Cyclohexanol dehydrogenation over Co/carbon nanotube catalysts and the effect of promoter K on performance

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Carbon nanotubes (CNT) were used as support medium to prepare Co catalysts for the selective dehydrogenation of cyclohexanol. Due to the unique structure and electronic property of CNT, Co/CNT possessed less acid sites than Co/activated carbon (AC). It seems to be easier to form multi-point complexes on Co/CNT than on Co/AC, resulting in a little higher selectivity to cyclohexanone and different distribution of by-products. The effect of K addition, attributed to electronic promotion, was also stronger on Co–K/CNT than on Co–K/AC.

KEY WORDS: cobalt; carbon nanotubes; cyclohexanol; dehydrogenation; cyclohexanone

1. Introduction

Cyclohexanone is an important intermediate in the industrial production of caprolactam. It is generally produced by catalytic dehydrogenation of cyclohexanol, where copper-based catalysts have been used extensively. However, dehydrogenation of cyclohexanol, an endothermic reaction, favors a high reaction temperature, while copper catalysts seriously sinter above 280 °C [1]. The studies are therefore divided into three groups: (1) changing the reaction system by adding gaseous oxidant (so-called oxidation route) [2]; (2) modification of the Cu catalyst by different promoters [3–5]; (3) development of Cu-free catalysts. As far as the third group is concerned, many Cu-free catalysts, such as Ni/ activated carbon (AC) [6], sulfated tin oxide [7] and Co/AC [8], have been reported to be more effective than the conventional Cu catalysts. Co/AC was found to be more active than other transition metals supported on AC.

Recently, carbon nanotubes (CNT) have attracted great interest due to their unique properties and potential application in various fields [9–12]. Using CNT as catalyst support medium, some meaningful results have been obtained. For example, Ru/CNT was used in the hydrogenation of cinnamaldehyde and up to 92% conversion of cinnamaldehyde to cinnamyl alcohol was observed [13]. Catalytic hydroformylation properties of CNT-supported Rh-phosphine were reported by Zhang et al. [14], and the results implied that the tubular channels and the hydrophobic surface of CNT played important roles in enhancing the activity of propene hydroformylation, especially the regioselectivity of butylaldehyde. More recently, Ru/CNT promoted by K was used for ammonia synthesis at atmospheric pressure and showed a promising result [15]. In this work, we investigated the catalytic activity of Co/CNT in the selective dehydrogenation of cyclohexanol to cyclohexanone and aimed to reveal the influence of the structure and electronic properties of CNT on the performance of the Co catalyst.

2. Experimental

CNT was produced by catalytic decomposition of C_2H_2 over Co/SiO_2, then purified by HNO_3 and HF treatment at room temperature. No other carbon materials and metal particles deposited on the CNT external surface, as evidenced by TEM image (see figure 1(a)). The 15 wt% Co/CNT was prepared by an incipient wetness technique: 1.0 g purified CNT was dispersed in an aqueous solution containing 0.8715 g $Co(NO_3)_2{\cdot}6H_2O$ by sonication treatment, then dried at 100 °C for 10 h and calcined at 480 °C for 3 h. The TEM image (see figure 1 (b) and (c)) of the as-prepared Co/CNT catalyst after a reduction treatment by H_2 at 480 °C for 2 h showed that metal particles were located on the surface of the tubes, with the size of 5–50 nm in diameter. In order to investigate the effect of K addition on Co catalysts, two methods were used to prepare Co–K/CNT catalysts: (I) the as-prepared Co/CNT catalyst was impregnated with an aqueous solution containing the desired amount of KNO_3, then dried at 80 °C (designated as Co–K/CNT-1); and (II) the as-prepared Co/CNT catalyst was reduced by H_2 at 480 °C for 2 h, followed by impregnation with a KNO_3 aqueous solution, then dried at 80 °C (designated as Co–K/CNT-2). The corresponding Co/AC was prepared by impregnation of AC with a $Co(NO_3)_2$ aqueous solution, followed by drying at 100 °C and calcination at 480 °C. The as-prepared Co/AC was impregnated with a KNO_3 aqueous solution, then dried at 80 °C (designated as Co–K/AC catalyst). Cyclohexanol dehydrogenation was carried out in a pulse-microcatalytic reactor, which was fixed at the inlet of

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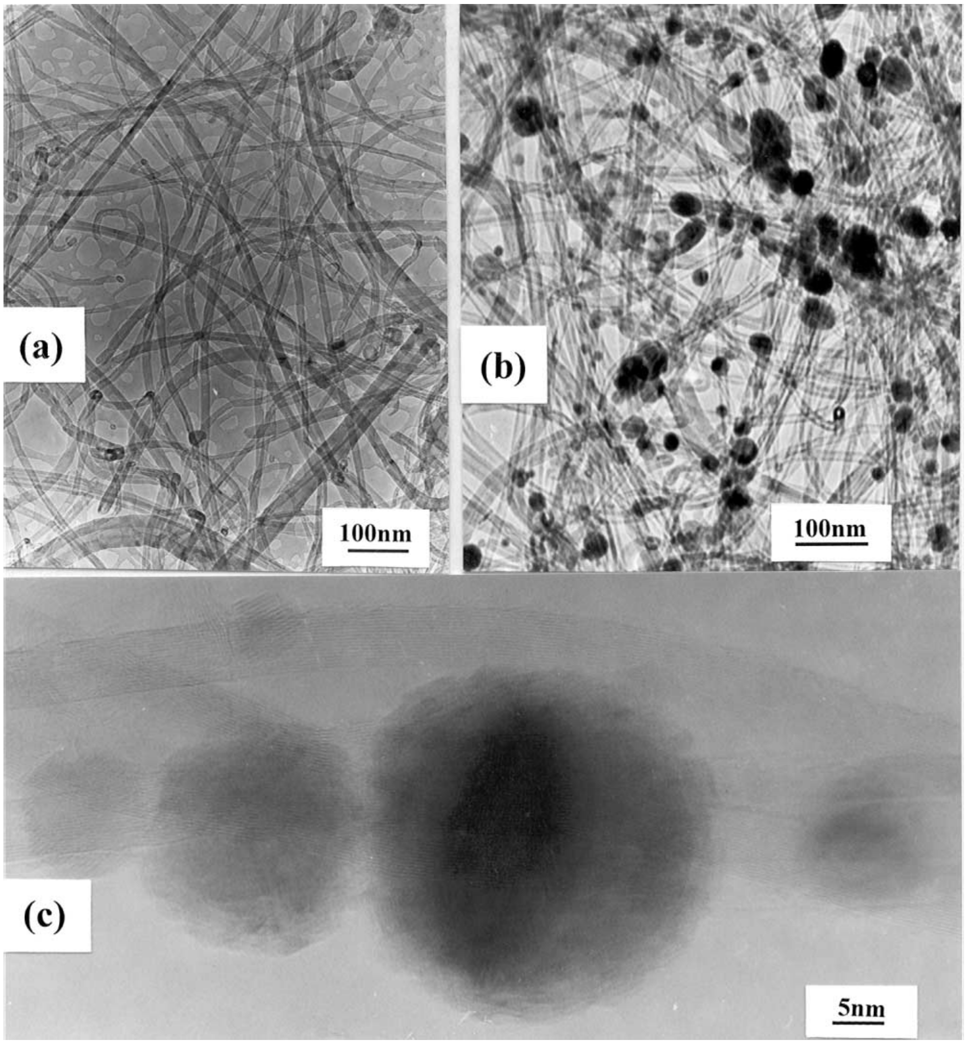


Figure 1. TEM images, recorded on a Jeol JEM-2010 microscope operating at an accelerating voltage of 200 kV, of (a) the purified carbon nanotubes, (b) the Co catalyst supported on carbon nanotubes and (c) several Co particles on the surface of a nanotube at a higher magnification.

a gas chromatograph (N_2 as carrier gas) for on-line analysis of reaction effluents. The activity of each catalyst was tested under the following conditions: temperature $T = 250\,^{\circ}\mathrm{C}$, N_2 flow rate is 25 ml/min, the height of the catalyst bed 4.5 cm, the weight of Co metal per reactant pulse 10 mg/μl. The catalysts Co/CNT, Co/AC, Co–K/AC and Co–K/CNT-1 were reduced *in situ* by H_2 at 480 °C for 2 h before reaction in contrast to no further treatment for Co–K/CNT-2.

3. Results and discussion

The catalytic performance of Co supported on two different carbon materials is shown in table 1, and figure 2 presents the typical deactivation curves of some catalysts with increasing number of pulse. The activity of Co catalysts in the selective dehydrogenation of cyclohexanol decreasing with process time in a fixed-bed reactor system has been reported by Uemichi et al. [8]. They attributed this to the deposition of cyclohexanone oligomers on the active sites. In our microcatalytic pulse system, catalyst deactivation can be also seen with increase in pulse number (figure 3). The selectivity to cyclohexanone, however, shows almost no change with process time (about 93 and 95% over Co/AC and Co/CNT, respectively). The major by-product over Co/AC catalysts is cyclohexene (about 4.0% caused by dehydration) with little phenol formation, while phenol (produced by deeper dehydrogenation) with almost the same amount as cyclohexene can be detected over Co/CNT catalysts. Formation of cyclohexene was usually attributed to the presence of acid sites (oxygen linked to the metal caused by incomplete reduction of metal oxide) on the catalyst surface, while the formation of multi-point complexes (scheme 1) was responsible for the phenol and cyclohexanone formation [16]. Our results suggest that, probably due to high capacity of H_2-uptake and unique structure of CNT, Co supported on CNT possesses higher degree of Co reduction, and multi-point complexes seem to be formed more easily on Co/CNT than on Co/AC catalysts, thus resulting in a little higher selectivity to cyclohexanone over Co/CNT and different distribution of by-products between the two types of catalysts.

Table 1
Initial activity of different catalysts in the dehydrogenation of cyclohexanol to cyclohexanone.

Catalyst[a]	Conversion (%)	Selectivity (%)				
		Cyclohexanone	Cyclohexene	Phenol	Benzene	Others
Co/CNT (15 : 0.0 : 85)	74.6	95.1	1.7	1.6	0.5	1.1
Co/AC (15 : 0.0 : 85)	72.2	93.2	4.2	0.4	0.7	1.5
Co–K/CNT-1 (15 : 2.0 : 85)	85.3	96.8	0.9	1.0	0.6	0.7
Co–K/CNT-1 (15 : 9.0 : 85)	16.9	96.0	1.2	1.1	0.7	1.0
Co–K/AC (15 : 2.0 : 85)	76.3	93.9	4.0	0.3	0.4	1.4
Co–K/AC (15 : 9.0 : 85)	15.6	94.1	4.3	0.1	0.5	1.0
Co–K/CNT-2 (15 : 2.0 : 85)	80.3	93.6	2.8	1.5	0.8	1.3
Co–K/CNT-2 (15 : 9.0 : 85)	14.5	94.1	2.6	1.3	0.6	1.4
Co/CNT (15 : 0.0 : 85)[b]	72.8	94.3	2.4	1.4	0.7	1.2

[a] Weight ratio of Co : K : CNT or AC in parentheses.

[b] This catalyst was obtained by reduction of Co/CNT by H_2 at 480 °C for 2 h before being loaded into the micro-catalytic reactor.

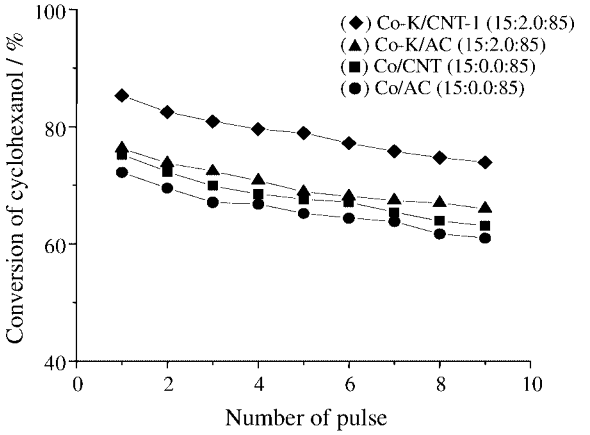
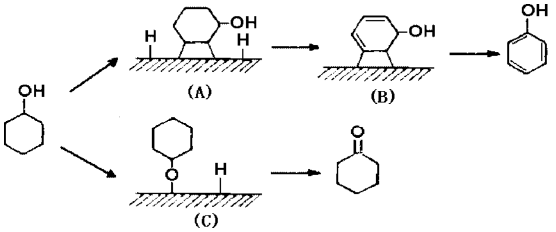


Figure 2. The typical deactivation curves of some catalysts with increasing number of pulse (one pulse every 15 min).



Scheme 1. Formation mechanism of phenol and cyclohexanone.

The effect of addition of K on the catalytic activity of Co catalysts supported on CNT and AC prepared by method (I) is also presented in figure 2 and table 1. With low K concentrations, an increase in activity can be observed on both Co/AC and Co/CNT. But, at higher level of K addition, the catalyst activity decreases dramatically, both on Co/AC and Co/CNT. Alkali doping has been generally interpreted in terms of electronic effect in some reaction systems such as ammonia synthesis and Fischer–Tropsch (FT) synthesis. In order to determine whether K addition affected the Co dispersion or K acts as an electron promoter, we prepared the K-promoted Co/CNT using method (II), in which it can be reasonably assumed that the impregnation of the Co/CNT catalyst in a solution of KNO_3 does not affect the Co dispersion. As shown in table 1, the results of activity test of these catalysts are consistent with the above observation: high cyclohexanol dehydrogenation activity at low levels of K promotion, very low activity with higher K concentration. The difference between the Co–K/CNT catalysts prepared by the two different methods is that Co–K/CNT-2 shows a little lower activity and selectivity (with about 3% cyclohexene formation) than Co–K/CNT-1. However, the activity and selectivity of Co–K/CNT-2 can be improved by an *in situ* treatment with hydrogen at 480 °C, suggesting that oxidation of Co particles on the Co–K/CNT-2 surface by exposure to air results in the decline of activity and selectivity. The above results indicate the influence of K addition on the Co catalyst may be associated with an electronic effect. This electronic effect could be explained according to the reaction mechanism (scheme 1) proposed by Richardson et al. [16]. The intermediate species (C), which desorbs as cyclohexanone, is formed through proton abstraction from the OH group by active sites on the catalyst. It may be reasonable to believe that more electron density of the active sites is favorable to proton abstraction and the transfer of an electron from K to the active sites results in a rise in the activity of the Co catalysts.

In table 1 and figure 2, we also observed an interesting result that the effect of K on Co/CNT was much higher than that on Co/AC. A stronger electronic effect on Co/CNTs than on Co/AC might be correlated with the remarkable electronic properties of carbon nanotubes. Theoretical calculations and experimental verification showed carbon nanotubes had a range of electronic behavior (metallic, semiconducting and semimetallic) [17]. Recent reports presented ballistic electron transport at room temperature in individual multi-walled nanotubes [18]. Thus, the carbon nanotubes used in this study might be good electron conductors, and electron transferring from K to the active sites improved the activity of Co–K/CNT.

The low catalytic activity of cobalt catalysts at high level of K promotion is just like the behavior of iron-based Fischer–Tropsch catalysts with alkali addition, which was attributed to lowering the reduction degree of iron by alkali addition. This inhibitory effect on reduction with alkali addition was supported by TG measurement [19]. However, the inhibitory effect does not exist in Co–K/CNT catalysts, as suggested by TPR results of these catalysts as well as the results of activity test that K addition did not result in preferential formation of cyclohexene which was produced on the acid sites caused by incomplete reduction of metal oxide. A possible explanation for this is that at high K concentration KNO_3 covers the active sites, leading to the remarkable decay of activity. Further work is necessary to elucidate this point and is carried out in our laboratory.

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References

[1] M. Dobrovolszky, P. Tétényi and Z. Paál, J. Catal. 74 (1982) 31.
[2] Y.M. Lin, I. Wang and C.T. Yeh, Appl. Catal. 41 (1988) 53.
[3] F.T.M. Mends and M. Schmal, Appl. Catal. A 151 (1997) 393.
[4] F.T.M. Mends and M. Schmal, Appl. Catal. A 163 (1997) 153.
[5] D.V. Cesar, C.A. Perez, V.M. Salim and M. Schmal, Appl. Catal. A 176 (1999) 205.
[6] Y. Uemichi, T. Sakai and T. Kanazuka, Chem. Lett. (1989) 777.
[7] M. Hino and K. Arata, Chem. Lett. (1990) 1737.
[8] Y. Uemichi, K. Shouji, M. Sugioka and T. Kanazuka, Bull. Chem. Soc. Jpn. 68 (1995) 385.
[9] H. Dai, J. Kong, C. Zhou, N. Franklin, T. Tombler, A. Cassell, S. Fan and M. Chapline, J. Phys. Chem. B 103 (1999) 11246.
[10] C. Park and R.T.K. Baker, J. Phys. Chem. B 103 (1999) 2453.
[11] G. Maurin, C. Bousquet, F. Henn, P. Bernier, R. Almairic and B. Simon, Chem. Phys. Lett. 312 (1999) 14.
[12] B.C. Satishkumar, A. Govindaraj, E.M. Volgl, L. Basumallick and C.N.R. Rao, J. Mater. Res. 12 (1997) 606.
[13] J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.S. Kumbhar, R. Putartre, P. Geneste, P. Bernier and P.M. Ajayan, J. Am. Chem. Soc. 116 (1994) 935.
[14] Y. Zhang, H.B. Zhang, G.D. Lin, P. Chen, Y.Z. Yuan and K.R. Tsai, Appl. Catal. A 187 (1999) 213.
[15] Y. Cai, J.D. Lin, H.B. Chen, H.B. Zhang, G.D. Lin and D.W. Liao, Chin. Chem. Lett. 11 (2000) 373.
[16] J.T. Richardson and W.C. Lu, J. Catal. 42 (1976) 275.
[17] T.W. Ebbsen, H. Lezec, H. Hiura, J.W. Bennet, H.F. Ghaemi and T. Thio, Nature 382 (1996) 54.
[18] S. Frank, P. Poncharal, Z.L. Wang and W.A. de Heer, Science 280 (1998) 1774.
[19] Q. Xu, D. He, M. Fujiwara, M. Tanaka, Y. Souma and H. Yamanaka, J. Mol. Catal. A 136 (1998) 161.