Bi-MCM-41 催化对氯甲苯选择氧化

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摘要: 合成了一系列 Bi 掺杂的 MCM-41 介孔分子筛, 运用电感耦合等离子体原子光谱, X 射线衍射, N_2 吸附脱附, 透射电镜和紫外可见光谱对其进行了表征, 并将其用于以 H_2O_2 为氧化剂, 乙腈为溶剂的对氯甲苯选择氧化反应中. 结果表明, Bi-MCM-41 即便在底物量较大时也表现出较高的催化活性. 浓缩反应液的检测结果表明, Bi 在反应过程中无明显流失, 同时该催化剂具有良好的循环使用性能.

关键词: Bi-MCM-41; 对氯甲苯; 氧化反应; 对氯苯甲醛

中图分类号: O643 　　　　**文献标识码**: A

Catalytic Selective Oxidation of 4-Chlorotoluene by Bi-MCM-41

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Abstract: A series of bismuth incorporated MCM-41 mesoporous samples were synthesized and characterized by inductive coupled plasma emission spectrometer (ICP), X-ray diffraction, N_2 adsorption/desorption, transmission electron microscopy, and UV-Vis spectroscopy. These samples catalyzed the selective oxidation of 4-chlorotoluene efficiently even on a large scale with H_2O_2 as oxidant in acetonitrile. No bismuth was detected by ICP in the condensed reaction mother liquid, and the recycle test proved the catalyst was stable.

Key words: Bi-MCM-41; 4-chlorotoluene; oxidation; 4-chlorobenzaldehyde

　　对氯苯甲醛是一种非常重要的有机合成中间体, 是许多合成染料、荧光增白剂、农药和医药产品的基本原料, 长期以来, 工业上采用对氯甲苯氯化氧化水解法来生产, 但该法会造成严重的环境污染[1~4]. 比较而言, 对氯甲苯选择氧化法具有较低的三废排放量、易操作和路线短等显著优点. 然而, 相对于甲苯选择氧化反应, 有关对氯甲苯氧化反应的报道却并不多[5~9]. Merga 等[10]研究了 $Fe(CN)^{3-}$ 作用下含苯基自由基的氧化反应, 并提出了可能的反应机理. 后来, Singh 等[11]发现, 钒硅分子筛可有效催化氧化对氯甲苯制备对氯苯甲醛. 基于 Co/Mn/Br 催化剂可高效催化甲苯氧化生成苯甲酸[12], Hu 等[13]将其应用到对氯甲苯氧化反应中, 发现催化剂同样具有较高的催化活性.

尽管对氯甲苯以及类似芳烃选择氧化的报道很多, 也取得了较大进展, 但尚有许多难题有待解决, 如所用均相催化剂的分离和回收, 大多数催化体系的效率较低等. 因此, 开发绿色高效的对氯甲苯催化氧化体系十分迫切.

介孔分子筛具有极高的比表面积、有序的孔道结构、较窄的孔径分布、较大且可调的孔体积和孔径, 因而备受关注[14,15]. 金属 Bi 是高效的气相氧化复合催化剂的重要组分[16,17], 本课题组曾将 Bi 引入 MCM-41 的骨架中, 制备了 Bi-MCM-41, 发现它在环己烷选择氧化反应中具有很高的催化活性[18,19]. 基于此, 本文制备了一系列的 Bi 含量更高的 Bi-MCM-41, 并进行了系统表征, 研究了它在对氯甲苯选择氧化反应中的催化活性, 开发了一个对氯甲苯氧化的高效绿色催化体系.

1 实验部分

1.1 催化剂的制备

将溴代十六烷基吡啶 (CPB, 分析纯, Aldrich)、去离子水、盐酸和硝酸铋于 50 ℃ 混合搅拌 30 min, 滴加正硅酸四乙酯 (TEOS, 分析纯, Aldrich), 磁力搅拌, 得到凝胶状混合物, 其摩尔比组成为 0.33CPB:1.0TEOS:7.5HCl:68H_2O:0.06~0.08Bi$(NO_3)_3$. 将所得凝胶在 50 ℃ 搅拌 24 h, 过滤, 用去离子水洗涤, 于 100 ℃ 干燥 3 h, 然后于 550 ℃ 焙烧 6 h, 即得不同 Bi 含量的 Bi-MCM-41 样品, 经测定 Bi 含量分别为 14.5%, 12.2%, 10.3% 和 8.3%.

1.2 催化剂的表征

铋的含量采用 Rigaku JY38S 型电感耦合等离子体 (ICP) 原子发射光谱仪进行测定. 样品的结构有序度和晶型采用 Rigaku D/Max 2400 型 X 射线衍射仪进行测定. 样品的孔结构采用 Micromeritics ASAP 2010 型比表面及孔径分析仪进行测定. 样品的形貌采用 JEOL-JEM 100 型透射电子显微镜 (TEM) 和 JSM-5600LV 型扫描式显微电镜 (SEM) 进行观察. 样品的光吸收范围采用 Shimadzu UV-240 型紫外-可见 (UV-Vis) 光谱仪进行测定.

1.3 催化剂的评价

对氯甲苯氧化反应在 50 ml 自制不锈钢反应器中进行, 向其中加入 2.0 g 对氯甲苯, 5.0 g 40% 的 H_2O_2, 25 ml 乙腈以及 50 mg Bi-MCM-41 催化剂, 加

热至 80~120 ℃ 密闭反应. 反应结束后, 样品采用 P.E. AutoSystem XL 型气相色谱和 Agilent 6890N/5973N 型气相色谱-质谱联用仪分析.

2 结果与讨论

2.1 样品的表征结果

由前期的研究结果可知[19], 所制备的 Bi-MCM-41 样品具有典型的六方孔道结构, 有序度较高. 图 1 为 12.2%Bi-MCM-41 样品的 N_2 吸附-脱附等温线. 由图可见, 样品具有典型的介孔吸附-脱附特征[20,21], 在相对压力为 0.5 时, 出现了明显的滞后环, 这与等温吸附-脱附 Ⅳ 型曲线一致. 样品的颗粒大小为 3~3.5 nm, 比表面积在 800 m²/g 以上.
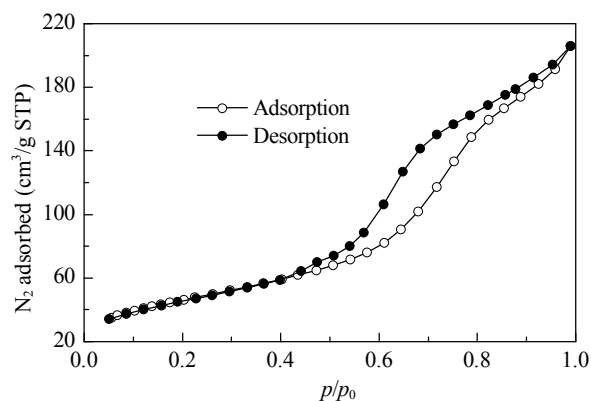

图 1 12.2%Bi-MCM-41 样品的 N_2 吸附/脱附等温线
Fig. 1. N_2 adsorption/desorption isotherm for 12.2%Bi-MCM-41 sample.

UV-Vis 谱对负载在分子筛骨架外的金属氧化物非常敏感: 分子筛骨架外的铋氧化物聚集体在 400 nm 处将出现一个较大的吸收峰, 而进入骨架且处于高分散状态的 Bi 会在 200 nm 处出现明显的吸收带. 图 2 为所制 Bi-MCM-41 样品的 UV-Vis 谱. 可以看出, 200 nm 处吸收峰非常明显, 而在 400 nm 处并未出现吸收峰, 表明金属铋都进入了分子筛骨架. 随着样品中 Bi 含量的增加, 在 240 nm 处出现较明显的肩峰, 这可能是由于 Bi 含量超过一定限度后, Bi 除了四配位外, 还可能存在其它配位形式.

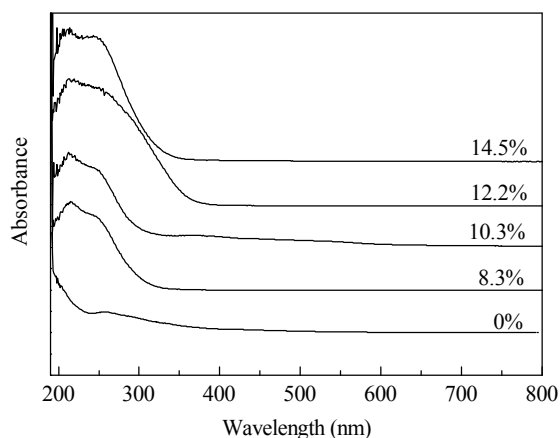综上可见, 合成的 Bi-MCM-41 具有典型的 MCM-41 孔道结构, 且所有 Bi 均进入了分子筛骨架中, 处于高分散状态. 图 3 为 12.2%Bi-MCM-41 样品的 TEM 照片. 由图可以看出, 样品中未出现氧化铋粒子.

图 2　不同 Bi 含量的 Bi-MCM-41 样品的 UV-Vis 谱
Fig. 2. UV-Vis spectra of Bi-MCM-41 samples with different Bi contents.
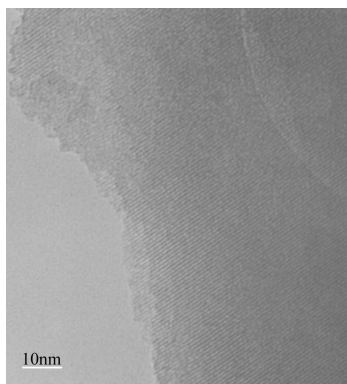

图 3　12.2%Bi-MCM-41 样品的 TEM 照片
Fig. 3. TEM image of 12.2%Bi-MCM-41 sample.

2.2　样品的催化性能

表 1 为各 Bi-MCM-41 样品上对氯甲苯氧化反

应结果. 可以看出, 不同 Bi 含量的 Bi-MCM-41 均具有较高的活性和对氯苯甲醛选择性, 其中以 12.2%Bi-MCM-41 最高. 这表明四配位金属铋可能是主要的催化活性中心. 还可以看出, 在这个催化体系中 O_2 不是有效的氧化剂; 改用其它溶剂时, 反应活性显著下降, 甚至得不到产物, 表明乙腈在体系中起着关键的作用, 但其作用机制尚不清楚.

另外, 当底物量加大时, Bi-MCM-41 依然保持着较高的催化活性, 甚至具有较高的分离收率(11.5%), 由此可见, 该催化体系具有较好的实际应用潜力.

图 4(a) 为反应时间对 12.2%Bi-MCM-41 催化剂上对氯甲苯氧化反应性能的影响. 可以看出, 对氯甲苯转化率随着时间的延长而增加, 但对氯苯甲醛选择性却略有下降. 但反应时间过长, 对氯甲苯转化率增加不大, 而对氯苯甲醛选择性却明显下降. 因此, 反应 7 h 为宜.

图 4(b) 为反应温度对 12.2%Bi-MCM-41 催化剂上对氯甲苯氧化反应性能的影响. 可以看出, 于 120 ℃ 反应时性能最佳, 超过这一温度, 对氯苯甲醛选择性开始显著下降.

本文还考察了 12.2%Bi-MCM-41 的循环使用性能. 结果发现, 该催化剂连续使用 4 次, 对氯甲苯转化率和对氯苯甲醛选择性未见明显降低. 反应后体系浓缩液检测结果表明, 反应过程中 Bi 没有明显的流失. 由此可见, Bi-MCM-41 是一种稳定高效的对氯甲苯氧化催化剂.

表 1　Bi-MCM-41 催化对氯甲苯选择性氧化反应性能
Table 1　Performance of Bi-MCM-41 catalyst for catalytic oxidation of 4-chlorotoluene

Entry	Catalyst	Coversion (%)	Selectivity (%)		
			4-Chlorobenzaldehyde	4-Chlorobenzyl alcohol	4-Chlorobenzoic acid
1	—	0.8	93.1	4.7	1.3
2	MCM-41	0.9	95.2	2.8	0.9
3[a]	14.5% Bi-MCM-41	2.7	78.5	10.5	6.2
4[b]	14.5% Bi-MCM-41	1.3	81.8	11.2	3.4
5	14.5% Bi-MCM-41	13.4	96.2	1.0	0.7
6	12.2% Bi-MCM-41	18.6	95.3	1.1	0.9
7	10.5% Bi-MCM-41	21.0	84.1	8.0	3.1
8	8.3% Bi-MCM-41	11.8	87.2	7.7	2.6
9[c]	12.2% Bi-MCM-41	15.2	91.0 (11.5[d])	4.8	2.8

Reaction conditions: 4-chlorotoluene 2.0 g, H_2O_2 (40%) 5.0 g, acetonitrile 25 ml, catalyst 50 mg, 120 ℃, 7 h, autogenous pressure.

[a] Without solvent.

[b] 1 MPa O_2.

[c] 4-Chlorotoluene 30.0 g, H_2O_2 (40%) 60 g, acetonitrile 400 ml, catalyst 0.75 g, 120 ℃, 7 h, autogenous pressure.
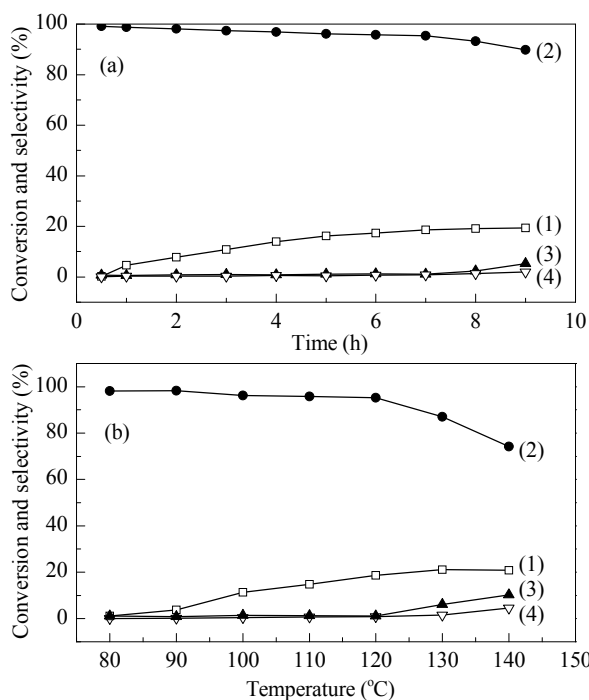
[d] Isolated yield (%).

图 4 反应时间和反应温度对 **12.2%Bi-MCM-41** 上对氯甲苯氧化性能的影响

Fig. 4. Effect of reaction time (a) and reaction temperature (b) on the conversion and selectivity over 12.2%Bi-MCM-41. (1) Conversion of 4-chlorotoluene; (2) Selectivity for 4-chlorobenzaldehyde; (3) Selectivity for 4-chlorobenzyl alcohol; (4) Selectivity for 4-chlorobenzoic acid.

3 结论

合成了一系列的高 Bi 含量的 MCM-41 介孔材料, 金属 Bi 高度分散于 MCM-41 骨架中, 且具有很好的有序度和典型的介孔结构. 在以 H$_2$O$_2$ 为氧化剂, 乙腈为溶剂的体系里, Bi-MCM-41 能高效地催化选择氧化对氯甲苯生成对氯苯甲醛, 且铋金属不流失, 可连续使用 4 次. 同时, 在底物量较大时, 该催化体系依然表现出较高的效率, 获得了良好的分离收率, 这表明该催化体系具有工业应用的潜力. 有关乙腈的作用机制, 催化剂内不同铋物种对反应的影响等目前还在研究中.

参 考 文 献

1 Yoo J S. *Appl Catal A*, 1996, **135**: 261
2 Walling C, Zhao C, El-Taliawi G M. *J Org Chem*, 1983, **48**: 4910
3 Selvam T, Singh A P. *J Chem Soc, Chem Commun*, 1995: 883
4 Partenheimer W. *Catal Today*, 1995, **23**: 69
5 Miki J, Osada Y, Konoshi T, Tachibana Y, Shikoda T. *Appl Catal A*, 1996, **137**: 93
6 龙丽萍, 赵建国, 杨利娴, 付名利, 吴军良, 黄碧纯, 叶代启. 催化学报 (Long L P, Zhao J G, Yang L X, Fu M L, Wu J L, Huang B Ch, Ye D Q . *Chin J Catal*), 2011, **32**: 904
7 罗晓明, 陈宁, 陈懿. 催化学报 (Luo X M, Chen N, Chen Y. *Chin J Catal*), 1988, **9**: 351
8 Popova M, Szegedi A, Németh P, Kostova N, Tsoncheva T. *Catal Commun*, 2008, **10**: 304
9 Kim K-J, Ahn H-G. *Appl Catal B*, 2009, **91**: 308
10 Merga G, Schuchmann H-P, Rao B S M, Vonsonntag C. *J Chem Soc, Perkin Trans*, 1996: 551
11 Singh A P, Selvam T. *Appl Catal A*, 1996, **143**: 111
12 Raju Burri D, Jun K-W, Yoo J S, Lee C W, Park S-E. *Catal Lett*, 2002, **81**: 169
13 Hu A-J, Lü C X, Wang H Y, Li B D. *Catal Commun*, 2007, **8**: 1279
14 Kresge C T, Leonowicz M E, Roth W J , Vartuli J C, Beck J S. *Nature*, 1992, **359**: 710
15 Selvam P, Bhatia S K, Sonwane C G. *Ind Eng Chem Res*, 2001, **40**: 3237
16 Bielanski A, Haber J. Oxygen in Catalysis. Amsterdam: Elsevier, 1991
17 Dumitriy D, Bârjega R, Frunza L, Macovei D, Hu T, Xie Y, Pârvulescu V I, Kaliaguine S. *J Catal*, 2003, **219**: 337
18 Qian G, Ji D, Lu G M, Zhao R, Qi Y X, Suo J S. *J Catal*, 2005, **232**: 378
19 Qian G, Luo X, Wang J M. *Microporous Mesoporous Mater*, 2008, **112**: 632
20 Zhou Z, Franz A W, Hartmann M, Seifert A, Thomas J J, Thiel W R. *Chem Mater*, 2008, **20**: 4986
21 Shi G J, Shen J Y. *Energy Fuels*, 2009, **23**: 320

英 译 文
English Text

4-Chlorobenzaldehyde is an important intermediate used in the synthesis of dyes, optical brighteners, agricultural chemicals, and pharmaceuticals. Traditionally, 4-chlorobenzaldehyde is synthesized on a large scale by the acid hydrolysis of chlorobenzal chloride, but this is a heavily polluting process [1–4]. As compared with the traditional method, the selective oxidation of 4-chlorotoluene to 4-chlorobenzaldehyde is an environmentally benign process because of the green, simplified operation, and short synthesis route. However, compared to the abundant research on toluene oxidation [5–9], there are few reports on this important process. Merga et al. [10] studied the oxidation of benzyl radicals by Fe(CN)$_6^{3-}$ and the corresponding possible mechanism. Singh et al. [11] reported that vanadium silicate molecular sieves can catalyze the oxidation of 4-chlorotoluene to 4-chlorobenzaldehyde effectively. It is well-known that a Co/Mn/Br catalyst is a highly efficient catalyst for the oxidation of toluene to benzoic acid [12],

and Hu et al. [13] found the catalyst is also effective for the selective oxidation of 4-chlorotoluene.

Although some research have been done on the selective oxidation of 4-chlorotoluene and some interesting results were obtained, there are many problems remaining, such as the separation and reuse of the catalyst, and low conversion and selectivity. The development of an efficient and green catalyst system is highly desired. Mesoporous materials, due to their high surface area, well defined regular pore shape, narrow pore size distribution, large pore volume, and tunable pore size in the range of 1.6–20 nm have attracted much attention [14,15]. Bismuth is a well known component of mixed oxide catalysts for gas phase oxidation [16,17]. In our early research, bismuth atoms were introduced into the framework of MCM-41, and it was shown that Bi-MCM-41 can catalyze the selective oxidation of cyclohexane efficiently [18,19]. In this paper, a series of Bi-MCM-41 were prepared and their catalytic activity in the selective oxidation of 4-chlorotoluene was studied. The purpose is to investigate the catalytic oxidation reaction and develop a practical highly effective green catalytic system.

1 Experimental

1.1 Catalyst preparation

The synthesis procedure was carried out as follows. Cetyl pyridine bromide (CPB, AR, Aldrich) deionized water, hydrochloric acid, and bismuth nitrate were mixed at 50 $^\circ$C and stirred for 30 min. Tetraethyl orthosilicate (TEOS, AR, Aldrich) was added to the above mixture with vigorous stirring to obtain a gel mixture. The molar composition of the gel was $0.33CPB/1.0TEOS/7.5HCl/68H_2O/0.06–0.08Bi(NO_3)_3$. The mixture was stirred for 24 h at 50 $^\circ$C. The resultant product was filtered and washed with deionized water, dried at 100 $^\circ$C for 3 h, and then calcined in air at 550 $^\circ$C for 6 h. Pure siliceous MCM-41 was synthesized with the same procedure except that no bismuth nitrate was added. The bismuth content (analyzed by ICP) of synthesized samples are 14.5%, 12.2%, 10.3%, and 8.3%.

1.2 Catalyst characterization

The bismuth content was analyzed by inductively coupled plasma (ICP) atomic emission spectroscopy (Rigaku JY38S). The crystalline phases were identified by X-ray diffraction (XRD) using a Rigaku D/Max 2400 diffractometer. The textural properties of the samples were evaluated from the adsorption-desorption isotherms of nitrogen using a Micromeritics ASAP 2010 apparatus. The morphology of the samples was analyzed by a transmission electron microscope (TEM, JEOL-JEM 100) and a scanning electron mi-

croscope (SEM, JSM-5600LV). UV-Vis spectra of the samples were recorded on a Shimadzu UV-240 spectrophotometer.

1.3 Catalyst evaluation

Catalytic oxidation of 4-chlorotoluene was carried out in a 50 ml stainless steel reactor equipped with a magnetic stirrer. In a typical reaction procedure, 4-chlorotoluene (2.0 g), H_2O_2 (40%, 5.0 g) and acetonitrile (25 ml) were mixed with the Bi-MCM-41 catalyst (50 mg) and heated to 80–120 $^\circ$C under autogenous pressure. After reaction, the reactants and products were analyzed by GC (P.E. AutoSystem XL) or GC-MS (Agilent 6890N/5973N).

2 Results and discussion

2.1 Characterization results

The XRD pattern of calcined Bi-MCM-41 [19] is similar to those reported in the literature, which indicated that the mesoporous molecular sieve synthesized had an ordered hexagonal cylindrical shape channel system.

A typical N_2 adsorption/desorption isotherm is given in Fig. 1. This confirmed the presence of complementary textural and framework confined mesoporosity [20,21], which is consistent with XRD results. The pore diameters were 3–3.5 nm. The surface area was over 800 m^2/g.

Diffuse reflectance UV-Vis spectroscopy is a very sensitive probe for the presence of extra-framework metal in zeolites. The bismuth oxide mixture showed a large absorption at 400 nm and bismuth atoms in tetrahedral coordination show an intense band centered at 210 nm (Fig. 2). Hence, it was clear that most of the Bi in the bismuth-containing MCM-41 samples had the tetrahedral coordination. In addition, a shoulder band centered at 240 nm was also observed. This suggested the existence of another kind of bismuth species, and it was assigned to hexa-coordinated bismuth species.

The XRD and UV-Vis results indicated that the samples have an ordered hexagonal cylindrical shape channel system and all bismuth atoms had entered the framework of Bi-MCM-41. These results were in agreement with the conclusion drawn from the TEM characterization (Fig. 3). In the TEM image, no particle of bismuth oxide was found.

2.2 Catalytic activity of the samples

The catalytic activities of different Bi-MCM-41 samples for 4-chlorotoluene oxidation are given in Table 1. Good to excellent conversion and selectivity were obtained. 12.2%Bi-MCM-41 was the most active. The results indi-

cated that tetrahedral coordination bismuth was the main active site. Oxygen is not effective oxidant for the catalytic system. Pure MCM-41 was also used as a catalyst but the conversion was much lower than Bi-MCM-41. In addition, we found that acetonitrile was necessary, which indicated that acetonitrile played an important role under the given conditions.

A large scale reaction was also carried out and an excellent isolated yield was obtained (11.5%, entry 9), which proved that the catalyst was quite efficient even on a large scale. The result indicated that the catalytic system can be used in a practical industrial process.

The effects of reaction time and temperature were studied and the results are shown in Fig. 4. The conversion of 4-chlorotoluene increased with time, while the selectivity for 4-chlorobenzaldehyde decreased slightly. In addition, too long a reaction time no longer increased the conversion and the selectivity for 4-chlorobenzaldehyde decreased remarkably when the reaction was carried out for more than 7 h. The investigation on the reaction temperature illustrated that the best temperature was 120 $^{\circ}$C, and at a higher reaction temperature, the selectivity for 4-chlorobenzaldehyde decreased.

A recycle test of the catalyst was also carried out with 12.2%Bi-MCM-41. No decrease was found in both conversion and selectivity when the catalyst was reused four times. In the leaching test, no bismuth was detected by ICP in the condensed reaction mother liquid. These studies proved that Bi-MCM-41 is a stable catalyst for the reaction.

3 Conclusions

A series of bismuth incorporated MCM-41 mesoporous samples were synthesized. ICP analysis confirmed the presence of bismuth in the product. Characterization by XRD, N_2 adsorption/desorption, and TEM revealed high crystallinity and uniformity of the mesopore structure, and UV-Vis investigations indicated that bismuth was highly dispersed in the silica-based framework structure. In catalytic tests, the samples efficiently catalyzed the selective oxidation of 4-chlorotoluene with H_2O_2 as oxidant in acetonitrile. The leaching and recycling tests proved that the catalyst was very stable. In addition, an excellent isolated yield in a large scale experiment indicated that the catalytic system can be used in a practical industrial process. Further study on the reaction such as the role of acetonitrile and the kind of bismuth species that is active is ongoing.