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A Novel Catalyst for the Selective Hydrogenation of Furfural to Furfuryl Alcohol

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MCM-41 supported CuO catalyst with high metal loading level and dispersion degree was prepared via a novel preparative method. The catalyst shows remarkable high activity and selectivity in the hydrogenation of furfural to furfuryl alcohol.

Furfuryl alcohol is an important raw material in the polymer industry and is generally produced by vapor-phase hydrogenation of furfural. However, the reduction results in a variety of possible products with different reducing degrees depending on the catalyst used. For over five decades, copper chromite has been the most successful commercial catalyst whereas the serious environmental pollution due to its toxicity is arousing public worries. Consequently, to prepare new catalysts free of chromium is of significant necessity and many papers have been published,[1–10] while rather limited researches have focused on molecular sieves as support for the active species. Seo et al.[11] investigated the hydrogenation of furfural over ion-exchanged Pd-CuY and Ni-CuY catalysts at 573 K and received high selectivity upon furfuryl alcohol but low conversion. To date other type of molecular sieves has not been involved yet.

Mesoporous MCM-41 is most promising in heterogeneous catalysis owing to its pore size and high specific surface area.[12] The present research herein aims to prepare a new environmentally benign catalyst with high activity for the selective hydrogenation of furfural to furfuryl alcohol, which owns MCM-41 as support and copper as main active composition with high loading level and dispersion degree. It is of obvious potential value in industry.

Zeolite-based exchanged catalyst was prepared as follows: MOR (Si/Al = 10) or Naβ (Si/Al = 15) was suspended in a mixed solution of $Cu(NO_3)_2$ and $La(NO_3)_3$ which was stirred at 363 K for 1 h and then the solid was filtrated and washed with water. This was repeated 3 times for enhancing the degree of ion exchange. The resultant solid was filtrated, dried, and calcined at 723 K for 4 h.

MCM-41 was synthesized according to the literature.[13] Quantified MCM-41 was suspended in boiling toluene and an excess of 3-aminopropyltrimethoxysilane (99%, ACROS) was added dropwise. The refluxing lasted for 8 h and the produced organofunctionalized MCM-41 was washed by ethanol and water. The as-synthesized material was added into $Cu(NO_3)_2$ solution or mixed solution of $Cu(NO_3)_2$ and $La(NO_3)_3$, and the mixture was continuously stirred for 6 h. Then, the ultrasonic wash was adopted to remove the physisorbed ions and to make the dispersion of active composition more homogeneous. The resultant solid was recovered by filtration, dried, and finally calcined at 773 K for 4 h.

Vapor-phase hydrogenation of furfural was performed in a fixed bed quartz chamber. The catalyst was first reduced in a 5% H_2 balance He flow at 623 K for 5 h. Furfural was injected at 1.4 $mL \cdot h^{-1}$ by a syringe pump (H_2:furfural molar ratio = 5:1). GHSV was maintained at 0.087 $mol \cdot h^{-1} \cdot g \cdot catalyst^{-1}$. The product mixture was collected hourly from an ice-cold trap and was analyzed by GC with a PEG-20M capillary column.

Furfural is reduced to furfuryl alcohol with equimolar hydrogen. Upon further hydrogenation, the furan ring becomes saturated, yielding tetrahydrofurfuryl alcohol and ring-opening products. Ni-based catalysts usually lead to further hydrogenation.[2] Table 1 lists the hydrogenation results over different catalysts in this work, showing only furfuryl alcohol and 2-methyl furan are yielded, which is in agreement with literatures.[1,11] This is probably because copper owns moderate reducing power which is comparative to deactivated nickel and thus is capable of avoiding over-hydrogenation, which clearly explains the superiority of copper-based catalysts. CuLa-MOR and CuLa-β catalysts resulted in extremely low yield of furfuryl alcohol and 2-methyl furan which may mainly attribute to the increasing acidity resulting from the H_2 reduction of Cu^{2+} which balances the negative charge of the zeolite framework.[9] In spite of low conversion, the selectivity of 2-methyl furan increases over MOR and Naβ supported catalysts with the rise of reaction temperature.

Table 1. Product distribution in the hydrogenation over the catalysts

Cat.	Cont./%		S_{BET}/ $m^2\,g^{-1}$	T/K	Conv. /%	Selectivity/%	
	Cu	La				furfuryl alcohol	2-methyl furan
CuLa-MOR	4.12	0.41	502	413	2.0	75.8	24.2
				453	2.1	62.3	37.7
CuLa-β	3.14	0.32	471	413	7.0	23.4	76.6
				453	9.5	18.5	81.5
CuLa /MCM-41	6.53	1.48	687	413	98.2	>99	—
				453	98.6	>99	—
Cu /MCM-41	6.40	—	675	413	63.2	>99	—
				453	70.1	>99	—

Different selectivities are reported as a consequence of varied catalyst composition and reaction conditions.[11,14,15] Applying MCM-41 as a support of Cu species and adopting organofunctionalization method, we've prepared CuLa/MCM-41 catalyst that exhibits remarkable high activity and selectivity to furfuryl alcohol, which is comparative to commercial copper–chromium catalyst. Compared with zeolites, the mesoporous structure is superior for the diffusion of molecules and can better avoid pore blocking. Meanwhile, the large pore size makes it possible for the preparative method in assembling different active species, such as organic groups which can coordinate with transition metal ions, resulting in high loading level and dispersion degree of catalytically active species. Table 1 shows the

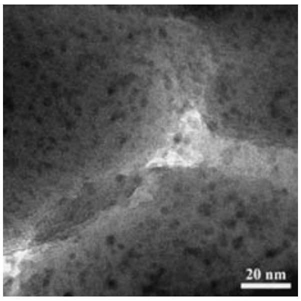

Figure 1. TEM photograph of CuLa/MCM-41.

composition and BET surface areas of the different catalysts. TEM photograph (Figure 1) indicates that metal oxides are dispersed homogeneously on the surface of MCM-41. Appropriate copper particle size might restrain over-hydrogenation of the furfural,[9] and therefore get the high selectivity for furfuryl alcohol.

According to the data in Table 1, the conversion is obviously increased when La is introduced as promoter. This is possibly because La is an electron donor which helps to increase the catalyst alkalinity and therefore is effective for the hydrogenation of C=O group.[9]

TPR is very persuasive in characterizing reducible catalysts.[16–18] Figure 2 shows H_2-TPR profiles of CuLa/MCM-41 and Cu/MCM-41. Two reduction peaks are observed at 533 and 718 K in the Cu/MCM-41 TPR profile, which might be from the reduction of CuO to Cu^0 located on external and internal surfaces, respectively. When La is introduced as promoter, the two reductions peaks move to lower temperatures of 483 and 672 K, indicating the easier reduction of CuO which mainly accounts for the increased activity of CuLa/MCM-41 catalyst.

The active sites of copper-containing catalysts as well as their functions in hydrogenation process have been so far extensively studied,[2,11] however the information is still inadequate. To our pity, it was impossible to collect in situ information of the active sites of the catalyst under the practical reaction conditions, leaving uncertainties about the real active site and its catalytic mechanism in reaction, which requires further investigation.

Deactivation of catalyst has been noticed in all of previous investigations,[14,15] and many explanations are presented e.g. coking on the catalyst surface, catalyst poisoning by either a reaction intermediate or a by-product, sintering under reaction conditions, and the change of copper charge during the reaction.

In the present investigation, CuLa/MCM-41 catalyst loses 32% of its activity after 8 h continuous employment; however its activity recovers to 85% of its origin after calcination at 573 K for 4 h. This better illuminates the premier reason for the catalyst deactivation being coking that jams the pore channels and overlaids the active sites of the supporting catalyst. And no reduction peaks were observed when the used catalyst was cooled in argon and then estimated in the in situ H_2-TPR test, implying that catalyst after reaction had not been oxidized and oxidation could not account for the catalyst deactivation.

The present research has originally immobilized active copper composition with high loading content and dispersion degree onto the mesoporous MCM-41 through an effective novel method which produces a new CuLa/MCM-41 catalyst. The catalyst shows remarkable high activity and selectivity of furfuryl alcohol in the hydrogenation of furfural which can be comparative to commercial catalyst and is of potential industrial value.

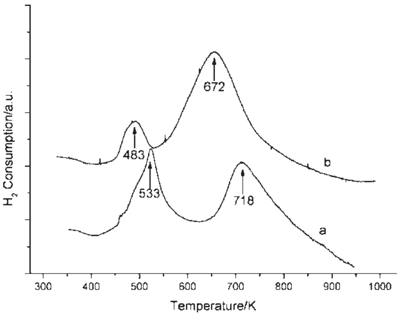

Figure 2. TPR profiles of (a) Cu/MCM-41 and (b) CuLa/MCM-41.

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