ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 3, pp. 407–413. © Pleiades Publishing, Ltd., 2009.
Published in Russian in Kinetika i Kataliz, 2009, Vol. 50, No. 3, pp. 428–433.

Catalytic Properties of Antimony-SBA-15 Materials in the Benzylation of Aromatics Reactions[1]

K. Bachari[a,b], A. Touileb[a], and O. Cherifi[b]

[a] *Centre de Recherche Scientifique et Technique en Analyses Physico-chimiques (C.R.AP.C), BP 248, Alger RP 16004, Alger, Algérie*

[b] *Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, BP 32, 16111, El Alia, U.S.T.H.B., Bab Ezzouar, Algérie*

e-mail: bachari2000@yahoo.fr

Received January 26, 2008

Abstract—Antimony-containing mesoporous SBA-15 with different Si/Sb ratio has been synthesized using a post-treatment procedure with an aqueous solution of $SbCl_3$ and characterized by elemental analysis, XRD method, N_2 adsorption measurements (BET and BJH theory) and FTIR spectroscopy. The benzylation of aromatics by benzyl chloride has been investigated over these solids. Indeed, the antimony-containing mesoporous SBA-15 showed both high activity and high selectivity for this reaction. More interesting is the observation that Sb-SBA-15 (35) catalyst is active and selective for large molecules like naphthenic compounds such as 2-methylnaphthalene and it can also be reused in the benzylation of benzene for several times. Kinetics of the benzene benzylation over these catalysts have also been investigated.

DOI: 10.1134/S0023158409030112

1. INTRODUCTION

Friedel–Crafts alkylations comprise a very important class of reactions which are of common use in organic chemistry. These reactions are habitually catalyzed by Lewis acids in liquid phase [1], and the substitution of liquid acids by solid acid catalysts is a challenging task. The alkylation of benzene by benzyl chloride is interesting for the preparation of substitutes of polychlorobenzenes used as dielectrics. In homogeneous phase this reaction is catalyzed at the industrial scale by $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, and H_2SO_4 [1–3].

The new environmental legislation pushes for the replacement of all liquid acids by solid acid catalysts which are environmentally more friendly catalysts and which lead to minimal pollution and waste [4, 5]. Indeed, several solid acid catalysts have already been proposed which are efficient catalysts such as: Fe-modified ZSM-5 and H-β zeolites; Fe_2O_3 or $FeCl_3$ deposited on micro-, meso and macro-porous supports [6]; Fe-containing mesoporous molecular sieves materials [7, 8]; Fe-, Zn-, Ga- and In-modified ZSM-5 type zeolite catalysts [9]; Ga- and Mg-oxides and chlorides derived from Ga–Mg-hydrotalcite [10]; Ga-SBA-15 [11]; Ga-HMS [12]; $InCl_3$, $GaCl_3$, $FeCl_3$, and $ZnCl_2$ supported on clays and Si-MCM-41 [13]; transition metal chloride supported mesoporous SBA-15 [14]; supported thallium oxide catalysts [15]; Sb-modified K10 [16]; solid superacid and silica-supported polytrifluoromethanesulfosiloxane [17]; Si-MCM–41-supported Ga_2O_3 and In_2O_3 [18]; H_2SO_4, HNO_3, and $HClO_4$/metakaolinite [19]; alkali metal salts and ammonium salts of Keggin-type heteropolyacids [20]; ion-exchanged clays [21]; Clayzic [22]; Cu-HMS [23]; solid superacids based on sulfated ZrO_2 [24]; HY [25]; Fe, Ce, W-modified H-β- zeolites [26]; H-ZSM-5 [27] and $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ supported on acidic alumina [28] for the benzylation of benzene and other aromatic compounds. In the present work, we report the benzylation of benzene reaction with benzyl chloride using a series of antimony-containing mesoporous SBA-15 with different Si/Sb ratio as catalyst. The kinetics of the reaction over these catalysts have been investigated and the reaction has been extended to other substrates like toluene, *p*-xylene, anisole, naphthalene and 2-methylnaphthalene.

2. EXPERIMENTAL

2.1. Materials

Samples were synthesized with tetraethyl orthosilicate (TEOS, Merck), poly(ethylene glycol)poly(propylene glycol)poly(ethylene glycol) tri-block copolymer (Pluronic P123, molecular weight = 5800, EO20PO70EO20, Aldrich), antimony trichloride ($SbCl_3$, Merck).

2.2. Catalysts Preparation

The SBA-15 sample was synthesized using poly(ethylene glycol)poly(propylene glycol)poly(ethylene glycol) tri-block copolymer as a structure direct-

[1] The article is published in the original.

Table 1. Chemical composition and characteristics of the catalysts

Sample	Chemical analysis		Surface area, $m^2\ g^{-1}$	ϕ_p^* , nm*
	Sb, wt %	Si/Sb		
SBA-15	–	–	1170.0	9.7
Sb-SBA-15 (55)	0.80	85.0	1137.0	9.2
Sb-SBA-15 (35)	2.98	38.8	1082.0	9.4
Sb-SBA-15 (15)	6.30	15.2	961.6	9.3

* ϕ_p is the mean pore diameter obtained from N_2 adsorption isotherms.

ing agent with the following molar gel composition: TEOS : 0.016P123 : 0.46HCl : 127H_2O. In a typical synthesis, 4 g of Pluronic P123 was added to 30 ml of water. After stirring for a few hours, a clear solution was obtained. 70 g of 0.28 M hydrochloric acid was added to it and the solution was stirred for another 2 h. Then, 9 g of tetraethyl orthosilicate was added and the resulting mixture was stirred for 24 h at 313 K. The solid product was recovered by filtration, washed with water for several times, and dried overnight at 373 K. Finally, the product was calcined at 823 K to remove the template. Furthermore, antimony-containing SBA-15 were synthesized by method of impregnation: 1 g SBA-15 was impregnated with 0.5 g of antimony trichloride $SbCl_3$ in 50 g deionised water under vigorous stirring for 12 h at room temperature. The obtained products were separated by centrifugation, washed with deionised water, dried in vacuum for 40 min at 423 K and then calcined at 673 K for 4 h. This loading procedure can be repeated for more than one times to pickup more antimony. The obtained samples were named as follows: Sb-SBA-15 (15), Sb-SBA-15 (35) and Sb-SBA-15 (55), respectively, corresponding to Si/Sb ratios of 15, 35, and 55.

2.3. Characterization of the Samples

Powder X-ray diffraction patterns were recorded on a SIEMENS D500 diffractometer with CuK_α radiation. The chemical compositions of the samples were determined by a combination of wet chemical methods and atomic absorption spectrometry (HITACHI Z 800).

The surface areas and pore diameters were determined from N_2 adsorption isotherms using a NOVA 2000 porosimeter (Quantachrome) instrument. FTIR spectra were collected at ambient conditions with a Perkin-Elmer 2000 spectrometer using the KBr method (1 g of sample to 100 g of KBr).

2.4. Catalytic Testing

The benzylation of benzene by benzyl chloride has been used as a model reaction for Friedel–Crafts alkylation catalytic properties. The reaction was carried out in a batch reactor between 343 and 353 K. The quantity of 100 mg of the solids was tested after an activation consisting of a heat treatment under air (2 l h^{-1}) up to 573 K. Directly after cooling, the catalysts were contacted under stirring with 15 ml of moisture-free liquid aromatic compound (or 2.5 ml of moisture-free aromatic compound mixed with 12.5 ml of moisture- free solvent) + 1.0 ml of benzyl chloride. The reaction was started by injecting benzyl chloride in the reaction mixture, containing catalyst and aromatic compound with or without solvent. Measuring quantitatively the HCl evolved in the reaction by acid–base titration (by absorbing the HCl carried by N_2 in a 0.1 M NaOH solution containing phenolphthalein indicator) followed the course of the reaction. The polybenzyl chloride (which is formed by the condensation of benzyl chloride) was isolated from the reaction mixture by the procedure given by Choudhary et al. [29]. In all the cases, the major product formed was mainly mono-benzylated compound along with polybenzyl chloride as side product depending upon the condition used. Samples were analyzed periodically on a gas chromatograph (HP-6890) equipped with a FID detector and a capillary column RTX-1 (30 m × 0.32 mm i.d.). The products were also identified by GC-MS (HP-5973) analysis.

3. RESULTS AND DISCUSSION

3.1. Characterization

The results of the chemical composition and characteristics of the catalysts are given in the Table 1. The antimony compositions of the solids corresponded relatively well to those fixed for the synthesis except at low antimony content (Sb-SBA-15 (55)) where a loss of antimony was observed. Most of the values of the specific surface areas of the solids were larger than 1000 ($m^2\ g^{-1}$), which were typical for mesoporous materials. When the antimony content increased, they

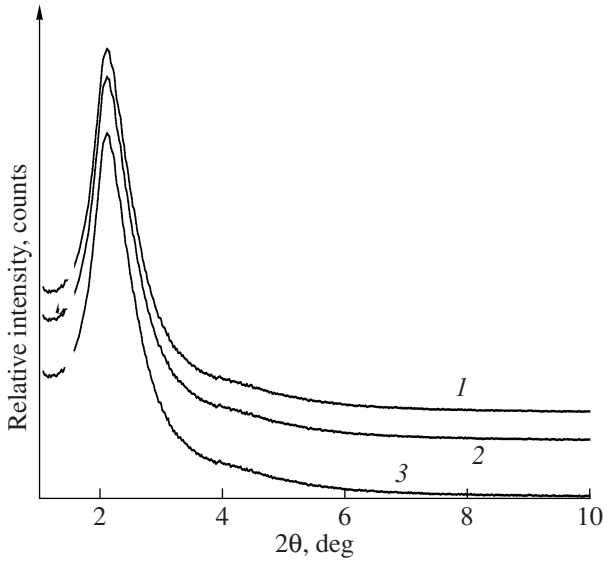

Fig. 1. XRD patterns of the Sb-SBA-15 samples in the domain of 1°–10° (2θ). n = Si/Sb = (*1*) 55, (*2*) 35, (*3*) 15.

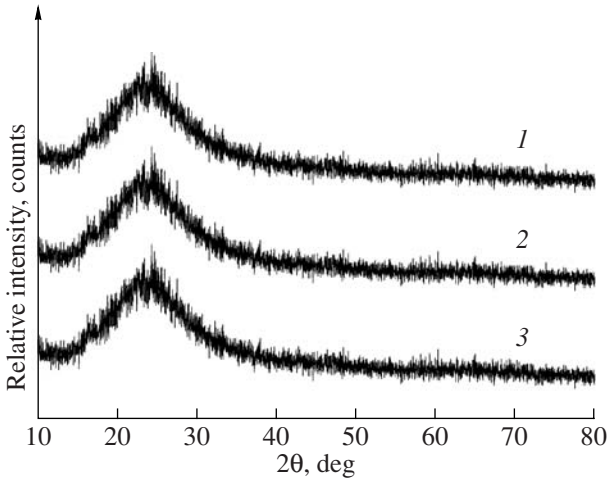

Fig. 2. XRD patterns of the Sb-SBA-15 samples in the domain of 10°–80° (2θ). n = Si/Sb = (*1*) 55, (*2*) 35, (*3*) 15.

decreased slightly. The average pore diameters calculated from N_2 adsorption isotherms using the BJH model are presented in Table 1. The N_2 adsorption isotherms of the samples revealed a uniform pore size. However, the presence of Sb in the framework of SBA-15 makes the average pore size decrease slightly.

The X-ray powder diffraction patterns of the solids showed a broad peak at 2θ = 2° (Fig. 1) characterizing a mesoporous material not well-crystallized. The intensity of the peak decreased slightly when the antimony content increased showing that the addition of antimony has not a negative effect on the crystallinity. Furthermore, no peak corresponding to Sb_2O_3 is observed in the 10° to 80° (2θ) (Fig. 2).

The IR spectra of SBA-15 and Sb-SBA-15 samples with different Si/Sb molar ratio are presented in Fig. 3. The absorption bands at about 475, 800, and 1090 cm^{-1} are attributed to a consequence of stretching vibrations of the SiO_4 tetrahedra [30]. In addition, the band at 960 cm^{-1} is clearly visible in the IR spectra of Sb-SBA-15 samples. This band is generally considered a proof of the incorporation of the heteroatom into the framework [31–34]. But the 960 cm^{-1} band also exists in the spectrum of the pure siliceous SBA-15 mesoporous molecular sieve, and this vibration absorption band at 960 cm^{-1} has also been detected in Si-MCM-41 and Si-MCM-48 molecular sieves [35, 36], which may be due to the abundance of silanol groups on the surface of the samples. There is still a debate about the nature of the absorption band at 960 cm^{-1}. However, the results in Fig. 3 show clearly that the band intensity at 960 cm^{-1} increases with Sb^{3+} ions incorporation into the framework, and this peak intensity enhances somewhat on increasing the Sb content in the samples.

3.2. Reaction Kinetics

The kinetic data for the benzene benzylation reaction in excess of benzene (molar ratio Bz/BzCl = 15) over the Sb-SBA-15(35) catalyst could be fitted well to a pseudo-first-order rate law: $\log[1/(1-x)] = (k_a/2.303)(t-t_0)$, where k_a is the apparent first-order rate constant, x—the fractional conversion of benzyl chloride, t—the reaction time and t_0—the induction period

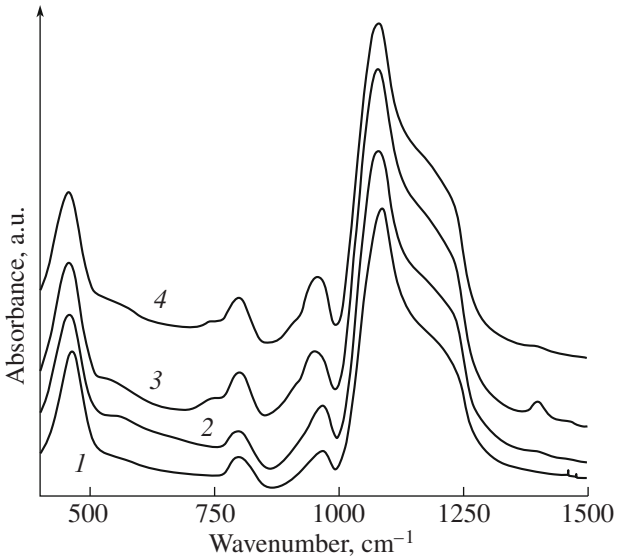

Fig. 3. FTIR spectra of the SBA-15 and the Sb-SBA-15 samples. (*1*) SBA, (*2*) Si/Sb = 55, (*3*) Si/Sb = 35, (*4*) Si/Sb = 15.

Table 2. Catalytic activities of Sb-SBA-15 (35) at different temperatures: 343, 348, and 353 K Bz/BzCl ratio = 15 and m_{cat} = 0.1 g

Temperature, K	Time*, min	Selectivity, %		Apparent rate constant $k_a \times 10^3$, min^{-1}
		diphenylmethane	polybenzylbenzene	
343	27.7	100.0	–	118.9
348	22.2	99.9	0.1	132.6
353	16.7	99.2	0.8	186.6

* Time required for 90% conversion of benzyl chloride.

Table 3. Influence of the molar ratio between benzene and benzyl chloride for the benzylation of benzene at 353 K over Sb-SBA-15 (35) catalyst

Benzene/benzyl chloride ratio	Time*, min	Selectivity, %	
		diphenylmethane	polybenzylbenzene
5	25.7	75.4	24.6
15	16.7	99.2	0.8

* Time required for 90% conversion of benzyl chloride.

Table 4. Catalytic properties of substituted benzenes and substituted naphthalene at 353 K over Sb-SBA-15 (35) catalyst m_{cat} = 0.1 g and substituted benzenes and naphthalene/BzCl = 15

Substituent	Apparent rate constant $k_a \times 10^3$, min^{-1}	Reaction products	Selectivity, %
Benzene	186.6	Diphenylmethane	99.2
Toluene	175.3	*para*-Benzylated	92
		ortho-Benzylated	7
		meta-Benzylated	1
p-Xylene	166.9	2,5-Dimethyldiphenylmethane	>99
Anisole	119.4	*para*-Benzylated	87
		ortho-Benzylated	11
		meta-Benzylated	2
Naphthalene	64.3	1-Benzylnaphthalene	82
		2-Benzylnaphthalene	18
2-Methylnaphthalene	58.4	1-Benzyl-2-methylnaphthalene	97
		6 further isomers*	3

* The isomers formed in minor amounts were identified by their mol peaks (GC-MS analysis).

corresponding to the time required for reaching equilibrium temperature. A plot of $\log[1/(1-x)]$ as a function of the time gives a linear plot over a large range of benzyl chloride conversions. The effect of temperature on the rate was studied by conducting the reaction at 343, 348, and 353 K under the standard reaction conditions (molar ratio Bz/BzCl = 15 and 0.1 g catalyst). The results of the effect of temperature on the rate showed that the catalytic performances of the catalyst strongly increased with the reaction temperature (Table 2). Indeed, the time for 90% conversion of benzyl chloride and the apparent rate constant k_a changed from 27.7 min and 118.9×10^{-3} min^{-1} at 343 K to, respectively, 16.7 min and 186.6×10^{-3} min^{-1} at 353 K. By contrast, the selectivity to diphenylmethane remains approximately constant. The activation energy estimated thus obtained was 98.7 kJ mol^{-1}. In fact, this value can probably suggest that no interference of diffusional limitations is existed. Two Bz/BzCl ratios have been investigated. The results obtained are reported on Table 3. It appears that the molar ratio between benzene and benzyl chloride has a strong influence on the selectivity to diphenylmethane. With a low ratio, the secondary reactions to dibenzylbenzenes and tribenzylbenzene were favored.

Results showing the influence of different substituent groups attached to aromatic benzene nucleus on the conversion of benzyl chloride in the benzylation of corresponding substituted benzenes at 353 K over the Sb-SBA-15 (35) catalyst are presented in Table 4. According to the classical mechanism of the Friedel–Crafts type acid catalyzed benzylation reaction, the benzylation of an aromatic compound is easier if one or more electron donating groups are present in the aromatic ring [1]. Hence, the order for the rate of benzylation for the aromatic compound is expected as follows: anisole > *p*-xylene > toluene ⩾ benzene. But, what is observed in the present case is totally opposite to that expected according to the classical mechanism. The first-order rate constant for the benzylation of benzene and substituted benzenes is in the following order: benzene > toluene > *p*-xylene > anisole. This indicates that, for this catalyst, the reaction mechanism is different from that for the classical acid catalyzed benzylation reactions. In fact, the probable redox mechanism for the activation of both benzyl chloride and benzene by these catalysts leading to the benzylation of benzene reaction is proposed:

$$m\text{Ø-CH}_2\text{Cl} + \text{M}^{n+} \rightleftharpoons m\text{Ø-CH}_2\text{Cl}^{+\bullet} + \text{M}^{(n-m)+},$$

$$m\text{Ø-CH}_2\text{Cl}^{+\bullet} \rightleftharpoons m\text{Ø-CH}_2^{+} + m\text{Cl}^{\bullet},$$

$$\text{M}^{(n-m)+} + m\text{Cl}^{\bullet} \rightleftharpoons \text{M}^{n+} + m\text{Cl}^{-},$$

where M = Sb; *n* and *m* = 3.

Table 5. Catalytic properties of the catalysts in the benzylation of benzene with benzyl chloride at 353 K, Bz/BzCl ratio = 15 and m_{cat} = 0.1 g

Catalyst	Time*, min	Selectivity, %		Apparent rate constant, $k_a \times 10^3$, min^{-1}
		diphenylmethane	polybenzylbenzene	
SBA-15	–	–	–	–
Sb-SBA-15 (55)	–	–	–	–
Sb-SBA-15 (35)	16.7	99.2	0.8	186.6
Sb-SBA-15 (15)	14.8	88.8	11.2	200.5

* Time required for 90% conversion of benzyl chloride.

The redox mechanism is similar to that proposed earlier for the benzene benzylation [13] and alkylation or acylation reactions [15, 21, 37]. Furthermore, in order to rule out the influence of a steric effect on the rate of reaction, we have applied the Taft relation [38]. According to this relation when a steric effect influences the reaction, there is a linear relation between the rate and the parameter E_s values considered to be representative of the size of the substituting group of the studied aromatic compounds. Using the E_s parameter tabulated by Charton [39] we have shown that such a relation did not exist. It was interesting to compare the solids with Sb-exchanged clays (K10-Sb calcined at 393 and 823 K) investigated earlier under similar conditions [16]. The Sb-SBA-15 is more active than K10-Sb. Indeed, the time required for the complete conversion of benzyl chloride was about 30 min for K10-Sb calcined at 393 K and 300 min for K10-Sb calcined at 823 K and was here about 16.7 min.

On the other hand, a comparison of the catalytic properties of the solids tested is presented in Table 5. The pure silicic compound (SBA-15) and the compound containing less antimony (Sb-SBA-15 (55)) were totally inactive. The other compounds showed an activity increasing with their antimony content. However, the selectivity to diphenylmethane at complete conversion of benzyl chloride decreased while the Sb content increased.

3.3. Effect of Solvent

To understand the role of solvent in benzylation of benzene by antimony-containing samples with benzyl chloride, the reaction was carried out with different solvents, such as dichloroethane and n-heptane. The reaction conditions and the results of benzene benzylation with Sb-SBA-15 (35) catalyst are presented in Table 6. The reaction rate is highest in the absence of any solvent. It is decreased when the solvent (via dichloroethane and *n*-heptane) is used, the decrease is quite large when *n*-heptane is used as a solvent but it is small for dichloroethane as a solvent. The observed solvent effect on the reaction rate is expected because of the competitive adsorption of both the reactants and the solvent on the catalyst. The results show that between the two solvents, dichloroethane is a better solvent for the benzylation reaction.

3.4. Recycling of the Catalysts

The stability of the catalysts has been studied by running the reaction successively with the same catalyst (Sb-SBA-15 (35)) under the same conditions without any regeneration between two runs. The reaction was first run under the standard conditions (benzene to benzyl chloride ratio of 15, 353 K) to the complete conversion of benzyl chloride. Then after a period of 10 min another quantity of benzyl chloride was introduced in the reaction mixture leading to the same benzene to benzyl chloride ratio. After the achievement of the second run, the same protocol was repeated a second time. The results, presented in Table 7, showed that

Table 6. Effect of solvent on the conversion of benzyl chloride at 353 K in the benzylation of benzene over Sb-SBA-15 (35), reaction mixture is 15 ml of moisture-free liquid aromatic compound (or 2.5 ml of moisture-free aromatic compound mixed with 12.5 ml of moisture- free solvent) + 1.0 ml of benzyl chloride and amount of catalyst is 0.1 g

Solvent	Time*, min	Apparent rate constant, $k_a \times 10^3$, min^{-1}
Without solvent	16.7	186.6
Dichloroethane	18.6	171.0
n-Heptane	24.8	126.8

* Time required for 90% conversion of benzyl chloride.

Table 7. Effect of recycling of the catalysts in the benzylation of benzene with benzyl chloride at 353 K over Sb-SBA-15 (35), Bz/BzCl ratio = 15 and m_{cat} = 0.1 g

Catalyst	Time*, min	Selectivity, %		Apparent rate constant, $k_a \times 10^3$, min^{-1}
		diphenylmethane	polybenzylbenzene	
Fresh	16.7	99.2	0.8	186.6
First reuse	17.3	97.3	2.7	180.3
Second reuse	18.1	95.3	4.7	175.8

* Time required for 90% conversion of benzyl chloride.

the catalyst could be used several times in the benzene benzylation process without a significant change of its catalytic activity.

3.5. Applications to Other Aromatic Alkylations

The Sb-SBA-15 (35) catalyst has been used with success for the alkylation of benzenic compounds as illustrated in Table 4 and discussed above. More interesting is the observation that this catalyst is active and selective for larger molecules like naphthenic compounds such as 2-methylnaphthalene (Table 4). The large pores of the mesoporous support permit the conversion of these molecules that could not be done on other supports.

4. CONCLUSIONS

In conclusion, the study of the benzylation of benzene and other aromatics with benzyl chloride using the antimony-containing mesoporous SBA-15 shows that these catalysts display remarkable activities for the this reactions. The mechanism involves a redox step at the reaction initiation and gives a greater independence to the effect of substituents. These catalysts can therefore be used with substrates of low reactivity. Moreover, the large pores of the mesoporous catalyst do not limit the size of the molecules that could be reacted.

REFERENCES

1. Olah, G.A., *Friedel–Crafts Chemistry*, New York: Wiley, 1973.
2. Olah, G.A., Prakash, G.K.S.J., and Sommer, J., *Superacids*, New York: Wiley, 1985.
3. European Patent 0422986, 1991.
4. Clark, J.H., Cullen, S.R., Barlow, S.J., and Bastock, T.W., *J. Chem. Soc., Perkin Trans.*, 1994, p. 1117.
5. Cao, J., He, N., Li, C., Dong, J., and Xu, Q., *Mesoporous Mol. Sieves*, 1998, vol. 117, p. 461.
6. Choudhary, V.R., Jana, S.K., and Mamman, A.S., *Microporous Mesoporous Mater.*, 2002, vol. 56, p. 65.
7. He, N., Bao, S., and Xu, Q., *Appl. Catal., A*, 1998, vol. 169, p. 29.
8. Bachari, K., Millet, J.M.M., Benaichouba, B., Cherifi, O., and Figueras, F., *J. Catal.*, 2004, vol. 221, p. 55.
9. Choudhary, V.R. and Jana, S.K., *Appl. Catal., A*, 2002, vol. 224, p. 51.
10. Choudhary, V.R., Jana, S.K., and Narkhede, V.S., *Appl. Catal., A*, 2002, vol. 235, p. 207.
11. El Berrichi, Z., Cherif, L., Orsen, O., Fraissard, J., Tessonnier, J.P., Vanhaecke, E., Louis, B., Ledoux, M.J., and Pham-Huu, C., *Appl. Catal., A*, 2006, vol. 298, p. 194.
12. Bachari, K. and Cherifi, O., *J. Mol. Catal. A: Chem.*, 2006, vol. 253, p. 187.
13. Choudhary, V.R. and Jana, S.K., *J. Mol. Catal. A: Chem.*, 2002, vol. 180, p. 267.
14. Bachari, K. and Cherifi, O., *J. Mol. Catal. A: Chem.*, 2006, vol. 260, p. 19.
15. Choudhary, V.R. and Jana, S.K., *J. Catal.*, 2001, vol. 201, p. 225.
16. Deshpande, A.B., Bajpai, A.R., and Samant, S.D., *Appl. Catal., A*, 2001, vol. 209, p. 229.
17. Zhou, D.-Q., Yang, J.-H., Dong, G.-M., Huang, M.-Y., and Jiang, Y.-Y., *J. Mol. Catal. A: Chem.*, 2000, vol. 159, p. 85.
18. Choudhary, V.R., Jana, S.K., and Kiran, B.P., *J. Catal.*, 2000, vol. 192, p. 257.
19. Sabu, K.R., Sukumar, R., Rekha, R., and Lalithambika, M., *Catal. Today*, 1999, vol. 49, p. 321.
20. Izumi, Y., Ogawa, M., and Urabe, K., *Appl. Catal., A*, 1995, vol. 132, p. 127.
21. Cseri, T., Bekassy, S., Rizner, S., and Figueras, F., *J. Mol. Catal. A: Chem.*, 1995, vol. 98, p. 101.
22. Barlow, S.J., Bastock, T.W., Clark, J.H., and Cullen, S.R., *Tetrahedron Lett.*, 1993, vol. 34, p. 3339.
23. Bachari, K. and Cherifi, O., *Catal. Commun.*, 2006, vol. 7, p. 928.
24. Koyande, S.N., Jaiswal, R.G., and Jayaram, R.V., *Ind. Eng. Chem. Res.*, 1998, vol. 37, p. 908.
25. Cog, B., Gourves, V., and Figueras, F., *Appl. Catal., A*, 1993, vol. 100, p. 69.
26. Narender, N., Krishna Mohan, K.V.V., Kulkarni, S.J., and Ajit Kumar Reddy, I., *Catal. Commun.*, 2006, vol. 7, p. 583.
27. Choudhary, V.R., Jana, S.K., and Kiran, B.P., *Catal. Lett.*, 1999, vol. 59, p. 217.
28. Salavati-Niasari, M., Hasanalian, J., and Najafian, H., *J. Mol. Catal. A: Chem.*, 1995, vol. 125, p. 33.

29. Choudhary, V.R., Jana, S.K., and Kiran, B.P., *Catal. Lett.*, 2000, vol. 64, p. 223.
30. Maria, D.A., Luan, Z.H., and Klinowski, J., *J. Phys. Chem.*, 1996, vol. 100, p. 2178.
31. Das, T.K., Chaudhari, K., Chandwadkar, A.J., and Sivasanker, S., *J. Chem. Soc., Chem. Commun.*, 1995, p. 2495.
32. Kitayama, Y., Asano, H., Kodama, T., Abe, J., and Tsuchiya, Y., *J. Porous Mater.*, 1998, vol. 5, p. 139.
33. Thangaraj, A., Kumar, R., Mirajkar, S.P., and Ratnasamy, P., *J. Catal.*, 1991, vol. 130, p. 1.
34. Sen, T., Chatterjee, M., and Sivasanker, S., *J. Chem. Soc., Chem. Commun.*, 1995, p. 207.
35. Chaudhari, K., Das, T.K., Rajmohanan P.R., Lazar, K., Sivasanker, S., and Chandwadkar, A.J., *J. Catal.*, 1999, vol. 183, p. 281.
36. Sayari, A., *Chem. Mater.*, 1996, vol. 8, p. 1840.
37. Brio, K., Bekassy, S., Agai, B., and Figueras, F., *J. Mol. Catal. A: Chem.*, 2001, vol. 151, p. 179.
38. March, J., *Advanced Organic Chemistry*, New York: Wiley, 1985.
39. Charton, B., *J. Am. Chem. Soc.*, 1975, vol. 97, p. 1552.