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A new solid acid catalyst grafting BF_3·Et_2O on mesoporous molecular sieve MCM-41

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A new Solid acid catalyst has been prepared by grafted BF_3·Et_2O on mesoporous molecular sieve MCM-41. The solid catalyst would effectively promote the opening reaction of epichlovohydrin with isobutanol to form 1-isobutoxy-3-chloropropanol, and showed a nice activity and selectivity.

KEY WORDS: Solid acid catalyst; BF_3·Et_2O; MCM-41; Epichlorohydrin; Isobutanol; 1-Isobutoxy-3-chloropropanol.

1. Introduction

Among the M41S family of mesoporous crystalline solids, MCM-41 is the most attractive mesoporous materials because of its characteristic structure of well-ordered hexagonal mesopores [1,2]. It is neccessary to introduce funtionality into MCM-41 structures, so surface modification techniques are enjoying a renewed interest, and it is clear that the pore walls of mesoporous materials are easily modified with either purely inorganic or hydrid, semi-organic functional groups[3, 4]. Progress in acid catalysis is legged behind, largely because of the low acid strength of Al-substituted mesoporous silicas such as Al-MCM-41[5], so scientists try to improve its acid strength by functionalised with sulfonic acid and supported with heteropoly acid on MCM-41[6,7].

In this paper, we are to report the preparation and characterization of MCM-41 supported BF_3Et_2O(designated as BF_3Et_2O/MCM-41), and the activity of the new solid acid catalyst towards the opening reaction of epichlorohydrin with isobutanol to form 1-Isobutoxy-3-chloropropanol was examined.

2. Experimental

MCM-41 was prepared according to the literature 2. The results of BET surface area and pore size measurement showed that the surface area and average pore radius of MCM-41 were 924.5 $m^2\ g^{-1}$ and 3.9 nm, respectively.

MCM-41 or SiO_2 supported $BF_3 \cdot Et_2O$ catalysts were easily prepared as follow: a mixture of precursor $BF_3 \cdot Et_2O$ (0.03–0.3 mol L^{-1}) diluted in 100 mL of ethanol, benzene, acetone or water (as solvent) and 1 g of MCM-41 or SiO_2 was stirred for 2 h under N_2 atmosphere at ambient temperature, and then dried slowly on a rotary evaporator at 50 °C. The $BF_3 \cdot Et_2O$ loading in the catalysts was varied from 0.03 to 0.3 mol g^{-1}. The surface area and average pore radius of the catalysts were 856.3 $m^2\ g^{-1}$ and 3.3 nm for 0.03 mol $BF_3 \cdot Et_2O$/MCM-41, 715.5 $m^2\ g^{-1}$ and 2.5 nm for 0.07 mol $BF_3 \cdot Et_2O$/MCM-41, 660.3 $m^2\ g^{-1}$ and 1.7 nm for 0.2 mol $BF_3 \cdot Et_2O$/MCM-41, respectively.

XRD measurement was performed on Rigaku/Max-IIIB diffractometer. FT-IR measurement was carried out on Nicolet 560 E.S.P.magna IR spectrophotometer.

In the presence of these catalysts, the opening reaction of epichlorohydrin with isobutanol was carried out at 90 °C. A typical reaction, a mixture of epichlorohydrin (10 mL), isobutanol (15 mL) and 0.3 g $BF_3 \cdot Et_2O$/MCM-41 was stirred in an oil bath at 90 °C for 12 h. After the reaction, the $BF_3 \cdot Et_2O$/MCM-41 catalyst was separated from the mixture by filtration. The filtrate was analyzed by GC.

3. Results and discussion

Figure 1 shows the XRD patterns of MCM-41 and 0.07 mol $BF_3 \cdot Et_2O$/MCM-41. The XRD results indicate that the synthesis of MCM-41 is consistent with literature 2. After grafting $BF_3 \cdot Et_2O$, the structure of MCM-41 is still maintained. However, the d_{100}-spacing value in the $BF_3 \cdot Et_2O$/MCM-41 catalysts with increasing $BF_3 \cdot Et_2O$ loading increases remarkedly, 36.78 for MCM-41 and 40.13 for 0.07 mol $BF_3 \cdot Et_2O$/MCM-41 respectively, which shows that the wall thickness of MCM-41 is thickened [8]. It perhaps

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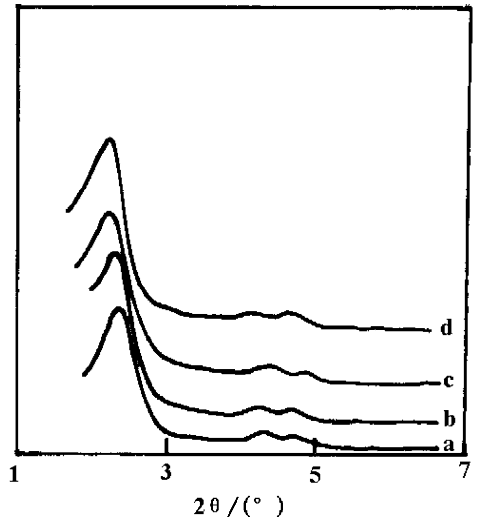


Figure 1. XRD patterns of MCM-41 and $BF_3 \cdot Et_2O$/MCM-41 (a) MCM-41; (b) 0.03 mol $BF_3 \cdot Et_2O$/MCM-41; (c) 0.07 mol $BF_3 \cdot Et_2O$/MCM-41; (d) 0.2 mol $BF_3 \cdot Et_2O$/MCM-41.

contributes to the BF_3 coordinate with the silanol group of MCM-41. FT-IR (figure2) also supports such a deduction that two peaks appear at 1300–1500 cm^{-1} which result from the B–O bond stretching mode[9], and the absorption peaks of B–O bond become apparent as the $BF_3 \cdot Et_2O$ loading increase, but B-F bond stretching mode would probably be obsured by the total background absorption of silica. Characterisation of the acid sites present on the surface was performed by recording FT-IR spectra following adsorption of the supported $BF_3 \cdot Et_2O$ catalysts with pyridine as shown in figure 3. These show that all the catalysts exhibit both Lewis and Bronsted acidity, as indicated by the strong adsorption band at 1440 cm^{-1} (Lewis sites), and those at 1593 cm^{-1} (Bronsted Sites). The adsorption band at 1593 cm^{-1} increase remarkedly with increasing the $BF_3 \cdot Et_2O$ loading. The remaining bands at 1461 and 1540 cm^{-1} are assigned to pyridine band at either Lewis or Bronsted sites. Bronsted acidity in solid acid catalysts normally arises from polarized $^{\delta-}O\text{–}H^{\delta+}$ sites. The observation of strong Bronsted acidity following attachment of a Lewise acid center to an oxide support has been reported in other system[10], and might be attributed to polarization of surface hydroxyl groups via an inductive effect of the electronegative F atoms on BF_3. So we believe that these spectroscopic results can be summarized by the model presented scheme 1.

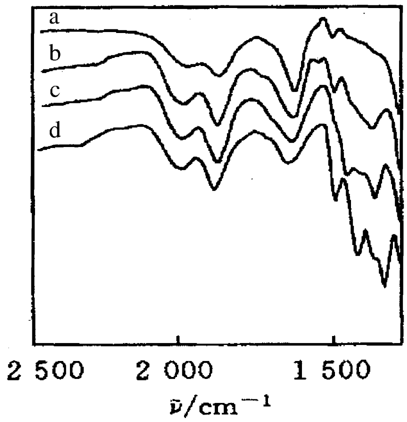


Figure 2. FT-IR spectra of MCM-41 and $BF_3 \cdot Et_2O$/MCM-41 (a) MCM-41; (b) 0.03 mol $BF_3 \cdot Et_2O$/MCM-41; (c) 0.07 mol $BF_3 \cdot Et_2O$/MCM-41; (d) 0.2 mol $BF_3 \cdot Et_2O$/MCM-41.

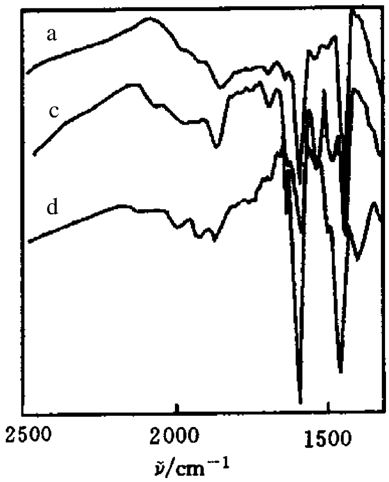
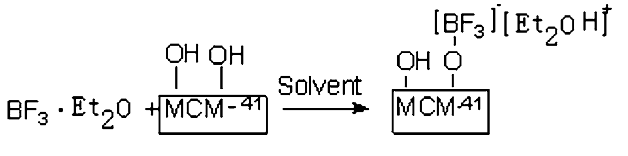


Figure 3. Pyridine-IR spectra on MCM-41 and $BF_3 \cdot Et_2O$/MCM-41 (a) MCM-41; (b) 0.07 mol $BF_3 \cdot Et_2O$/MCM-41; (c) 0.2 mol $BF_3 \cdot Et_2O$/MCM-41.



Scheme 1.

The catalytic activity of these supported BF_3 samples was tested using the opening reaction of epichlorohydrin with isobutanol, the results are listed in tables 1–3. table 1 shows the epichlorohydrin conversions and selectivities towards 1-Isobutoxy-3-chloropropanol obtained after 12 h reaction time. It is clear that the $BF_3 \cdot Et_2O$/MCM-41 and $BF_3 \cdot Et_2O/SiO_2$ catalysts prepared in ethanol exhibit high catalytic activitity and selectivity, and their catalytic activities decrease and selectivities towards 1-Isobutoxy-3-chloropropanol increase after washed with ethanol. The loss of activity on washing the catalysts with according solvent may result from the weak adsorbent $BF_3 \cdot Et_2O$ on the surface of MCM-41 and SiO_2 washed away. From table 2, it shows that epichlorohydrin conversions increase with increasing $BF_3 \cdot Et_2O$ loading, and but the selectivities towards 1-Isobutoxy-3-chloropropanol decrease slightly. The activity can thus be correlated with the number and strenth of Bronsted acid sites identified on

Table 1
Catalytic properties of $BF_3 \cdot Et_2O$/MCM-41, SiO_2

Catalyst	Epichlorohydrin conversion, %	1-Isobutoxy-3-chloropropanol selectivity, %
SiO_2	–	–
MCM-41	7.0	~100
0.07 mol $BF_3 \cdot Et_2O/SiO_2$	47.5 (26.6)[a]	96.0 (100)[a]
0.07 mol $BF_3 \cdot Et_2O$/MCM-41	59.0 (25.0)[a]	96.0 (100)[a]

[a] Catalyst was washed with ethanol for many times.

Table 2
Effect of $BF_3 \cdot Et_2O$ loading on acid catalytic properties

Catalyst	Epichlorohydrin conversion, %	1-Isobutoxy-3-chloropropanol selectivity, %
0.03 mol $BF_3 \cdot Et_2O$/MCM-41	25.0	98.0
0.07 mol $BF_3 \cdot Et_2O$/MCM-41	59.0	96.0
0.2 mol $BF_3 \cdot Et_2O$/MCM-41	80.1	95.5
0.3 mol $BF_3 \cdot Et_2O$/MCM-41	87.2	95.4

Table 3
Effect of solvent used in preparation process of catalyst on acid catalytic performane of 0.07 mol $BF_3 \cdot Et_2O$/MCM-41

Solvent	Epichlorohydrin conversion, %	1-Isobutoxy-3-chloropropanol selectivity, %
Benzene	87.2 (67.0)[a]	95.6 (~100)[a]
Acetone	78.3 (35.0)[a]	94.0 (~100)[a]
Ethanol	59.0 (25.0)[a]	96.0 (~100)[a]
Water	17.2 (–)[a]	100 (–)[a]

[a] Catalyst was washed with according solvent for many times.

these catalysts using FT-IR. From table 3, it shows that the activity of the $BF_3 \cdot Et_2O$/MCM-41 catalyst prepared in benzene is superior to other samples. In addition, their catalytic activities decrease and selectivities towards 1-Isobutoxy-3-chloropropanol increase after washed with according solvent, too. It is not difficult to find that the activity of catalysts depends greatly on the polarity of the solvent, nonpolar solvent is superior to polar solvent. We think that there are two reasons: first is that polar solvent coordinating to BF_3 is more stronger than nonpolar solvent, which results in the decrease of the ability of silanol group coordinating with BF_3; secondly, due to the channel of MCM-41 is hydrophobic, the amount of MCM-41 absorbing nonpolar solvent is larger than polar solvent.

In conclusion, we have synthesized a new form of supported boron trifluoride which is easy to prepare and handle, shows unusually high Bronsted acidity, and exhibits considerable catalytic activity.

Acknowledgments

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