Polish J. Chem., **78**, 861–868 (2004)

Effect of Residual Na on Cu-ZnO Catalyst in Dehydrogenation of 2-Butanol

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(Received April 29th, 2003; revised manuscript February 26th, 2004)

A series of residual Na on Cu-ZnO catalysts were prepared by co-precipitation method. The effect of residual Na on catalysts was examined in dehydrogenation of 2-butanol. The catalysts were characterized by BET, ICP, XRD, TPR and XPS techniques. The TPR result showed that residual Na made CuO exists in different phases, the higher the content of Na the harder the reduction of CuO. For reduced or used catalyst with a high content of Na, the XPS result indicated that Na diffused to the catalyst surface and inhibited the interaction between Cu and ZnO. The sharp decrease in catalytic activity by Na incorporation could be interpreted mainly in terms of the copper particle size increasing during reaction. Interaction between Cu and ZnO could have stabilized the copper species. The Na free catalyst shows high and stable activity in dehydrogenation of 2-butanol.

Key words: Na, Cu-ZnO catalyst, dehydrogenation, 2-butanol

The dehydrogenation of 2-butanol to yield methyl-ethyl-ketone (MEK) is an important industrial process. MEK is a widely used industrial solvent. Many investigations found that copper-based catalysts are quite effective for the dehydrogenation of 2-butanol [1–5]. Arsalane *et al.* [1] investigated the $CuTh_2(PO_4)_3$ in 2-butanol conversion. It was found that the dehydrogenation process was related to the migration of Cu^+ ions toward the surface and their replacement in the structure by protons under catalytic reaction conditions. Keuler *et al.* [2] studied the effects of support type (MgO and SiO_2) and copper loading on MEK yield, and the effects of reaction temperature, 2-butanol feed flow rate and catalyst particle size were also investigated. Benarafa *et al.* [3] characterized the active sites of calcium-copper and calcium-sodium-copper phosphates in dehydrogenation of 2-butanol, and they proved that the active sites are the Cu^{2+} ions hosted by the Ca (4) sites.

The effect of alkali upon heterogeneous catalysts was studied [6–15]. The main action of alkali was used in different ways, such as neutralized acid centers, increase the selectivity or specificity, increase the activity and prolong the effective lifetime of the catalyst. The effect of alkali on copper-based catalysts in methanol synthesis has been studied [10–13]. Nunan *et al.* [13] found that the promoter Cs on Cu/ZnO can improve the activity of methanol synthesis. Dantas *et al.* [9] studied the effect of alkali metals on the synthesis of higher alcohols using copper based model catalysts.

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Díez *et al*. [6] and Thomasson *et al*. [15] studied the acid-base properties of alkali-promoted MgO catalysts on decomposition of 2-propanol, 2-butanol and 2-methyl-3-butyl-2-ol.

In this work, we studied the effect of residual Na on the co-precipitated Cu–ZnO catalysts for the dehydrogenation reaction of 2-butanol. The effect of Na on the interaction between Cu and ZnO and the effect on the conversion of 2-butanol and the selectivity 5-methyl-3-heptanone were studied in detail.

EXPERIMENTAL

Catalyst preparation: Catalyst precursors were prepared by conventional co-precipitation method. The aqueous solution of sodium carbonate was added to an aqueous solution, containing copper and zinc nitrates (Cu:Zn molar ratio = 2:1) with constant stirring. The precipitation temperature was maintained at 333 K, and the final pH was kept at 7.0 ~ 8.0. The precipitate was aged for 1 h in the parent liquid, followed by filtration and washing with different volume distilled water. Thus, the precursors with different Na content were obtained. The results are given in Table 1 (the catalysts number was a–e). The precipitate was then dried at 393 K overnight and calcined in air at 623 K for 6 h. The prepared catalysts were reduced in a 30% hydrogen/nitrogen mixed gas at flow rate of 30 ml/min and at 573 K. The reduced and reacted catalysts were protected in Ar.

Table 1. Characteristics of Cu-ZnO catalysts with various Na contents.

Catalyst No.	Na – content (wt%)	Specific surface area (m^2/g)	Cu – crystallite size (nm)	
			After reduction	After reaction
a	8.3	0.7	–	428
b	3.2	6.5	146	246
c	1.8	7.6	129	131
d	1.1	10.5	112	132
e	0	17.3	74	74

Catalyst characterization: The specific surface areas (m^2g^{-1}) of the cataysts were measured by N_2 adsorption at 77 K (BET method), using a Micromeritics ASAP 2010 instrument. The chemical composition of the samples was determined by using ICP-PLASMA 1000. Powder X-ray diffraction (XRD) patterns were obtained with a SHIMADZU/XRD-6000 diffractometer using CuKα (λ = 0.15418 Å) radiation. Temperature-programmed reduction (TPR) was carried out in a conventional TPR system. The dry samples of about 0.02 g were reduced in a mixture of 5% H_2/Ar gas at a flow-rate 30 cm^3 min^{-1}. X-ray photoelectron spectroscopy spectra (XPS) of catalysts were made on a ESCA LAB MKII (VG Co. England) XPS spectrometer with Mg Kα radiation of 1253.6 eV. The C (1s) line at 284.6 eV was used as an internal standard for correction of binding energies.

Catalytic activity test: The catalytic dehydrogenation of 2-butanol was carried out in a fixed-bed flow reactor, constructed of a 0.6 cm I.D. stainless-steel tube and equipped with a thermocouple in the catalyst bed. Suitable catalyst was used in the experiment and the GHSV was kept at 1000 h^{-1}. 2-Butanol was fed into the reactor by a plunger pump and vaporized at the upper part of the reactor. The effluents of the reaction were analyzed by an on-line gas chromatograph with a flame ionization detector and a PEG 20000 column.

RESULTS AND DISCUSSION

Catalysts characteristics: Fig. 1 presents the XRD patterns of the calcined and reduced catalysts with different content of Na. For catalyst with a high content of Na, most of copper oxide (Fig. 1 A1), is reduced to cuprous oxide (Fig. 1 B1), and sodium nitrate (Fig. 1 A1) is reduced to sodium nitrite (Fig. 1 B1). For catalyst with a low content of Na, there still exists a small proportion of sodium nitrate (Fig. 1 A2) on calcined catalyst. After reduction the copper oxide changes into metallic copper (Fig. 1 B2) and sodium nitrate disappears [10]. For the sodium free catalyst, copper oxide changes into copper completely after reduction (Fig. 1 B3). The XRD result indicates, that the including of Na on catalysts made copper oxide difficult to be reducted. The particles size of metallic copper is listed in Table 1. We can find, that the higher the content of Na, the bigger the particles size of copper over the reduced and reacted catalysts (Table 1 a–d). For Na free catalyst, particle size of copper does not change before and after reaction (Table 1 e). It indicates, that the existing of Na could have inhibited the interaction between Cu and ZnO and the result is the increase of the metallic copper. Similar phenomena were also found by other authors in the alkali metals promoted catalysts [6,10–12,15]. About the interaction between Cu and ZnO over Cu-ZnO catalysts, which were prepared by coprecipitation method, has been reported already [16–19].

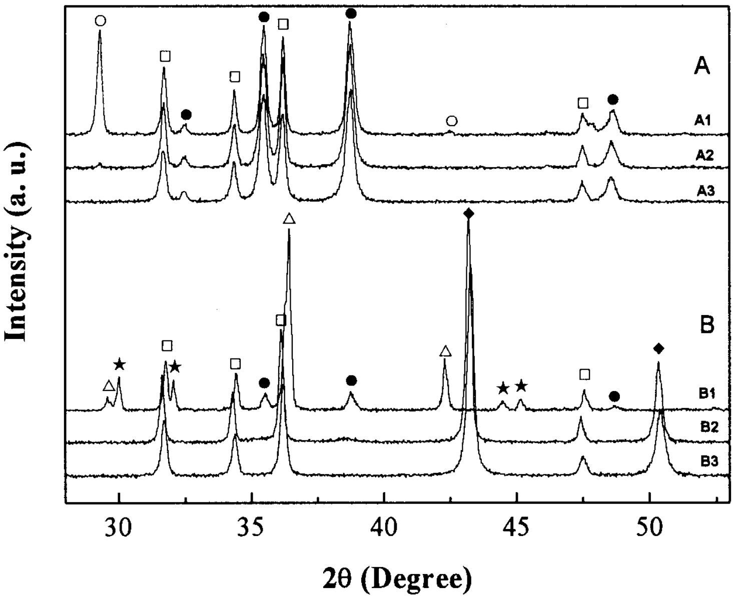

Figure 1. XRD patterns of catalysts with different content of Na: A are the patterns of calcined catalysts a (A1), b (A2), and e (A3); B are the patterns of reduced catalysts a (B1), b (B2), and e (B3). ○ sodium nitrate, □ zinc oxide, ● copper oxide, △ cuprous oxide, ★ sodium nitrite, ◆ metallic copper.

The TPR results of catalysts with different content of Na are shown in Fig. 2. It is observed, that Na affect the reducibility of copper oxide. If decreasing Na, the TPR peaks shift to lower temperature. For catalyst (a) (Fig. 2 a), two peaks can be found at 793 K and 853 K, just similar to the reduction of pure CuO and Cu_2O [10]. Two main overlap peaks can be found for catalysts (b)–(d). These peaks are attributed to the reduction of CuO, and the different temperature of peaks can be explained by the varied morphology of CuO, *i.e.* well dispersion and bulky CuO [20–23], and it may be also considered as different particle sizes of CuO [24]. We also find, that the well dispersed (or small particle sizes) CuO increase with Na content decreasing (Fig. 2 b–d). Two small shoulder peaks can be found for catalyst (b). The peak at 679 K associates with the reduction of bulk like CuO and the peak at 476 K corresponds to reduction of highly dispersed CuO [23]. For the catalyst (e), the main reduction peak at 550 K means that dispersion of CuO is better than others. The results of TPR indicate that the presence of Na makes the reduction of CuO more difficult. The result of BET also proves, that the catalyst with a high content of Na shows serious agglomerate (Table 1). For the Na free catalyst, some interaction exists between CuO and ZnO and this interaction may disperse CuO well, so the reduction of CuO is easy.

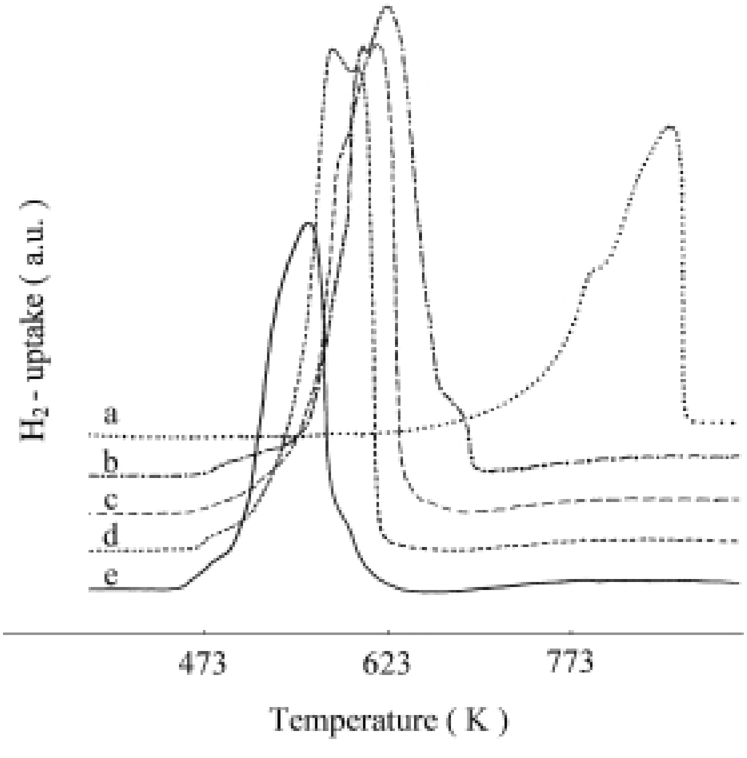

Figure 2. TPR profiles of catalysts with different content of Na: profiles a–e are catalysts, a–e calcined at 623 K for 4 h, respectively.

The results of elements analysis of catalysts by XPS (the results of ICP included as reference) are shown in Table 2. In this Table, it can be seen clearly that the concentration of Na on the surface of reduced and used catalysts is higher, than that in the bulk of catalysts, and the concentration of Na increases on the catalysts surface after reaction. It indicates, that under reduction or reaction conditions, Na can easily diffuse to the surface of catalysts. For the catalyst (a), used the concentration of Na is five to seven times higher than the concentration of copper or zinc. The ratio of sodium to copper or zinc on the surface decreases with decreasing of Na content. The concentration of ZnO on the reacted catalyst surface is higher than that before use. Poels *et al.* [25] has reported, that high reduction temperature results in a larger ZnO surface enrichment in $Cu/ZnO/SiO_2$ catalyst, used in methyl acetate hydrogenolysis reaction. On the contrary, the copper concentration is lower than that before use except for catalyst (a) and (e). This may be due to the increase of the copper particles size during reaction (see Table 1). Na weakens the interaction between copper and zinc oxide, thus copper particle size increases under this reaction conditions. For Na free catalyst (e), the copper concentration is higher than that before use, this may be leads by the interaction between copper and zinc oxide, and may facilitate the copper dispersion.

Table 2. The components of catalysts analyzed by ICP and XPS (wt%).

Element	a			b			c			d			e		
	ICP	XPS		ICP	XPS		ICP	XPS		ICP	XPS		ICP	XPS	
		B	A		B	A		B	A		B	A		B	A
Na	8.3	28.5	30.1	3.2	8.1	17.5	1.8	9.9	18.1	1.1	10.2	13.9	0	0	0
Cu	32	4.1	6.5	43	20.8	8.4	46	21.7	12	44	20.1	13.3	50	22.1	23.1
Zn	20	3.3	4.4	27	8.9	10.7	28	8.7	12	28	11.3	13.3	30	20.3	22.3

a–e: No. of catalyst; B: catalysts before reaction; A: catalysts after reaction.

Catalytic activity: Fig. 3 shows the conversion of 2-butanol as a function of reaction time at 563 K over the catalysts. For the catalyst (a), it shows inactivity in dehydrogenation of 2-butanol (Fig. 3 a). This can be explained by the catalyst serious agglomeration with high content of Na (Table 1), and this catalyst is difficult to reduce (Fig. 2 a), the Cu_2O is the main component over catalyst after reduction (Fig.1 B1). Cu_2O exhibits no activity for dehydrogenation of 2-butanol. The catalyst (b) is quickly inactive during reaction. This can be explained that Cu^0 is the main component on catalysts surface (Fig. 1 B2), thus the conversion is high at the beginning of the reaction, with running of reaction the Cu^0 particles size increases quickly (Table 1). This may happen because the increasing of Na concentration on catalyst surface (Table 2). The low content and free Na catalysts are slowly inactive and stable activity (Fig. 3 c–e). It is because that with deceasing of Na the interaction between Cu and

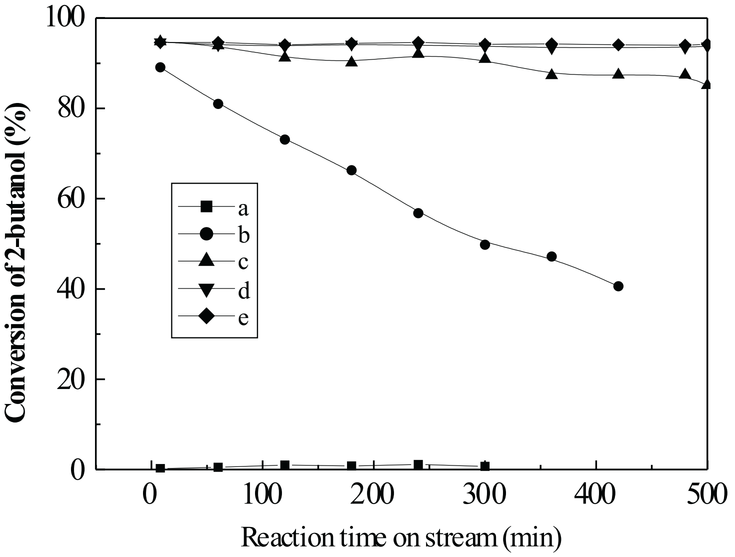

Figure 3. The conversion of 2-butanol for catalysts with different content of Na: a–e are catalysts, a–e reacted at 563 K, respectively.

ZnO becomes strong and Cu is dispersed and stabled on catalyst surface, so the Cu particle size does not increase after reaction (Table 1), and the conversion of 2-butanol is stable during reaction as test.

Fig. 4 shows the selectivity of the by-product 5-methyl-3-heptanone changing with the time on stream at 563 K. The selectivity of 5-methyl-3-heptanone is negligible for catalyst (a) (Fig. 4 a). For catalysts (b) and (c), we find that the selectivity of 5-methyl-3-heptanone is high at beginning of the reaction, and then decreasing to zero after reaction for 150 min and 250 min respectively (Fig. 4 b, c). For catalyst (d), the selectivity also decreases at the beginning of the reaction, but it reaches a stable value after 100 min reaction (Fig. 4 d). For the Na free catalyst, the selectivity of 5-methyl-3-heptanone is higher than others, although it decreases during the reaction. The result indicates that existing of Na over the catalysts can affect the by-product selectivity, little content of Na over catalyst is favorable to decreasing the by-product and corresponding increasing the selectivity of MEK.

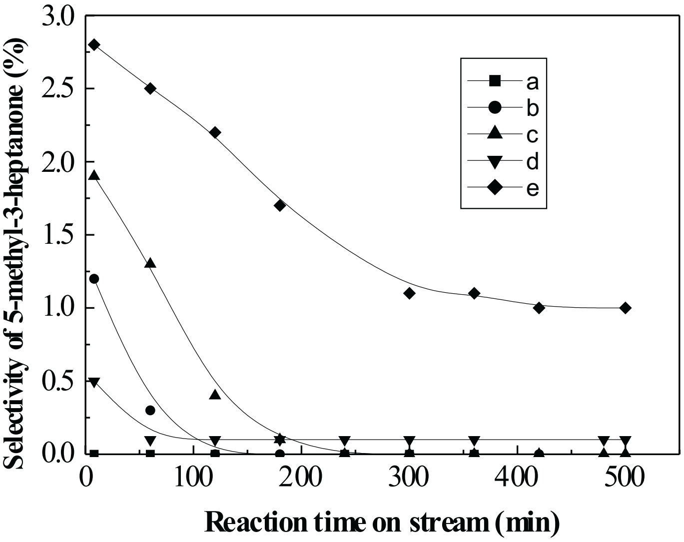

Figure 4. The selectivity of 5-methyl-3-heptanone for catalysts with different content of Na: a–e are catalysts, a–e reacted at 563 K, respectively.

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