).
24. F. Pepe, C. Angeletti and S. De Rossi, *J. Catal.*, **118**, 1 (1989).