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Journal of Catalysis 227 (2004) 448–458
JOURNAL OF CATALYSIS
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Liquid-phase Beckmann rearrangement of cyclohexanone oxime over mesoporous molecular sieve catalysts

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Received 9 June 2004; revised 30 July 2004; accepted 7 August 2004

Abstract

A series of mesoporous molecular sieves with various SiO_2/Al_2O_3 ratios have been applied to the liquid-phase Beckmann rearrangement of cyclohexanone oxime. The influences of solvent, aluminum content, aluminum-incorporating method, and catalyst structure on the catalytic performance have been investigated. Benzonitrile has been found to be a suitable solvent. The surface silanol groups ineffectively catalyze the rearrangement, whereas the acid sites generated by incorporation of aluminum improve the activity and the selectivity to ε-caprolactam remarkably. Moreover, an Al-containing MCM-41 catalyst prepared by the postsynthetic method using $AlCl_3$ as an aluminum precursor exhibits higher lactam selectivity than a directly synthesized one. For a given aluminum content, MCM-41 shows superior performance to beta zeolite and other mesoporous catalysts, SBA-1 and SBA-15. It has been suggested that a sufficient amount of acid sites with appropriate strength is of importance to the liquid-phase Beckmann rearrangement.

Keywords: Beckmann rearrangement; Acidity; Mesoporous molecular sieves; Benzonitrile

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime is an important process for the production of caprolactam, a starting material for the manufacture of nylon-6. The conventional rearrangement carried out industrially in fuming sulfuric acid is well known as an environmentally unfriendly process. This is particularly owing to a large amount of ammonium sulfate produced as a by-product from the subsequent neutralization of the oleum. To solve this problem, a variety of heterogeneous catalysts have been developed and applied to the vapor-phase rearrangement [1–13]. However, control of the selectivity and elongation of the catalysts life in such systems appear to be a serious issue because of the drastic experimental conditions required. Sumitomo Chemical has recently industrialized the vapor-phase Beckmann rearrangement using silicalite-1 as catalyst. To solve the problem of a rapid deactivation of the catalyst, a fluidized bed system is employed. Alternatively, this problematic disadvantage might be overcome by carrying out the rearrangement in the liquid phase at lower temperatures.

Although performance in the rearrangement over a number of solid acid catalysts under vapor-phase conditions has put forward several hypotheses on the active sites, they are still the subject of controversy. The strong Brønsted acid sites of the zeolite were formerly reported to preferentially catalyze the rearrangement [1], but the later works showed that it accelerates the formation of by-products [14,15]. Subsequently, it was suggested by a majority of researchers that the weakly acidic hydroxyl groups [16,17] or the acid sites with weak to intermediate strength [3,9–11] were active and selective for the formation of caprolactam, while Sato and co-workers proposed that the neutral silanol groups located on the external surface of highly siliceous H-ZSM-5 are the catalytically active sites [2].

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doi:10.1016/j.jcat.2004.08.008

The catalytic performance of the zeolites in the liquid-phase rearrangement was previously investigated by Corma and his co-workers; PhCl was reported to be a good solvent when the reaction was carried out at 132 °C [18]. Under similar reaction conditions, Camblor et al. found that over beta zeolites the nitriles, the by-products usually observed under the vapor-phase conditions, were not detected in the liquid-phase reaction and that the rearrangement of bulkier oximes, such as acetophenone oxime, was more favorable than that of cyclohexanone oxime [19]. Furthermore, the results showed that the presence of Brønsted acid sites in the catalysts contributed to a high activity and selectivity to lactam, whereas nonacidic silanol groups were claimed to be responsible for the formation of hydrolysis products.

MCM-41, one of the mesoporous molecular sieve M41S members possessing a 2-d hexagonal arrangement of unidimensional channels, has been studied intensively for characterizations, modifications, and catalysis. Large-pore channels varying from 15 to 100 Å, high thermal stability, large sorption capacity, and high surface area with a large amount of surface SiOH groups provide MCM-41 with attractive applications in several fields. Recently, MCM-41 was reported to be an effective catalyst for the vapor-phase Beckmann rearrangement of cyclohexanone oxime [9]. Its acidity varied by the aluminum content influenced the hydrophilicity/hydrophobicity and altered the catalytic performance depending upon the diluent used.

Here, we first applied MCM-41 to the liquid-phase rearrangement of cyclohexanone oxime using a variety of solvents. The influences of aluminum content, aluminum-incorporating method, and mesoporous structure, including MCM-41, SBA-1, and SBA-15, were studied. Furthermore, the catalytic performance of the mesoporous molecular sieves was compared to that of microporous zeolitic materials.

2. Experimental

2.1. Catalysts synthesis and modification

Pure-silica MCM-41 (Si-MCM41) and Al-containing MCM-41 (Al-MCM41) were hydrothermally synthesized by the method of gel equilibrium adjustment reported by Kim et al. [20]. Pure-silica SBA-1 (Si-SBA1) and pure-silica SBA-15 (Si-SBA15) were synthesized under acidic conditions following the procedure described by Che et al. [21] and by Zhao et al. [22], respectively. Postsynthetic incorporation of aluminum into pure silica mesoporous molecular sieves was achieved by using $AlCl_3$ [23] or $Al(OPr^i)_3$ [24] as an aluminum source. Hereafter, the grafted catalysts are designated as PAl-X-OPr and PAl-X-Cl where X denotes type of mesoporous molecular sieve, and OPr and Cl represent the aluminum sources of $AlCl_3$ and $Al(OPr^i)_3$, respectively. Beta zeolite was prepared by hydrothermal synthesis according to the procedure stated by Perez-Pariente et al. [25]. Before being employed as a catalyst, the sample was converted into the proton form by ion exchange twice with 1 M NH_4NO_3 solution at 80 °C for 2 h, followed by calcination at 500 °C for 4 h.

2.2. Characterizations

The catalyst structures were confirmed by X-ray powder diffraction (XRD) on a MacScience MX Labo powder diffractometer equipped with Cu$K\alpha$ radiation. Elemental composition was determined by means of induced couple plasma (ICP). Nitrogen adsorption technique (Belsorp 28SA sorptionmeter) was applied to determine surface area (S_{BET}), pore volume (V_P), and pore diameter (D_P). Before the characterization, a sample was evacuated at 200 °C for 3 h. D_P was calculated according to the BJH method with the corrected Kelvin equation.

Ammonia-temperature-programmed desorption (NH_3-TPD) was performed on a Bel Japan Multitask-TPD analyzer. After a sample (50 mg) was pretreated in a helium stream at 500 °C for 1 h and exposed to 20 Torr of NH_3 at 100 °C, the desorption of NH_3 was measured with a mass number 16 by an Anelva Q-Mass detector by heating the sample from 100 to 600 or 800 °C at a ramping rate of 10 °C min^{-1}.

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. The sample (30 mg) was pressed into a self-supported wafer with a diameter of 20 mm. The wafer was set in a quartz IR cell that was sealed with CaF_2 windows and connected to a vacuum system. After the wafer was evacuated at 500 °C for 1 h, it was exposed to pyridine vapor at 100 °C and equilibrated at the same temperature for 30 min. The desorption of pyridine was carried out stepwise at 100, 350, and 500 °C for 1 h at each temperature. All the spectra after the desorption were collected at room temperature.

2.3. Reaction procedure

A freshly calcined catalyst (100 mg) was pretreated "in situ" by heating in a 50-ml three-necked round-bottom flask equipped with a reflux condenser at 200 °C under pressure below 1 Torr for 2 h. A mixture of cyclohexanone oxime (100 mg), n-decane (50 mg) as the internal standard, and a solvent (20 ml) was then poured into the flask. The reaction was carried out with a magnetic stirrer at 130 °C under nitrogen. A series of solvents, chlorobenzene (PhCl), benzonitrile (PhCN), acetophenone (MPK), acetonitrile (MeCN), dimethyl sulfoxide (DMSO), and N,N-dimethylformamide (DMF) were used for the reaction. In the case of MeCN, the reaction temperature was maintained at 80 °C. The reaction products were analyzed by a gas chromatograph equipped with a 30-m capillary column of PEG.

3. Results and discussion

3.1. Structure of catalysts

The structural order of mesoporous catalysts is shown by XRD patterns in Fig. 1. The patterns of calcined Si-MCM41 and Al-MCM41 possessed four well-resolved diffraction peaks, indicating a highly long-ranging ordered hexagonal mesostructure. Also, the characteristic diffraction peaks consistent with the reported patterns were observed in the cubic *Pm3n* Si-SBA1 and hexagonal *p6mm* Si-SBA15 (not shown). After the postsynthetic modification of the pure silica mesoporous molecular sieves, the highly well-ordered patterns were still retained on Al-grafted catalysts while there was a small decrease in the intensity of the diffraction peaks. Furthermore, specific surface area and pore volume were reduced concomitantly with a slight enlargement of unit cell parameter, as shown in Table 1. These observations are similar to those previously presented by Mokaya and Jones [24].

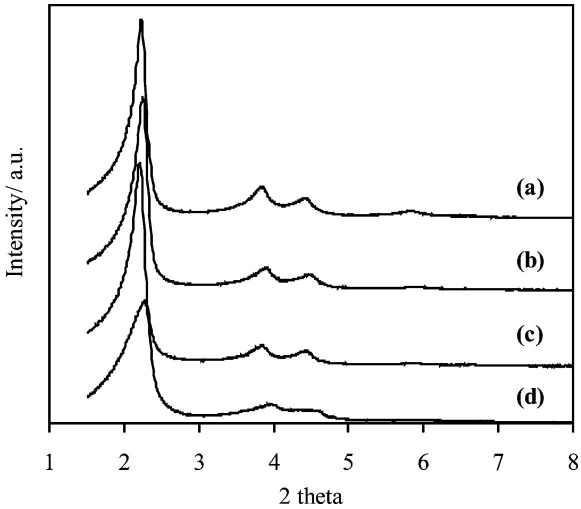
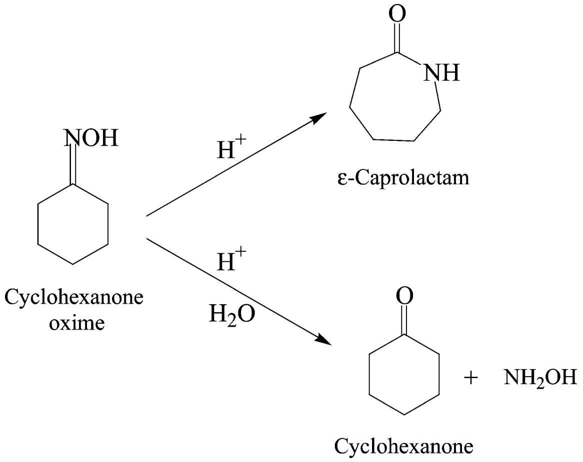


Fig. 1. XRD patterns of MCM-41 catalysts Si-MCM41 (a), PAl-MCM41-Cl (b), PAl-MCM41-OPr (c), and Al-MCM41 (d).

3.2. Influences of solvents

The product distribution from the liquid-phase rearrangement over Al-MCM41 in various aprotic solvents with different polarities is shown in Table 2. It can be seen that a poor activity was observed for the reaction in the solvents with a high dielectric constant, DMSO and DMF. It is not surprising since such solvents, having not only high polarity but also high basicity, adsorb strongly on the catalyst surface, decreasing the accessibility of oxime to the active sites. When the reaction was carried out in MPK and PhCl, the oxime conversion was comparable but the product distribution was quite different. Unlike the previous results reported by Corma and co-workers [19], cyclohexanone, a by-product formed by hydrolysis of cyclohexanone oxime (Scheme 1), was found to be the major product and the selectivity to the lactam was very low in PhCl. The difference in the nature of the catalysts used might account for this discrepancy.

Interestingly, the activity and selectivity to the lactam were remarkably improved when the rearrangement was performed in PhCN. Moreover, the amount of cyclohexen-1-



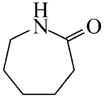
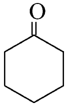
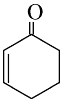
Scheme 1. Beckmann rearrangement and hydrolysis of cyclohexanone oxime to ε-caprolactam and cyclohexanone, respectively.

Table 1
Characteristics of mesoporous molecular sieve catalysts

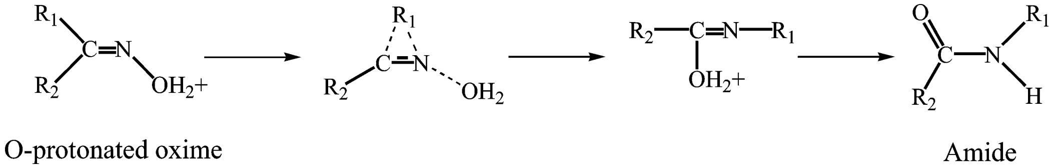
Catalyst[a]	a_0[b] (Å)	D_p[c] (Å)	S_{BET} ($m^2 g^{-1}$)	S_{ext}[d] ($m^2 g^{-1}$)	V_p[e] ($mm^3 g^{-1}$)
Si-MCM41	45.7	28.2	1013	50.1	830
Al-MCM41 (47)	44.5	27.8	1003	66.7	784
PAl-MCM41-OPr (24)	46.1	26.6	884	58.0	664
PAl-MCM41-OPr (53)	46.0	27.6	957	52.4	726
PAl-MCM41-Cl (54)	46.1	27.6	935	49.6	712
Si-SBA1	88.1	22.4	984	31.2	622
PAl-SBA1-OPr (53)	85.4	22.4	896	32.2	560
Si-SBA15	110	80.6	640	98.1	1056
PAl-SBA15-OPr (50)	106	78.2	530	85.3	951

[a] Number in parentheses presents the SiO_2/Al_2O_3ratio.
[b] Unit cell parameter.
[c] Pore diameter determined by the BJH method with the corrected Kelvin equation.
[d] External surface area.
[e] Pore volume.

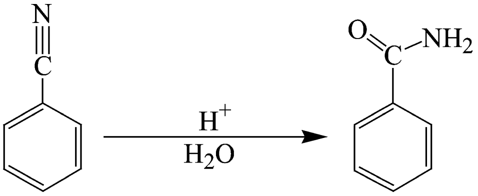
Table 2
Product distribution in the liquid-phase Beckmann rearrangement over Al-MCM41 (47) catalyst in various solvents[a]

Solvent	ε[c]	Conv. (%)	Selectivity (%)				
							Others[d]
Benzonitrile	25.2	50.6	89.1	10.9	0.0	0.0	0.0
Chlorobenzene	5.6	28.8	23.3	66.1	5.6	1.8	3.2
Acetophenone	17.3	26.5	18.0	59.4	0.0	0.0	22.6
Acetonitrile[b]	37.5	13.0	21.0	79.0	0.0	0.0	0.0
Dimethyl sulfoxide	49.0	5.0	100.0	0.0	0.0	0.0	0.0
N,*N*-Dimethylformamide	36.7	0.0	0.0	0.0	0.0	0.0	0.0

[a] Reaction conditions: temperature, 130 °C; time, 5 h; catalyst amount, 0.1 g; oxime:catalyst:solvent = 1:1:200 (weight).
[b] Reaction temperature: 80 °C.
[c] Dielectric constant.
[d] Mostly dimers; octahydrophenazine and tetrahydrocarbazole.



Scheme 2. Formation of amide via the acid-catalyzed Beckmann rearrangement of an oxime.



Scheme 3. Acid-catalyzed hydrolysis of PhCN to benzamide.

one, nitriles, and dimers was negligible even after the rearrangement was carried out for 24 h. These advantages should be attributed to two particular aspects of PhCN. The first one is appropriate polarity and basicity, intermediate between those of DMSO/DMF and MPK/PhCl. This should result in a balanced adsorption on the catalyst surface, on one hand, and promote effectively the desorption of the lactam produced from the acid sites, increasing the reaction rate and prohibiting the formation of nitriles and dimers, on the other hand. Recently, Chung and Rhee studied the influences of the competitive adsorption between 4-hydroxyacetophenone oxime and a series of solvents with different dielectric constants on the catalytic performance of beta zeolites [26]. A solvent molecule was claimed to have another important role in stabilizing a protonated oxime and then accelerate the rearrangement by migrating water molecule (as leaving group), forming nitrilium species and amide eventually (Scheme 2). The effectiveness of this feature is likely to be related to the polarity of solvent. If this is the case, it is not surprising that the rearrangement in PhCN with relatively high polarity is fast and more selective to the lactam than that in MPK and PhCl.

Another aspect is the ability of PhCN to react with water through an acid-catalyzed hydrolysis reaction, giving benzamide as the product (Scheme 3). A trace of water may be present in the reaction system as a residue remaining after even drying the solvent by molecular sieve 4A. Fig. 2 plots the lactam yield, the cyclohexanone yield and the amount of benzamide against the oxime conversion. It can be seen that a linear relationship could be established in all cases. This result implied that the benzamide formation is closely related to the formation of the lactam and cyclohexanone. Indeed, since both cyclohexanone and benzamide are produced through hydrolysis reactions occurring in parallel in the system, one may expect a competitive consumption of water between the oxime and PhCN. According to Table 2, 19% cyclohexanone formed when PhCl was used as the solvent was decreased by 13% to 6% in PhCN. This coincided with the amount of benzamide produced, 14% (at 50.6% oxime conversion in Fig. 2). Thus, it is likely that the PhCN hydrolysis removed water, which was supposed to hydrolyze the oxime, and then mitigated the formation of cyclohexanone. Moreover, we found that, to run the reaction for longer time until the oxime conversion was nearly unchanged, there was no further increase in the amount of benzamide. This suggested another relationship between the PhCN hydrolysis and the conversion of the oxime to the corresponding lactam and cyclohexanone.

To clarify the unique characteristics of this solvent, the hydrolysis of PhCN was extensively studied. According to Scheme 4, Al-MCM41 catalyst was suspended in PhCN, without the addition of the oxime, and treated at 130 °C for 5 h. The catalyst was subsequently recovered by filtration

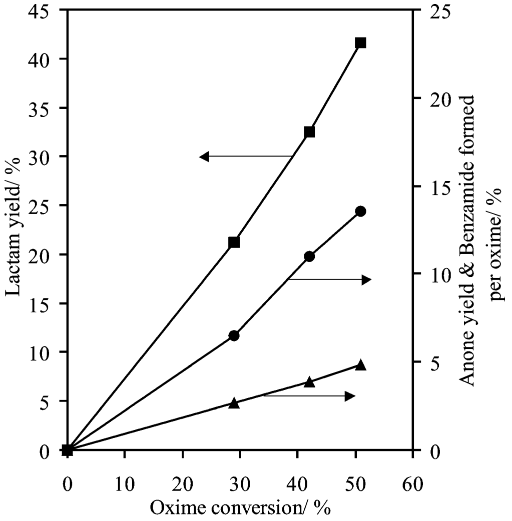
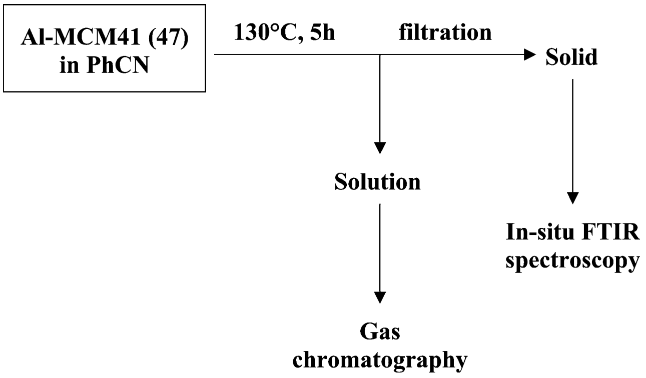


Fig. 2. Change in the lactam (■), cyclohexanone (▲), and benzamide (●) formation with the oxime conversion from the Beckmann rearrangement of cyclohexanone oxime over Al-MCM41 (47) catalyst. Reaction conditions: solvent, PhCN; for others, see Table 2.



Scheme 4. Supplementary experiment to investigate the formation of benzamide on Al-MCM41 (47) catalyst.

and dried at room temperature. The amount of benzamide in the reaction solution was investigated by the gas chromatography. Surprisingly, it was found that only a trace amount of benzamide was detectable in the solution (0.0091 mmol). That is about 12 times lower than the amount observed under the typical reaction conditions (0.115 mmol). Furthermore, adding a subtle amount of water (1.22 mmol) did not significantly influence the hydrolysis of PhCN. Possibly, the majority of benzamide product tightly adsorbed on the acid sites because of its relatively high basicity, and thus could not be liberated by PhCN solvent itself.

Instead of gas chromatography, the catalyst after treatment was characterized by means of FTIR spectroscopy. Fig. 3 shows the spectrum of the treated catalyst after evacuation at room temperature for 1 h. The presence of the band around 1659 cm^{-1}, corresponding to C=O stretching, indicated unambiguously the formation of benzamide on the catalyst. Moreover, the band at around 1560 cm^{-1}, which was not observed for the solution of benzamide in PhCN, appeared and could be related to the N–H deformation of benzamide adsorbed on the Brønsted acid sites. Its broad character may be due to the presence of Brønsted centers with different strengths. Lasperas et al. found a directly proportional relationship between the catalytic activity and the Brønsted acidity in the synthesis of aromatic amides over faujasite catalysts [27]. It was reported that the strong Brønsted acid sites are the active centers for the conversion of nitriles to the corresponding amides.

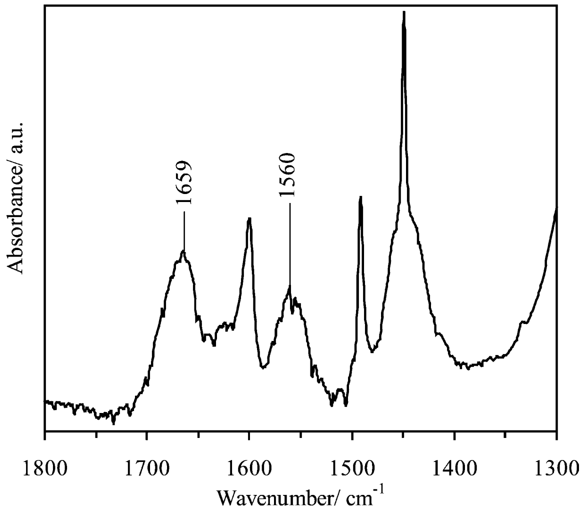


Fig. 3. FTIR spectrum of Al-MCM41 (47) after treatment with PhCN at 130 °C for 5 h.

Once the hydrolysis of PhCN is catalyzed by the Brønsted sites, a strong adsorption of benzamide formed is anticipated. The presence of a more basic compound, i.e., the oxime, may be required to liberate the amide product from the acid sites. However, whether this is practical or not depends on the strength of the sites where the benzamide is adsorbed. By using TGA to characterize the catalyst applied to the reaction using PhCN as the solvent, it was found that the DTA curve exhibited a sharp peak at 360 °C with a small shoulder at around 330 °C, mainly assigned to the decomposition of the lactam and benzamide, respectively (Fig. 4). The retention of these amides up to 330 °C on the catalyst indicated their adsorption on the rather strong acid sites, implying that they could not be easily liberated by the PhCN solvent as well as the oxime reactant. Besides, the relatively large amount of the lactam remaining at higher temperature suggested its relatively high basicity and having much difficulty in desorbing.

It is common to believe that the relatively strong acid sites catalyze both the rearrangement of oxime [1,18,19] and the hydrolysis of PhCN more actively [27]. However, due to much higher basicity of the oxime, it adsorbs preferentially on these sites followed by the Beckmann rearrangement to the corresponding lactam. As a result, only a small amount of PhCN can be hydrolyzed to benzamide. Upon the formation of these amide products on the strong acid sites, their desorption hardly occurred, rendering the sites rapidly deactivated at the early stage of the reaction course. The rearrangement and PhCN hydrolysis then proceed mostly on

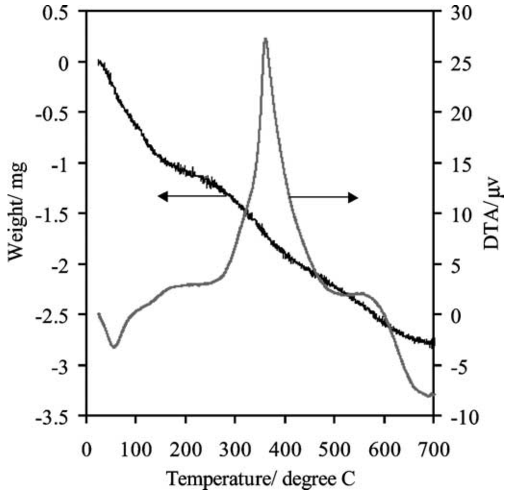


Fig. 4. Thermogravimatric analysis (TGA) of Al-MCM41 (47) catalyst after used in the Beckmann rearrangement of cyclohexanone oxime.

the remaining relatively weak sites, where the desorption can be possibly facilitated by the oxime reactant or PhCN solvent. Therefore, the benzamide observable from gas chromatography (Fig. 2) could be similarly formed on the weak acid sites responsible for the rearrangement and hydrolysis of the oxime. The increase in all products with increasing oxime conversion supported this hypothesis (Fig. 2). In addition, the results provided by pure silica Si-MCM41 catalyst suggested that not only the lactam and cyclohexanone were produced but also the PhCN hydrolysis could be catalyzed to some extent by even weakly acidic silanol groups (–Si–OH).

3.3. *Influences of aluminum contents*

The oxime conversion and the selectivity to the lactam obtained over MCM-41 catalysts with different SiO_2/Al_2O_3 ratios are illustrated in Fig. 5. Obviously, Si-MCM41 exhibited a low activity and selectivity to the lactam. Since the pure-silica catalyst possesses a neutral silicate framework, the surface silanol groups must take full responsibility for the catalytic activity, indicating that the liquid-phase rearrangement of cyclohexanone oxime is not favorable on the silanol groups. The oxime conversion and the lactam selectivity were remarkably improved over the Al-grafted catalysts, and both increased with increasing aluminum content. These results show that a sufficient amount of acid sites is important in achieving an effective rearrangement.

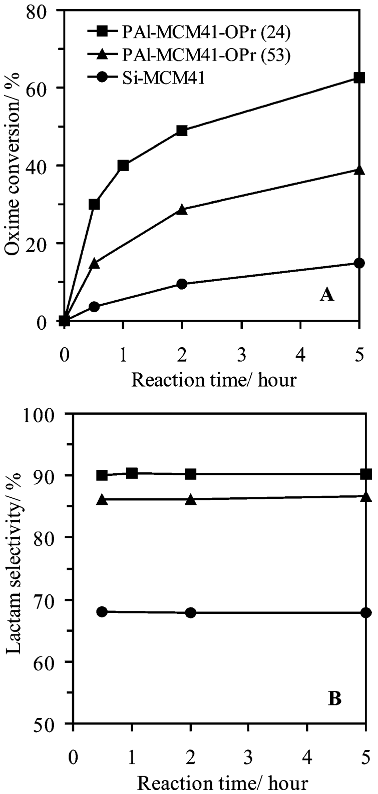


Fig. 5. Influences of aluminum content on the oxime conversion (A) and the selectivity to lactam (B) in the Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: solvent, PhCN; for others, see Table 2.

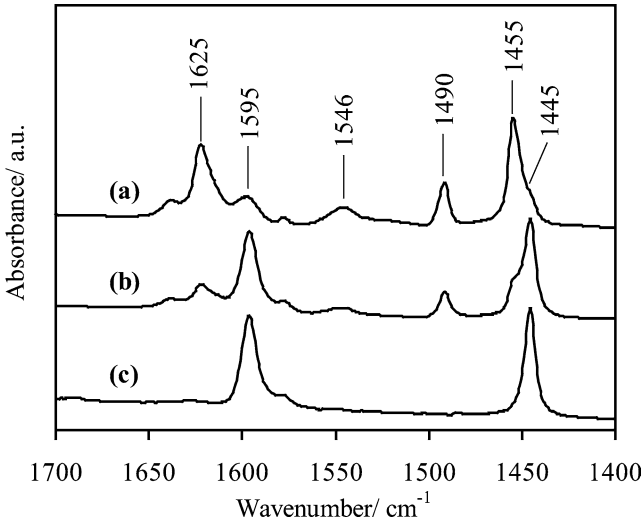


Fig. 6. FTIR spectra PAl-MCM41-OPr (24) (a), PAl-MCM41-OPr (53) (b), and Si-MCM41 (c) after the pyridine adsorption and desorption at 100 °C.

Besides the acid amount, the influences of acid type and acid strength should be also taken into account. According to pyridine-adsorbed FTIR spectra in Fig. 6, Si-MCM41 showed only the bands at 1595 and 1445 cm^{-1} owing to the pyridine hydrogen bonded to the surface silanol groups. These bands totally disappeared upon raising the desorption temperature to 350 °C, in agreement with weak acid strength of the silanol groups. In contrast, the bands at 1625 and 1546 cm^{-1}, assigned to the pyridinium ion on Brønsted acid sites, and at 1455 cm^{-1}, corresponding to Lewis acid sites [28,29], were observed for the Al-grafted catalysts. In addition, pyridine adsorbed on these corresponding sites with a significant amount still existed on both catalysts after the desorption at 350 °C. With increasing aluminum content, the intensity of these bands increased, while that of the bands at 1595 and 1445 cm^{-1} decreased simultaneously.

The low activity and selectivity to the lactam over the silanol sites should be due to their acid strength insufficient to catalyze the rearrangement of the oxime appreciably. This is also supported by the high selectivity to cyclohexanone, which can be preferentially formed even on nonacidic silanol groups [19], when the reaction was catalyzed by the pure-silica catalyst. Indeed, the postsynthetic grafting of aluminum generates the acid sites onto the pure-silica material simultaneously at the expense of the weakly acidic silanol groups (Fig. 6). As a result, the oxime molecules are more effectively protonated on the acid sites related to the Al species, and then the rearrangement to the lactam product is highly active and selective.

Our results are contrary to the study reported on the vapor-phase rearrangement over highly siliceous H-ZSM-5, where the neutral silanol groups were assumed to be the catalytically active sites [2]. This is presumably attributed to the difference in the reaction conditions. The higher temperatures required for the desorption of lactam product in the vapor phase would sharply accelerate the rearrangement. Therefore, it is not necessary to catalyze the rearrangement on relatively strong acid sites, which in contrast lead to a strong adsorption of reactant and product molecules and result in the formation of by-products and rapid deactivation [11]. Even though the operating temperatures under the liquid-phase conditions are much lower than those under the vapor-phase conditions, the desorption of lactam can occur smoothly in the presence of a suitable solvent. From our study it can be seen that at moderate temperatures an appropriate rearrangement of the oxime could not be achieved on a catalyst without relatively strong acidity, suggesting that the energy barrier needed to activate the reaction intermediate could be crossed only by using the strong acid.

3.4. *Influences of aluminum-incorporating methods*

Recently, a postsynthetic Al-grafted MCM-41 catalyst was reported to have a higher activity in the cracking of cumene than a directly synthesized one [24]. This was elucidated by the higher Brønsted acidity generated from the postsynthetic grafting, since the acid sites are exposed and more available to the guest molecules, whereas the conventional direct synthesis embeds a part of aluminum content within the silicate walls, rendering the acid sites inaccessible. In Fig. 7, the activity and the selectivity to the lactam in the oxime rearrangement were compared between the directly synthesized and the postsynthetic Al-grafted MCM-41 catalysts at a similar SiO_2/Al_2O_3 ratio. It was evident that both PAl-MCM41-Cl and PAl-MCM41-OPr showed a lower oxime conversion than Al-MCM41 at 5 h. These results did not show the advantage of the postsynthetic incorporation of aluminum as noted above.

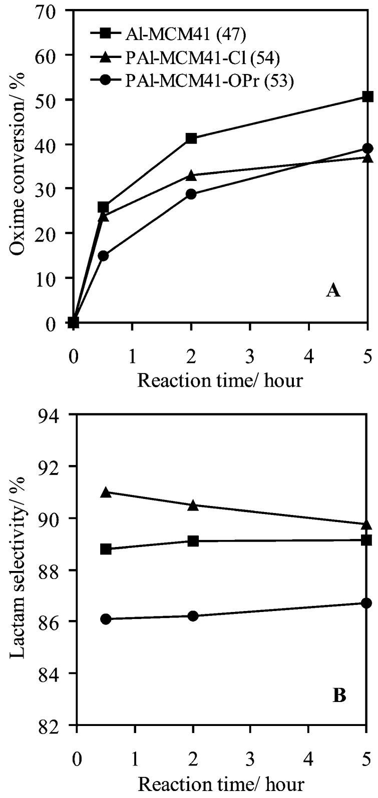


Fig. 7. Influences of aluminum-incorporating method on the oxime conversion (A) and the selectivity to lactam (B) in the Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: solvent, PhCN; for others, see Table 2.

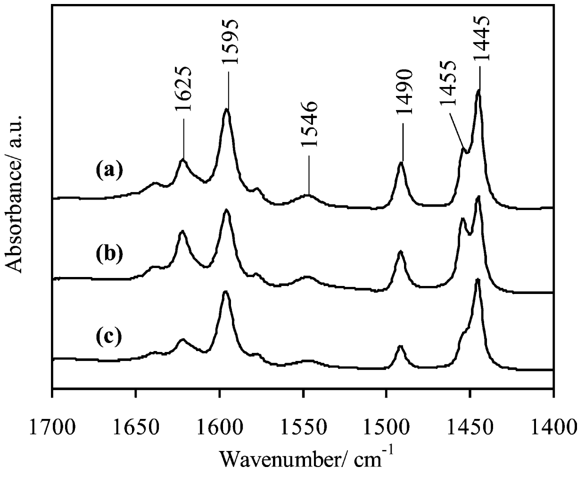


Fig. 8. FTIR spectra of Al-MCM41 (47) (a), PAl-MCM41-Cl (54) (b), and PAl-MCM41-OPr (53) (c) after the pyridine adsorption and desorption at 100 °C.

The inferior activity of PAl-MCM41-Cl and PAl-MCM41-OPr to Al-MCM41 is attributed to a lower acidity of both the Al-grafted catalysts, as indicated by the FTIR spectra in Fig. 8. Furthermore, to characterize the acidity of the catalysts, NH_3-TPD measurement was performed. It revealed that the acid amount of PAl-MCM41-Cl (0.26 $mmol\,g^{-1}$) and PAl-MCM41-OPr (0.14 $mmol\,g^{-1}$) was much lower than that of Al-MCM41 (0.51 $mmol\,g^{-1}$), which is closer to the Al content (0.60 $mmol\,g^{-1}$). This suggests that ca. 57 and 76% of the aluminum added in the postsynthetic modification for PAl-MCM41-Cl and PAl-MCM41-OPr, respectively, exist on the catalysts as nonframework species, indicating the difficulty in incorporation of aluminum by the postsynthesis. This should be attributed to the presence of a small amount of adventitious water in the modification system, although the solvent used was carefully dried according to the procedure originally reported in the literature [23,24]. When such water is present, the hydrolysis of aluminum sources, a water-sensitive precursor, occurs considerably faster than the grafting reaction. Consequently, the aluminum is not anchored to the silicate wall with high dispersion but partly forms aluminum oxide on the surface of the catalyst.

Al-containing MCM-41 directly synthesized with repetition of pH adjustment was recently reported to have a larger amount of tetrahedral aluminum as well as a higher activity in the acylation of 2-methoxynaphthalene with acetic anhydride, than the samples prepared without pH adjustment [30]. Redissolution and recrystallization of aluminosilicate framework during the period of pH adjustment were suggested to result in the homogeneous distribution of tetrahedral aluminum and a progressive condensation of hydroxyl groups in the MCM-41 framework structure. Accordingly, compared to those synthesized by the conventional methods, one could expect that the amount of aluminum species occluded inside the silicate wall of MCM-41 synthesized by the pH adjustment method should be small. Hence, in our study the advantage of Al grafting over the direct incorporation method on the catalytic activity may not be pronounced as previously reported.

In contrast to PAl-MCM41-OPr, PAl-MCM41-Cl exhibited a comparable activity to Al-MCM41 up to 30 min but the curve change in the oxime conversion with time of PAl-MCM41-Cl leveled off more rapidly at longer reaction times (Fig. 7A), indicating a relatively fast deactivation. This result should be related to the difference in acid strength. The FTIR spectra obtained from PAl-MCM41-Cl (Fig. 9A) and PAl-MCM41-OPr (Fig. 9B) after the pyridine desorption at different temperatures showed that even after the evacuation at 500 °C, a relatively large amount of pyridine still remained on PAl-MCM41-Cl, as shown by the bands at 1546 and 1455 cm^{-1}. This reveals the presence of strong Brønsted acid sites as well as strong Lewis sites due to trigonal chloride-attached Al species on the catalyst modified by using $AlCl_3$ as the precursor. These strong acid sites should catalyze the rearrangement of the oxime rapidly, giving a high conversion at the initial stage of the reaction. However, as described above, the lactam product formed strongly adsorbs on these sites, accelerating the deactivation on the catalyst.

PAl-MCM41-Cl gave the highest lactam selectivity up to 91% at 30 min, which then slightly decreased to 89% at 5 h whereas the other two catalysts exhibited a lower selectivity (Fig. 7B). This result should be related to the presence of relatively strong acid sites in PAl-MCM41-Cl as noted above, converting the oxime more selectively to the lactam but being susceptible to deactivation. Besides the low oxime conversion due to the small amount of acid sites, PAl-MCM41-OPr was not selective, giving the lactam selectivity of 86%. This result should be attributed to the presence of small amount of sites with strong strength (Fig. 9B), indicating that using $Al(OPr^i)_3$ as the precursor does not generate strong acid sites on the catalyst.

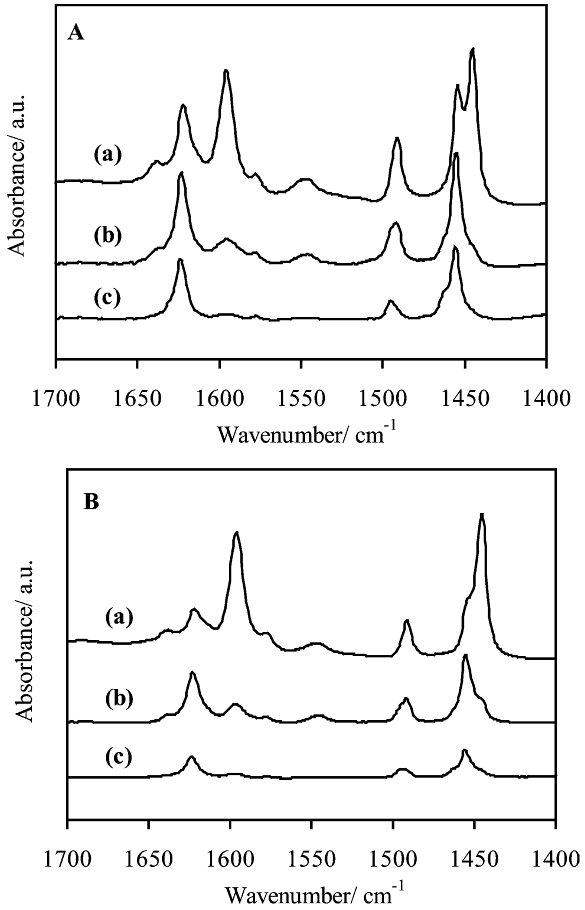


Fig. 9. FTIR spectra of PAl-MCM41-Cl (54) (A) and PAl-MCM41-OPr (53) (B) after the adsorption of pyridine at 100 °C and desorption at 100 (a), 350 (b), and 500 °C (c).

3.5. *Influences of catalyst structures*

As a large-pore zeolitic material, beta zeolite with a three-dimensional 12-membered ring channel system was applied to the reaction and its catalytic performance is shown in Fig. 10. It can be seen that Al-MCM41 exhibited higher oxime conversion, while H-Beta gave higher selectivity to the lactam at the initial stage of reaction. The presence of 3 interconnecting channels with different pore opening sizes, 6.6 × 6.7 and 5.6 × 5.6 Å, in beta zeolite would exclude the diffusion limitation. Thus, this reaction result should be related to the difference in acidity. Since it is well known that, besides a higher acid amount, the Brønsted acid sites of beta zeolite are more acidic than those of Al-containing MCM-41, they should initially accelerate the rearrangement at a high rate and ε-caprolactam is preferentially formed.

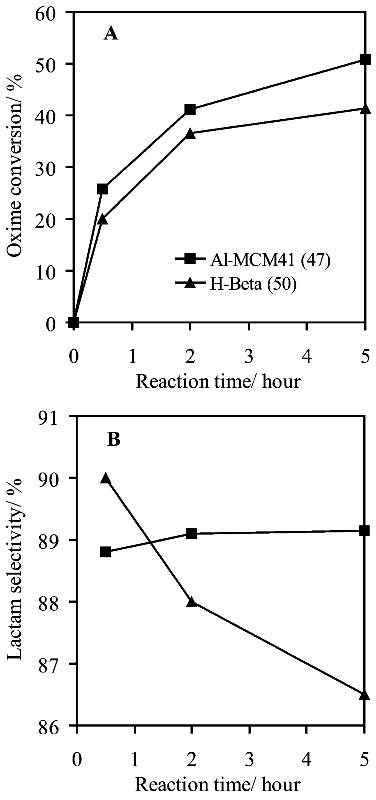


Fig. 10. Comparison of the oxime conversion (A) and lactam selectivity (B) between Al-MCM41 and H-Beta in the Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: solvent, PhCN; for others, see Table 2.

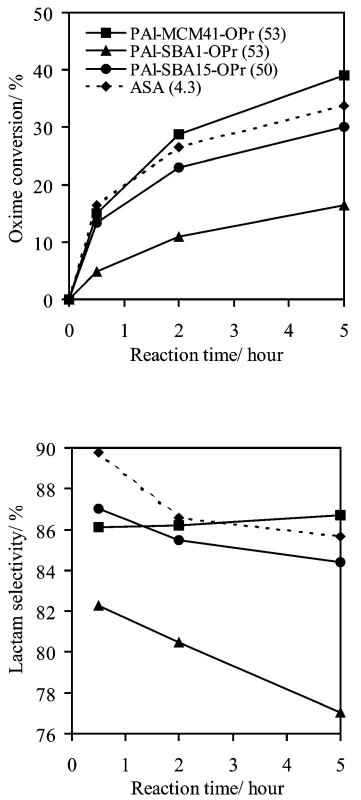


Fig. 11. Influences of catalyst structure on the oxime conversion (A) and the selectivity to lactam (B) in the Beckmann rearrangement of cyclohexanone oxime. Reaction conditions: solvent, PhCN; for others, see Table 2.

However, the problem of rapid deactivation was encountered, as evidenced by a relatively fast decrease in the oxime conversion and the lactam selectivity accompanied with an increase in the cyclohexanone formation with time (Fig. 10), and a lower material balance (not shown) when H-Beta was used as a catalyst. On the other hand, the steady selectivity to the lactam remaining at 89% through the reaction course, in addition to the relatively high oxime conversion, over Al-MCM41 indicated that the acid sites present on this catalyst possess an appropriate strength, which are more suitable for catalyzing the liquid-phase Beckmann rearrangement of cyclohexanone oxime.

Contrary to zeolitic materials, mesoporous materials possess an amorphous aluminosilicate or silicate framework with accessible channels of diameter > 20 Å, which allows the oxime molecules to pass through with less restriction. It is interesting to study how the structures of different mesoporous molecular sieves with a similar aluminum content influence the rearrangement. Although the channel wall of mesoporous materials is amorphous, the catalytic performance of the mesoporous catalysts was different from that of amorphous silica-alumina (ASA) with an average pore diameter ca. 80 Å (Fig. 11). Compared to PAl-MCM41-OPr, ASA exhibited a higher activity at 30 min, but the conversion became lower with increasing reaction time. Besides, the selectivity to lactam over ASA decreased rapidly, while that over PAl-MCM41-OPr slightly increased and was constant at 5 h. The results obtained from ASA were also the case of the rearrangement over PAl-SBA15-OPr. It was observed that ASA and PAl-SBA15-OPr had even larger amounts of acid sites (0.55 and 0.18 mmol g^{-1}, respectively) than PAl-MCM41-OPr (0.14 mmol g^{-1}).

Despite the similar hexagonal mesostructure (*p6mm*) to MCM-41, SBA-15 possesses larger pore sizes and pore volumes, but its specific surface area is lower (Table 1). It is well known that the lower negative charge density on the zeolite framework enhances the acid strength; for a given aluminum content the aluminosilicate material with larger specific surface area (lower acid density) has the acid sites with higher Brønsted acidity. Accordingly, it could be expected that the acid sites on PAl-MCM41-OPr are stronger than those on PAl-SBA15-OPr, because the acid density of the former is 0.15 µmol m^{-2}, whereas that of the latter is 0.34 µmol m^{-2}. This is supported by the FTIR spectra in Fig. 12.

Upon increasing the desorption temperature to 350 °C the adsorbed pyridine seemed to be desorbed from the acid sites on PAl-SBA15-OPr more easily (Fig. 12B), indicating a low acid strength of PAl-SBA15-OPr compared to PAl-MCM41-OPr. Since the Beckmann rearrangement of an oxime molecule is commonly believed to be initiated by protonation at the oxime group, the acid sites on PAl-SBA15-

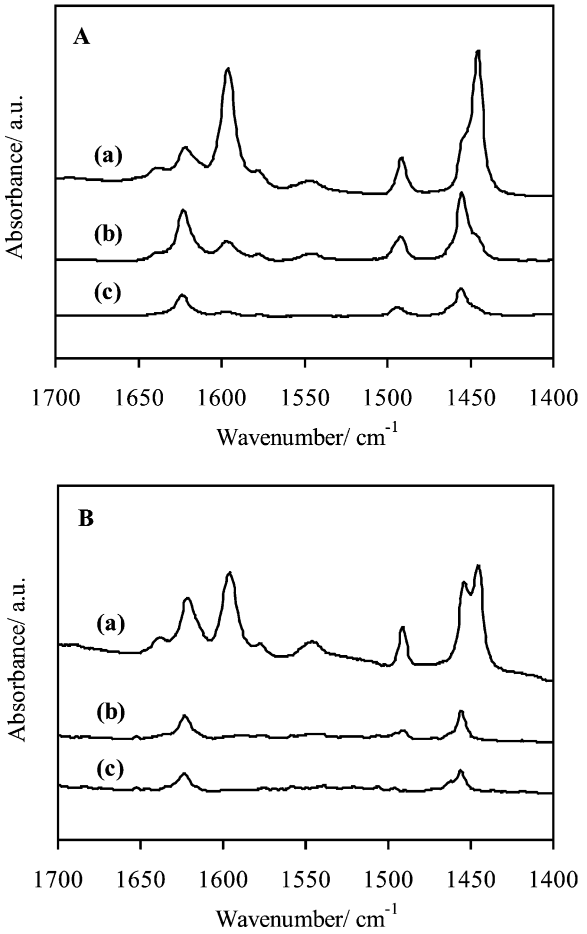


Fig. 12. FTIR spectra of PAl-MCM41-OPr (54) (A) and PAl-SBA15-OPr (50) (B) after the adsorption of pyridine at 100 °C and desorption at 100 (a), 350 (b), and 500 °C (c).

OPr should be less effective for the oxime protonation than those on PAl-MCM41-OPr. At the early stage of the reaction, even though the catalytic performance of PAl-SBA15-OPr was comparable to that of PAl-MCM41-OPr owing to the catalysis on the acid sites with relatively high strength, but as those sites became deactivated in a short time, the acid sites with weak strength then became mainly responsible for catalyzing the rearrangement. As a consequence, over PAl-SBA15-OPr the activity was lowered, accompanied with an increase in the selectivity to cyclohexanone. Thus, the similar reaction results to PAl-SBA15-OPr observed over ASA with specific surface area of 290 $m^2\,g^{-1}$ should be also ascribed to the presence of weak-strength acid sites relating to the high acid density (1.90 $\mu mol\,m^{-2}$) and/or its amorphous nature.

PAl-SBA1-OPr, having a cubic *Pm3n* mesostructure with three-dimensional channel system, showed very low activity and selectivity to the lactam, compared to other mesoporous catalysts with similar aluminum contents. This result should be attributed to its less acidity due to the difficulty in grafting of aluminum by the postsynthesis method, as described above. Characterizing the acid content by NH_3-TPD indicated that the amount of acid sites on PAl-SBA1-OPr was only 0.08 $mmol\,g^{-1}$. It is worth noting that even starting with a SiO_2/Al_2O_3 ratio of 20 in the postsynthetic suspension using $Al(OPr^i)_3$ as the aluminum source, we obtained Al-containing SBA-1 with the ratio of only around 50.

The pore structures of beta and mesoporous molecular sieve catalysts seem to influence indirectly the catalytic performance in the liquid-phase Beckmann rearrangement of cyclohexanone oxime due to their channel systems with large pore-opening diameters, allowing the oxime reactant and the lactam product to diffuse with less restriction. However, compared to Al-containing mesoporous materials with amorphous wall, the crystalline framework of beta zeolite renders the acid sites relatively strong, catalyzing more actively and selectively the rearrangement but being deactivated rapidly by the strong adsorption of the lactam produced. Although the channel wall of Al-containing MCM-41 is amorphous in nature, the presence of relatively strong acid sites on more condensed framework linkage resulting from the hydrothermal treatment promotes the rearrangement more effectively compared to disordered amorphous silica-alumina.

3.6. Reuse of catalysts

In this study, Al-MCM41 catalyst after use in the reaction was recovered, washed with PhCN, and calcined at 550 °C in a muffle furnace. The XRD pattern revealed that the ordered hexagonal mesostructure of regenerated catalyst was retained (not shown). Fig. 13 shows the catalytic performance of Al-MCM41 after being reused several times. It can be seen that there was no significant decrease in the oxime conversion and selectivity to the lactam, indicating the stability and reusability of this catalyst in the liquid-phase Beckmann rearrangement.

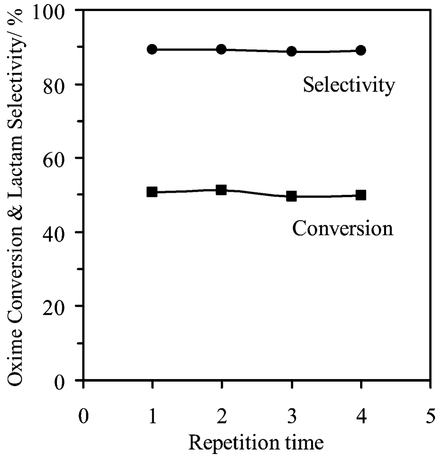


Fig. 13. Catalytic performance of Al-MCM41 (47) after reusing several times. Reaction conditions: solvent, PhCN; for others, see Table 2.

4. Conclusions

PhCN is a suitable solvent for the liquid-phase Beckmann rearrangement of cyclohexanone oxime: the lactam yield is improved, the formation of cyclohexanone is retarded, and the ring-opening reaction and polymerization of the oxime are prohibited. Besides a suitable basicity and polarity, the ability of PhCN to remove some residual water through the acid-catalyzed hydrolysis reaction over weak acid sites is an important key to enhance the lactam selectivity. The rearrangement is not appreciatively catalyzed on the surface silanol sites because of their insufficient acid strength. The incorporation of aluminum into the silicate framework of mesoporous materials generates the acid sites, which are considerably more active and selective to the lactam. The oxime conversion and the lactam selectivity are increased with increasing acid amount. Furthermore, an Al-containing MCM-41 catalyst, which is prepared by the postsynthetic modification using $AlCl_3$ as a precursor, promotes the formation of the lactam more selectively than directly synthesized ones. This should be due to the presence of relatively strong acid sites relating to trigonal chloride-attached Al species. In conclusion, Al-containing MCM-41 with high surface area, providing an appropriate acid density and acid strength, is an effective catalyst for the liquid-phase Beckmann rearrangement.

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