Bismuth-Containing SBA-15 Mesoporous Silica Catalysts for Solvent-Free Liquid-Phase Oxidation of Cyclohexane by Molecular Oxygen

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Bismuth (Bi)-containing SBA-15 mesoporous silica catalysts, Bi/SBA-15, with different Bi loadings were synthesized by a direct hydrothermal method. The materials were characterized in detail by various techniques. Powder-X-ray-diffraction (PXRD), N_2-adsorption/desorption, and transmission-electron-microscopic (TEM) analyses revealed that the well-ordered hexagonal structure of SBA-15 is maintained after Bi incorporation. Diffuse-reflectance UV/VIS, *Raman*, and X-ray photoelectron spectroscopy (XPS) showed that the incorporated Bi-atoms are highly dispersed, most of them entering the internal surface of SBA-15. The new, very stable catalysts were found to be highly efficient for the oxidation of cyclohexane in a solvent-free system, molecular oxygen (O_2) being used as oxidant.

1. Introduction. – Since the mesoporous silica molecular sieve termed 'SBA-15' was synthesized by *Zhao et al.* in 1998 [1], such a material has attracted considerable attention due to their tunable pore diameters, thicker walls, high hydrothermal stabilities, and potential applications in a wide variety of fields. However, a drawback of pure siliceous mesoporous molecular sieves lies in their inherent inert nature toward various organic transformations [2]. The introduction of heteroatoms into the framework of silica is mandatory for the formation of catalytically active sites in mesoporous molecular sieves. In recent years, several studies have been dealing with the incorporation of heteroatoms such as Cr [3], Mn [4], Ti [5], Fe [6], Zr [7], Ga [8], Al [5e,h][9], and V [10] in the framework of SBA-15 by direct-synthesis or post-synthesis grafting, and most of these materials have been tested for their catalytic activities in a certain reaction. However, to the best of our knowledge, no research has been reported so far on the incorporation of bismuth (Bi) into the framework of SBA-15.

The selective oxidation of cyclohexane is an industrially important reaction, because its oxidation products, *i.e.*, cyclohexanol and cyclohexanone, are important intermediates in the production of adipic acid and caprolactam, which are used to manufacture *Nylon-6* and *Nylon-66* polymers [11]. Recently, the use of redox-type molecular sieves as catalysts for the selective oxidation of cyclohexane with O_2 in a solvent-free system has attracted great interest [12].

In the present study, we synthesized, for the first time, Bi-containing SBA-15 mesoporous materials by a direct hydrothermal method. The new materials were characterized by numerous physico-chemical methods, including inductively coupled plasma-emission spectroscopy (ICP), powder X-ray diffraction (PXRD), N_2-adsorption/desorption, transmission electron microscopy (TEM), diffuse-reflectance UV/VIS spectroscopy, *Raman* spectroscopy, and X-ray photoelectron spectroscopy (XPS). Finally, the catalytic performance of Bi-containing SBA-15 was tested in the selective oxidation of cyclohexane in a solvent-free system, using O_2 as oxidant.

2. Experimental. – 2.1. *Catalyst Preparation.* The Bi-containing SBA-15 (Bi/SBA-15) material was synthesized using tetraethyl orthosilicate (TEOS) and $Bi(NO_3)_3 \cdot 5\ H_2O$ as silica and bismuth precursors, resp. The nonionic triblock copolymer surfactant $EO_{20}PO_{70}EO_{20}$ (*P_{123}*; *Aldrich*) was used as structure-directing agent, conc. aq. HCl being used as the acid source. All reagents were used as received. In a typical synthesis of Bi/SBA-15, *P_{123}* (2 g) was dissolved in H_2O (12.5 ml) to get a clear soln. Then, 0.86M aq. HCl soln. (58.6 ml) was added, and the mixture was stirred for 1 h. Then, TEOS (4.25 g) and $Bi(NO_3)_3$ (5 ml) acidic soln. [Si/Bi 20 : 1, 30 : 1, 50 : 1, and 70 : 1 (molar ratio); conc. aq. HCl/H_2O 2 : 3 (*v*/*v*)] were added, and the resulting mixture was stirred for 24 h at 313 K. Then, it was transferred into an autoclave and allowed to crystallize over 24 h at 373 K under static conditions. The resulting solid was filtered, washed several times with H_2O, and dried overnight at 373 K. The rel. molar composition of the gel was 1 equiv. of TEOS, 0.014 – 0.05 equiv. of $Bi(NO_3)_3$, 0.017 equiv. of *P_{123}*, 3.65 equiv. of HCl, and 203 equiv. of H_2O. Finally, the solid was calcined at 823 K in air for 6 h to remove the template completely. According to the four different Bi contents in Bi/SBA-15 (as analyzed by ICP), the catalyst samples were labeled *A* – *D*, resp. (see *Table 1* below).

For comparisons, pure siliceous SBA-15 was also synthesized according to [1]. In a typical experiment, *P_{123}* (2 g) was dispersed in H_2O (15 g) and 2M aq. HCl (60 g) with stirring, followed by addition of TEOS (4.25 g) to the homogeneous soln. This gel was stirred at 313 K for 24 h, and then crystallized at 373 K for 24 h. The resulting solid was filtered, washed, and dried overnight at 373 K. Finally, the solid was calcined at 823 K in air for 6 h to remove the template completely.

2.2. *Catalyst Characterization.* The Bi contents of catalysts *A* – *D* were quantified by inductively coupled plasma-emission spectroscopy (ICP). A working soln. was prepared by 100-fold dilution of a stock soln. (1 mg/ml Bi) with 3% (*v*/*v*) aq. HNO_3. Calibration solns. of 1, 2, 4, 6, and 8 μg/ml Bi concentrations were prepared by diluting the working soln. with 3% aq. HNO_3, and blank reagent (3% HNO_3) was used for zero calibration (blank). For ICP-AES analysis, the Bi/SBA-15 catalyst (50 mg) was dissolved in 40 wt-% aq. HF (1.5 ml) and 65 wt-% aq. HNO_3 (1.5 ml) in a polytetrafluoroethylene pot. Thereafter, the residue of HF and HNO_3 was evaporated to dryness by heating the above mixture at 393 K. Then, the pot was cooled to r.t. Finally, 3% HNO_3 was added to dissolve the Bi species to a final volume of 100 ml, and the resulting soln. was analyzed on a *Rigaku JY38S* ICP-AES spectrometer. From these data, the Bi content in the catalysts were calculated.

The following other techniques were also used. Powder-X-ray-diffraction (PXRD) patterns were recorded on a *Rigaku D/Max-2400* diffractometer, using CuK_α radiation ($\lambda = 0.15418$ nm) in the 2θ range of 0.5 to 10° (low-angle diffraction) and 2 to 80° (wide-angle diffraction), resp. Nitrogen (N_2)-adsorption/desorption experiments were performed at 77 K in a *Micromeritics ASAP-2010* apparatus. The samples were pretreated overnight at 423 K at a pressure of 1.33×10^{-4} Pa before measurement. Transmission electron microscopy (TEM) measurements were made on a *Jeol-JEM-100* electron microscope. Diffuse-reflectance UV/VIS spectra were recorded on a *Shimadzu UV-240* spectrometer, and *Raman* spectra were recorded on a *Nicolet Raman-910* spectrometer. X-Ray photoelectron spectroscopy (XPS) was performed on a *Vgescalab-210* spectrometer.

2.3 *Catalytic Oxidation.* The catalytic oxidation of cyclohexane was carried out in a 100-ml stainless-steel reactor equipped with a magnetic stirrer. In a typical procedure, cyclohexane (8 ml, 74 mmol) was mixed with Bi/SBA-15 (40 mg) and heated to 413 K under an O_2 atmosphere (1.0 MPa). After the reaction, the catalyst was separated, and the products were analyzed by GC (*Perkin-Elmer AutoSystem XL*) or by GC/MS (*Agilent 6890N/5973N*). For comparison, the same oxidation was also conducted with SBA-15 proper.

2.4. *Leaching and Recycling Tests.* To test the stability of the Bi/SBA-15 catalysts *A* – *D*, we carried out leaching studies by two methods. Method I included that the catalyst was separated from the reaction mixture by filtration after stirring for 12 h at r.t. under 1 MPa O_2, and then the mother liquid was immediately allowed to react further at 413 K under 1 MPa O_2 in the *absence* of catalyst. After the reaction, the soln. was analyzed by GC immediately. The Bi contents of the mother liquid and the used catalyst were determined by ICP-AES. Method II was similar as method I, but the catalyst was separated by filtration from the reaction mixture after 12 h under 1 MPa of N_2 at 413 K.

Recycling tests were carried out by repeatedly using Bi/SBA-15 in four consecutive reactions. Once the reaction was finished, the catalyst was separated by filtration from the mixture, washed with acetone, dried, and used again in the next catalytic run under the same reaction conditions.

3. Results and Discussion. – 3.1. *Catalyst Characterization.* 3.1.1. *Powder X-Ray Diffraction.* In *Fig. 1*, the low-angle PXRD patterns of the four Bi/SBA-15 catalyst samples *A* – *D* with different Si/Bi ratios are shown. SBA-15 and the Bi/SBA-15 samples all show three well-resolved diffraction peaks in the *2θ* range of 0.5 – 2°, which correspond to the (100), (110), and (200) reflections. The PXRD patterns match well with those reported for SBA-15 [1] [13], indicating that the synthesized materials have an ordered two-dimensional (2D) *p6mm* hexagonal mesostructure.

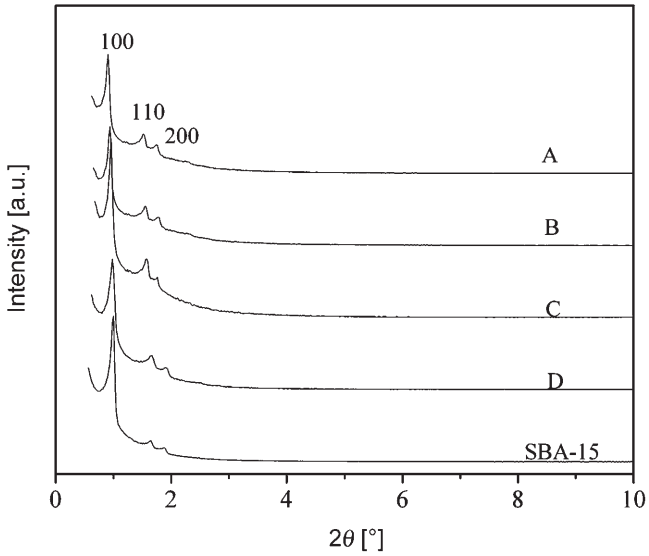

Fig. 1. *Powder-X-ray-diffraction* (PXRD) *patterns of SBA-15 and Bi/SBA-15 catalysts.* For catalyst details, see *Table 1.*

Table 1 lists the d_{100} spacing and hexagonal unit-cell parameter a_0, as calculated from the (100) peak. As can be seen, the unit-cell parameter for the Bi/SBA-15 samples are higher than for SBA-15, and increase significantly with increasing Bi content. Such expansion of the unit-cell parameter indicates the successful incorporation of Bi in the framework. Expansion of the unit-cell parameter was observed before for Ga/SBA-15 [8b – c] and Ti/SBA-15 [5d]. In addition, no peaks corresponding to bulk bismuth oxide phase are observed in the X-ray diffractograms in the 2θ domain of 2 – 80° (*Fig. 2*).

Table 1. *Analytical Data of Different Bi/SBA-15 Samples*

Sample	Si/Bi	Bi Content (wt-%)	d_{100} [Å]	A_{BET} [m^2/g]	D_{BJH}[a]) [Å]	a_0[b]) [Å]	V_{BJH}[a]) [cm^3/g]
A	20:1	1.87	98.84	693.93	73.48	114.13	1.33
B	30:1	1.22	94.94	643.84	66.18	109.63	1.18
C	50:1	0.76	92.83	778.72	61.92	107.19	1.22
D	70:1	0.47	90.37	867.32	58.66	104.35	1.22
SBA-15	∞	–	89.66	847.13	54.89	103.53	1.21

[a]) Calculated from the N_2-desorption isotherm. [b]) XRD Lattice parameter calculated from the formula $a_0 = 2d_{100}/\sqrt{3}$.

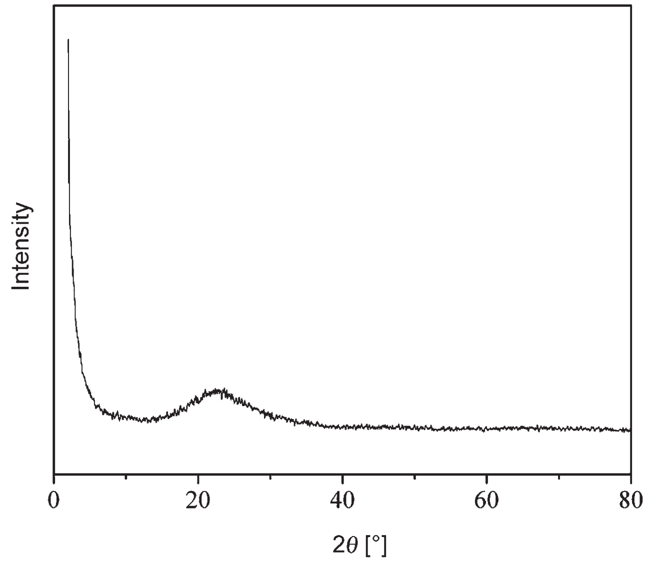

Fig. 2. *Wide-angle PXRD pattern of Bi/SBA-15 catalyst* (sample *A*)

3.1.2. *N_2 Adsorption/Desorption.* The N_2-adsorption/desorption isotherms for the Bi/SBA-15 samples are shown in *Fig. 3*, and the textural properties are collected in *Table 1*. All materials give typical irreversible type-IV adsorption isotherms, with a H1-type hysteresis loop according to the *IUPAC* classification [14]. As the relative pressure increases ($P/P_0 > 0.6$), all isotherms exhibit a sharp inflection, corresponding to capillary condensation of N_2 within uniform mesopores, where the P/P_0 position of the inflection point is correlated to the diameter of the mesopore. The capillary condensation is shifted to higher P/P_0 values when increasing the Bi content of the sample. This can be attributed to an increase of pore diameter with increasing Bi content (*Table 1*).

In addition, the BET surface area and pore volume of the Bi/SBA-15 samples are comparable with those of SBA-15. Similar results have been observed for Al/SBA-15 [5e]. These observations suggest that the synthesized Bi/SBA-15 samples have highly ordered mesostructures, in agreement with the PXRD results.

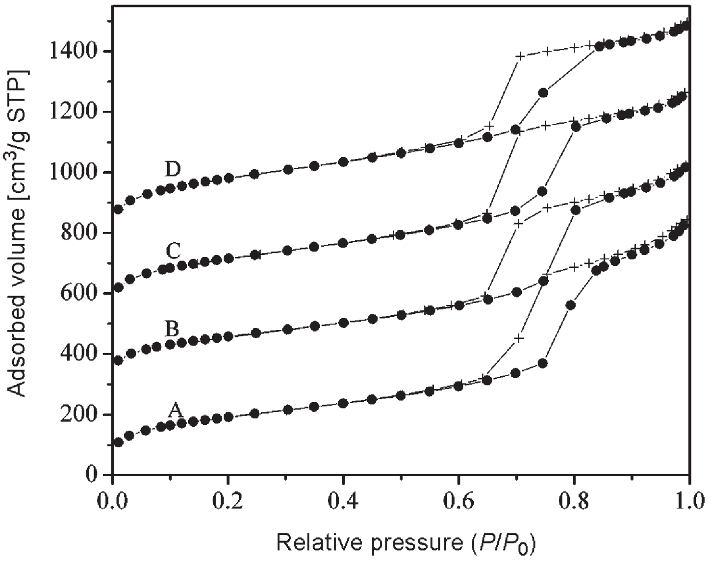

Fig. 3. *N_2-Adsorption/desorption isotherms of Bi/SBA-15 catalysts* (see *Table 1*). ●: Adsorption; +: desorption.

3.1.3. *Transmission Electron Microscopy.* As shown in *Fig. 4*, the TEM image of Bi/SBA-15 (sample *D*) shows well-ordered hexagonal arrays of mesoporous channels, which further confirms that the Bi/SBA-15 sample has a 2D *p6mm* hexagonal structure. The distance between two consecutive centers of hexagonal pores estimated from the TEM images is *ca.* 11 nm, and the pore diameter is *ca.* 6 nm, which is in agreement with the XRD results and the N_2-adsorption/desorption measurements (*Table 1*).

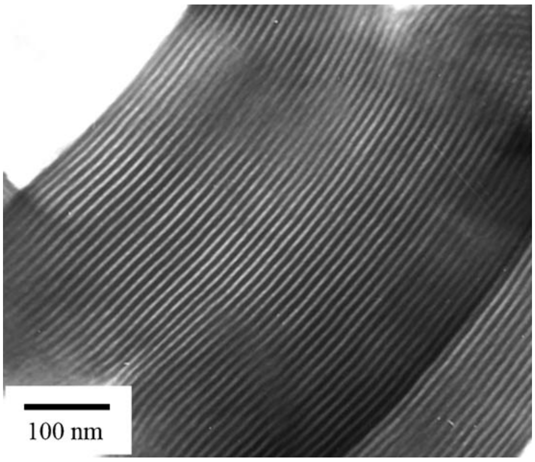

Fig. 4. *Transmission-electron-microscope* (TEM) *image of Bi/SBA-15* (sample *D*)

3.1.4. *Diffuse-Reflectance UV/VIS Spectroscopy.* This extensively used method is one of the best techniques to detect the framework and extra-framework metal species in molecular sieves [15]. The UV/VIS spectra of the Bi/SBA-15 samples are shown in *Fig. 5*. An absorption band is observed at *ca.* 215 nm for all the Bi/SBA-15 samples *A* – *D*, and its intensity was found to increase with increasing Bi content. This absorption band is attributed to ligand-to-metal charge transfer (LMCT) from an O^{2-} to an isolated Bi^{3+} ion in a tetrahedral configuration. This indicates the presence of tetrahedral, isolated Bi^{3+} ions in the SBA-15 mesoporous framework. Furthermore, as for sample *A*, the shoulder at *ca.* 250 nm indicates the presence of hexacoordinated Bi species. In Bi_2O_3, where there is full connectivity of Bi–O–Bi linkages, the LMCT shifts to lower wavelength (*ca.* 400 nm) [16]. These results indicate that there is no bismuth oxide in the Bi/SBA-15 samples and that Bi-atoms enter the framework of Bi/SBA-15.

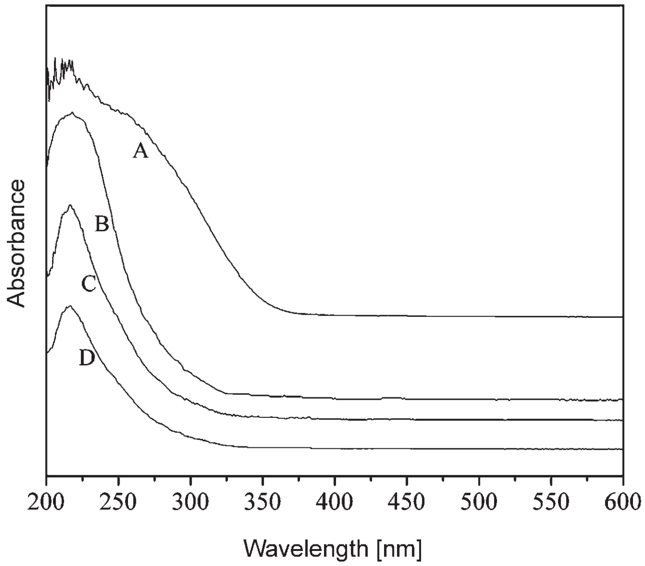

Fig. 5. *Diffuse-reflectance UV/VIS spectra of Bi/SBA-15 catalysts.* For catalyst details, see *Table 1.*

3.1.5. *Raman Spectroscopy.* In *Fig. 6*, the *Raman* spectra for Bi/SBA-15 and crystalline Bi_2O_3 are shown. Crystalline Bi_2O_3 is a very strong *Raman* scatterer, with intense peaks at *ca.* 2136, 1724, 1410, 449, and 315 cm^{-1}. As for the Bi/SBA-15 samples, the absence of these intense peaks indicates that the Bi is highly dispersed in the silica-based framework. This result is in agreement with the conclusion drawn from the UV/VIS spectra (see above).

3.1.6. *X-Ray Photoelectron Spectroscopy.* XPS was used to analyze the surface chemical composition of the catalysts. For bismuth oxide, the Bi 4 f_7 peak centered at *ca.* 159.8 eV is very typical [17]. However, it is worth noting that no obvious Bi signals are detected by XPS for any of the Bi/SBA-15 samples. A typical spectrum for sample *A* is shown in *Fig. 7.* It could be estimated that most of the Bi enters the internal surface or framework of SBA-15.

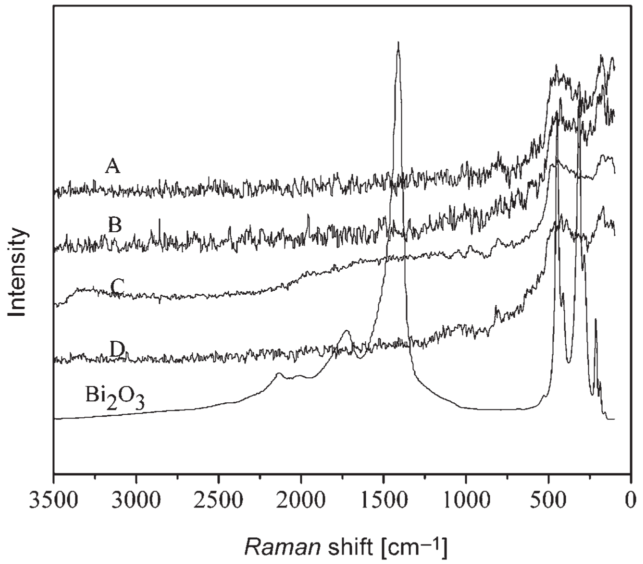

Fig. 6. Raman *Spectra for Bi/SBA-15 and Bi_2O_3 catalysts.* For catalyst details, see *Table 1.*

3.2. *Catalytic Activity.* The catalytic activity of the Bi/SBA-15 samples *A*–*D* in terms of cyclohexane oxidation in the presence of O_2 (1 MPa) at 413 K are collected in *Table 2*. GC/MS Analysis indicated that the main by-products of the reaction are adipic acid and some esters. The blank reaction, carried out with SBA-15 proper, afforded no oxidative products (*Table 2*, *Entry 1*). Hence, the excellent catalytic activity observed with Bi/SBA-15 arises from the presence of active Bi sites in the catalysts (*Entries 2*–*6*).

Earlier, many heterogeneous solid catalysts were used for cyclohexane oxidation with O_2 as oxidant [18]. However, most of these catalysts depend on the type of solvent used, and to accelerate the initiation step, a co-catalyst or initiator is usually essential. Here, Bi/SBA-15 showed excellent catalytic activity in the *absence* of solvent and co-catalyst, *i.e.*, just in the presence of O_2. Therefore, our catalytic system is environmentally friendly.

As shown in *Table 2*, among the Bi/SBA-15 catalysts, sample *B* (1.22 wt-% Bi) showed the best activity for the oxidation of cyclohexane. After 4 h, the conversion of cyclohexane was 16.9%, and the cyclohexanol/cyclohexanone ratio was 19:74 (*Entry 3*). Higher Bi content did not lead to better results for cyclohexane oxidation. Furthermore, we observed that cyclohexanol selectivity decreased with increasing conversion of cyclohexane. This might be attributed to the much higher activity of cyclohexanol, which could be oxidized to more-stable products such as cyclohexanone and adipic acid, with increasing activity of the catalyst in the systems.

In recent years, some other redox molecular sieves as catalyst were reported for the above reaction, including Ce/AlPO-5 [12c], Co/ZSM-5 [12d], Fe/AlPO [12e], [Cr]MCM-41 and [Cr]MCM-48 [12f], and $C_{27}ClC_{15}$ [12h]. In these catalytic systems,

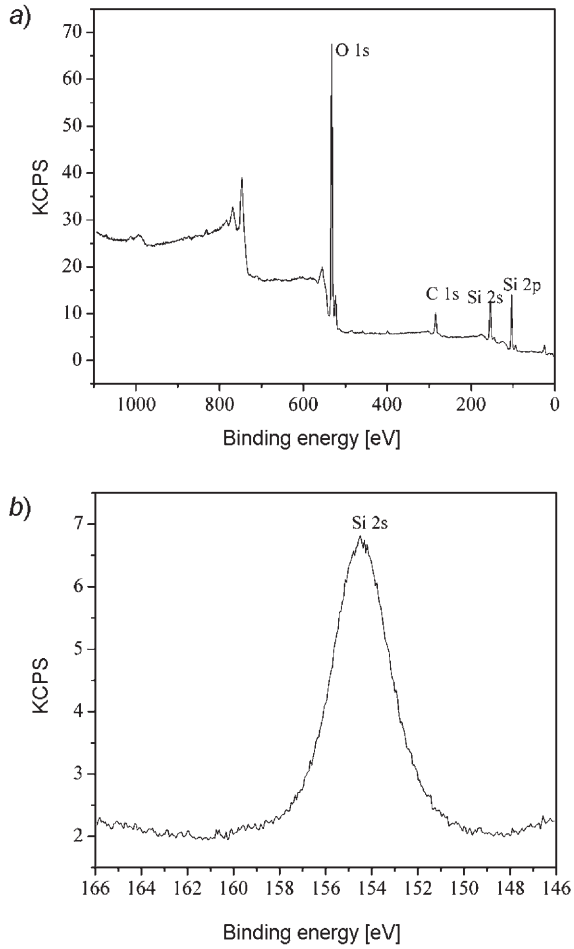

Fig. 7. a) *X-Ray photoelectron spectrum* (XPS) *of Bi/SBA-15* (sample *A*). b) *Expansion of the Si 2s signal.*

the conversion of cyclohexane was lower than 15%, with a total KA-oil[1]) selectivity of more than 90%. It was reported that Au/SBA-15 [12i,j] is very efficient in this reaction, with a cyclohexane conversion of 18% and a total KA-oil selectivity of 93%. However, gold (Au) is a noble metal, whose application is seriously limited for economic reasons. Compared with these catalysts, Bi/SBA-15 is an excellent and considerably cheaper catalyst for the selective oxidation of cyclohexane by O_2.

The effect of reaction time was also investigated. As shown in *Fig. 8*, the conversion of cyclohexane (■) and the relative amount of cyclohexanone (▲) increased with increasing reaction time, whereas the percentage of cyclohexanol (●) decreased. However, too long a reaction time led to a decrease in overall selectivity, with only a

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[1]) Industrial term for the amount of cyclohexanol and cyclohexanone formed.

Table 2. *Cyclohexane Oxidation in the Presence of Bi/SBA-15 and other Catalysts.* Conditions (for Bi/SBA-15): 40 mg catalyst, 8 ml C_6H_{12}, 413 K, 1 MPa O_2, no solvent.

Entry	Catalyst	*t* [h]	Conv. [%]	Selectivity [%]		Ref.
				Cyclohexanol	Cyclohexanone	
1	SBA-15	6	0	–	–	this work
2	Bi/SBA-15 (*A*)	4	10.7	32	63	this work
3	Bi/SBA-15 (*B*)	4	16.9	19	74	this work
4	Bi/SBA-15 (*B*)[a])	4	16.6	21	72	this work
5	Bi/SBA-15 (*C*)	4	13.4	23	71	this work
6	Bi/SBA-15 (*D*)	4	12.3	27	66	this work
7	Ce/AlPO-5	4	13	40	51	[12c]
8	Co/ZSM-5	4	7.5	46	46.4	[12d]
9	Fe/AlPO	24	7.5	86.6	7.0	[12e]
10	[Cr]MCM-41 or [Cr]MCM-48	6	< 10	~20	~70	[12f]
11	$C_{27}ClC_{15}$	6	8.0	29	63	[12h]
12	Au/SBA-15	6	18	18	75	[12i,j]

[a]) Results after the fourth successive run with the same catalyst.

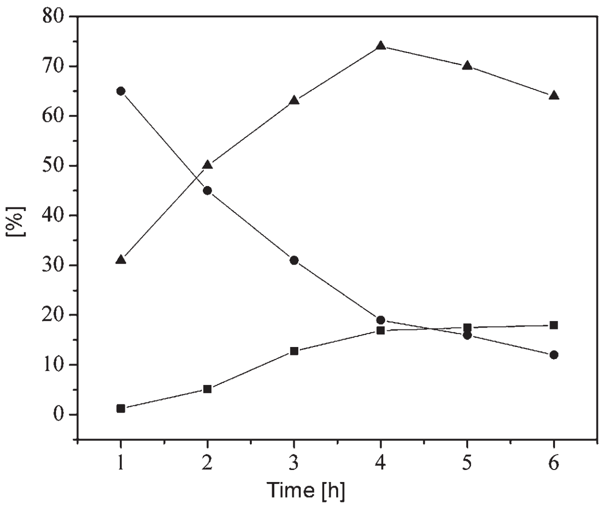

Fig. 8. *Effect of reaction time on the conversion and selectivity of cyclohexane oxidation in the presence of Bi/SBA-15* (sample *B*) *as catalyst.* Conditions: 74 mmol cyclohexane, 40 mg catalyst, 1 MPa O_2, 413 K. Legend: conversion (■), cyclohexanol selectivity (●), cyclohexanone selectivity (▲).

slight increase in conversion. Therefore, the appropriate reaction time is 4 h under our experimental conditions (see *Experimental*).

In *Fig. 9*, the influence of reaction temperature is illustrated. With increasing temperature, the conversion of cyclohexane was found to increase slightly. But at higher reaction temperatures, the total selectivity decreased. Therefore, the optimum reaction temperature was determined as 413 K (140°).

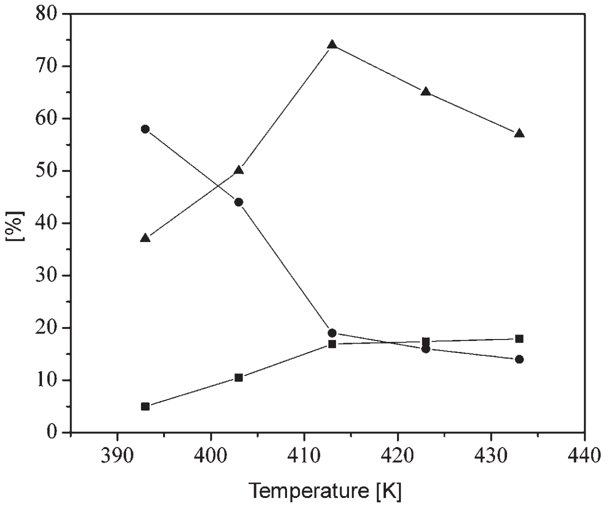

Fig. 9. *Effect of reaction temperature on the conversion and selectivity of cyclohexane oxidation in the presence of Bi/SBA-15* (sample *B*) *as catalyst.* Conditions and legend as in *Fig. 8.*

3.3. *Leaching and Recycling Studies.* In ICP-AES analyses of the mother liquid and the used catalysts, we did not detect any leaching of Bi from Bi/SBA-15, and no oxidative products in the reaction solution were detected by GC. These results indicate that the Bi/SBA-15 catalyst is very stable. We also carried out catalyst-recycling experiments. Thus, upon repeated use (up to four times) of sample *B* of Bi/SBA-15, either conversion or selectivity hardly changed (*Table 2*).

4. Conclusions. – We have elaborated the first synthesis of Bi-containing SBA-15 mesoporous materials, prepared by a direct hydrothermal method. The resulting Bi/SBA-15 catalysts were thoroughly characterized, and found to exhibit a two-dimensional *p6mm* hexagonal mesostructure, the Bi-atoms being highly dispersed in the silica-based framework. The Bi/SBA-15 catalysts, with different Bi loading, showed excellent catalytic activity in the selective oxidation of cyclohexane under solvent-free conditions, molecular oxygen (O_2) being used as oxidant. Compared with other redox molecular-sieve catalysts (except those containing noble metals such as Au/SBA-15), a higher cyclohexane conversion (16.9%) and a product yield of 15.7% were achieved. Both reaction time and temperature were found to influence the catalytic performance. The Bi catalyst is very stable and can be readily reused without loss of activity.

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