Catalysis Letters Vol. 100, Nos. 3–4, April 2005 (© 2005)
DOI: 10.1007/s10562-005-3460-2

Reactions of turpentine using Zr-MCM-41 family mesoporous molecular sieves

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Received 07 October 2004; accepted 15 November 2005

The mesoporous molecular sieve Zr-MCM-41 was synthesized under hydrothermal conditions. Zr-MCM-41 material was impregnated using sulfuric acid to prepare SO_4^{2-}/Zr-MCM-41. The obtained materials were characterized by XRD, FT-1R, N_2 adsorption/desorption and NH_3-TPD analysis technique. The results indicated that SO_4^{2-}/Zr-MCM-41 was of better mesoporous structure, long range ordering and crystallites, and that SO_4^{2-} existed in the skeleton of Zr-MCM-41 and enhanced its acidity. SO_4^{2-}/Zr-MCM-41 were firstly used as catalyst in the esterification of terpineol. The catalytic results were compared with those obtained by using sulfuric acid (33%), HY, HZSM-5 and SO_4^{2-}/ZrO_2 as catalysts. It was showed that SO_4^{2-}/Zr-MCM-41 were not only of better catalytic activity and selectivity, but also of better regenerable performance. The effects of synthesis methods of catalysts and Si/Zr mole ratio on catalytic properties were also studied. In addition, $AlCl_3$ was supported on the synthesized mesoporous molecular sieves to get composite catalysts that were firstly used to catalyze the polymerization of α-pinene. It was showed that the catalytic result of the *composite catalyst* was better than that $AlCl_3$ alone.

KEY WORDS: mesoporous molecular sieves; terpineol; α-pinene; esterification; polymerization.

1. Introduction

α-Pinene is the main constituent of turpentine oil. When treated with water in the presence of acid, α-pinene is mainly hydrated to terpineol. Terpineol can be esterificated to terpinyl acetate that is an important and widely used synthetic perfume of citric and lavender scents. Terpinyl acetate is traditionally manufactured in the presence of phosphoric acid. However, the drawbacks of such a process include too large amount of usage, serious corrosive and environmental problems.

α-Pinene polymer can be obtained by cationic polymerization. As a kind of excellent viscosifier, it is of better resistance to aging, higher cohesive force, better resistance to heat and atoxicity. α-Pinene polymer is widely used in the fields of adhesive agent, coating and mimeograph ink, etc. When treated with Lewis acids such as $AlCl_3$, the polymerization of α-pinene is extremely slow and only lower oligomers can be obtained. The low reactivity of α-pinene is due to lack of the highly reactive exo-methylene double bond that exists in the β-isomer. Therefore, in addition to the major catalyst, some kinds of activators are usually used in polymerization of α-pinene in order to stabilize the chain-growing carbonium and extend its residence time during which the chain-growing carbonium can react with other α-pinene monomer to get polymer higher molecular weight. Jiang *et al.* [1] used $AlCl_3/SbCl_3$ binary catalyst to get relatively high molecular weight of α-pinene polymer. However, the reaction must be carried out at lower temperature (−15 °C) because the polymerization was so rapid at higher temperature that the obtained product was mainly dimer.

Mesoporous molecular sieves designed as M41S were firstly reported in 1992 [2–4] by American Mobil Company. These materials possess a hexagonal arrangement of uniformly sized unidimensional mesoporous. An exciting property of these materials is the possibility of controlling the internal diameter of the mesopores between 2 and 10 nm by varying the chain length of the micellar surfactant template. Their high thermal and hydrothermal stability, uniform size and shape of the pores, and large surface areas make them of interest as catalysts. For example, when used in Diels–Alder reaction of anthracene with *p*-benzoquinone, the catalytic activity of MCM-41 was higher than that of HY, the conversion was only 2.2% on HY, but was 70.9% on MCM-41 [5]. α-*n*-Amylcinnamaldehyde was prepared with higher selectivity by MCM-41 than by Beta zeolite because the former is of larger pore size than the latter [6]. The conversion of Friedel-Crafts alkylation between 2,4-ditertbutyl phenol and cinnamyl alcohol was more than 60% when using MCM-41 as catalyst, but the conversion was only 7% on microporous molecular sieve such as HY [7]. Therefore, MCM-41 will be a potential catalyst suitable to catalyze reactions of larger substrates.

When used in the Friedel-Crafts acylation of 2-methoxynaphthalene, the catalytic activity of MCM-41

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was very low because of the poorer acidity of MCM-41. If the Na^+ in MCM-41 was exchanged by H^+, the catalytic activity was obviously improved and the conversion was over 55% [8]. It was also reported that the catalytic activity of MCM-41 could be improved by introducing some transition metals such as Ti [9,10], V[11,12] Cr[13], Zr [14] and Mo[15] in its skeleton. However, after above improvements, the catalytic activity of MCM-41 was not high enough for some reactions because its acidity was still poorer. Therefore, it is necessary to further enhance the acidity of MCM-41 in order to expend its application fields.

In this study, the mesoporous molecular sieves Zr-MCM-41 were synthesized under hydrothermal conditions. Zr-MCM-41 materials were impregnated using sulfuric acid to prepare SO_4^{2-}/Zr-MCM-41. The obtained materials were characterized by XRD, FT-IR, N_2 adsorption/desorption and NH_3-TPD analysis techniques. SO_4^{2-}/Zr-MCM-41 were firstly used as catalyst in the esterification of terpineol. The catalytic results were compared with those obtained by using sulfuric acid (33%), HY, HZSM-5 and SO_4^{2-}/ZrO_2. It was showed that SO_4^{2-}/Zr-MCM-41 was not only of better catalytic activity and selectivity, but also of better regenerable performance. The effects of preparation methods of catalysts and Si/Zr mole ratios on catalytic properties were studied. Moreover, $AlCl_3$ were supported on the synthesized mesoporous molecular sieves to get composite catalysts that were firstly used to catalyze the polymerization of α-pinene. It was showed that the catalytic activities of the composite catalysts were better than that of $AlCl_3$ alone.

2. Experimental

2.1. Synthesis of catalysts

Zr-MCM-41 was synthesized by hydrothermal method. The mole ratio of reactants was 0.0125–0.06 $Zr(SO_4)_2$: 0.67 Na_2SiO_3: silica gel: 0.20 CTMABr: $102H_2O$, following the procedure reported in the previous paper [14].

Six different SO_4^{2-}/Zr-MCM-41 were prepared. (A) Using 0.25 mol/L H_2SO_4 to infuse uncalcined Zr-MCM-41. (B) Using 0.25 mol/L H_2SO_4 to infuse calcined Zr-MCM-41. (C) Using 0.25 mol/L $(NH_4)_2SO_4$ to infuse uncalcined Zr-MCM-41. (D) Using 0.25mol/L $(NH_4)_2SO_4$ to infuse calcined Zr-MCM-41. (E) Grinding $(NH_4)_2SO_4$ solid with uncalcined, Zr-MCM-41. (F) Grinding $(NH_4)_2SO_4$ solid with calined Zr-MCM-41. All above six sieves were prepared by filtering, drying at 100 °C for 12 h and calcining at 550 °C for 3 h.

The mesoporous molecular sieve (1 g) CCl_4 were added into a bottle, then $AlCl_3$(3 g) was added. The mixture was stirred for 30 min, and then dried a vacuum dryer for 2 h.

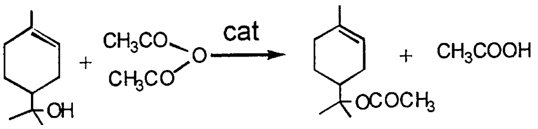
2.2. Characterization

X-ray powder diffraction patterns of the samples were obtained on an XB-3A instrument using monochromatic Cu K_α radiation(λ0.15418 nm). It was operated at 40 kV and 100 mA. The experimental conditions correspond to step width of 0.02° and scan speed of 2°/min. It should be noticed that the diffraction must be operated at narrow seam and diffraction region $2\theta = 2–10$. IR spectra were recorded using a Nicolet 510P FT-IR spectrometer in the range of 2000–800 cm^{-1}, using KBr powder containing ca. 1 wt% of sample. N_2 adsorption–desorption isotherms were measured at Micromeritics ASAP 2000. Surface area was calculated using BET method based on adsorption data in the partial pressure (P/P_0) range 0–0.1 and the pore diameter and pore volume were determined from the amount of N_2 adsorbed at $P/P_0 = 1$ using BJH method. The NH_3-TPD data were collected using a chembet 3000 analyzer. About 200 mg sample was activated in flowing He at 500 °C for 2 h, then cooled to 120 °C under continuous evacuation. The sample was equilibrated with gaseous NH_3 at 0.04 kPa, then ramped up at 10 °/min while He was flowing through the reactor at 20 cm^3/min.

2.3. Catalytic experiments

2.3.1. Esterification of terpineol

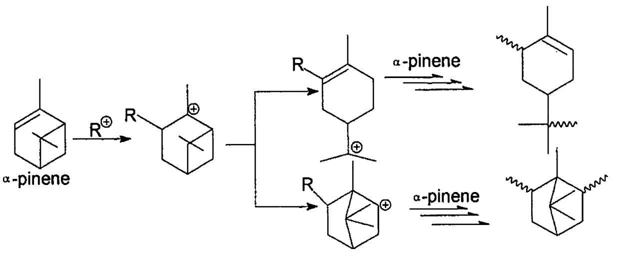
The catalyst (1 g) was added into a mixture of terpineol and acetic anhydride, and the reaction was carried out in a flask with an electronic stirred at reaction temperature for 6 h. After reaction, the mixture was filtered and the filtrate was washed by Na_2CO_3 solution to pH > 8. Then the organic supernatant was collected and washed by water to pH = 7. The organic supernatant was dried by anhydrous magnesium sulfate, filtered get clear organic solution and analyzed with Gas Chromatograph of GC-122 using a flame-ionization detector and a capillary column of DB-5. The reaction Scheme (1) is followed:



Scheme 1. Equation of esterification.

2.3.2. The polymerization or α-pinene

The catalyst and solvent were added into a flash, then α-pinene was dropped slowly with stirring at 25–30 °C for 4 h. The reaction mixture was filtered and α-pinene resin was obtained after removing solvent by distillation. The product was evaluated by its soft paint temperature, which was measured by SDY-2806 asphalt soft point temperature machine according to circular ball method. The reactions were showed in Scheme 2.



Scheme 2. Equation of polymerization.

3. Results and discussion

3.1. XRD

Figure 1 shows the powder X-ray diffraction patterns of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B). It can be noted that Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B) exhibit the typical hexagonal lattice corresponding to that reported by Beck [2]. It shows three low-angle peaks in the region $2\theta = 1.5$–10, corresponding to (100), (110) and (200) reflections. Compared the peak intensify and width of Zr-MCM-41 with that of SO_4^{2-}/Zr-MCM-41(B), SO_4^{2-}/Zr-MCM-41(B) is of the same long range ordering and crystallites as Zr-MCM-41[16].

Therefore, there is no obvious influence on mesoporous structure after introducing SO_4^{2-}.

3.2. FT-IR Spectroscopy

The IR spectra of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B) were showed in figure 2. The broad bands at 1630 and 1650 cm^{-1} may be attributed to surface silanol groups and adsorbed water molecules [17]. SO_4^{2-}/Zr-MCM-41(B) exhibits absorption band at 1364 cm^{-1} corresponding to S=O. For solid super acidic catalyst such as SO_4^{2-}/MxOy, the band of S=O is at 1380 cm^{-1} that is often regard as the characteristic band of SO_4^{2-} in the solid super acidic catalysts [18–21]. The band at 1364 cm^{-1} of SO_4^{2-}/Zr-MCM-41(B) is attributed to the interaction between SO_4^{2-} and metallic element. With the increase of metallic element, this band becomes more intense [22]. All these mean that SO_4^{2-} exists in the skeleton of Zr-MCM-41. In the IR spectra, the asymmetric and symmetric stretching vibration bands of framework Si–O–Si appeared at about 1090 and 789 cm^{-1} [23].

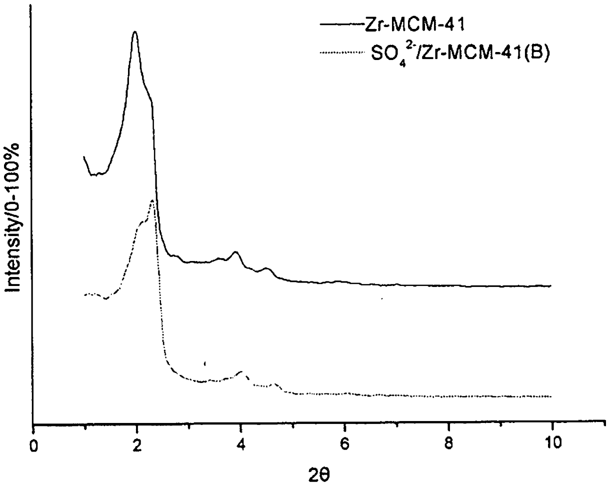


Figure 1. XRD power patterns of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41 (B).

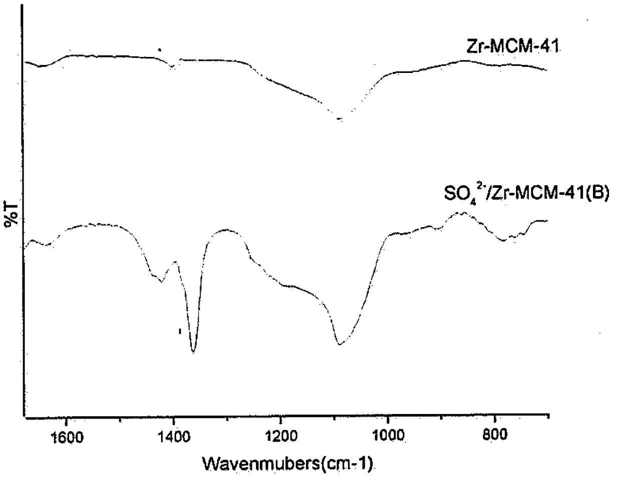


Figure 2. FT-IR spectra of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B).

3.3. N_2 adsorption–desorption isotherms

Figures 3 and 4 show the isotherms of nitrogen adsorption-desorption on Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B). In accordance with those of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B) materials, all samples exhibit a well-expressed hysteresis of loop type IV, which means that all of the samples are of good mesoporous structural ordering and a narrow pore size distribution. A slow increase in nitrogen uptake at low relative pressure corresponding to monolayer–multilayer adsorption on the pore walls, and adsorption curve is identical with desorption curve, which indicates that

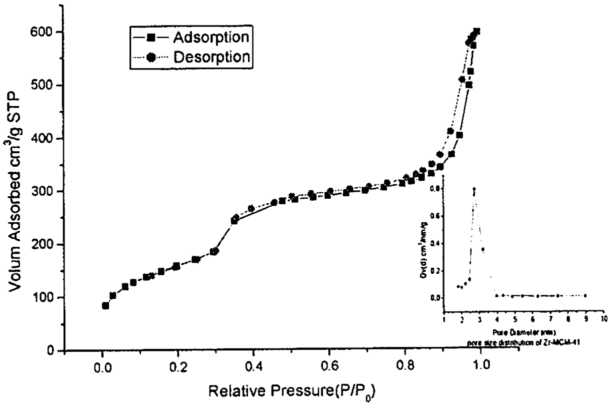


Figure 3. N_2 adsorption–desorption isotherms and pore size distribution of Zr-MCM-41.

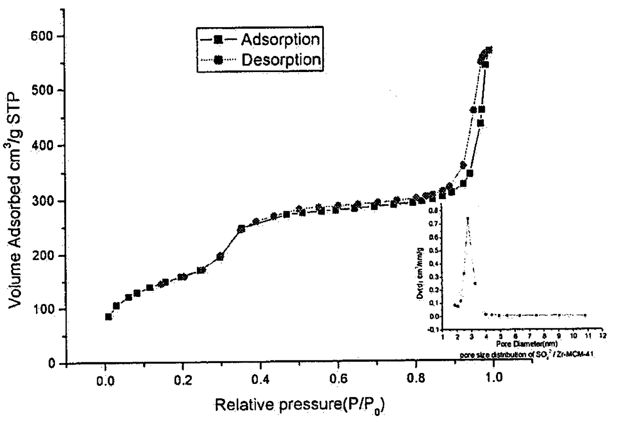


Figure 4. N_2 adsorption–desorption isotherms and pore size distribution of SO_4^{2-}/Zr-MCM-41(B).

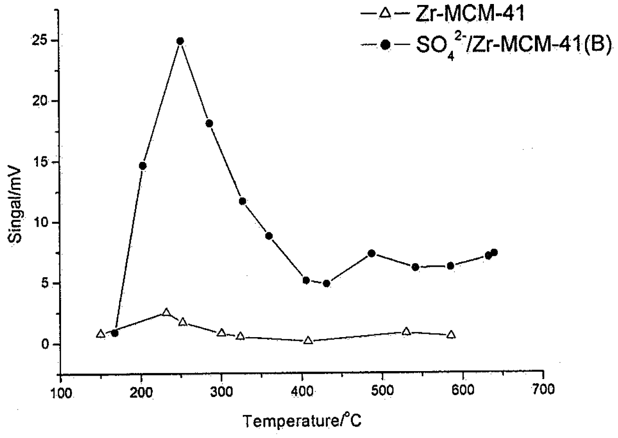


Figure 5. NH_3-TPD of SO_4^{2-}/Zr-MCM-41(B) and Zr-MCM-41.

materials possess broad mesoporous structure. A hysteresis loop exhibits at high relative pressure corresponding to capillary condensation. The surface area, pore diameter and pore volume are given in table 1. It can be noted that there are no significant difference of surface area, pore diameter and pore volume between Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B), which means that SO_4^{2-} do not affect the mesoporous structure. It is in good agreement with the results of XRD.

3.4. NH_3-TPD

The NH_3-TPD profiles of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B) are shown in figure 5. It can be seen that there is only one peak at low temperature for Zr-MCM-41, whereas a very strong peak at the same low temperature and a middle strong peak at high temperature are observed for SO_4^{2-}/Zr-MCM-41(B). The appearance or a high temperature peak indicates that new strong acid sites might be generated on the surface after impregnating SO_4^{2-}. From the area of peaks, the amount of the strong acid and poor acid for SO_4^{2-}/Zr-MCM-41 are obviously more than these for Zr-MCM-4I. It is suggested that SO_4^{2-} greatly increased the acidity and amount of acid of Zr-MCM-41.

Table 1
Character of Zr-MCM-41 and SO_4^{2-}/Zr-MCM-41(B)

Sample	Zr-MCM-41	SO_4^{2-}/Zr-MCM-41(B)
d-Spacing value (nm)	3.94	3.80
Unit cell parameter(nm)[a]	4.55	4.39
BET (m^2/g)	577.26	576.74
BJH(a)D (nm)	2.79	2.72
BJH(a)V (cm^3/g)	0.22	0.21

[a] Unit parameter (a_0) = $2d_{100}/3^{1/2}$.

3.5. Model reactions

3.5.1. Esterification of terpineol

3.5.1.1. Variation with preparing methods of SO_4^{2-}/Zr-MCM-41

Table 2 shows the effects of different preparing methods on the activity and selectivity of SO_4^{2-}/Zr-MCM-41 in esterification of terpineol under the same conditions. The catalyst, which possesses the best activity and selectivity, is SO_4^{2-}/Zr-MCM-41(B). Using SO_4^{2-}/Zr-MCM-41(B) as catalyst, the conversion of terpineol is 87.7% and the selectivity of terpinyl acetate is 91.7%. In a word, the activity and selectivity of SO_4^{2-}/Zr-MCM-41 which is synthesized using SO_4^{2-} to impregnate calcined Zr-MCM-41 is better than those of is synthesized using SO_4^{2-} to impregnate uncalcined Zr-MCM-41. It is suggested that SO_4^{2-} incorporation affect the long rang ordering of Zr-MCM-41 to some degree. The structure of calcined Zr-MCM-41 is more stable than that of uncalcined Zr-MCM-41. Therefore, when using SO_4^{2-} to impregnate uncalcined Zr-MCM-41, although the acidity of Zr-MCM-41 was improved, the activity and selectivity of SO_4^{2-}/Zr-MCM-41 dropped because its structure was destroyed. SO_4^{2-} can bond well with the frame of Zr-MCM-41 when using 0.25mol/L H_2SO_4 to infuse calcined Zr-MCM-41. That the catalytic activity of sulfated Zr-MCM-41 obtained using 0.25 mol/L H_2SO_4 was better than that of sulfated Zr-MCM-41 using 0.25 M $(NH_4)_2SO_4$ is owing to the stronger acidity and the better dispersion of H_2SO_4 than those of $(NH_4)_2SO_4$. The catalytic activity of SO_4^{2-}/Zr-MCM-41 prepared by impregnating was better than that of by grinding, which is because SO_4^{2-} could contact with Zr-MCM-41 more easily in solution than in solid. In short, the best preparing method of SO_4^{-2}/Zr-MCM-41 was using 0.25 M H_2SO_4 to impregnate calcined Zr-MCM-41.

Table 2
Variation with preparing methods of SO_4^{2-}/Zr-MCM-41[a]

SO_4^{2-}/Zr-MCM-41	Product constituent (%)			Conversion (%)	Selectivity (%)[b]
	Terpinene	Terpineol	Terpinyl acetate		
A	16.9	72.0	11.1	28.0	39.6
B	7.3	12.3	80.4	87.7	91.7
C	38.7	58.6	2.7	41.4	6.5
D	48.1	19.5	32.4	80.5	40.3
E	45.0	50.0	5.0	50.0	10.0
F	35.5	16.5	48.0	83.5	57.7

[a] Reaction conditions: terpineol:acetic anhydride = 1:1.75 (mol:mol), terpineol 0.2 mol, temperature 60 °C, time 6 h, catalyst l g.
[b] Selectivity to terpinyl acetate.

Table 3
Variation with different catalysts[a]

Catalysts	Product constituent (%)			Conversion (%)	Selectivity (%)[b]
	Terpinene	Terpineol	Terpinyl acetate		
H_2SO_4(33%)	34.4	19.4	46.2	80.6	57.3
SO_4^{2-}/ZrO_2	12.4	22.5	65.1	77.5	84.0
HY	10.5	89.2	0.3	10.8	2.9
HZSM-5	14.5	81.4	4.1	18.6	22.0
Zr-MCM-41	19.4	78.0	2.6	22.0	11.8
SO_4^{2-}/Zr-MCM-41(B)	7.3	12.3	80.4	87.7	91.7

[a] Reaction conditions: terpineol:acetic anhydride = 1:1.75 (mol:mol), terpineol 0.2 mol, temperature 60 °C, time 6 h, catalyst l g.
[b] Selectivity to terpinyl acetate.

Table 4
Variation with Si/Zr mole ratio[a]

Si/Zr	Product constituent (%)			Conversion (%)	Selectivity (%)[b]
	Terpinene	Terpineol	Terpinyl acetate		
1/0.0125	11.5	64.3	24.2	35.7	67.7
1/0.05	7.3	12.3	80.4	87.7	91.7
1/0.06	42.2	3.5	54.3	96.5	56.3

[a] Reaction conditions: terpineol:acetic anhydride = 1:1.75 (mol:mol), terpineol 0.2 mol, temperature 60 °C, time 6 h, catalyst l g.
[b] Selectivity to terpinyl acetate.

3.5.1.2. Catalytic activities of different kinds of catalysts

From table 3 it can be seen that SO_4^{2-}/Zr-MCM-41(B) possesses the best catalytic activity among these catalysts, the conversion of terpineol is 87.7% and the selectivity to terpinyl acetate is 91.7%. The catalytic activity and selectivity of SO_4^{2-}/Zr-MCM-41(B) is better than those of Zr-MCM-41. It is indicated that SO_4^{2-} has a great effect on improving the catalytic property of Zr-MCM-41. The catalytic activity of SO_4^{2-}/Zr-MCM-41(B) is better than hose of microporous molecular sieves such as HY, HZSM-5, solid super acid SO_4^{2-}/ZrO_2 and H_2SO_4(33%). It is suggested that the acidity and the ordering mesoporous structure of SO_4^{2-}/Zr-MCM-41(B) contribute to the increasing of the conversion of larger molecular reactant and the selectivity of target product.

3.5.1.3. Variation with Si/Zr mole ratio

According to table 4, Si/Zr can greatly affect the catalytic activity of SO_4^{2-}/Zr-MCM-41(B). With increasing the Si/Zr from 1/0.025 to 1/0.06, the conversion ascended from 35.7% to 96.5% while the selectivity increased first then decreased, which indicated that Zr increasing could enhance the acidity of catalyst but the too strong acidity could lead to produce a lot of terpinene and decrease the selectivity of aim product.

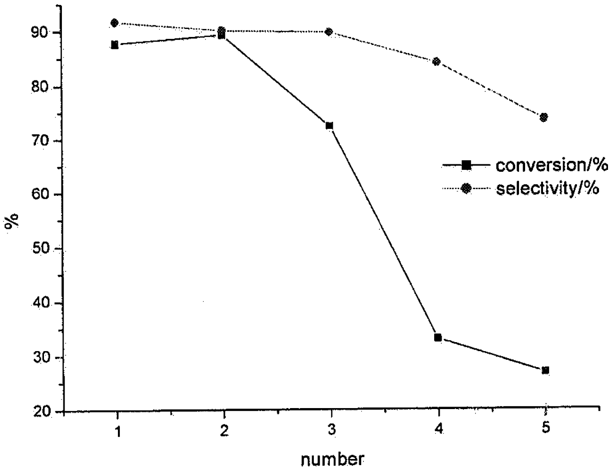


Figure 6. Lifespan of catalyst. a. Reaction condition: terpineol:acetic anhydrate = 1:75 (mol:mol), terpineol 10.2 mol, temperature 60 °C, time 6 h, catalyst 1 g.

3.5.1.4. *Lifespan of catalyst*

After being used five times, the activity and selectivity of the catalyst obviously declined and the color of catalyst turned from white to slight yellow, which meant that catalyst was deactivated. When the deactivated catalyst was activated by calined at 550°C for 3 h and reused in the esterification of terpineol, the conversion was 85.6% and the selectivity of terpinyl acetate was 90.5%, and its color turned to white again. The deactivation of the catalyst may be due to the formation of coking and make the activity of catalyst decreased. After the coking was eliminated, the activity and the selectivity of catalyst could be recovered. The result was shown in Figure 6.

3.5.2. *The polymerization of α-pinene*

From table 5 it can be seen that the catalytic activity of the composite catalysts are greatly dependent on the kind of support. If microporous molecular sieves were used as supports to get composite catalysts, the reaction could only synthesize little lower oligmers and the conversion of α-pinene was very poor. When the composite catalyst obtained by supporting $AlCl_3$ on SO_4^{2-}/Zr-MCM-41(B) was used in the polymerization of α-pinene, the reaction was very quickly and a lot of low oligmers was obtained so that the product was of lower soft point temperature. However, when $AlCl_3$/Zr-MCM-41 was used as composite catalyst in the reaction, the soft point temperature of the α-pinene polymer could reach 103.5 °C, which indicated that the acidity and structure of Zr-MCM-41 was suitable for supporting $AlCl_3$ to catalyze this reaction.

4. Conclusions

The mesoporous molecular sieve Zr-MCM-41 was synthesized under hydrothermal condition. Zr-MCM-41 material was impregnated using sulfuric acid to prepare SO_4^{2-}/Zr-MCM-41. The obtained materials were characterized by XRD, FT-IR, N_2 adsorption/desorption and NH_3-TPD analysis technique. The results indicated that SO_4^{2-}/Zr-MCM-41 were of better mesoporous structure, long range ordering and crystallites, and SO_4^{2-} existed in the skeleton of Zr-MCM-41 and increased its acidity.

SO_4^{2-}/Zr-MCM-41 was firstly used as catalyst in the reaction of terpineol esterification. The catalytic result was compared with those obtained by using sulfuric acid (33%), HY, HZSM-5 and SO_4^{2-}/ZrO_2. It was showed that SO_4^{2-}/Zr-MCM-41 was not only of better catalytic activity and selectivity, but also of better regenerable performance.

$AlCl_3$ was supported on the synthesized mesoporous molecular sieves to get composite catalysts that were firstly used to catalyze the polymerization of α-pinene. It was showed that $AlCl_3$/Zr-MCM-41 was of the best catalytic result.

Acknowledgments

Thanks for the support of National Natural Science Foundation of China (No. 30070608) and Research Foundation of Shandong Province for Excellent Young Scientists.

Table 5
Variation with different kinds of catalysts[a]

Catalysts	Soft p.t (°C)	Yield %	acid value mgKOH/g	Saponification value (mgKOH/g)	Iodine value (gI/100 g)
$AlCl_3$	86	89.5	1.0	1.43	49
$AlCl_3$/HY[b]	–	–	–	–	–
$AlCl_3$/HZSM-5[b]	–	–	–	–	–
$AlCl_3$/Zr-MCM-41	103.5	92.3	0.9	1.32	43
$AlCl_3/SO_4^{2-}$/Zr-MCM-41(B)	72	88.3	1.0	1.38	52

[a] Reaction conditions: α-pinene 33 g, toluene 52.9 g, $AlCl_3$ 3 g, mesoporous molecular sieves 1 g, temperature 25–30 °C, time 4 h.

[b] Only get low oligmers.

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