Highly effective Cu-HMS catalyst for hydroxylation of phenol

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Transition metals copper and titanium substituted mesoporous silicas (Cu-HMS and Ti-HMS) were synthesized at ambient temperature by using dodecylamine (DDA) surfactant as templating agent. XRD measurements prove that incorporating titanium and especially copper into the mesostructures causes the d_{100} peaks of mesoporous silicas to become shifted to lower angles, indicating progressive expansion of the lattice d-spacings upon heteroatoms Ti and especially Cu incorporating. FT-IR measurements indicate that the calcined Cu-HMS and Ti-HMS samples all exhibit a weaker absorption band near 960 cm^{-1} which may be rather a fingerprint of the heteroatom on the matrix of [SiO_4] units whatever its crystallization state. Cu-HMS possesses relatively high catalytic activity for the hydroxylation of phenol with 30% aq. H_2O_2 in aqueous solution (about 36% phenol conversion and more than 95% selectivity for dihydroxybenzene isomers), but Ti-HMS has no catalytic activity under the same reaction conditions. The product distribution obtained from Cu-HMS is completely different from that of the microporous titanium silicalite zeolites (TS zeolites). This is attributed to the porous structural differences between Cu-HMS and TS zeolites. The catalytic activity of the Cu-HMS is strongly dependent on the nature of the solvent; the Cu-HMS does not have any catalytic activity in the presence of organic solvents such as methanol or acetone instead of water. A reusing test of the recovered Cu-HMS indicates that the recovered catalyst suffers almost loss of activity and must be regenerated by calcination in air at 873 K in order to recover its activity.

Keywords: Cu-HMS, Cu-substituted mesoporous silicas, phenol, hydroxylation, catalytic oxidation

1. Introduction

Various transition metal substituted microporous silicalites such as TS-1 [1], TS-2 [2], VS-2 [3] and mesoporous silicas such as Ti-HMS [4], Zr-HMS [5], Cu-HMS [6] have found applications in the catalytic oxidation of a variety of organic compounds with aqueous hydrogen peroxide (H_2O_2) as an oxygen source. Apart from their unique catalytic properties, these thermally stable materials can be recycled many times without any loss of activity. The direct liquid peroxide hydroxylation of phenol is very important in theory and application. TS-1 zeolites are the best catalysts for the hydroxylation of phenol with 30% aq. H_2O_2 in methanol or acetone among the reported catalysts. However, the following faults limit the practical application of the microporous TS zeolites: (1) the synthesis of the TS zeolites is much more difficult and expensive than that of the mesoporous silicas containing transition metals; (2) the factors affecting the catalytic activity of the microporous TS zeolites are very complex [7] as various TS samples synthesized by different researchers strongly differ in oxidative activity [7–10] with some TS samples possessing lower catalytic activity; and (3) large amount of organic solvents used in the reaction system such as methanol or acetone causes definite environmental pollution. Therefore, it is very necessary to develop a novel environment-friendly catalyst.

Here, we report a convenient preparation of Cu-HMS with a higher catalytic activity for the hydroxylation of phenol with 30% aq. H_2O_2 in aqueous solution.

2. Experimental

2.1. Preparation of the catalysts

Cu-HMS was synthesized via a neutral S^oI^o templating pathway using dodecylamine (DDA) as the surfactant, ethanol (EtOH) as a co-solvent, tetraethyl orthosilicate (TEOS) and $Cu(NH_3)_4^{2+}$ ($Cu(OAC)_2 + NH_3{\cdot}H_2O$) as Si and Cu sources, respectively. In a typical preparation, the TEOS/$Cu(NH_3)_4^{2+}$ in ethanol solution was added dropwise to the solution of DDA in water and ethanol under vigorous stirring. The molar composition of the reaction mixtures was $0.02Cu : 1.0Si : 0.2DDA : 9.0EtOH : 72H_2O$. The reaction mixture was aged at room temperature (293 K) under vigorous stirring for 24 h in order to obtain the crystalline product. For comparative purposes, we have also synthesized Ti-HMS by replacing $Cu(NH_3)_4^{2+}$ with titanium tetra-butoxide (TBOT), and HMS by omitting the transition metal source in the above preparations. The obtained samples were filtered, washed thoroughly with ethanol, dried at 393 K for 4.0 h, and calcined at 873 K for 6 h in air prior to use.

2.2. Characterization of the catalysts

The catalysts thus obtained (Cu-HMS, Ti-HMS and HMS) were studied through X-ray powder diffraction and FT-IR spectroscopy. Their pore volumes and metal contents were measured with CCl_4 absorption measurements and with chemical analysis, respectively. The XRD measurements were carried out with a Siemens D-500 diffractometer with Cu Kα radiation ($\lambda = 1.542$ Å) and a scan speed of 2° (2θ) min^{-1}. The infrared measurements were carried out with a Nicolet 510P spectrometer, using KBr pellets.

2.3. Catalytic testing

For the study of their catalytic properties, the mesoporous samples were introduced along with phenol in a three-necked flask with a condenser. In a typical run, 0.94 g of phenol, 0.05 g of catalyst and 10.8 g of water were added to the reactor. When the mixture was heated to the reaction temperature under vigorous stirring, 1.14 g of a 30% aq. H_2O_2 was added dropwise to the reactor in 10 min. The reaction products were analyzed by GC on an XE-60 capillary column with a FID.

3. Results and discussion

The low-angle powder XRD patterns of the calcined mesoporous materials (Cu-HMS, Ti-HMS and HMS) only featured a strong first-order (d_{100}) diffraction peak accompanied by broader, unresolved higher order reflections, indicating that these materials possess a mesostructures with the lack of long-range order. The lack of long-range order exhibited by these materials is attributed to the weak H-bonding forces that govern the neutral S^oI^o assembly process and to the corresponding small scattering domain sizes [11] (see figure 1). As the transition metals are incorporated into the mesostructures, the d_{100} peaks of the materials become shifted to lower diffraction angles and slightly broad, indicating progressive expansion of the lattice d-spacings upon heteroatoms Cu and Ti incorporating (see figure 1 and table 1). The CCl_4 uptakes measured on the Ti-HMS and especially the Cu-HMS samples are larger than that of HMS (table 1). This indicates that the heteroatoms substituted silica has larger channels than pure silica. This result is consistent with the results of XRD characterizations. The FT-IR results of the untreated materials shown in figure 2 show that the intensity of C–H stretching bands of DDA inside the channels does not significantly change as the heteroatoms are incorporated into the mesostructures. This indicates that the incorporation of the heteroatom little affects the templating effects of the DDA reagent for assembling mesostructures. When the DDA reagent was removed by calcination in air, a weak absorption band near 960 cm^{-1} was observed in the spectrum of Cu or Ti incorporated HMS materials (figure 2). Although the assignment of the 960 cm^{-1} band is still disputed [12,13], more evidence, in that a very similar band is observed in titanium siloxane polymers [14], in mixed oxides [15] or in TiO_2-grafted on silica [16], supports that the characteristic IR band is due to a modification of SiO_4 units indirectly related to the presence of heterometals. Therefore, the IR band at 960 cm^{-1} is rather a fingerprint of heteroatoms on a matrix of [SiO_4] units whatever its crystallization state.

Catalytic reaction

The catalytic activities of the Cu-HMS and TI-HMS in the oxidation of phenol with water as solvent are listed in

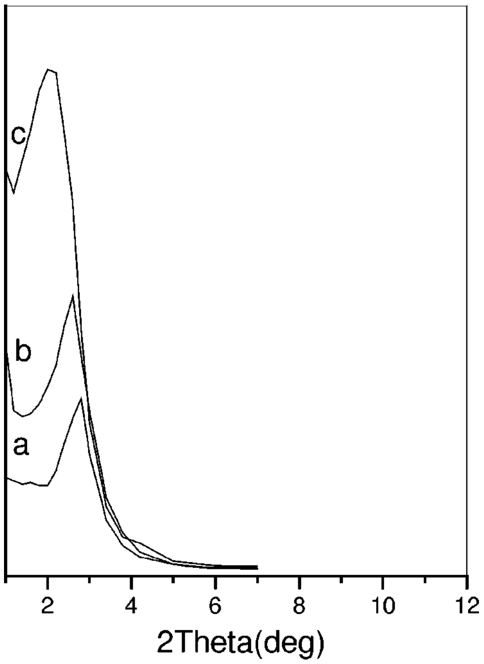

Figure 1. Powder XRD patterns of calcined mesoporous materials: (a) HMS, (b) Ti-HMS and (c) Cu-HMS.

Table 1
Characterized results of transition metals incorporated HMS.

Sample	Metal loading (mol%)		XRD results[a] (Å)		FT-IR results[b]		CCl_4 uptake[c]
	Gel.	Product	d_{100}	a	A band int.	B band site (cm^{-1})	($\text{ml}\,\text{g}^{-1}$)
HMS	–	–	31.4	36.2	0.238	–	0.42
Ti-HMS	1.96	2.12	35.1	40.5	0.220	956.8	0.48
Cu-HMS	1.96	1.97	43.6	50.4	0.239	964.5	0.52
TS-2[d]	3.83	3.00	–	–	–	962.6	–

[a] $a = 2\sqrt{3}\,d_{100}$.
[b] The C–H stretching bands of dda surfactant (2959, 2928 and 2856 cm^{-1}) and the fingerprint of the transition metal incorporated HMS, respectively. The relative intensity of A bands was calculated on the basis of the intergral area of A bands/the intergral area of Si–O stretching bands (1082 cm^{-1}).
[c] Measured by CCl_4 absorption apparatus at 298 K.
[d] From [8].

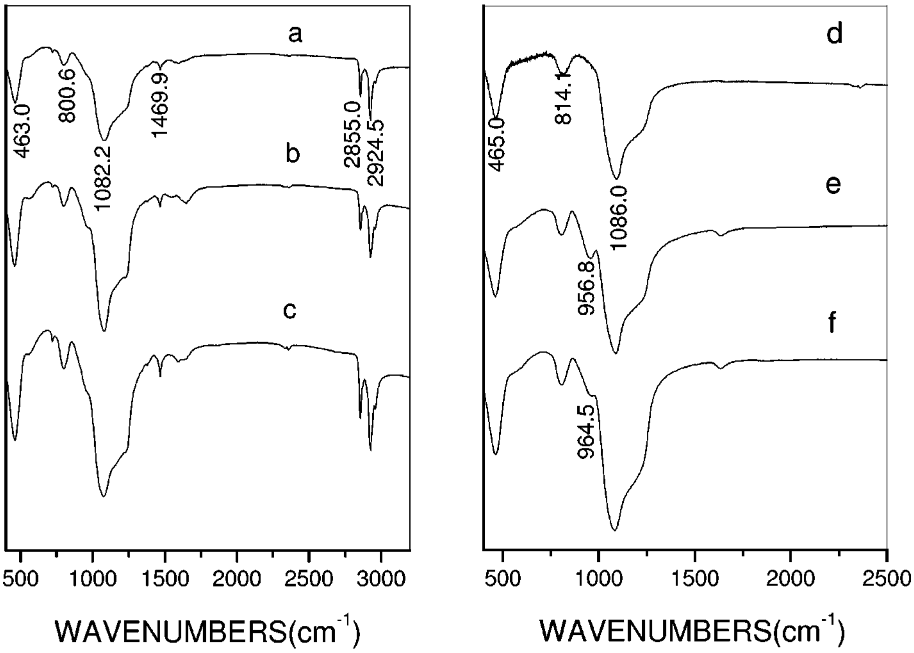

Figure 2. FT-IR spectra of uncalcined and calcined mesoporous materials: (a) uncalcined HMS, (b) uncalcined Ti-HMS, (c) uncalcined Cu-HMS, (d) calcined HMS, (e) calcined Ti-HMS and (f) calcined Cu-HMS.

Table 2
Results of hydroxylation of phenol over Cu-HMS.

Catalyst	Solvent	Reaction temp. (K)	Reaction time (h)	Phenol conv. (mol%)	Product distributions[a] (%)			
					Cat.	Hyd.	Other	Cat./Hyd.
Cu-HMS	H_2O	313	2	3.9	66.4	30.8	2.8	2.2
			4	7.1	68.2	28.5	3.3	2.4
		333	2	23.5	72.9	24.7	2.4	3.0
			4	35.8	65.0	31.0	4.0	2.1
		353	2	38.4	63.0	33.9	3.1	1.9
			4	38.7	63.5	33.5	3.0	1.9
		373	2	37.0	63.6	32.3	4.1	2.0
			4	36.5	64.6	30.5	4.9	2.1
Cu-HMS[b]	H_2O	333	4	2.3	99.2	–	0.8	
Cu-HMS[c]	H_2O	333	4	32.7	65.5	30.6	3.9	2.1
Cu-HMS	Methanol	333	4	0.0	–	–	–	–
	Acetone	333	4	0.0	–	–	–	–
Ti-HMS	H_2O or methanol	333	4	0.0	–	–	–	–
TS-2	Methanol	333	4	6.2	50.8	48.2	1.0	1.1

[a] Cat. and Hyd. indicate catechol and hydroquinone, respectively, Other indicates unidentified tar products.
[b] Recovered Cu-HMS was not activated prior to reuse.
[c] Recovered Cu-HMS was activated by calcination in air at 773 K for 4 h prior to reuse.

table 2, and compared to that of TS-2 zeolite with methanol as solvent. Product analyses show that phenol is selectively oxidized by H_2O_2 at 333–373 K to a mixture of the dihydroxybenzenes catechol and hydroquinone (more than 36% phenol conversion and 95% selectivity for dihydroxybenzene isomers) and a small amount of unidentified tar products (less than 5.0% tar products), but Ti-HMS in the presence of H_2O or methanol solvent has no catalytic activity. By comparing the catalytic properties of Cu-HMS and TS-2, it is discovered that Cu-HMS is by far more active than TS-2 (the conversion of phenol is 35.8% over Cu-HMS and 6.2% over TS-2 at 333 K), and relatively more active than TS-1 zeolites previously reported by other researchers [7,10]. The product distributions observed for Cu-HMS are different from that of TS zeolites such that catechol always prevails with a selectivity higher than 62% on Cu-HMS and is almost equal to hydroquinone on TS-2 (catechol : hydroquinone $= 1:0.95$). A possible reason which may account for such a difference is that the one-dimensional mesostructure of Cu-HMS which is completely different from the three-dimensional microstructure of the microporous TS zeolites shows a non-shape-selective oxidation for the hydroxylation of phenol. When hydrogen peroxide is added to the solution, phenol molecules are rapidly oxidized over the Cu species outside and inside the channels of Cu-HMS to yield an excess of catechol, the most thermodynamically favored isomer. Another explanation could be that hydroquinone is preferably consumed in the secondary formation of tar products.

The influences of the solvent on the catalytic activity of TS-1 has been reported [17]. Here, we also discovered that the catalytic activity of Cu-HMS is strongly dependent on the nature of the solvent. When methanol or acetone, which are previously used as the standard solvent for the hydroxylation of phenol over the microporous TS zeolites, is used as the solvent instead of water, Cu-HMS shows no catalytic activity. The reason may be due to the completely different activation mechanism between Cu-HMS and TS zeolites. Liu et al. [6] propose that the Cu^{2+} species on Cu-HMS may first activate H_2O_2 to form OH radicals, and then, the OH radicals oxidize phenol to dihydrobenzenes. The radical mechanism proposed still needs to be confirmed by further experimental proofs.

The temperature test indicates that the catalytic activity of Cu-HMS increases as the reaction temperature increases from 313 to 353 K. Furthermore, selectivity to dihydrobenzenes and the catechol to hydroquinone ratio are little affected as the reaction temperature varies. The temperature test further proves that the product compositions observed from Cu-HMS are only controlled by thermodynamics and not controlled by diffusion dynamics.

Reusing of the recovered catalyst indicates that the catalytic activity of the used Cu-HMS is little before the regeneration, and can be almost recovered after the regeneration. A reasonable explanation may be because Cu-HMS with larger channels has little effects of the channel constraints on the formation and transformation of the brown tar species (formed as a result of the reaction of hydrogen peroxide with dihydroxybenzenes) inside the channels of Cu-HMS. The tar species gradually poisons the Cu^{2+} active sites inside and outside the channels, and finally, leads to the loss of activity of the catalyst. Therefore, in order to recover the catalytic activity, the used catalyst is necessary to be regenerated by the calcination to remove the poisoning molecules.

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