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Highly active Cu-based catalysts on carbon nanofibers for isopropanol dehydrogenation

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Abstract

Cu/CNF and Cu/CeO_2/CNF catalysts have been synthesized and characterized on different nanostructured carbon nanofibers (CNF). The samples have been tested in isopropanol dehydrogenation. Cu/CNF show similar activity to Cu catalysts supported on activated carbon. Cu/CeO_2 nanotubes have been synthesized on the CNF surfaces. The Cu/CeO_2 nanotubes exhibit much higher activity and lower activation energy than Cu/CNF. The selectivity towards acetone depends on the fraction of CeO_2 in the composites. High activity and selectivity has been achieved with a $Cu_{12}Ce_5$/CNF catalyst.

Keywords: Copper; Cerium; Carbon nanofibers; Isopropanol; Dehydrogenation

1. Introduction

Isopropanol dehydrogenation is a simple and thus useful model reaction for testing dehydrogenation/hydrogenation activity. Recently, carbon has successfully been applied as a support for Cu catalysts in isopropanol dehydrogenation in a renewed effort to replace Cu-chromite [1]. Rioux and Vannice [1] prepared Cu catalysts with activated carbon supports subjected to high temperature and nitric acid treatment. The catalysts had dispersions in the range 2–17%. Cu (5 wt.%) on activated carbon treated at 1223 K showed the highest turnover frequency. Carbon nanofibers (CNFs) have recently received increasing interest in application as a catalyst support, since CNFs have many unique properties [2]. One of the most outstanding features is that the surface of the fibers is present as graphite edges which are thought to give a strong interaction between the support and the active phase. This property is also reported for Cu deposited on CNF [2]. Ma et al. [2] found that Cu particles adopt a relatively thin, faceted morphology on different types of graphite nanofibers, indicating a strong metal–support interaction. This was reflected by a high degree of stability with respect to particle sintering. In addition, oxides such as CeO_2 have been reported to enhance the reduction of Cu and the activity of the catalysts through the interaction between Cu atoms and the oxide [3,4]. The present work deals with preparation, characterization and testing of CNF supported Cu-based catalysts in isopropanol dehydrogenation. A highly active catalyst of Cu/CeO_2 nanotubes was prepared using CNF as template.

2. Experimental

Three types of carbon nanofibers synthesized in our laboratory, namely platelet (P), carbon filaments (CF) and herringbone (HB) were used as catalyst supports [5]. The HB support was oxidized by boiling in HNO_3 (65%)-solution for 10 min. The carbon filaments and platelet supports used for the CeO_2-modified catalysts were oxidized in air at 250 °C overnight.

Cu catalysts with 10 wt.% loading were prepared by incipient wetness (IW) impregnation and deposition–precipitation (DP). For impregnation, the required amount

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Table 1
Catalyst properties and activities at 448 K, P_{Ipa} = 4.4 kPa

	Cu-loading	Cu surface area, TGA (m^2/g)	Dispersion, TGA (%)	*D*, TGA (nm)	*D*, XRD[a] (nm)	*D*, XRD[b] (nm)	Activity (μmol/g s)	TOF ($s^{-1} \times 100$)	E (kcal/mol)	$S_{acetone}$, 423 K (%)	$S_{acetone}$, 473 K (%)
IW/HB	9.61	1.78	2.8	39.8	19.2	–	0.52	1.23	21.3	100	100
DP/HB-HNO_3	7.92	0.84	1.6	68.9	11.5	22.7	0.11	0.58	21.6	–	–
DP/CF	4.35	0.80	2.8	39.8	–	–	0.10	0.55	27.5	100	100
DP/P	4.77	1.43	4.5	24.5	10.3	22.5	1.00	2.97	38.1	0	0.35
$Cu_{12}Ce_5$/P-air	9.68	9.10	13.6	8.10	–	8.9	5.61	2.71	13.3	100	92
$Cu_{17}Ce_{17}$/P-air	15.25	8.17	8.3	13.3	–	38.8 (9.1)[c]	8.79	4.43	–	75	46
$Cu_{17}Ce_{17}$/CF-air	–	–	–	–	–	–	8.49	–	10.9	83	57

HNO_3 and air indicate oxidant used in preparation, $Cu_{12}Ce_5$/P-air indicates 12 wt.% Cu and 5% Ce on platelet support, which was oxidised by air.
[a] Crystal size determined by the Crysize software.
[b] Crystal size determined from the Scherrer equation.
[c] CeO_2 particle size in parenthesis.

of precursor salt ($Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in distilled water and added dropwise to the CNF-supports, followed by drying overnight at 110 °C. The CeO_2-modified Cu catalysts were prepared by incipient wetness impregnation corresponding to Cu/Ce amounts of 17:17 and 12:5 wt.% using $Cu(NO)_3 \cdot 3H_2O$ and $Ce(NO)_3 \cdot 6H_2O$ as precursors. Remaining water and gases in the pores of CNFs were removed under vacuum before impregnation. The deposition precipitation (DP) was performed by dissolving CNF in distilled water followed by the addition of an aqueous solution containing $Cu(NO_3)_2 \cdot 3H_2O$ (equivalent to 10 wt.% Cu) and urea (molar ratio, urea/Cu: 5:1). The solutions were mixed and stirred for 30 min at 50 rpm, then heated to 100 °C in 30 min, held at this temperature for 20 h [6] before being cooled to room temperature, filtered, redispersed twice and dried overnight at 100 °C. Both the IW- and the DP-catalysts were calcined at 250 °C for 1 h in air and reduced for 6 h at 250 °C in hydrogen (N_2/H_2, 1:1).

The supports and catalysts were characterized by temperature programmed oxidation (TPO), X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM), and the details have been described elsewhere [5]. The surface area of Cu was determined by means of N_2O decomposition at 363 K [7]. The activity tests were performed by means of temperature scanning experiments [8] in a quartz reactor using a partial pressure of isopropanol of 4.4 kPa. The reactor temperature was programmed in the range of 25–200–25 °C at a ramping rate of 2 °C/min, where the effluent was analyzed continuously by a mass spectrometer. Approximately, 0.2 g of catalyst was loaded into the reactor. The samples were reduced for 6 h at 250 °C in hydrogen ($N_2/H_2$1:1) prior to reaction. Isopropanol feeding was obtained by bubbling argon through a gas saturator containing isopropanol (vapor pressure at 25 °C). The experiments showed neglectable activity of CNF and CeO_2/CNF. One of the main advantages of the CNF supported catalysts is the relatively high surface area which is practically free of micropores and thus eliminates diffusion limitations. The absence of diffusion limitations in the present work has been confirmed by the Weiz–Prater criterion.

3. Results and discussions

The detailed characterization data for the prepared catalysts are shown in Table 1. The metal/oxide loading was determined in the TGA by removing CNF in air. The metal catalyst residue in CNF, determined by a blank run was subtracted. The Cu-loading in the Cu/oxide/CNF nanocomposites was calculated by assuming a Cu/Ce ratio of 12:5 and 17:17 wt.% added into the solution during preparation. The results clearly indicate that the Cu-loading depends on the preparation methods and oxidation of CNF, but less on CNF structure. By impregnation, almost all the Cu precursors deposited on the surface of the CNF had reasonable dispersions, even the samples without pre-oxidation. However, the deposition–precipitation method depends significantly on the functionalization of the CNF by oxidation. The surface groups on the CNF surface such as –COOH, –OH, C=O which are introduced by oxidation are important to obtain the interaction required for good distribution of the metal-precursor [9]. Oxidation of the HB-fibers in nitric acid gave a larger deposition of Cu. However, a deeper oxidation appears to be necessary to obtain the desired Cu-loading by deposition–precipitation. In addition, a high loading (total, 34 wt., $Cu_{17}Ce_{17}$) has been achieved by impregnation of functionalized CNF by air oxidation.

Determining Cu crystal size precisely is not straightforward. Three different techniques including chemisorption, XRD and TEM have been employed in the present work, giving diverging results by the different techniques. A TEM-image of the IW/HB sample is shown in Fig. 1A, indicating that the Cu particles on the fiber are generally well dispersed but highly disordered, as shown in Fig. 1Am. The average Cu size is about 20 nm, which is close to the value determined by the software CRYSIZE in XRD [5]. However, the Cu crystal size seems to be overestimated when using the Scherrer equation. Chemisorption of N_2O gave a much larger Cu crystal size (39.8 nm). The reason for this deviation is still not very clear. Table 1 show that the dispersion of Cu on CNF found from chemisorption is

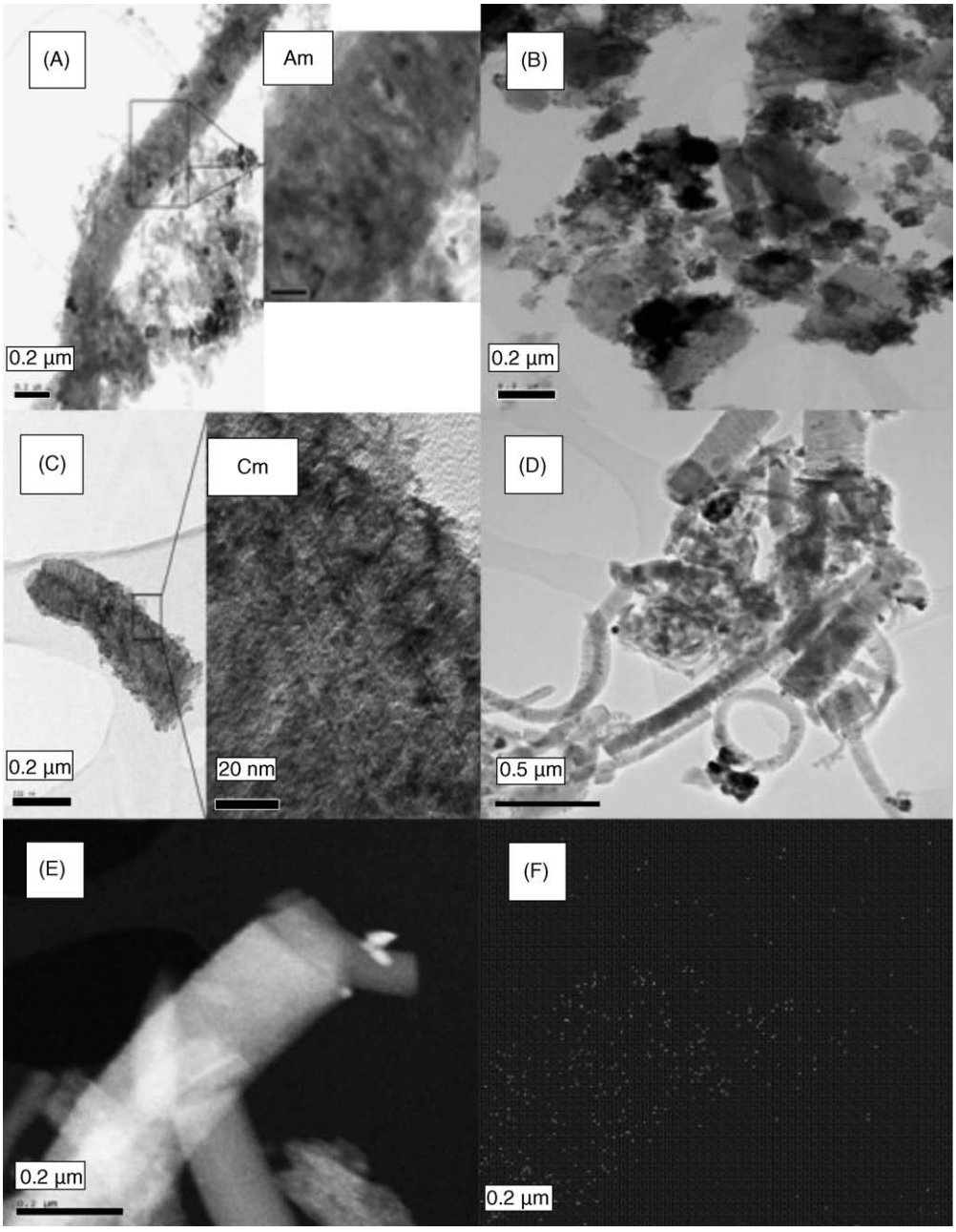

Fig. 1. TEM and STEM images of IW/HB, $Cu_{17}Ce_{17}$/P-air and $Cu_{12}Ce_5$/P-air. (A) TEM of IW/HB-fiber; (Am) area in A magnified; (B) TEM overview image $Cu_{17}Ce_{17}$/P-air; (C) TEM of fiber $Cu_{17}Ce_{17}$/P-air; (Cm) area in C magnified; (D) TEM overview image $Cu_{12}Ce_5$/P-air; (E) dark field STEM of $Cu_{12}Ce_5$/P-air fiber; (F) cerium EDX mapping of a CNF.

typically about 1.6–4.5%, similar to the reported values for activated carbon [1] and CNF [2]. An interesting observation from Table 1 is that cerium oxide significantly enhances the Cu dispersion. However, it should be pointed out that dispersion data on Cu/CeO_2/CNF determined by chemisorption is uncertain since reduction in hydrogen may also reduce Ce^{4+} to Ce^{3+}, which can decompose N_2O [10].

The distribution of Cu in $Cu_{17}Ce_{17}$/P-air is shown in the TEM-images in Fig. 1B and C, indicating a dual distribution pattern. Part of the Cu is well dispersed on the CNF surface (Fig. 1C), while large Cu clusters are found between the fibers (Fig. 1B), possibly due to the relatively high loading of Cu (17 wt.%). These clusters are most likely the main contributors to the large Cu crystal size measured by XRD. Although the Cu-loading is higher in $Cu_{17}Ce_{17}$/P-air, a lower intensity is found for the Cu peak than for Cu/CNF in Fig. 2, indicating that only a small part of Cu formed large clusters. All techniques confirm significantly higher dispersion on $Cu_{12}Ce_5$/P-air. Fig. 1D shows a typical TEM-image of $Cu_{12}Ce_5$/P-air, where it is difficult to see highly crystalline Cu particles. It is therefore believed that a large fraction of the Cu must be less ordered and/or deposited as particles not

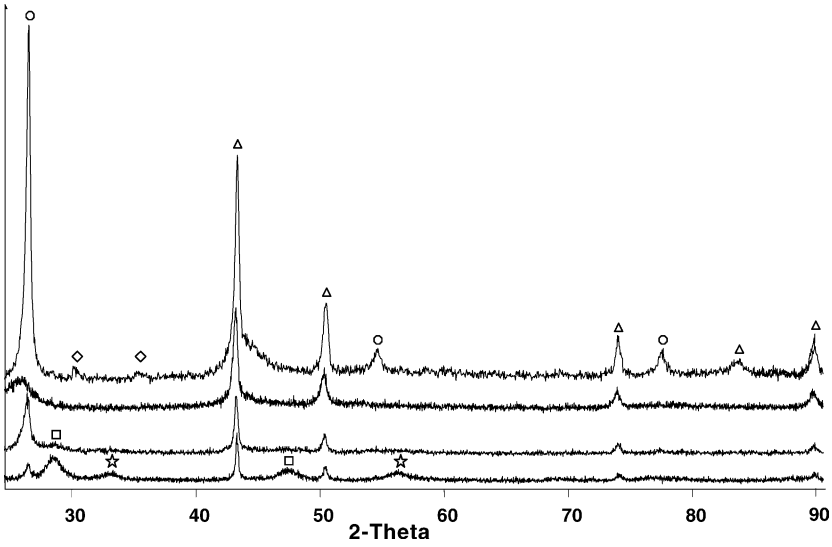

Fig. 2. XRD patterns from top to bottom of: DP/P, DP/HB-HNO3, $Cu_{12}Ce_5$/P-air and $Cu_{17}Ce_{17}$/P-air. Graphite (○); Cu (△); Cu_2O (◇); CeO_2 (□); CeO_2/Ce (☆).

visible due to the limitation in resolution of the microscope. Unfortunately, the distribution of Cu could not be assessed by EDX mapping due to interference from the Cu-containing TEM sample holder.

An interesting observation from the diffractograms in Fig. 2 is that the $Cu_{12}Ce_5$/P-air catalyst does not exhibit any peaks corresponding to Ce or CeO_2, while the $Cu_{17}Ce_{17}$/P-air contains peaks corresponding to both, with CeO_2 crystal size about 9 nm. EDX analysis of areas with visible particles and areas without visible particles on the sample confirmed the presence of cerium. By inspecting Fig. 1C and D, a Cu/CeO_2 layer on the platelet is clearly observed. The layer is further confirmed by a STEM dark field image (Fig. 1E) of a fiber in the $Cu_{12}Ce_5$/P-air sample, and an EDX elemental mapping of cerium in Fig. 1F. These results indicate that cerium is evenly distributed on the fibers leading to the formation of CeO_2 nanotubes. This observation is in agreement with a previous study on the activity of CuO/CeO_2–TiO_2 in methanol dehydrogenation [4]. Small amounts of CeO_2 resulted in the deposition of a uniform layer of CeO_2. As the amount of CeO_2 was increased, formation of bulk-like CeO_2 particles was observed. Some of the Cu atoms were believed to interact with these species, and thereby changing the activity of the catalyst.

The results summarized in Table 1 show that Cu/CeO_2/CNF nanocomposites have significantly higher activity than the Cu/CNF catalysts. The Cu/CNF catalysts have activity similar to Cu on activated carbon treated in nitric acid [1]. The selectivity to acetone is close to 100% on most of the Cu/CNF catalysts except for DP/P, which shows relatively high selectively to propene. The high selectivity to propene cannot be explained by surface acidity of the platelet, since the amount of O-groups determined by TPD was very low. TPR (not reported here) results showed that Cu on platelet is more difficult to reduce than Cu on other structured CNF. Two steps of reduction ($Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu^{0}$) were observed on this sample, where the last step requires a temperature higher than 300 °C. The presence of Cu^{2+} and Cu^{+1} may lead to high selectivity to propene, since our preliminary experiments on CuO powder showed high dehydration activity.

The selectivity of Cu/CeO_2/CNF nanocomposites was found to be dependent on the fraction of CeO_2 and on the temperature. The increased selectivity to propene at higher temperatures is most likely a result of higher activation energy for dehydration than for dehydrogenation [1]. The ceria, however, appears to promote the dehydration reaction. In a study of isopropanol dehydrogenation on simple metal oxides [11], it was found that Ce_2O_3 gave a higher dehydration activity than CeO_2 during isopropanol conversion in a hydrogen rich atmosphere. Acidic sites catalyze the dehydration, but the Ce_2O_3 was found to be less acidic than CeO_2. Ceria was, therefore, believed to exhibit a redox-ability contributing to the dehydration [11].

The isopropanol dehydrogenation has been extensively studied on Cu catalysts by Rioux and Vannice [1], at an isopropanol partial pressure 1.9 kPa. It was found that reaction is almost independent of the isopropanol partial pressure at low temperatures ($T < 175$ °C). Therefore, it is possible to directly compare the literature values with the present results. The activity of $Cu_{17}Ce_{17}$/P-air at 144 °C was 6.7 μmol/g s (78% selectivity) while the activity of $Cu_{17}Ce_{17}$/CF1-air was 7.2 μmol/g s (87% selectivity). This is higher than what is found for a commercial Cu-chromite catalyst with substantially higher Cu-loading (41 wt.% Cu): 4.1 μmol/g s [1]. The $Cu_{12}Ce_5$ with 100% selectivity does not have comparable activity at such low temperatures. At 175 °C, the activity of this catalyst is 5.6 μmol/g s whereas the activity of the commercial Cu-chromite is 10.6 μmol/g s. However, the CeO_2-modified catalyst exhibited about twice

the activity of the best Cu/activated carbon catalyst reported [1].

The activation energy of Cu/CNF is in the range 21–28 kcal/mol, which is in good agreement with previously reported values [1]. However, the activation energy on Cu/CeO_2/CNF is considerably lower (about 13 kcal/mol). Both higher TOF and lower activation energy on Cu/CeO_2/CNF suggest a possible ceria-assisted reaction mechanism. It has been proved that the O-atoms in a metal oxide can adsorb hydrogen, and thus, enhance the breakage of the C–H bond in the dehydrogenation of alkanes [12]. It is therefore reasonable to assume that the alcohol is chemisorbed on Cu through its O-atom, and that H can adsorb on an adjacent O-atom in CeO_2. This may weaken the OH-bond, and consequently, promote the reaction. However, a more detailed study is needed to verify the reaction mechanism.

4. Conclusions

Cu/CeO_2 nanotubes have been synthesized on the CNF surfaces, where CNF serves as a template. Such nanocomposites are found to be highly active for the dehydrogenation of isopropanol to acetone. The presence of CeO_2 enhanced the reduction and dispersion of Cu, and lead to higher turnover frequencies. Selective dehydrogenation has been achieved on the $Cu_{12}Ce_5$ nanotubes. However, excess CeO_2 enhanced hydration activity, and thereby, reduced the selectivity. Activities of Cu/CNF were found to be similar to that found for active carbon supported Cu catalysts. The nanostructure of CNF changes the selectivity but has no significant effect on the activity.

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