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Bismuth-containing MCM-41: synthesis, characterization, and catalytic behavior in liquid-phase oxidation of cyclohexane

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Abstract

Bismuth-containing MCM-41 was directly synthesized in strongly acidic media with CPBr as the template. It was shown, for the first time, by ICP, XRD, N_2 adsorption/desorption, TEM, SEM, ^{29}Si MAS NMR spectra, UV–vis DRS, and Raman spectroscopy that all of the samples have high surface area and good crystallinity, and all bismuth atoms in Bi-MCM-41 are highly dispersed in the silica-based structure. In addition, XPS spectroscopic data indicate that most of the bismuth enters the internal surface or framework of MCM-41. In the catalytic test, Bi-MCM-41 was found to be a very efficient catalyst for the oxidation of cyclohexane, with oxygen as oxidant, in a solvent-free system, and it behaves truly as a heterogeneous catalyst.

Keywords: Mesoporous molecular sieves; Bismuth; Characterization; Catalyst; Cyclohexane oxidation

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1. Introduction

Functionalization of hydrocarbons by selective oxidation is a very useful reaction and is of growing importance for the modern chemical industry. Cyclohexane, is oxidized to cyclohexanol and cyclohexanone, which are very important chemical intermediates since they are used as starting materials in the preparation of adipic acid and caprolactam, which are used in the manufacture of nylon-66 and nylon-6 polymers [1,2]. Furthermore, they are also used as good solvents for many chemical substances. In practice, oxidation of cyclohexane to cyclohexanol and cyclohexanone is now carried out with air as an oxidant without catalyst or with a cobalt salt catalyst on an industrial scale worldwide. However, these processes have their shortcomings – cyclohexane conversion was lower than 5%, and general yields of cyclohexanol and cyclohexanone were lower than 80%. For these reasons, the selective oxidation for cyclohexane has been studied comprehensively, and because of stringent ecological requirements, more emphasis is given to the catalytic oxidation in liquid phase with molecular oxygen and hydrogen peroxide in preference to non-environmentally friendly metal oxides. There is no doubt that molecular oxygen is the cheapest and cleanliest oxidant. However, the technology with which cyclohexane has been oxidized by O_2 to produce cyclohexanol and cyclohexanone has not been improved very well up to now.

Studies of the oxidation of cyclohexane into cyclohexanol and cyclohexanone with O_2 as oxidant have demonstrated important progress [3–17]. However, these systems display shortages and their applications are limited; either H_2O_2 or TBHP was used as a co-catalyst to accelerate the initiation step of the oxidation, or a large amount of organic solvent was used.

Recently, some new catalytic systems have been developed for cyclohexane oxidation with O_2 as oxidant. Using a nanosized iron oxide in the pores of mesoporous material (titania) as a catalyst, Nina et al. [18] reported that cyclo-

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hexane could be oxidized under mild conditions. The main products were cyclohexanol and cyclohexanone. However, the systems included a large amount of isobutyraldehyde and used acetic acid as a co-catalyst. Good results were obtained with the use of NHPI derivatives as catalysts and air as oxidant [19], but the preparation of catalysts is complex, and some co-catalysts were also used. Selvam et al. used systems with (Cr) MCM-41 [20] and (Fe) MCM-41 [21] as catalysts and obtained excellent results for the selective oxidation of cyclohexane. Unfortunately, acetic acid was used as a solvent, and initiator (methyl ethyl ketone) was also used in the systems. Can-cheng Guo et al. reported on the oxidation of cyclohexane with cobalt porphyrins as catalysts and air as oxidant in solvent-free systems [22]. The results indicated that the catalytic systems are very efficient for the reaction. However, cobalt porphyrins used as catalysts are much expensive.

For most processes of the oxidation of cyclohexane, the solvent plays an important role in the activity of catalysts. However, there is no doubt that the use of solvent leads to many environmental problems. Up to now, the development of solvent-free systems is still a challenge, and only a few systems have been reported [6,7,19,22]. More recently, we reported on the oxidation of cyclohexane with Au/ZSM-5 [23] and Au/MCM-41 [24] as catalysts and O_2 as an oxidant in a solvent-free system. The results indicated that Au/ZSM-5 and Au/MCM-41 are very efficient catalysts for the oxidation of cyclohexane. But it was also found that the leaching of gold nanoparticles from the ZSM-5 sieve is quite serious. In further research, therefore, we are attempting to find more stable and efficient catalysts for the oxidation of cyclohexane.

The MCM-41 mesoporous molecular sieve has attracted the attention of researchers in catalysis because of its large pores, high surface area, and thermal stability, and many metal-substituted MCM-41 mesoporous molecular sieves have been used as effective catalysts for various kinds of reactions [25–32]. More recently, Dumitriu et al. prepared a series of Bi-ZSM-5 by introducing Bi during ZSM-5 synthesis, and these catalysts were tested in the liquid-phase oxidation of benzene, toluene, and cyclohexane, with hydrogen peroxide as oxidant [33]. Up to now, however, little research has been reported on the incorporation of Bi into the framework of mesoporous materials.

Metal-substituted mesoporous molecular sieves are usually prepared under basic conditions, and reports of the successful preparation of metal-doped mesoporous materials under acidic conditions are very few [34–39]. In this paper, we report on a series of bismuth-substituted MCM-41 mesoporous materials synthesized under strongly acidic conditions ($[H^+] = 6$ mol/l); the Bi-MCM-41 samples were characterized by numerous physical-chemical methods, including inductively coupled plasma emission spectrometry (ICP), powder X-ray diffraction (PXRD), nitrogen adsorption/desorption, transmission electron microscopy (TEM), scanning electron microscopy (SEM), ^{29}Si CP-MAS NMR spectra, diffuse-reflectance UV–visible (UV–vis) spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The catalytic behavior of the Bi-MCM-41 was also investigated by cyclohexane oxidation with O_2 as oxidant in a solvent-free system.

2. Experiment

2.1. Catalyst preparation

All reagents used were of AR grade, and the synthesis procedure was carried out as follows. Cetyl pyridine bromide (surfactant), deionized water, hydrochloric acid and bismuth nitrate were mixed at 323 K and stirred for 30 min. TEOS was added to the above mixture with vigorous stirring to obtain a gel mixture. The molar composition of the gel was 0.33 CPBr/1.0 TEOS/7.5 HCl/68 H_2O/0.06–0.08 $Bi(NO_3)_3$. After the mixture was stirred for about 24 h at 323 K, the resultant product was filtered and washed with deionized water, dried at 373 K for 3 h, and then calcined in air at 823 K for 6 h. Pure siliceous MCM-41 was synthesized with the same procedure, except that no bismuth nitrate was added. According to the different bismuth content in the MCM-41 (analyzed by ICP), the catalysts were labeled A, B, C, and D.

2.2. Catalyst characterization

The physical properties of bismuth-containing mesoporous materials were confirmed by ICP (Rigaku JY38S), PXRD (D/Max 2400 Rigaku), N_2 adsorption/desorption (Micromeritics ASAP 2010), transmission electron microscopy (TEM) (JEOL-JEM 100 microscope), scanning electron microscopy (SEM) (JSM-5600LV), ^{29}Si CP-MAS NMR spectra (Bruker DSX-300), UV–vis spectroscopy (Shimadzu UV-240), Raman spectroscopy (Nicolet Raman 910), and XPS (Vgescalab 210).

2.3. Catalytic cyclohexane oxidation reactions

The catalytic oxidations were carried out in a 25-ml stainless-steel reactor equipped with a magnetic-type stirrer. In a typical reaction procedure, cyclohexane (18.5 mmol) was mixed with Bi-MCM-41 catalyst (10 mg) and heated to 140 °C in a 1 MPa O_2 atmosphere. After reaction, the reactants and products were directly analyzed by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6890N/5973N).

2.4. Leaching and recycling tests

The leaching tests were carried out in the 25-ml stainless-steel reactor equipped with a magnetic-type stirrer; two methods were used. Method a was as follows: the catalyst was separated from the reaction mixture after 24 h by filtration under 0.1 MPa air at reaction temperature. The mother

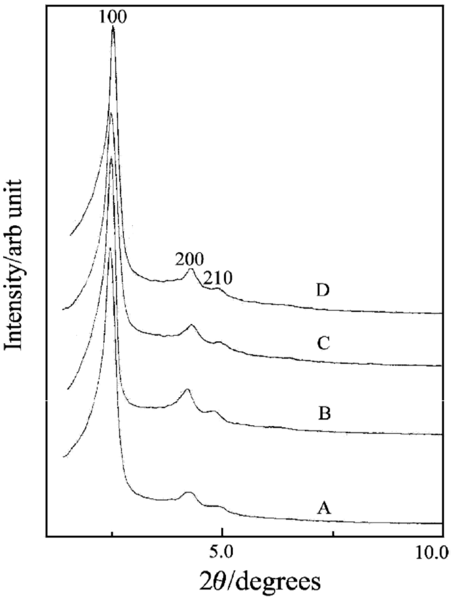

Fig. 1. The XRD patterns of Bi-MCM-41 catalysts with different Bi content: (A) 6.1 wt%, (B) 2.1 wt%, (C) 1.4 wt%, (D) 0.55 wt%.

liquid was immediately allowed to react further in the absence of the catalyst. After reaction, the reaction mixture was analyzed by GC immediately. Furthermore, the Bi content in the mother liquid was also determined by ICP-AES. Method b was the same as Method a, but the catalyst was separated from the reaction mixture after 4 h by filtration under 1.0 MPa Ar at 150 °C.

Recycling tests with repeated use of Bi-MCM-41 in three consecutive reactions were carried out. The catalyst was removed from the reaction mixture after 4 h by filtration, washed with acetone, dried at 393 K for 6 h, and subjected to the next catalytic run, with the same molar ratio substrate under the same reaction conditions.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Powder X-ray diffraction

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of calcined Bi-MCM-41. As displayed in Fig. 1, the XRD is similar to those reported in the literature, indicating that the mesoporous molecular sieve synthesized had an ordered hexagonal cylindrical channel system. Table 1 lists the d_{100} spacing and hexagonal unit cell parameters (a_0). From Table 1 it has been found that the unit parameters a_0 [calculated from (100) peak] of Bi-MCM-41 increased in comparison with their pure silica analogue. This observation confirms the presence of bismuth in the framework. Finally, no evidence of bismuth oxide is found in the X-ray diffractograms in the 0–50° 2θ domain.

3.1.2. N_2 adsorption/desorption

Fig. 2 shows the N_2 adsorption/desorption isotherm and corresponding pore size distribution curve for the Bi-MCM-41 samples. For all of the samples, the isotherms were quite similar and exhibited complementary textural and framework-confined mesoporosity, as indicated by the presence of two separate. One is the $p/p_0 = 0.3$–0.45 region, indicative of framework-confined mesopores, and the other one is at $p/p_0 \geqslant 0.9$, corresponding to capillary condensation in the interpartical pores. The second separate is not as distinct, and it indicates that the ratio of the surface area and pore volume corresponding to the interpartical pores is much smaller [40,41]. The position of inflection in the $p/p_0 = 0.2$–0.35 region depends on the diameter of the mesopores, and its sharpness indicates the uniformity of the narrow pore size distribution [42].

3.1.3. Transmission electron microscopy and scanning electron microscopy

Transmission electron microscopy (TEM) images of Bi-MCM-41 are shown in Fig. 3. TEM of the calcined sample shows a regular hexagonal array of uniform channels, which is characteristic of MCM-41. It confirms the presence of a well-ordered hexagonal structure. This is entirely consistent with the XRD results.

Scanning electron microscopy (SEM) is used to determine the particle size and particle morphology of the synthesized materials. SEM pictures of the Bi-MCM-41 (A) and Bi-MCM-41 (B) samples, given in Fig. 4, are typical for the mesoporous metallosilicates and show the morphology of spherical particles. The particle size of samples ranges from 1 to 3 µm. It is clear that most of the particles are spherical, although some agglomerates are detected.

Table 1
Analytic data of Bi-MCM-41 samples

Sample	Si/Bi gel	Bi products (wt%)	$d(100)$ (Å)	Surface area (m^{-2}/g)	APD[a] (Å)	a_0[b] (Å)	Average pore wall thickness (Å)
A	15	6.1	35.1	1016	30.5	40.5	10.0
B	30	2.1	35.6	1091	32.3	41.4	9.1
C	50	1.4	37.7	1183	32.3	43.5	11.2
D	75	0.55	36.8	1072	34.4	42.5	8.1
MCM-41	∞	0	34.4	1089		39.7	

[a] APD, average pore diameter.

[b] a_0, the lattice parameter calculated from XRD data using the formula $a_0 = 2d_{100}/\sqrt{3}$. Pore wall thickness (Å), a_0 − APD.

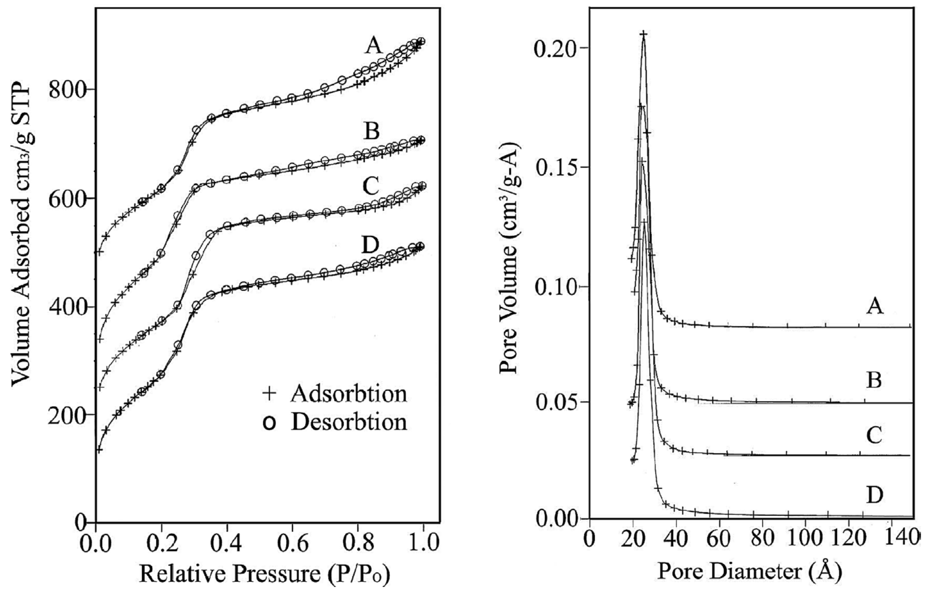

Fig. 2. N_2 adsorption/desorption isotherm and pore size distribution for the various samples.

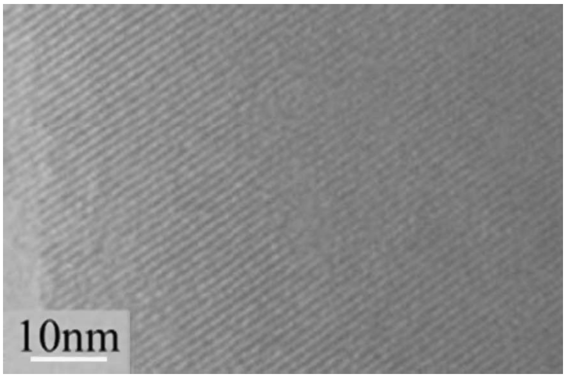

Fig. 3. TEM photograph of Bi-MCM-41 sample (B).

Because XRD, N_2 adsorption/desorption, TEM, and SEM do not provide any direct evidence regarding the extent to which bismuth has been incorporated into the framework, other techniques were used to characterize the Bi-MCM-41.

3.1.4. ^{29}Si NMR characterization

Generally, ^{29}Si MAS NMR spectroscopy is a suitable tool for elucidating the incorporation of guest atoms into the siliceous framework. Therefore, the Bi-MCM-41 sample was studied with ^{29}Si spectra. Fig. 5 shows the spectra of the calcined samples of pure Si-MCM-41 and Bi-MCM-41 (B). The peaks around −110 ppm (Q_4), −102 ppm (Q_3), and −93 ppm (Q_2) were observed for both the pure Si-MCM-41 and Bi-MCM-41 (B). The comparison of the spectra of the bismuth-containing sample with the pure Si-MCM-41 shows clearly that the $(Q_2 + Q_3)/Q_4$ ratio is considerably increased for the bismuth-containing materials. The peak around −102 ppm (Q_3) could belong to Si (3Si, 1Bi) species, and the increase in the peak around −93 ppm (Q_2) could be attributed to the incorporation of bismuth atoms into the MCM-41 framework and the formation of Si (2Si, 1Bi, 1OH) or Si (2Si, 2Bi). These results indicate that the silicon is in close proximity to bismuth and point to an incorporation of isolated bismuth atoms into the MCM-41 framework.

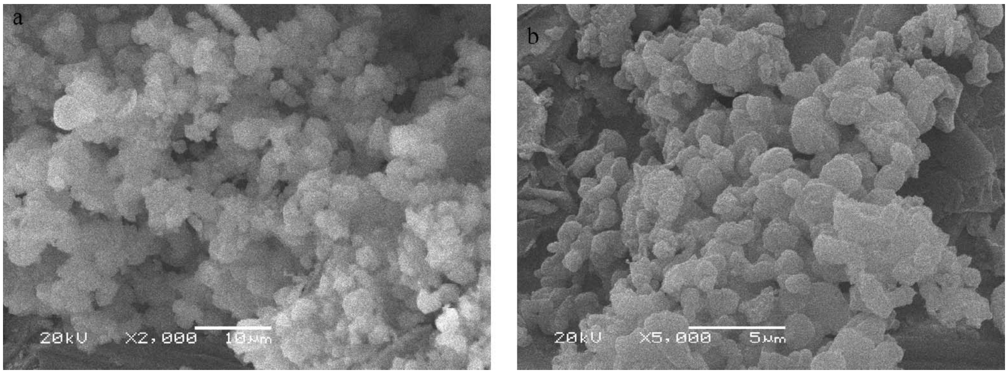

Fig. 4. SEM of images of (a) Bi-MCM-41 (A), (b) Bi-MCM-41 (B).

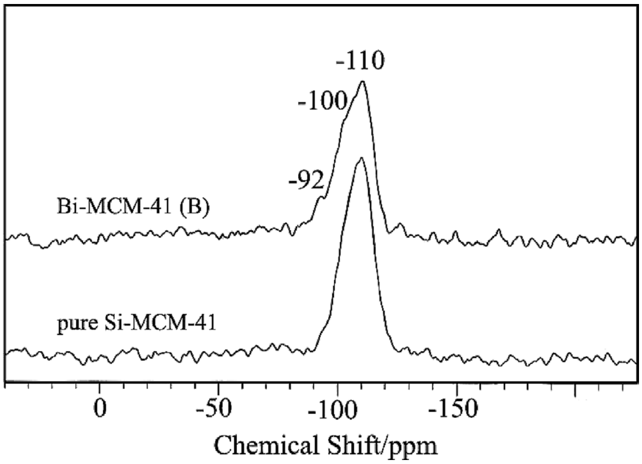

Fig. 5. ^{29}Si MAS NMR spectra of pure Si-MCM-41and Bi-MCM-41 (B).

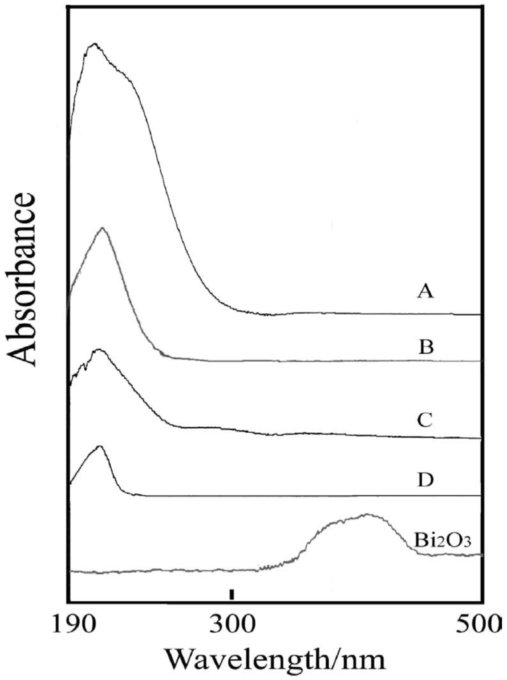

Fig. 6. UV–vis spectra for the Bi-MCM-41 catalysts and Bi_2O_3: (A) 6.1 wt%, (B) 2.1 wt%, (C) 1.4 wt%, (D) 0.55 wt%.

3.1.5. Diffuse-reflectance UV–vis spectroscopy

Diffuse-reflectance UV–vis spectroscopy is a very sensitive probe for the presence of extra-framework metal in zeolites. UV–vis spectra for Bi-MCM-41 samples are shown in Fig. 6. All of the bismuth-containing MCM-41 samples showed an intense band centered at ∼ 210 nm; its intensity increases with an increase in the Bi content of the samples, which reveals the presence of bismuth atoms in tetrahedral coordination. In addition to this bond, a shoulder band centered at ∼ 240 nm was also observed on sample A, and it indicates the existence of another kind of bismuth species at high Bi contents, which may be assigned to hexa-coordinated bismuth species. However, the diffuse-reflectance UV–vis spectra for a silica and bismuth oxide mixture shows a large absorption at ca. 400 nm. The results indicate that there is no bismuth oxide in the Bi-MCM-41 samples, and all bismuth atoms enter the framework of Bi-MCM-41.

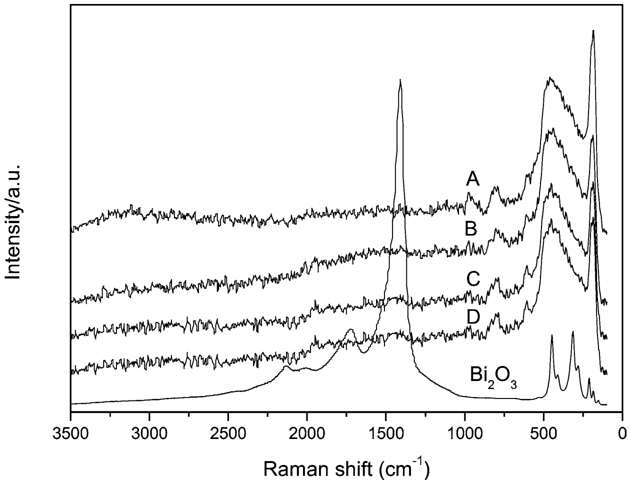

Fig. 7. Raman spectra for the Bi-MCM-41 catalysts and Bi_2O_3: (A) 6.1 wt%, (B) 2.1 wt%, (C) 1.4 wt%, (D) 0.55 wt%.

3.1.6. Raman spectroscopy

Fig. 7 shows Raman spectra for Bi-MCM-41 and crystalline Bi_2O_3. Crystalline Bi_2O_3 is a very strong Raman scatterer, so the absence of intense peaks at ca. 2134, 1723, 1409, 448, and 315 cm^{-1} (in Bi_2O_3) indicates that the bismuth was highly dispersed in the silica-based framework structure. This result is in agreement with the conclusion drawn from the UV–vis spectra and ^{29}Si MAS NMR spectroscopy.

3.1.7. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemical composition of the catalyst samples. For bismuth oxide, the Bi $4f_7$ peak centered at about 160 eV is very typical. However, it is very surprising that no obvious signals of bismuth were detected from XPS analysis for any of the Bi-MCM-41 samples. A typical spectrum for the Bi-MCM-41 samples is shown in Fig. 8. Because bismuth cannot be detected when the content of bismuth is lower than 0.4% (the sensitivity of the XPS machine) and only the external surface could be detected by the XPS, it could be estimated that most of the bismuth enters the internal surface or framework of MCM-41.

3.2. Catalytic behavior

The catalytic performances in the cyclohexane oxidation reactions at 150 °C are given in Table 2. Good to excellent conversion and selectivity were obtained at 150 °C in 1.0 MPa O_2 over Bi-MCM-41 catalysts with different bismuth contents. GS-MS analysis indicates that the main byproducts contain adipic acid and some esters. The blank reaction was carried out with pure Si-MCM-41 as catalyst, and

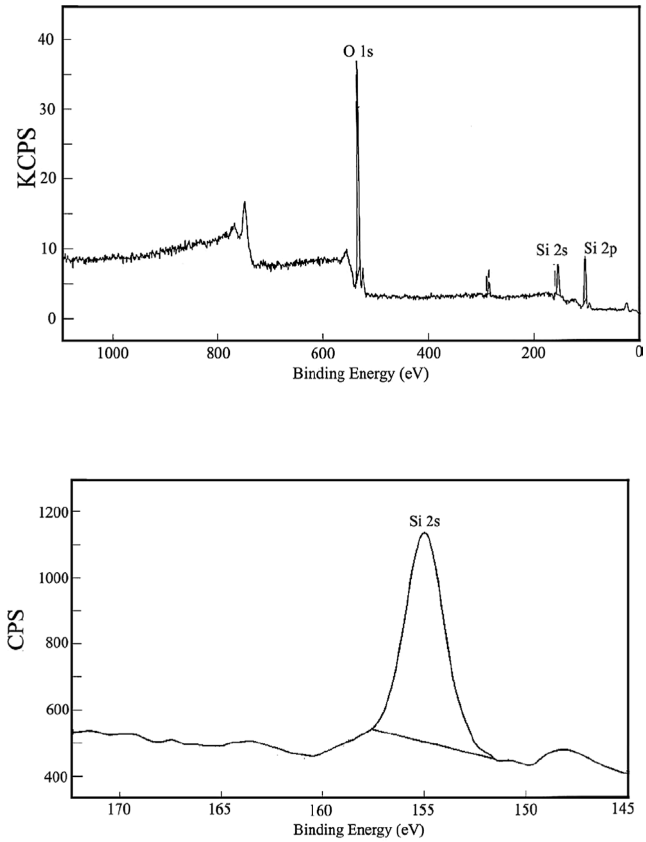

Fig. 8. XPS spectra of Bi-MCM-41 (A).

Table 2
Cyclohexane oxidation over Bi-MCM-41 catalyst

Entry	Catalyst	*T* (h)	Conversion (%)	Selectivity (%)	
				Cyclohexanol	Cyclohexanone
1	MCM-41	5	No reaction		
2[a]	A	4	No reaction		
3	A	4	9	36	62
4	B	4	12.5	22	72
5	C	4	17	19	72
6	D	4	12	70	
7 [21]	Fe-MCM-41	12	62	–	–
8 [20]	Cr-MCM-41	12	86.5	97.2	–

[a] Reaction carried out under 1 MPa Ar.

no oxidative products were detected by GC analysis. Thus, it is clear that the bismuth ions present in MCM-41 play a catalysis role in the reaction. Among the Bi-MCM-41 catalysts, the catalyst (C) (1.4 wt% bismuth) shows the best activity for the oxidation of cyclohexane, and a higher bismuth content in the catalysts does not lead to better results for the cyclohexane oxidation. The reason for this observation is not yet clear, and it may be due to the change in the kind of bismuth species or the distribution of bismuth in the catalyst with increasing bismuth content. For a comparison, the data for cyclohexane oxidation with Fe-MCM-41 [21] and Cr-MCM-41 [22] as catalysts are also listed in Table 2. It can be found that Fe-MCM-41 and Cr-MCM-41 are very efficient catalysts for cyclohexane oxidation with oxygen as oxidant. However, it should be noted that a large amount of acetic acid was used as a solvent, and methyl ethyl ketone was used as an initiator in their systems. Thus, compared with Fe-MCM-41 and Cr-MCM-41, Bi-MCM-41 is a more environmentally friendly catalyst.

A series of comparisons for the conversion of cyclohexane and the selectivity of cyclohexanol and cyclohexanone over catalysts with different bismuth contents were made under the reaction conditions depicted above (re-

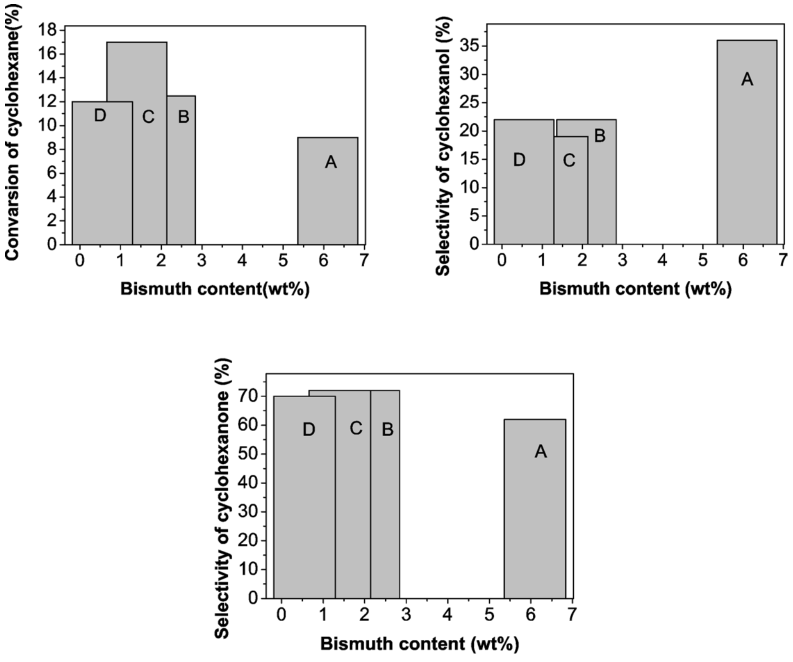

Fig. 9. Effect of bismuth content in the catalysts on the conversion and selectivity.

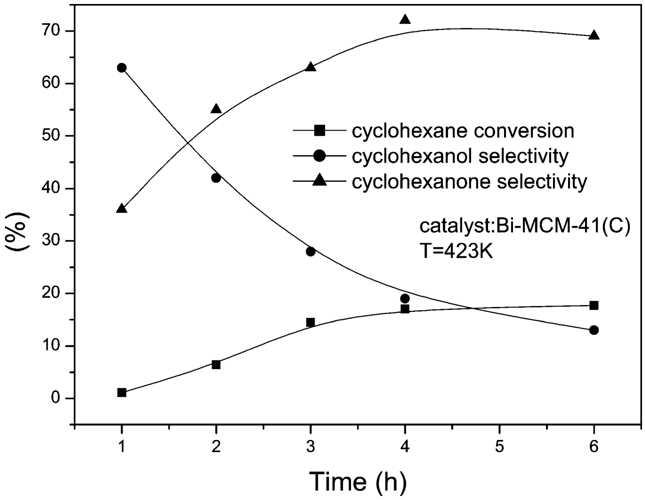

Fig. 10. Effect of reaction time on the conversion and selectivity over Bi-MCM-41 (C).

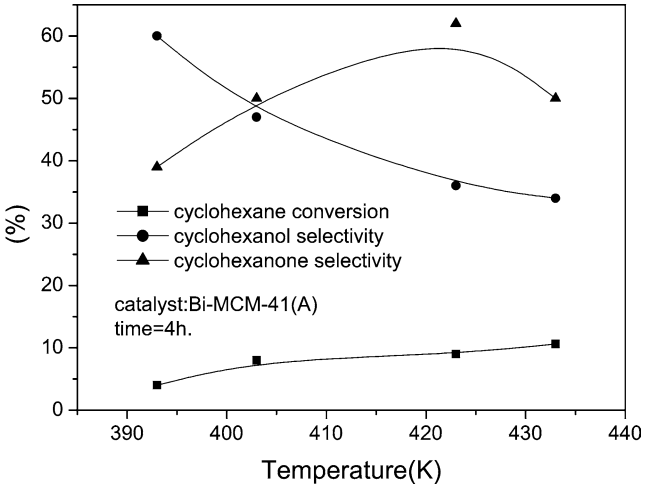

Fig. 11. Effect of reaction temperature on the conversion and selectivity over Bi-MCM-41 (A).

action time 4 h). The reaction results are given in Fig. 9. It could be observed in the figure that the selectivity of cyclohexanol decreases with increasing conversion of cyclohexane, it might be attributed to the much higher activity of cyclohexanol; and it could be oxidized to the more stable products such as cyclohexanone and adipic acid, with increasing activity of the catalyst in the systems.

The effect of reaction time over the Bi-MCM-41 catalyst was also investigated; Fig. 10 shows the results. The conversion of cyclohexane and the selectivity of cyclohexanone increase with increased time, and the selectivity of cyclohexanol decreases. In addition, too long a reaction time leads to a decrease in total selectivity with a slight increase in conversion.

Fig. 11 illustrates the influence of reaction temperature. With increasing reaction temperature, the conversion increases slightly, and at higher reaction temperatures, the selectivity of cyclohexanol and cyclohexanone decreases.

Table 3
Leaching and recycling tests over the Bi-MCM-41 catalysts

Method	Catalyst	*T* (h)	Conversion (%)	Selectivity (%)	
				Cyclohexanol	Cyclohexanone
a	A	4	No reaction		
b	A	4	No reaction		
b	B	4	No reaction		
b	C	4	No reaction		
b	D	4	No reaction		
a	Au/ZSM-5	3	5	24	68
a	Au/MCM-41	4	10	23	70
R[a]	C	4	16.8	21	72

[a] Reaction results for the third run.

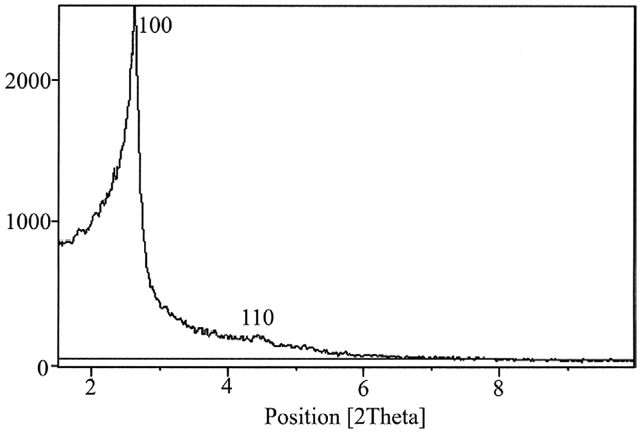

Fig. 12. The XRD pattern of recycled Bi-MCM-41 catalyst (C).

Two methods (a and b) were used in the leaching test. After the Bi-MCM-41 catalysts were separated from the reaction mixture under the given conditions, no bismuth was detected by ICP-AES analysis in the mother liquid for method a or b. The reaction results for leaching and recycling tests are listed in Table 3. With the use of method a and b, no oxidative products were detected by GC with Bi-MCM-41 as catalysts in the leaching tests. The result reconfirms that the leaching of bismuth in the catalysts is too slight to catalyze cyclohexane oxidation. This is well supported by the ICP-AES analysis, where no obvious change in bismuth content was noticed for the recycled catalysts (the sensitivity of the analysis is 0.034 µg/ml). In addition, the recycled catalyst (C) was characterized by XRD (Fig. 12), and it is clear that the catalyst still has characteristics typical of a mesoporous (hexagonal) MCM-41 structure.

As a comparison, Au/ZSM-5 (Au loading:1.3 wt%) and Au/MCM-41 (Au loading 1.21 wt%) were also used as catalysts in leaching tests, it can be seen that the leaching of active metal in the Au/ZSM-5 and Au/MCM-41 is quite serious. Catalyst recycling experiments were carried out with repeated use of Bi-MCM-41(C), and there is no obvious difference in either conversion or selectivity between the first and third runs. To summarize, the leaching and recycling tests revealed that Bi-MCM-41 catalysts are very stable and behave truly as a heterogeneous catalyst. The stability of the

Bi-MCM-41 could be attributed to the distribution of bismuth in the Bi-MCM-41; that is, most of the bismuth entered the internal surface or framework of MCM-41, as revealed by XPS.

4. Conclusion

A series of bismuth-containing MCM-41 mesoporous material samples were synthesized under strongly acidic conditions. ICP analysis confirmed the presence of bismuth in the product. Characterization of the material by XRD, N_2 adsorption/desorption, TEM, and SEM revealed high crystallinity, uniformity in the mesopore structure, and a high surface area. ^{29}Si NMR, UV–vis, and Raman spectroscopy investigations indicated that bismuth is highly dispersed in the silica-based framework. Furthermore, XPS spectroscopic data indicate that most of the bismuth enters the internal surface or framework of MCM-41. In the catalytic test, Bi-MCM-41 is found to be a very efficient catalyst for the oxidation of cyclohexane with oxygen as oxidant in a solvent-free system, and the catalytic systems are environmentally friendly. In addition, Bi-MCM-41 catalyst in the systems is very stable, and it behaves truly as a heterogeneous catalyst.

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