

# Comparative study of benzylation of benzene using benzyl chloride in the presence of pillared bentonite; ion-exchanged and pillaring solution impregnated montmorillonite K10

Devendrapratap U. Singh, Shriniwas D. Samant\*

Organic Chemistry Research Laboratory, University Institute of Chemical Technology, N.M. Parikh Marg, Matunga, Mumbai 400 019, India

Received 8 February 2003; received in revised form 24 August 2003; accepted 30 September 2003

Available online 16 September 2004

## Abstract

Montmorillonite K10 was modified with pillaring solutions of Fe, Al and Zr (K10-MPLS). The catalysts were activated at 120 and 550 °C. The resultant catalysts were used for the Friedel–Crafts benzylation of benzene with benzyl chloride under mild experimental conditions. Amongst them, K10-FePLS120 catalyst showed both high activity and selectivity for the benzylation reaction at room temperature (28 °C). The catalyst can also be reused in the benzylation for several times. The activities of these catalysts were compared with those of Fe<sup>3+</sup>-, Al<sup>3+</sup>- and Zr<sup>4+</sup>-exchanged montmorillonite K10 and Fe-, Al- and Zr-pillared bentonite catalysts. The benzylation of various monosubstituted benzenes was carried out using K10-FePLS120.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Pillaring solution modified K10; Ion exchange; Pillared clays; Friedel–Crafts benzylation; Benzyl chloride; Diphenylmethane

## 1. Introduction

Friedel–Crafts reaction is ubiquitous in fine chemicals, intermediates and petrochemical industries. Strongly acidic catalysts are normally employed in the Friedel–Crafts reaction. However, not only are polyalkylations and rearrangements generally difficult to avoid [1], but also these homogeneous catalysts (e.g. HF, AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, BF<sub>3</sub>) pose several problems such as difficulty in the separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. Development of reusable “environment friendly solid acid catalysts”, having high activity in the Friedel–Crafts reaction is, therefore, of great practical importance. Hence, efforts are being made to replace homogeneous acid catalysts by solid acid catalysts, such as sulfated zirconia [2], zeolites [3], metal cation exchanged clay [4,5], pillared clays [6] and heteropoly acids [7]. Good results have been obtained using zinc chloride impregnated montmorillonite K10, called

clayzic [8]. It is the most effective catalyst to catalyze alkylation of aromatic hydrocarbons and the process has been commercialized. Fe-containing molecular sieves catalysts, reported by Nongue et al. [9] are very active benzylation catalysts, with a monobenzylated product selectivity of 100%, and better thermal stability (>850 °C). Cseri et al. [5] used ion-exchanged K10 in the alkylation of aromatic hydrocarbons. Among these catalysts, the superiority of Fe<sup>3+</sup> cations over Al<sup>3+</sup> cations was surprising; particularly on the background of the reversal of reactivity in their homogeneous counterparts. It indicated that the catalysts containing reducible cations (Fe<sup>3+</sup>, Sn<sup>4+</sup>, Cu<sup>2+</sup>) exhibited high activity, in spite of their low number of Lewis acid sites when benzyl chloride was used as the alkylating agent. Hence, a redox mechanism has been proposed for the benzylation reaction, as against the conventional carbenium ion mechanism.

Pillared clays find wide applications in the field of catalysis [10,11]. Choudary et al. reported iron-pillared clays (Fe-PILCs) [6] as efficient catalysts for benzylation reaction of arenes with benzyl chloride. These catalysts exhibited conversion with a greatly reduced amount of catalyst

\* Corresponding author. Tel.: +91 22 24145616; fax: +91 22 24145614.  
E-mail address: [samantsd@udct.org](mailto:samantsd@udct.org) (S.D. Samant).

in a shorter reaction time. However, Fe-PILCs, as investigated by Pinnavaia and coworkers [12], are quite labile even under ambient conditions. Aging the material for a period of 3 months at 25 °C resulted in the loss of 001 ordering due to redistribution of iron and the concomitant change in the degree of cation polymerization. X-ray energy disperse spectroscopy indicated that some iron migrates to the particle edges upon aging. This lability will lead to trouble in applications, like redistribution in gallery height, resulting from the redistribution of iron and will influence the selectivity of reaction products. In view of this, we decided to modify montmorillonite K10 by impregnating K10 with the pillaring species of different metal ions (K10-MPLS). The procedure used was expected to lead to the impregnation of polyoxocations of different metal ions on the surface of K10. This approach offers several advantages over pillared clays (PILCs): (1) the time required for the preparation of the catalyst is less as compared to the time required for the preparation of PILCs; (2) drastic reduction in the metal ion/clay ratio and (3) less amount of water to be handled. We have recently reported high activity of K10-FeO120 and K10-FeA120 for the Friedel–Crafts benzylation of benzene with benzyl chloride [13]. In addition to this, the effect of activation temperature on the catalytic activity was also studied. We compared the activity of the pillaring species-impregnated catalysts (K10-MPLS) with metal ion-exchanged catalysts (K10-MA) and pillared catalysts (M-PILCs), using the benzylation reaction of benzene with benzyl chloride as a probe reaction.

## 2. Experimental

### 2.1. Preparation of catalysts

Montmorillonite K10 was obtained from M/s. Aldrich (manufactured by Sud-Chemie AG). The chemical composition (wt.%) of the clay (main elements) was Al<sub>2</sub>O<sub>3</sub>: 14.6; SiO<sub>2</sub>: 67.6; Fe<sub>2</sub>O<sub>3</sub>: 2.9; MgO: 1.8. The BET surface area was 220 ± 20 m<sup>2</sup>/g and the micropore volume was 0.1 m<sup>3</sup>/g. Bentonite was also obtained from M/s. Aldrich. The chemical composition (wt.%) of the bentonite clay (main elements) was Al<sub>2</sub>O<sub>3</sub>: 20.10; SiO<sub>2</sub>: 70.9; Fe<sub>2</sub>O<sub>3</sub>: 3.38; MgO: 2.5; CaO: 1.27. The BET surface area was 26.6 m<sup>2</sup>/g.

*Metal pillared clay.* Al, Zr [14] and Fe-pillared bentonite [12] were prepared as reported in the literature.

*K10-MPLS catalyst.* Pillaring solutions (500 ml) of Al, Zr [14] and Fe [12] were prepared. Montmorillonite K10 (10 g) was added to it over a period of 10 min. The resultant slurry was stirred at room temperature for 5 h. The clay was filtered, washed with deionized water till free from Cl<sup>-</sup> ions, dried in an oven at 80 °C and crushed to a fine powder.

*K10-MA catalyst.* To an anhydrous metal chloride (15 g), dissolved in deionized water (60 ml), montmorillonite K10 (10 g) was added over a period of 10 min. The resultant slurry was stirred at room temperature for 5 h. The clay was filtered,

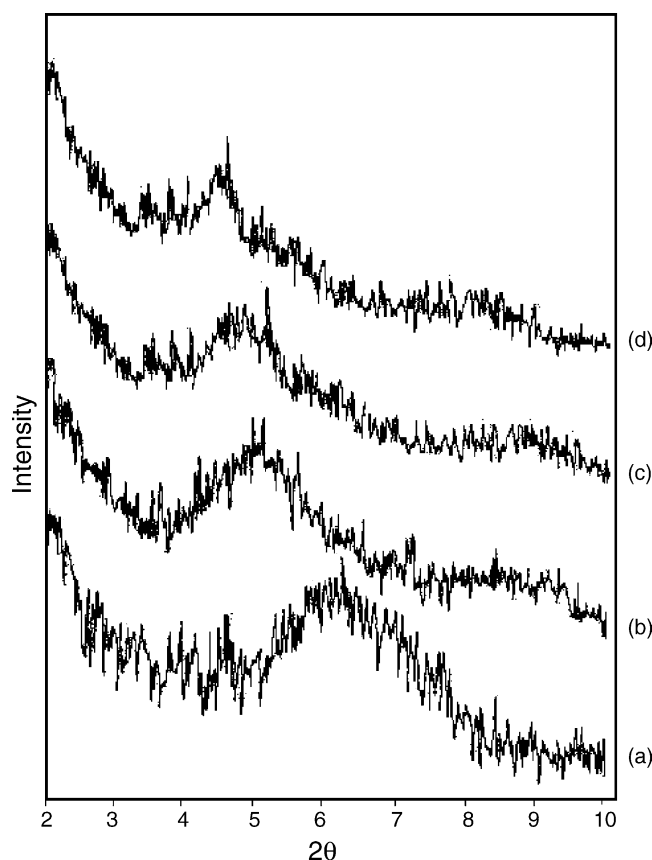


Fig. 1. X-ray diffraction pattern of: (a) Na-bentonite; (b) Al-pillared bentonite; (c) Zr-pillared bentonite; (d) Fe-pillared bentonite.

washed with deionized water till free from Cl<sup>-</sup> ions, dried in an oven at 80 °C, and crushed to a fine powder. Each catalyst was activated at 120 and 550 °C for a period of 5 h. The catalysts were then preserved in a vacuum desiccator and used when necessary after overnight activation at 120 °C.

### 2.2. Characterization

Powder X-ray diffraction patterns of pillared bentonite catalysts (Fig. 1) and pillaring solution impregnated montmorillonite K10 (Fig. 2) were recorded on a JEOL JDX-8030 X-ray diffractometer using Cu Kα radiation. Fig. 1 confirms the pillaring and shows the basal spacing in the range of 18–20 Å. Fig. 2 shows no pillaring effect, and confirms the impregnation of the pillaring species on the surface of montmorillonite K10.

Fe<sup>3+</sup> content of the catalysts (Table 1) was determined as reported by Cheng et al. [15].

### 2.3. Reactions

All the reactions were carried out in a round bottom flask (25 ml), equipped with a reflux condenser, a calcium chloride guard tube, a magnetic stirrer and a provision for sample withdrawal.

Table 1  
Benzylation of benzene with benzyl chloride at 80 °C

Catalyst	Fe (%)	Time (min)	Conversion of BzCl (%)	Monobenylation (%)	Dibenylation (%)
K10-FeA120	1.12	15	100	93.8	6.2
K10-FePLS120	4.8	2	100	90.1	9.9
Fe-PILC120	20.6	5	100	91.2	8.8

Substrate = 10 mL, benzyl chloride = 6.25 mmol (0.72 mL), catalyst = 0.1 g.

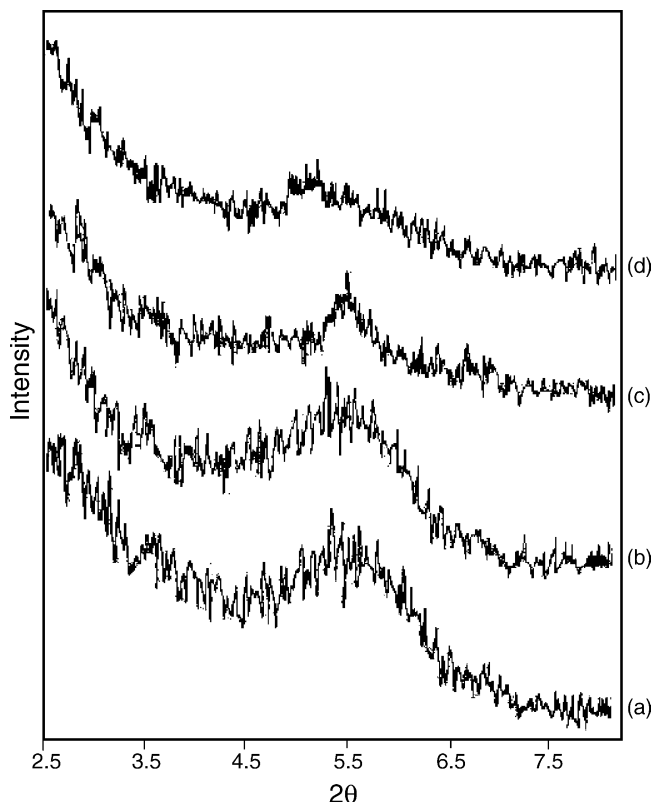


Fig. 2. X-ray diffraction pattern of: (a) K10; (b) K10-AIPLS; (c) K10-ZrPLS; (d) K10-FePLS.

To a catalyst (0.1 g) preactivated overnight in air at 120 °C, in the reaction flask itself, an arene (10 ml) and benzyl chloride (0.72 ml, 6.25 mmol) were added and the flask heated in a thermostated oil bath, preset at 80 °C. The 0.2 ml of the reaction mixture was accurately withdrawn at specific time intervals and filtered through a sintered glass funnel (G-4). The catalyst was washed with acetone, and the filtrate, after making-up the volume to 1 ml, was analyzed using a GC (Chemito 2865 Gas Chromatograph), equipped with flame ionization detector, 10% OV-17 column (Scheme 1).

### 3. Results and discussion

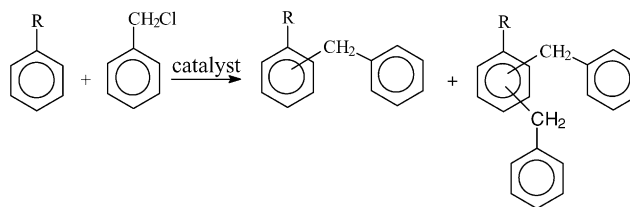
The Fe-, Al- and Zr-pillaring solution impregnated montmorillonite K10 catalysts were compared with ion-exchanged montmorillonite K10 and pillared bentonite catalysts for their performance in catalyzing the benzylation of benzene with benzyl chloride at 80 °C (Table 2). The pillaring solution im-

pregnated montmorillonite K10 catalysts were found to be superior than the other catalysts. K10-FePLS120 was found to be the most active catalyst (100% conversion of benzyl chloride in ~2 min at 80 °C), whereas, K10-FeA120 and Fe-PILC120 required 15 and 5 min, respectively, for the complete conversion of benzyl chloride. With K10-AIPLS120 and K10-ZrPLS120 the reaction was slower, but these catalysts showed better activity as compared to the corresponding ion-exchanged and pillared catalysts.

#### 3.1. Effect of activation on the acidity of the catalysts

Purnell et al. [16] have reported the effect of thermal treatment on the nature of acidity and catalytic properties of metal cation exchanged clays. The calcination of such catalysts was found to suppress both the Lewis and Bronsted acidity. However, the decrease in the Bronsted acidity is more pronounced than in the Lewis acidity. When the clay is calcined at 500 °C and above, it shows only Lewis acidity. Figueras et al. [17] have shown that major structural changes occur in K10 when it is subjected to heat treatment at higher temperatures. The exchangeable cations present in the interstitial spaces of the clay may get incorporated into the structural framework of the clay. The obvious effect of this behavior was that, the reactive species that are present in the interstitial region, and are not accessible to the reactants to undergo reaction, lose their accessibility and thus, results in poor catalysis of the reaction. Thus, all the catalysts were calcined at 550 °C, to find the effect of calcination on the activities of catalysts. K10-FePLS550 required 30 min for the 100% conversion of the benzyl chloride, whereas K10-FeA550 and Fe-PILC550 required 120 and 45 min, respectively.

On the above background, it is easier for Fe in the case of K10-FeA and Fe-PILC to get incorporated into the structural framework than in the case of K10-FePLS. As a result, the accessibility of the reactive sites for the alkylating agent to form a complex and undergo reaction was more in the case of K10-FePLS than in K10-FeA and Fe-PILC.



R = -H, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, -CH(CH<sub>3</sub>)<sub>2</sub>, -OCH<sub>3</sub>, -Cl, -Br

Scheme 1. Friedel-Crafts benzylation of arenes with benzyl chloride.

Table 2  
Benzylation of benzene with benzyl chloride using different catalysts at 80 °C

Catalyst	Time (min)	Conversion of BzCl (%)	Selectivity (%)	
			Monobenylation	Dibenylation
K10-FePLS120	2	100	90.1	9.9
K10-AlPLS120	420	55.3	95.3	4.7
K10-ZrPLS120	420	93.1	91.4	8.6
K10-FeA120	15	100	93.8	6.2
K10-AlA120	420	32.0	100	0
K10-ZrA120	420	36.9	100	0
Fe-PILC120	5	100	91.2	8.8
Al-PILC120	420	16.4	98.8	0.2
Zr-PILC120	420	85.8	92	8
K10-FePLS550	30	100	94.9	5.1
K10-AlPLS550	420	7.6	100	0
K10-ZrPLS550	420	3.6	100	0
K10-FeA550	120	100	92.5	7.5
K10-AlA550	420	20.1	100	0
K10-ZrA550	420	8.53	100	0
Fe-PILC550	45	100	93.4	6.6
Al-PILC550	420	0.8	100	0
Zr-PILC550	420	10.0	100	0

Substrate = 10 mL, benzyl chloride = 6.25 mmol (0.72 mL), catalyst = 0.1 g.

### 3.2. Effect of metal

From the reduction potential values (Table 3), it can be seen that, the reduction potentials of  $\text{Al}^{3+}$  and  $\text{Zr}^{4+}$  are very low. Thus, it is difficult for  $\text{Al}^{3+}$  and  $\text{Zr}^{4+}$  to take part in a redox reaction and the reaction may proceed through the classical carbocation mechanism. This was indeed reflected in the low activity of K10-Al, K10-Zr, Al-pillared and Zr-pillared bentonite catalysts. The reduction potential of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is +0.771 eV. This value is much higher than the reduction potentials of  $\text{Al}^{3+}$  and  $\text{Zr}^{4+}$ . On the basis of the high reduction potential of  $\text{Fe}^{3+}$  and the unusually high activity of K10-Fe and Fe-pillared catalysts as compared to other metals used, it is likely that the reaction might be proceeding through a redox mechanism.

### 3.3. Effect of $\text{Fe}^{3+}$ content and the active species

The iron content of different catalysts is shown in Table 1. It should be noted that even though the  $\text{Fe}^{3+}$  content in K10-FePLS120 is much less than in Fe-PILC120, the former was found to be a better catalyst than the latter. This can be explained on the basis of the better accessibility of polyoxocations of Fe on the surface of montmorillonite K10 (K10-FePLS120) than in Fe-PILC120, where polyoxocations are

Table 3  
Comparison of the ionic radius and reduction potential of various metal ions

Cation	Ionic radius (Å)	Reduction potential (eV)	
		Reduced species	Potential
$\text{Fe}^{3+}$	0.64	$\text{Fe}^{2+}$	+0.771
$\text{Al}^{3+}$	0.51	Al	-1.662
$\text{Zr}^{4+}$	0.79	Zr	-1.55

present between the layers of the bentonite. Choudary et al. have emphasized the importance of polyoxocations in the benzylation reaction [6] by comparing Fe-pillared clay with  $\text{Fe}^{3+}$ -exchanged clay. Fe-pillared clay is more active than  $\text{Fe}^{3+}$ -exchanged clay, although both of these catalysts contain the same amount of Fe.

### 3.4. Effect of reaction temperature

At 80 °C, all the three catalysts, viz. K10-FePLS120, K10-FeA120 and Fe-PILC120, were equally effective and gave 100% conversion of benzyl chloride in relatively less time; therefore, the comparison of the catalysts was not meaningful at 80 °C. Hence, we carried out the reaction at lower temperatures of 60, 40 °C and RT (28 °C) (Table 4). At 60 and 40 °C, K10-FePLS120 and Fe-PILC120 catalysts, showed 100% conversion of benzyl chloride in 5 min, whereas K10-FeA120 required 420 min for the complete conversion of benzyl chloride at 60 °C. K10-FeA120 showed a marked difference in its activity at 40 °C and only 9% conversion of benzyl chloride was achieved in 420 min. As K10-FePLS120 and Fe-PILC120, both showed good activity at 40 °C, we decided to carry out the reaction at room temperature. At room temperature (28 °C), the results were surprising. K10-FePLS120 and Fe-PILC120 showed 100% conversion of benzyl chloride in 5 and 10 min, respectively.

From the above observations, K10-FePLS120 was found to be the best catalyst for this reaction. Using this catalyst, the benzylation of substituted benzenes was carried out at 80 °C. Conversion and *ortho/para* selectivity observed in these reactions are shown in Table 5. The 100% conversion of benzyl chloride was achieved within 15 min with good *para*-selectivity, without formation of the dibenzylated products.

Table 4  
Mono- and dibenylation of benzene in the reaction of benzene with benzyl chloride at different temperatures

Catalyst	Room temperature		40 °C		60 °C		80 °C					
	Conversion of BzCl (%)	Selectivity (%)		Conversion of BzCl (%)	Selectivity (%)		Conversion of BzCl (%)	Selectivity (%)				
		Mono	Di		Mono	Di		Mono	Di			
K10-FePLS120	100 (5)	98.6	1.4	100 (5)	91.0	9.0	100 (5)	96.5	3.5	100 (2)	90.1	9.9
K10-FeA120	–	–	–	9.1 (420)	100	0	100 (420)	95.9	4.1	100 (15)	93.8	6.2
Fe-PILC120	100 (10)	98.7	1.3	100 (5)	96.6	3.4	100 (5)	91.1	8.9	100 (5)	91.2	8.8

Figures in parentheses indicate the time in min.

Table 5  
Benzylation of monosubstituted aromatic compounds with benzyl chloride using K10-FePLS120 at 80 °C

Substrate	Selectivity (%) <sup>a</sup>		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Toluene	36.3	0	63.7
Ethylbenzene	35.3	0	64.7
Cumene	16.8	15.1	68.1
Anisole	44.0	0	56.0
Chlorobenzene	21.6	0	78.4
Bromobenzene	35.6	0	64.4

Substrate = 10 mL, benzyl chloride = 6.25 mmol (0.72 mL), catalyst = 0.1 g, time = 15 min, conversion of BzCl = 100%.

<sup>a</sup> Dibenylation did not take place.

### 3.5. Recyclability

Recyclability of the catalyst was studied up to five cycles (Table 6), using K10-FePLS120 at 80 °C. The catalyst after completion of each cycle was recovered by filtration and used for the next cycle after activation at 120 °C overnight. K10-FePLS120 showed 100% conversion of benzyl chloride in each cycle, within 5 min without loss of activity and selectivity.

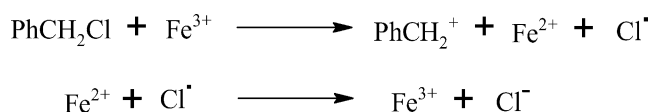
### 3.6. Mechanism

Cseri [18] suggested the possibility of a redox mechanism, because the catalyst containing reducible cations (Fe<sup>3+</sup>, Sn<sup>4+</sup>, Cu<sup>2+</sup>) exhibited high activity, in spite of the low number of Lewis acid sites when benzyl chloride was the alkylating agent. The existence of radicals was substantiated by ESR study carried out by Cativiela et al. [19]. In consonance with this, the high activity observed with the reducible cations (Fe<sup>3+</sup>) could be ascribed to a different initiation of the reac-

Table 6  
Recyclability of K10-FePLS120 catalyst

Cycle number	Conversion of benzyl chloride (%)	Monobenzylation (%)	Dibenzylation (%)
1	100	91.6	8.4
2	100	94.9	5.1
3	100	95.6	4.4
4	100	94.7	5.3
5	100	90.0	10.0

Substrate = 10 mL, benzyl chloride = 6.25 mmol (0.72 mL), catalyst = 0.1 g, time = 5 min.



Scheme 2. Proposed redox mechanism.

tion, for instance homolytic rupture of the carbon–chlorine bond followed by the oxidation of the radical (Scheme 2).

## 4. Conclusion

Pillaring species supported montmorillonite K10 catalysts were more active than their ion-exchanged and pillared counterparts. Among them the activity and selectivity of K10-FePLS120 was found to be the best. The high activity of the K10-FePLS120 was ascribed to better accessibility of Fe-polyoxocations supported on the surface of montmorillonite K10. The catalyst was found to be recyclable.

## Acknowledgements

The authors are grateful to TIFR, Mumbai, for XRD facility. DUS is grateful to G.D. Gokhale Charitable Trust for a fellowship.

## References

- [1] G.A. Olah, Friedel–Crafts Chemistry, Wiley, New York, 1973.
- [2] G.D. Yadav, T.S. Thorat, P.S. Kumbhar, Tetrahedron Lett. 34 (1993) 529.
- [3] B. Coq, V. Gourves, F. Figueras, Appl. Catal. A 100 (1993) 69.
- [4] P. Laszlo, A. Mathy, Helv. Chim. Acta 70 (1987) 577.
- [5] T. Cseri, S. Bekassy, F. Figueras, S. Rinzer, J. Mol. Catal. A: Chem. 98 (1995) 101.
- [6] B.M. Choudary, M.L. Kantam, M. Sateesh, K.K. Rao, P.L. Santhi, Appl. Catal. A: Gen. 149 (1997) 257.
- [7] Yusuke, O. Mayumi, U. Kazuo, Appl. Catal. A 132 (1995) 127.
- [8] J.H. Clark, S.R. Cullen, S.J. Barlow, T.W. Bastock, J. Chem. Soc., Perkin Trans. 2 (1994) 117.
- [9] H. Nongue, B. Shulin, X. Qinhua, Appl. Catal. A: Gen. 169 (1998) 29.
- [10] R. Burch (ed), Catal. Today 2 (2–3) (1988) 185–366.
- [11] R. Molina, A. Schutz, G. Poncelet, J. Catal. 145 (1994) 79.
- [12] E.G. Rightor, M.S. Tzou, T.J. Pinnavaia, J. Catal. 130 (1991) 29.

- [13] S.G. Pai, A.R. Bajpai, A.B. Deshpande, S.D. Samant, *J. Mol. Catal. A: Chem.* 156 (2000) 233.
- [14] W. Matthes, F.T. Madsen, G. Kahr, *Clays Clay Miner.* 47 (5) (1999) 617.
- [15] K.L. Cheng, T. Kurtz, R.H. Brag, *Anal. Chem.* 24 (1952) 1640.
- [16] J.H. Purnell, J.M. Thomas, P.A. Diddams, J.A. Ballantine, W. Jones, *Catal. Lett.* 2 (1989) 125.
- [17] F. Figueras, C. Cativiela, J.M. Fraile, J.I. Gracia, J.A. Mayoral, L.C. Menorval, E. Pires, *Stud. Surf. Sci. Catal.* 83 (1994) 391.
- [18] T. Cseri, S. Bekassy, F. Figueras, E. Cseke, L.C. de Menorval, R. Dutartre, *Appl. Catal. A: Gen.* 132 (1995) 141.
- [19] C. Cativiela, J.M. Fraile, J.I. Mayoral, F. Figueras, L.C. de Menorval, P.J. Alonso, *J. Mol. Catal.* 137 (1992) 394.