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Short Communication

Dehydrogenation of cyclohexanol on copper containing catalysts: The role of the support and the preparation method

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ABSTRACT

SiO_2 and Al_2O_3 supported copper catalysts were prepared by "chemisorption–hydrolysis" or incipient wetness impregnation methods and investigated by XRD, TG-TPR, UV–vis diffuse reflectance and FTIR spectroscopy. Formation of finely dispersed copper oxide species was registered for the samples prepared by "chemisorption–hydrolysis" method, while a significant amount of XRD detectable copper oxide phase is registered for the SiO_2 impregnated one. The latter materials possess higher catalytic selectivity in cyclohexanol dehydrogenation to cyclohexanone.

1. Introduction

Cu-based catalysts are of industrial importance in the synthesis of methanol, steam reforming of methanol, synthesis of cyclohexanone from cyclohexanol etc. [1–3]. Dehydrogenation of cyclohexanol to cyclohexanone is a very important industrial process because cyclohexanone is an intermediate used in the production of caprolactam. The reaction is endothermic but the increase of the reaction temperature to above 280 °C accelerates the sintering of copper because the commercial catalyst contains large amounts of copper [2–10]. To overcome this disadvantage, catalysts with low copper loading have been developed, which yielded cyclohexanone below a reaction temperature of 280 °C. A number of investigations have been focused on determining the influence of the support, the method of preparation, and the metal loading on the activity and selectivity of the catalysts, with the goal of enhancing the alcohol conversion [1–13]. Stohmeier et al. [14] examined the surface properties of impregnated Cu/Al_2O_3 catalysts and found that at low copper loading (<10 wt.%) copper ions form well-dispersed species, connected to the support, whereas at higher copper content, segregation of bulk-like CuO occurs. However, according to [1] copper particles in silica supported catalysts are highly dispersed in the catalyst, the Cu content of which is 20 wt.% or less. Some of the discrepancies in the results and in the interpretation can be attributed to the wide range of experimental conditions and catalyst preparation procedures. Both surface acid–base characteristics and redox properties of the catalysts influence their activity and selectivity in dehydrogenation of cyclohexanol.

In the present study, we focus on the effect of the support (SiO_2 and Al_2O_3) and the preparation method ("chemisorption–hydrolysis" or incipient wetness impregnation) on the catalytic behavior of copper modified samples in cyclohexanol dehydrogenation.

2. Experimental

2.1. Synthesis

SiO_2 (Grace, BET = 300 m^2/g) and Al_2O_3 (Puralox ScFa/140/L3 (La = 3%), Sasol, BET = 126 m^2/g) were used as supports of copper oxide which was introduced by two methods — "chemisorption–hydrolysis" (CH) and incipient wetness impregnation (WI). The SiO_2 and Al_2O_3 supported samples were prepared by "chemisorption–hydrolysis" according to the procedure described in [15]. The modified samples were calcined in air at 673 K for 4 h and they were designed as CuO/SiO_2(CH), and CuO/Al_2O_3(CH).

The second series was obtained by incipient wetness impregnation technique with copper nitrate. The precursor was decomposed by calcination in air at 773 K for 2 h for CuO/SiO_2 and CuO/Al_2O_3. The modified samples, prepared by impregnation method, were designated as CuO/SiO_2(WI), and CuO/Al_2O_3(WI). In all cases the Cu content was ca. 6–8 wt.% .

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2.2. Characterization

X-ray diffractograms were recorded on Philips PW 1810/1870 diffractometer applying monochromatized CuK_α radiation (40 kV, 35 mA).

The TPR–TG investigations were performed in a Setaram TG92 instrument.

Diffuse reflectance spectra of the samples in the UV–vis region were registered using a Jasco V-650 UV–vis spectrophotometer equipped with integrating sphere. All spectra were recorded under ambient conditions.

FTIR of adsorbed pyridine (Py) were registered on a Biorad FTS-40 FTIR spectrophotometer.

2.3. Catalytic activity measurements

Prior to the catalytic test the samples were pretreated for 1 h in nitrogen up to 673 K. Cyclohexanol dehydrogenation was studied at atmospheric pressure using a fixed-bed flow reactor, 95% nitrogen and 5% hydrogen as carrier gas and 30 mg of sample. The nitrogen/hydrogen stream (20 ml/min) passed through a saturator filled with cyclohexanol and equilibrated at 342 K ($n_{N2+H2}/n_{cyclohexanol}=38$), WHSV of 1 h^{-1}, P = 1 atm. The activity was determined at 513 K after 60 min time on stream. On-line analysis of the reaction products was performed using HP-GC with a 25 m HP-35 capillary column. The turnover frequency (TOF) was calculated as the converted number of cyclohexanol molecules per metal atom per second.

3. Results and discussion

3.1. Physico-chemical characterization of the samples

XRD patterns collected for the studied samples indicate reflections typical of CuO only for CuO/SiO_2(WI) (not shown). No reflections of crystalline copper oxide phases are registered on CuO/Al_2O_3, prepared by both methods due to the formation of finely dispersed copper oxide species. Stronger copper interaction with the support could be concluded in the case of the Al_2O_3 supported samples. Formation of CuO with particle size of about 23 nm is registered for CuO/SiO_2(WI).

DR UV–vis spectroscopy was applied to understand the nature and the coordination of the copper oxide species in the studied samples. The spectra of the studied samples are presented in Fig. 1. The first maximum, observed at about 250 nm, is related to charge-transfer between mononuclear Cu^{2+} ion and oxygen, whereas the maxima around 350 and 450 nm can be ascribed to the charge transfer between Cu^{2+} cluster and oxygen in $[Cu–O–Cu]_n$ surface species [16–19]. The bands characteristic for mononuclear Cu^{2+}, as well as for the $[Cu–O–Cu]_n$ cluster species are more intense in the spectrum of the CuO/Al_2O_3(CH) sample prepared by "chemisorption–hydrolysis" method in comparison to its impregnated analogue. The shift of the band to higher wavelength (>400 nm) for the CuO/SiO_2(WI), and CuO/Al_2O_3(CH) samples (Fig. 1) is due to the presence of polymerized copper oxide species. At the same time, the intensive band at 700 nm in the spectra of the CuO/SiO_2(WI) can be attributed to the presence of crystalline CuO phase, which is in accordance with XRD data (see above). The differences in the nature and the oxidative state of copper sites, which are formed on the modified samples, could be ascribed to the variations in the modification procedure and the nature of the applied support. So, the "chemisorption–hydrolysis" method provides predominantly the formation of copper ions and $[Cu–O–Cu]_n$ cluster species, while the impregnation method leads to the formation of crystalline CuO nanoparticles on the silica support as well.

More information on the state of copper oxide species is obtained by TPR–TG experiments (Fig. 2). The reduction profiles of the copper-containing catalysts depend on the support material used and the method of their preparation. The copper-containing SiO_2 and Al_2O_3 samples prepared by both methods possess clearly defined low-temperature reduction peaks in the region of 410–500 K attributed to Cu(II) → Cu(0) reduction. The presence of a clearly defined high-reduction peak at 770 K is registered only for CuO/SiO_2(WI) (Fig. 2). The extent of reduction is 100% for all studied samples. The narrow reduction peak with maximum at 450 K, registered for CuO/Al_2O_3 (CH) and CuO/SiO_2(CH), with a small shoulder at 500 K for the latter, is related to the more homogenous distribution of copper oxide species prepared via CH method on the supports. The presence of two overlapping peaks with maxima at 410–420 K and 460 K in TPR–TG profiles of the CuO/SiO_2(WI) and CuO/Al_2O_3(WI) samples (Fig. 2) is due to the formation not only of finely dispersed copper oxide species but of CuO as a separate phase as well.

Summarizing the above observations we could conclude that the reduction of copper oxide species occurs at a low temperature (410–500 K) and in a narrower temperature interval for the samples prepared by "chemisorption–hydrolysis" method in comparison to their copper analogues prepared by impregnation. Probably, the formation of different types of copper oxide species by the two applied methods is responsible for the different reduction behavior.

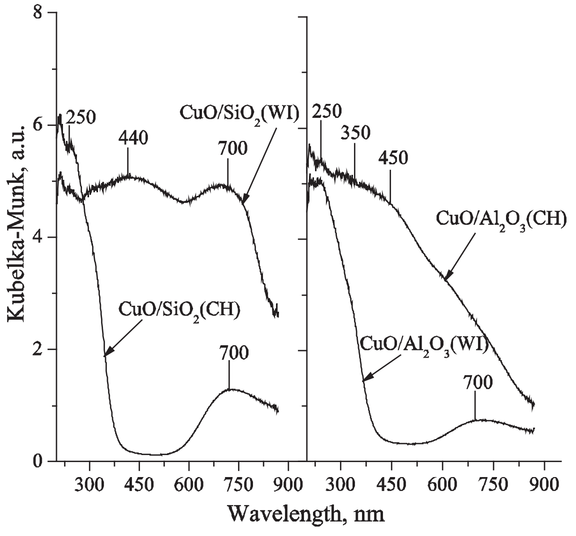

Fig. 1. UV–vis spectra of the copper samples.

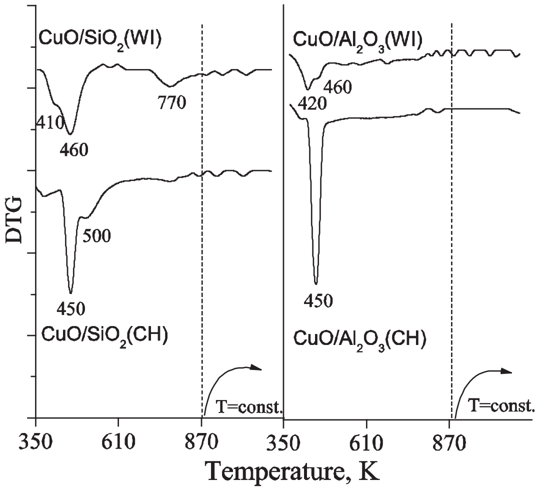

Fig. 2. TPR–TG profiles of various copper modified samples.

This assumption is also supported by the XRD and DR UV–vis data, where formation mainly of isolated copper ions and copper oligomers in the case of samples prepared by "chemisorption–hydrolysis" method and additionally presence of larger in size and amount crystalline copper oxide particles for the samples prepared by incipient wetness impregnation method was found.

One of the most informative techniques for the detection of Lewis and Brönsted acid sites is FT-IR spectroscopy of adsorbed pyridine (Py). Bands typical of Py adsorbed on Lewis acid sites are hardly detectable on the initial Al_2O_3 support (spectra 3 in Fig. 3), there are only very weak features at 1449 and 1611 cm^{-1} attributable to Py coordinatively bound to weak Lewis sites [20]. The copper loading of copper on Al_2O_3 support induces substantial changes in the FTIR spectra (Fig. 3, spectra 1, 2). The spectra of CuO/Al_2O_3(CH) and CuO/Al_2O_3(WI) samples show the presence of absorption bands located at 1449/1611 cm^{-1} typical of Py adsorbed on Lewis acid sites [20,21]. While CuO/Al_2O_3(WI) sample spectra basically behaves like CuO/Al_2O_3(CH), the acidic properties of CuO/SiO_2(WI) are similar to those of the silica support, i.e. no bands of adsorbed pyridine on Lewis acid sites are registered (Fig. 3, spectra 4–6). The bands at 1449/1611 cm^{-1} are observed on FTIR spectrum of CuO/SiO_2(CH), more probably because of the formation of isolated copper ions in it, interacting as Lewis acid sites.

To sum up CuO/SiO_2(CH), CuO/Al_2O_3(CH) and CuO/Al_2O_3(IW) samples show the presence of Lewis acidic sites, whereas CuO/SiO_2 (IW) shows no acidity and is similar to the silica support. The FTIR results are in good accordance with the data from XRD and DR UV–vis spectroscopy, confirming that copper oxide is formed as a separate phase on SiO_2 by incipient wetness impregnation method. Therefore it does not influence the surface acidity, whereas the isolated copper ions formed on SiO_2 by "chemisorption–hydrolysis" method are responsible for the Lewis acidity of the sample.

3.2. Catalytic activity for cyclohexanol dehydrogenation

In Fig. 4 and Table 1 the catalytic activities of copper containing materials in cyclohexanol dehydrogenation at 513 K are presented. High catalytic activity is registered for CuO/SiO_2(CH) and CuO/Al_2O_3 (CH) samples and the former one possesses higher selectivity to cyclohexanone. Their analogues prepared by impregnation show lower catalytic activity. The higher selectivity to cyclohexene observed for CuO/Al_2O_3(CH) and CuO/Al_2O_3(WI) samples (Fig. 4) is probably due to the acid sites of the alumina support, responsible for the dehydration process. The dehydrogenation reaction of cyclohexanol to cyclohexanone is favored on CuO/SiO_2(CH) and CuO/SiO_2(WI). The FTIR spectra of adsorbed pyridine (Fig. 3) are in good accordance with the catalytic data. Formation of high amounts of phenol (Fig. 4) is observed on the SiO_2 and Al_2O_3 supported samples prepared by "chemisorption–hydrolysis" method. According to the literature the Lewis acid–base pairs react with an alcohol molecule to generate an adsorbed long-lived alkoxy intermediate [19,22]. The surface oxygen species act as Lewis bases, which extract hydrogen from cyclohexanol and the intermediates. At the same time, copper oxide species act as Lewis acid sites to stabilize the adsorbed negatively charged intermediates. The XRD and UV–vis data of all the spent catalysts are presented in Fig. 5. The catalysts were purged in nitrogen to ambient temperature to avoid their reoxidation, followed by XRD and UV–vis measurements. The formation of crystalline Cu_2O (27 nm) is registered on CuO/SiO_2(WI), whereas no copper oxide phase is detected on the spent CuO/SiO_2(CH) (Fig. 5A). The reduction of CuO to Cu_2O in the spent CuO/SiO_2(WI) sample was proven by UV–vis measurement, where the shift of the band at 700 nm to 400–500 nm range is registered (Fig. 5B). The latter is assigned to Cu_2O layers formation [15]. However, the UV–vis spectrum of the CuO/SiO_2(CH) sample shows a shift of the band at 250 nm to higher wavelength (>300 nm), indicative of the formation of copper clusters and finely dispersed metallic copper.

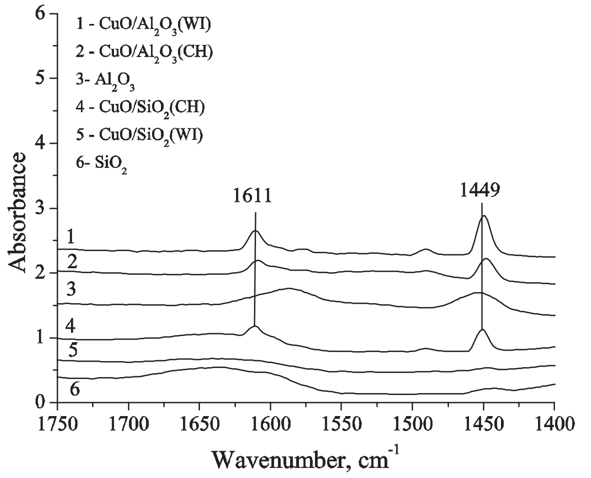

Fig. 3. FTIR pyridine adsorption spectra of CuO/Al_2O_3(CH), CuO/Al_2O_3(WI), CuO/SiO_2(CH) and CuO/SiO_2(WI) samples after evacuation at 673 K and pyridine desorption at 373 K .

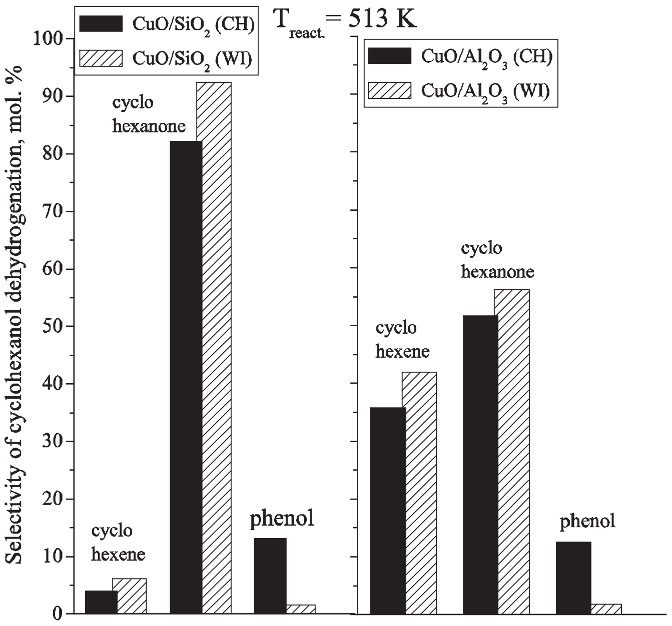

Fig. 4. Catalytic activity at 513 on the studied materials.

The UV–vis spectrum of the spent CuO/Al_2O_3(WI) sample also shows the band at 400–500 nm region and a shift of the bands above 600 nm present in the spectrum of the fresh sample to lower wavenumbers (Fig. 5B). These effects could be ascribed to the Cu^+ and metallic copper formation during the catalytic reaction. A well-defined band at 580 nm is observed in the spectrum of the spent CuO/Al_2O_3(CH) sample, indicative for metallic copper formation (Fig. 5B). The formation of very finely dispersed metallic copper in the spent CuO/Al_2O_3(CH) catalyst was proved by XRD (Fig. 5A). The copper species in CuO/SiO_2(WI) remain finely dispersed after the catalytic test and they are not detectable by XRD (Fig. 5A).

Table 1
Catalytic activity of the samples in cyclohexanol dehydrogenation at 513 K.

Samples	CuO/SiO_2(CH)	CuO/SiO_2(WI)	CuO/Al_2O_3(CH)	CuO/Al_2O_3(WI)
TOF, s^{-1}	0.0969	0.0818	0.0952	0.0634

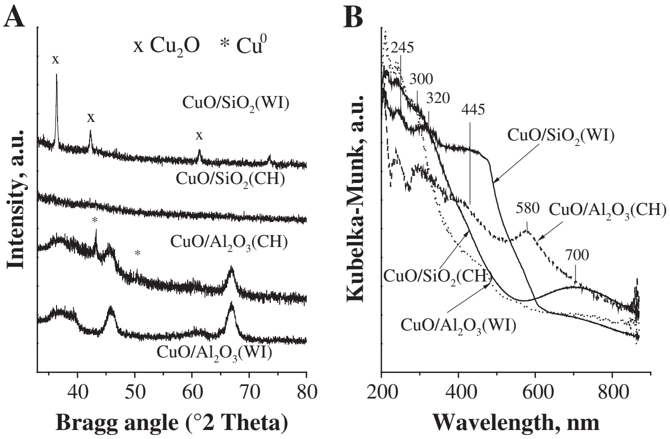

Fig. 5. XRD patterns (A) and UV Vis spectra (B) of CuO/SiO_2(CH) and CuO/SiO_2(WI) after the catalytic test.

On the basis of these observations and the catalytic data we can conclude that Cu^+ are the active sites for cyclohexanol dehydrogenation to cyclohexanone. Fridman et al. [4,5] also found that Cu^+ are the most active species in Cu–Zn catalyst in cyclohexanol dehydrogenation to cyclohexanone. The higher selectivity to phenol is observed on the SiO_2 and Al_2O_3 supported samples prepared by "chemisorption–hydrolysis" in comparison to that of the impregnated ones. The interpretation of the phenol formation in the literature [4,5,19,22] is ambiguous and two possible routes are suggested — directly from cyclohexanol (direct route) and through dehydrogenation of cyclohexanone (consecutive route). According to Fridman et al. [4,5] Cu^+ are the active sites for cyclohexanol dehydrogenation to cyclohexanone, whereas zero-valent copper species are the active sites for the formation of cyclohexanone and phenol. The applied physicochemical methods show that Cu^+ are predominantly formed and stabilized on SiO_2 and Al_2O_3 catalysts prepared by impregnation. We assume that the higher amount of the formed phenol on the samples prepared by the CH method is due to the initial presence in these samples of a higher amount of more finely dispersed Cu^{2+} ions and clusters. They can be easily reduced to finely dispersed metallic copper under the reaction medium, whereas stabilized Cu_2O species are responsible for the higher cyclohexanol conversion to cyclohexanone. The results presented by us support the direct route of phenol formation. Additional catalytic experiment with CuO/SiO_2(CH), pretreated in hydrogen at 523 K, shows significant decrease in the selectivity to phenol (not shown). This result can be explained by the agglomeration of metallic copper formed during the reduction pretreatment procedure. The formation of a higher amount of phenol was observed only on CuO/SiO_2(CH) without reduction pretreatment. This effect could be explained with the formation of finely dispersed metallic copper by the reaction medium.

4. Conclusion

The method of modification and the support used (SiO_2 and Al_2O_3) strongly influence the state of the obtained copper oxide species. In contrast to the incipient wetness impregnation procedure, the "chemisorption–hydrolysis" method facilitates the formation of higher amounts of finely dispersed and readily reducible copper ions and copper cluster species $[Cu–O–Cu]_n$ that provide higher catalytic activity in cyclohexanol dehydrogenation This effect is more pronounced, when SiO_2 is used as a support. The higher catalytic selectivity to cyclohexanone of the CuO/SiO_2 sample, prepared by incipient wetness impregnation method, is due to the formation of finely dispersed Cu^+ and their stabilization on the support material.

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