Journal of Catalysis **205,** 221–225 (2002)
doi:10.1006/jcat.2001.3435, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

# $AlCl_3$-Grafted Si–MCM-41: Influence of Thermal Treatment Conditions on Surface Properties and Incorporation of Al in the Structure of MCM-41

Vasant R. Choudhary[1] and Kshudiram Mantri

*Chemical Engineering Division, National Chemical Laboratory, Pune—411 008, India*

Received July 16, 2001; revised September 14, 2001; accepted September 29, 2001

**Grafting of $AlCl_3$ onto Si–MCM-41 using the reaction of anhydrous $AlCl_3$ from its $CCl_4$ solution with terminal Si–OH groups of Si–MCM-41 under reflux at two different concentrations of $AlCl_3$ relative to Si–MCM-41 has been studied. The influence of thermal-treatment conditions (viz., temperature and gas atmosphere, such as vacuum, static or flowing air, and flowing $N_2$) on bulk and surface properties of the $AlCl_3$-grafted Si–MCM-41 has also been investigated. The $AlCl_3$-grafted Si–MCM-41 samples before and after thermal treatment were characterized by Fourier transform infrared, $^{27}$Al magic-angle spinning nuclear magnetic resonance, X-ray photoelectron spectroscopy, and energy disperse X-ray analysis (EDAX) analysis and also for their surface area and concentration of strong acid sites (measured in terms of the pyridine chemisorbed at 400°C). The incorporation of tetrahedral Al in the MCM-41 structure with the creation of strong acid sites could be accomplished by thermally treating the $AlCl_3$-grafted Si–MCM-41, particularly in a flow of $N_2$ at 400°C.** 

*Key Words:* **$AlCl_3$-grafted Si–MCM-41; incorporation of Al in MCM-41; thermally treated $AlCl_3$-grafted Si–MCM-41.**

## INTRODUCTION

Aluminium chloride (an important Lewis acid catalyst) can be immobilized by grafting it onto the surface of inorganic solids (1–6). $AlCl_3$ grafting can be accomplished by using the reaction of anhydrous $AlCl_3$ from nonaqueous solvent with inorganic solids, which creates HCl as a side product. Recently, the grafting of $AlCl_3$ onto Si–MCM-41 was reported to produce a highly active Lewis acid catalyst for Friedel–Crafts alkylation reactions (7, 8). Earlier studies (3) showed that $AlCl_3$ grafting by refluxing anhydrous $AlCl_3$ in $CCl_4$ solution with $SiO_2$ results in both 4- and 6-coordinated Al species on the silica surface. Very recently, Jun and Ryoo (7) observed the incorporation of Al in its tetrahedral and octahedral symmetry for $AlCl_3$-grafted KIT-1 (a mesoporous aluminosilicate molecular sieve with a disordered three-dimensional channel network).

Si–MCM-41 (a mesoporous silica) has a highly defective structure with different types of terminal Si–OH groups (9, 10). It is therefore interesting to study the reaction of anhydrous $AlCl_3$ with the terminal Si–OH groups of Si–MCM-41 for incorporating Al into the structure of MCM-41. The present work was undertaken for this purpose and also for studying the influence of thermal-treatment temperature and gas atmosphere on the incorporation of Al in its tetrahedral and octahedral symmetry and surface properties of the $AlCl_x$-grafted Si–MCM-41.

## EXPERIMENTAL

Synthesis and characterization of Si–MCM-41 (high-silica MCM-41) is given elsewhere (11). $AlCl_x$-grafted Si–MCM-41 was prepared by reacting anhydrous $AlCl_3$ with the terminal Si–OH groups of Si–MCM-41, as follows: A mixture of 10 g of Si–MCM-41 and 250 ml of dry $CCl_4$ was refluxed for 1.5 h, while bubbling moisture-free $N_2$ (30 $cm^3$ $min^{-1}$) through the mixture to remove traces of moisture. Then 4.6 g (34.5 mmol) or 1.33 g (10 mmol) of anhydrous $AlCl_3$ (Aldrich) was added to the mixture and the resulting mixture was refluxed under the $N_2$ flow for 3 h. The HCl gas evolved in the reaction between the $AlCl_3$ and the terminal Si–OH groups of Si–MCM-41 was measured quantitatively using an acid–base titration (by absorbing the HCl gas in an aqueous NaOH solution) as a function of time. After the reaction, the $AlCl_x$-grafted Si–MCM-41 was filtered and washed with hot $CCl_4$ under dry $N_2$ and the filtrate was analyzed for its $AlCl_3$ content. The catalyst was dried under vacuum at 80°C and then stored in a desiccator. The $AlCl_x$-grafted Si–MCM-41 was thermally treated at different temperatures under $N_2$ and flowing or static air.

The resulting solid material was characterized for its surface area (using a Surface Area Analyzer, Quantachrome, USA), bulk and surface Al/Si and Cl/Al ratios (by EDAX and XPS, respectively), and $Al_{(tetrahedral)}/Al_{(octahedral)}$ ratio from $^{27}$Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) (using a Bruker MSL 300-MHz NMR

[1] To whom correspondence should be addressed. Fax: (+91)-20-5893401/5893355. E-mail: vrc@ems.ncl.res.in.



0021-9517/02 $35.00

under the following conditions: static field = 7.1 $T$, spin rate = 3 kHz $s^{-1}$, pulse angle = 1 $\mu$s, and delay time = 100 ms). The strong acid sites on the thermally treated material were measured in terms of the pyridine chemisorbed at 400°C, using the GC pulse technique (12). The IR spectra of the $AlCl_x$-grafted Si–MCM-41 was obtained using the Nujol technique with a Shimadzu FTIR spectrometer (Model 8300).

## RESULTS AND DISCUSSION

### *Grafting of $AlCl_3$ on Si–MCM-41*

Data on the HCl evolved in the reaction between the terminal Si–OH groups of Si–MCM-41 and anhydrous $AlCl_3$ as a function of the reaction period are presented in Fig. 1. The reaction was stopped when there was no more HCl evolution (i.e., after 3 h) in the reaction.

For $AlCl_3$ concentrations of 1.0 and 3.45 mmol $g^{-1}_{(Si-MCM-41)}$, Al grafting on Si–MCM-41 was 1.0 and 3.2 mmol $g^{-1}_{(Si-MCM-41)}$, respectively, and the Cl/Al ratio of the grafted $AlCl_x$-species was 0.83 and 1.43, respectively (Table 1). The change in the Cl/Al ratio from three to one indicates that, in the grafting of $AlCl_3$, more than one terminal hydroxyl group is involved.

Figure 2 shows that the IR band at about 3730 $cm^{-1}$, which corresponds to –OH groups of Si–MCM-41, is decreased or vanishes after the grafting. This is consistent with the fact that the –OH groups are consumed in the above reactions.

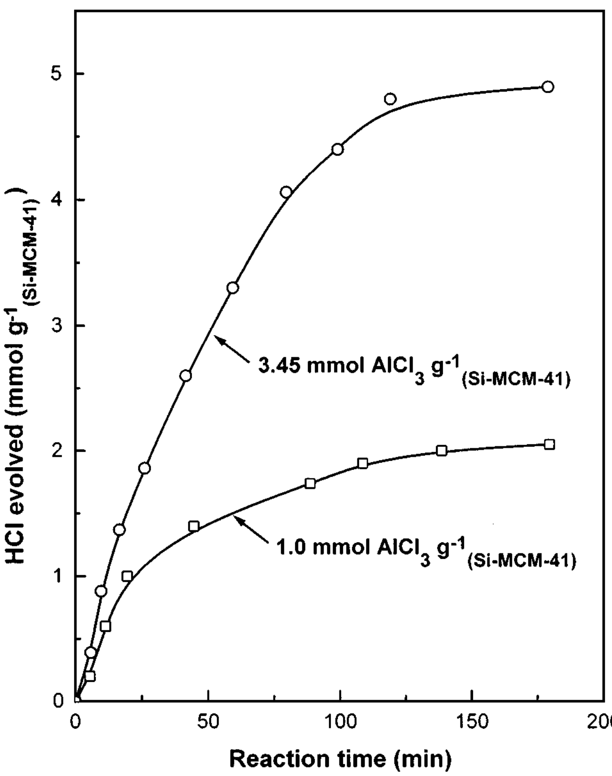


**FIG. 1.** HCl evolved in the grafting of $AlCl_3$ on Si–MCM-41 at different concentrations of $AlCl_3$ in the reaction mixture.

X-ray photoelectron spectrometry XPS analysis showed that the Cl/Al ratio at the external surface of the $AlCl_3$-grafted Si–MCM-41 is lower than the bulk Cl/Al ratio (Table 1). This indicates the involvement of more terminal Si–OH groups from the external surface than from the hexagonal mesoporous channels of the Si–MCM-41 in $AlCl_3$ grafting. This is expected because of the presence of a larger number of terminal Si–OH groups at the external surface of Si–MCM-41. Also the surface Al/Si ratio is much higher than the bulk Al/Si ratio (Table 1). This shows that the grafting reactions occur to a larger extent at the external surface compared to that in the mesoporous channels. This is also expected because of the larger terminal Si–OH groups present at the external surface of Si–MCM-41. Based on surface and bulk Cl/Al ratios, the Al-containing species formed in the grafting are as follows:

1. For the higher $AlCl_3$ concentration (3.45 mmol $g^{-1}_{(Si-MCM-41)}$) used in the grafting, in the mesoporous channels (→Si–O)$AlCl_2$ (I) and $(\rightarrow Si–O)_2AlCl$ (II) and at the external surface $(\rightarrow Si–O)_2AlCl$ (II) and $(\rightarrow Si–O)_3Al$ (III)
2. For the lower $AlCl_3$ concentration (1.0 mmol $g^{-1}_{(Si-MCM-41)}$) used in the grafting, in the mesoporous channels $(\rightarrow Si–O)_2AlCl$ (II) and $(\rightarrow Si–O)_3Al$ (III), with II > III, and at the external surface $(\rightarrow Si–O)_3Al$ (III) and $(\rightarrow Si–O)_2AlCl$ (II), with III > II

The $^{27}$Al MAS NMR spectra of the $AlCl_3$-grafted Si–MCM-41 are shown in Figs. 3a and 4a. In both cases, two peaks, one at close to 0 ppm and the second at about 54 ppm, are observed. The first and second peaks show the formation of 4-coordinated (tetrahedral) and 6-coordinated (octahedral) Al, respectively, in the $AlCl_3$ grafting. The $Al_{(tetrahedral)}/Al_{(octahedral)}$ ratios in the two $AlCl_3$-grafted samples are quite different; it is higher for the sample prepared using the lower concentration of $AlCl_3$ (Table 1).

Incorporation of tetrahedral Al into the structure of Si–MCM-41 using its reaction with aluminium alkoxide in nonaqueous medium has also been reported earlier (13, 14).

### *Effect of Thermal-Treatment Conditions*

$^{27}$Al MAS NMR spectra of the $AlCl_3$-grafted Si–MCM-41 (Al/Si = 0.06 and 0.17), showing the influence of thermal-treatment conditions (viz., temperature and gas atmosphere) on the relative concentration of the octahedral and tetrahedral Al, are presented in Figs. 3 and 4. The corresponding values of $Al_{(tetrahedral)}/Al_{(octahedral)}$, obtained by comparing the area of the NMR peak at about 54 ppm to that at 0 ppm, are included in Table 1. Data on surface composition (Cl/Al and Al/Si ratios at the external surface) and strong acid sites (measured in terms of the pyridine chemisorbed at 400°C) for the thermally

**TABLE 1**

**Effect of Thermal-Treatment Conditions on Bulk and Surface Properties of $AlCl_x$-Grafted Si–MCM-41 Prepared Using Two Different Concentrations of $AlCl_3$ in the Grafting**

| Concentration of $AlCl_3$ (mmol $g^{-1}$) | Thermal-treatment conditions | | | Al/Si ratio | | $Al_{(tetrahedral)}/Al_{(octahedral)}$ | Cl/Al Ratio | | Acidity (mmol $g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | Gas atmosphere | Temperature (°C) | Time (h) | Bulk | At external surface | | Bulk | At external surface | |
| 1.0 | Vacuum | 80 | 12 | 0.06 | 0.31 | 1.53 | 0.83 | 0.20 | — |
| | Air | 500 | 1 | — | — | 4.5 | 0.02 | 0.01 | 0.06 |
| | $N_2$ | 400 | 1 | — | — | 6.4 | 0.13 | 0.05 | 0.08 |
| 3.45 | Vacuum | 80 | 12 | 0.17 | 0.43 | 0.84 | 1.43 | 0.85 | — |
| | Air | 500 | 1 | — | — | 4.6 | 0.04 | 0.02 | 0.13 |
| | $N_2$ | 400 | 1 | — | — | 8.2 | 0.20 | 0.08 | 0.27 |
| | $N_2$ | 800 | 1 | 0.17 | 0.006 | ≈0.0 | 0.087 | ≈0.0 | ≈0.0 |

treated samples are also included in Table 1. The influence of thermal-treatment conditions (viz., temperature and gas atmosphere) on thermal stability of the $AlCl_3$-grafted Si–MCM-41 (Al/Si = 0.17, measured in terms of surface area) is shown in Fig. 5.

From the above results, the following important observations can be made:

1. Thermal treatment of both $AlCl_3$-grafted Si–MCM-41 samples at 400°C in $N_2$ and at 500°C in air causes a transformation of octahedral Al into tetrahedral Al to an appreciable extent (Table 1). However, at the higher temperature (800°C) no presence of tetrahedral Al is observed. Thermal treatment at 800°C (under $N_2$ flow) does not affect significantly the surface area but it transforms all the tetrahedral Al present in the $AlCl_3$-grafted Si–MCM-41 into octahedral Al, mostly in the form of $Al_2O_3$. The strong acidity, which is expected due to the presence of tetrahedral Al in zeolites (15, 16), is quite consistent with the changes in the tetrahedral Al caused by the thermal treatments.

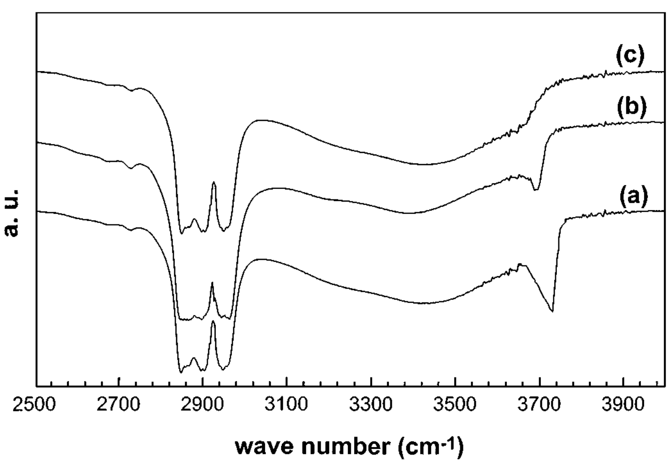


**FIG. 2.** IR spectra of Si–MCM-41 (a) and $AlCl_3$-grafted Si–MCM-41 obtained using $AlCl_3$ concentrations of 1.0 mmol $g^{-1}_{(Si–MCM-41)}$ (b) and 3.45 mmol $g^{-1}_{(Si–MCM-41)}$ (c) in the grafting.

2. With an increase in treatment temperature, both bulk and surface Cl/Al ratios of the $AlCl_3$-grafted Si–MCM-41 are decreased (Table 1), the decrease being more pronounced in the presence of air. This is expected because of the further reaction of $AlCl_x$ species with surface hydroxyls or with the oxygen from air, leading to the formation of $AlO_x$ species during thermal treatment. Also, after the high-temperature (800°C) treatment, the surface Al/Si ratio is reduced drastically, indicating the migration of $AlO_x$ species from the external surface to the mesoporous channels of the MCM-41 during thermal treatment.

3. The Si–MCM-41 with or without $AlCl_3$ grafting shows highest thermal stability in the presence of flowing

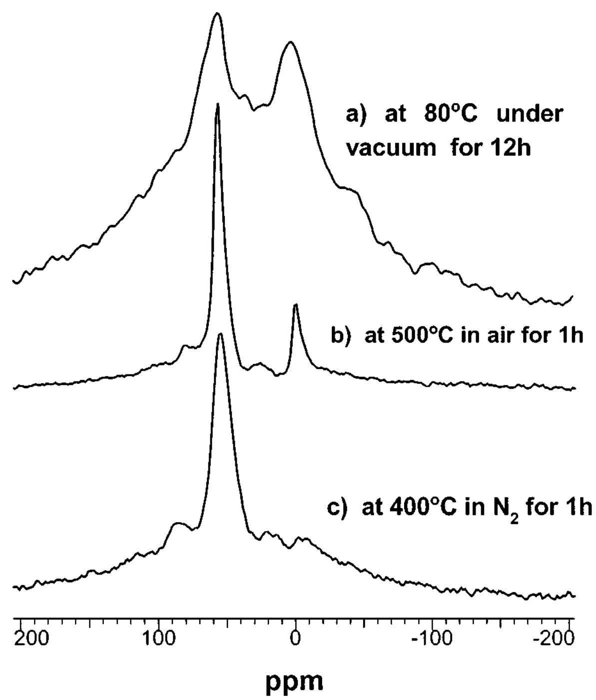


**FIG. 3.** $^{27}Al$ MAS NMR of the $AlCl_3$-grafted Si–MCM-41 (with Al/Si bulk ratio of 0.06) thermally treated under various conditions.

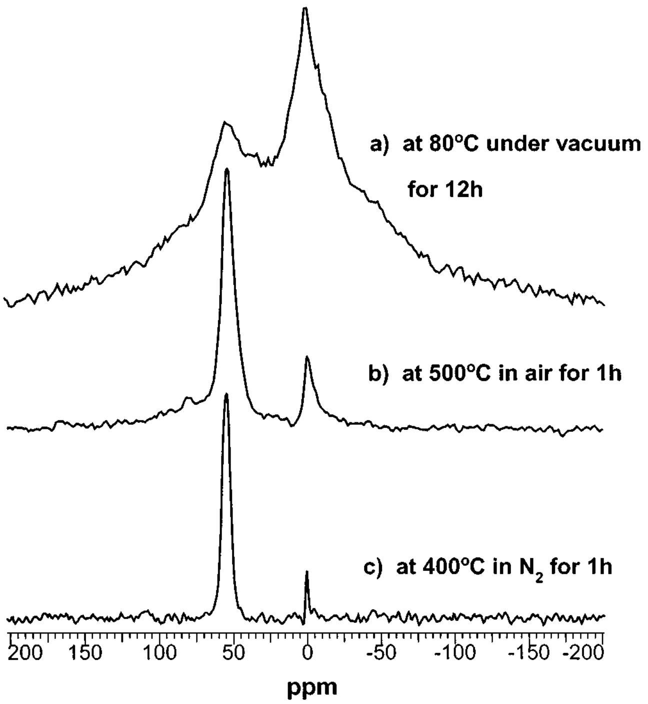


**FIG. 4.** [27]Al MAS NMR of the $AlCl_3$-grafted Si–MCM-41 (with Al/Si bulk ratio of 0.17) thermally treated under various conditions.

$N_2$ and lowest thermal stability in static air (Fig. 5). The observed increase in surface area with increasing temperature in the presence of flowing $N_2$ (Fig. 5b) is expected because of the removal of adsorbed water from the $AlCl_3$-grafted Si–MCM-41 at the higher temperatures. The presence of oxygen, particularly when it is accompanied by moisture (which is the case when the thermal treatment is given under static air), during thermal treatment at higher temperatures (above 600°C) is detrimental to both the $AlCl_3$-grafted Si–MCM-41 and the parent Si–MCM-41.

The above results indicate that the surface properties of $AlCl_3$-grafted Si–MCM-41 are influenced by both the temperature and the environment used in the thermal treatment.

## CONCLUSIONS

Surface and bulk composition (Al/Si and Cl/Al ratios) and relative concentrations of tetrahedral and octahedral Al in $AlCl_3$-grafted Si–MCM-41 depend strongly on the concentration of $AlCl_3$, relative to Si–MCM-41, used in the grafting. These compositional properties, and the acidity and surface area (or stability) of the $AlCl_3$-grafted Si–MCM-41, are strongly influenced by the thermal-treatment

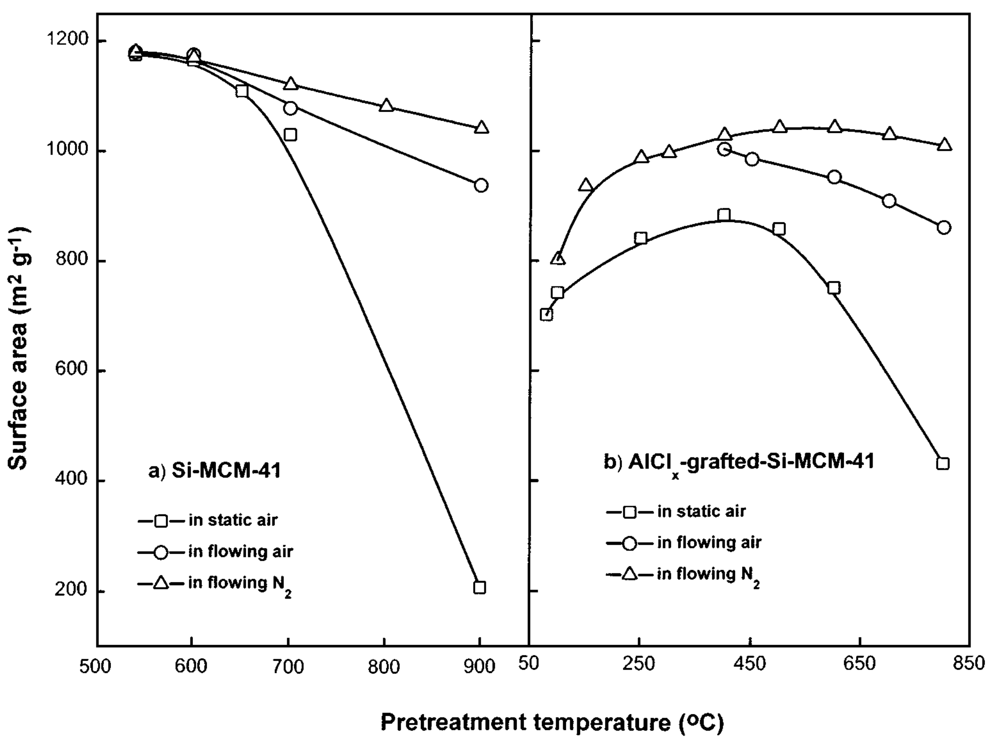


**FIG. 5.** Thermal stability (as expressed by retention of surface area) of (a) Si–MCM-41 and (b) $AlCl_3$-grafted Si–MCM-41 (with Al/Si bulk ratio = 0.17) (thermal treatment under various gas atmospheres carried out for 1 h).

conditions (viz., temperature and gas atmosphere). The thermal treatment to the $AlCl_3$-grafted Si–MCM-41, particularly at 400°C in a flow of $N_2$, results in the incorporation of tetrahedral Al in the MCM-41, creating strong acid sites.

## ACKNOWLEDGMENTS

The authors are grateful to Dr. P. R. Rajmohonan and Ms. R. Gupta for the NMR, Mr. A. B. Mandale for the XPS, and Mr. S. Ray for the IR spectra. One of the authors (K. Mantri) is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for a senior research fellowship.

## REFERENCES

1. Krzywicki, A., and Marczewski, M., *J. Chem. Soc., Faraday Trans.* **76**, 1311 (1980).
2. Drago, R. S., and Getty, E. E., *J. Am. Chem. Soc.* **110**, 3311 (1988).
3. Getty, E. E., and Drago, R. S., *Inorg. Chem.* **29**, 1186 (1990).
4. Clark, J. H., Martin, K., Teasdale, A. J., and Barlow, J., *J. Chem. Soc., Chem. Commun.* 2037 (1995).
5. Clark, J. H., Price, P. M., Martin, K., Macquarrie, D. J., and Bastock, T. W., *J. Chem. Res. Synop.* 430 (1997).
6. Price, P. M., Clark, J. H., Martin, K., Macquarrie, D. J., and Bastock, T. W., *Org. Process Res. Dev.* **2**, 221 (1998).
7. Jun, S., and Ryoo, R., *J. Catal.* **195**, 237 (2000).
8. Hu, X., Foo, M. L., Chuah, G. K., and Jaenicke, S., *J. Catal.* **195**, 412 (2000).
9. Chen, J., Li, Q., Xu, R., and Xiao, F., *Angew. Chem. Int. Ed. Engl.* **34**, 2694 (1995).
10. Jentys, A., Phan, N. H., and Vinek, H., *J. Chem. Soc., Faraday Trans.* **92**, 3287 (1996).
11. Choudhary, V. R., and Mantri, K., *Langmuir* **16**, 8024 (2000).
12. Choudhary, V. R., and Nayak, V. S., *Appl. Catal.* **4**, 31 (1982).
13. Mokaya, R., and Jones, W., *J. Chem. Soc., Chem. Commun.* 2185 (1997).
14. Mokaya, R., and Jones, W., *Phys. Chem. Chem. Phys.* **1**, 207 (1999).
15. Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature (London)* **309**, 589 (1984).
16. Weisz, P. B., *Ind. Eng. Chem. Fund.* **25**, 53 (1986).