

Regioselective *ortho*-C-cyclohexylation of phenols with cyclohexanol in the presence of transition metal modified zeolite-H β

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Abstract

The cyclohexylation of various phenols with cyclohexanol as an alkylating agent in the presence of Ti⁴⁺, Sb³⁺, Fe³⁺, Sn⁴⁺, Al³⁺, and Zr⁴⁺ metal modified zeolite-H β catalysts was carried out. The best catalyst was Sn⁴⁺ exchanged H β , activated at 120 °C (H β -SnA120), which displayed a selectivity of more than 95% towards 2-cyclohexylphenol. The reaction was found to proceed through the formation of cyclohexyl phenyl ether. Cyclohexylation of different phenols has also been studied.

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Keywords: Cyclohexylation; 2-Cyclohexylphenol; Ion-exchanged; Zeolite-H β

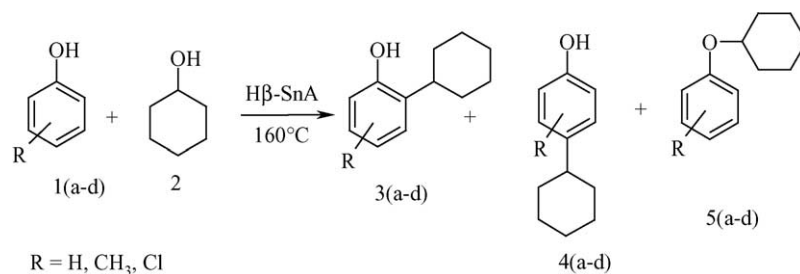
1. Introduction

Since its discovery in 1877 [1–3], Friedel–Crafts alkylation has been recognized as one of the most important tools for introducing an alkyl substituent into an aromatic ring [4,5]. Various transition metal halides (AlCl₃, FeCl₃, SnCl₄, and TiCl₄) are used as Lewis acids for the alkylation reaction. Use of these conventional catalysts has various disadvantages, like tedious work-up procedure, non-reusability, formation of hazardous side products, and mainly lack of selectivity. These disadvantages can be minimized by using solid acid catalysts. Particularly, zeolites have proved to be versatile catalysts in the petrochemical industry and in the manufacture of fine chemicals and chemical intermediates, as highly shape-selective catalysts [6–11]. Since the last decade, our group has been working towards the development of environmentally benign acidic catalysts for the Friedel–Crafts reaction [12–16].

Alkylated phenols and their derivatives are of great commercial importance, having a variety of applications in

the surfactant, dyestuff and the pharmaceutical industries [17]. 2-Cyclohexylphenol is an important intermediate in dyestuff preparation. It is also useful in the preparation of 2-phenylphenol, which is an important disinfectant as well as fungicide. There are reports of cyclohexylation of phenol using cyclohexene, many of which are vapour phase reactions [18–21]. When the alkylation of phenol by cyclohexene is carried out at a low-temperature cyclohexyl phenyl ether is the predominant product [22]. However, not much work has been reported on the alkylation of phenol using cyclohexanol. Very few catalysts have been used for the alkylation of phenol using cyclohexanol, such as cation-exchange resin KU-2, H β -zeolite and other conventional Lewis and Brønsted acids [23–25]. Also, the reported methods show a maximum of 60% selectivity for 2-cyclohexylphenol. It is well known that in the alkylation of phenol, C-alkylation requires stronger acid sites than those for O-alkylation [26,27]. In the cyclohexylation of phenol, the crucial point is the regioselectivity. In the present work, we have modified H β -zeolite through aqueous ion exchange with Ti⁴⁺, Sb³⁺, Fe³⁺, Sn⁴⁺, Al³⁺, and Zr⁴⁺ cations and used the resulting catalysts for the C-cyclohexylation of phenols with cyclohexanol (Scheme 1). The reaction is completed to form three products, 3–5.

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Scheme 1. cyclohexylation of phenol by cyclohexanol using H β -SnA catalyst.Table 1
Characterization of the ion-exchanged catalysts

Catalyst	Metal content (%)	Surface area (m ² /g)	Pore diameter (Å)	Total pore volume (cm ³ /g)	Ionic radius of metal (pm)	Electronegativity of metal cation on pauling scale (eV)
H β -120	–	510.5	17.5	0.217		
H β -SnA120	6.7	454.6	33.5	0.380	83.0	1.96
H β -SbA120	9.4	332.6	47.7	0.397	74.0	2.05
H β -ZrA120	6.9	425.5	41.3	0.365	86.0	1.33
H β -AlA120	8.3	415.6	38.7	0.345	67.5	1.61
H β -TiA120	6.3	417.9	39.9	0.417	74.5	1.54
H β -FeA120	9.1	351.4	35.5	0.312	78.5	1.83

2. Experimental

2.1. Catalyst preparation

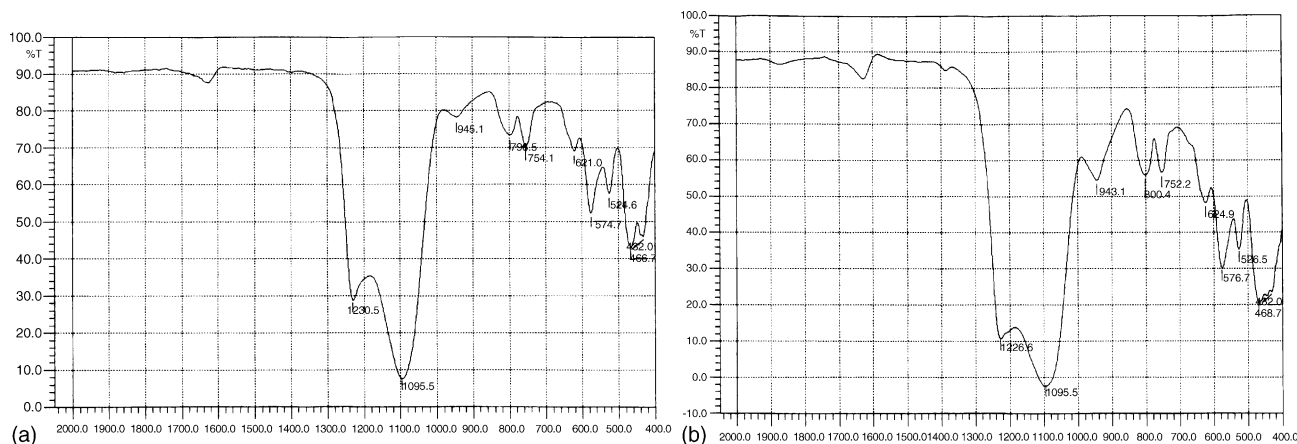
To an anhydrous metal chloride (15 g) dissolved in deionized water, H β -zeolite (10 g) (Sud-chemie, SiO₂/Al₂O₃ = 15) was added over a period of 10 min. The slurry was stirred at room temperature (30 °C) for 5 h. The resultant catalyst was filtered, washed with deionized water till free from Cl⁻ ions and activated at 120 °C to obtain H β -MA120 (M = metal) catalyst. Thus, a series of catalysts was prepared by exchanging Ti⁴⁺, Sb³⁺, Fe³⁺, Sn⁴⁺, Al³⁺, and Zr⁴⁺ ions with H β -zeolite. The catalyst were preserved in a desiccator and used after activation at 120 °C overnight in the reaction flask itself.

2.2. Catalyst characterization

The metal-exchanged H β -zeolites were characterised for the properties surface area, pore volume, pore diameter (BET analysis), amount of each metal exchanged (ICP analysis), with the ionic radius and the electro-negativity of the respective cations (Table 1).

The most active catalyst H β -SnA120 was further characterized by FT-IR, XRD, ¹¹⁹Sn NMR techniques.

The FT-IR of H β and H β -SnA120 catalyst were recorded using a Shimadzu 3800 FT-IR spectrophotometer. There is no significant change in the spectra of H β -zeolite and that of H β -SnA120 (Fig. 1). Hence, we may say that the metal ion incorporated had not formed bonds with a metal (Al/Si) present in the zeolite.

Fig. 1. FT-IR spectra of: (a) H β catalyst and (b) H β -SnA120.

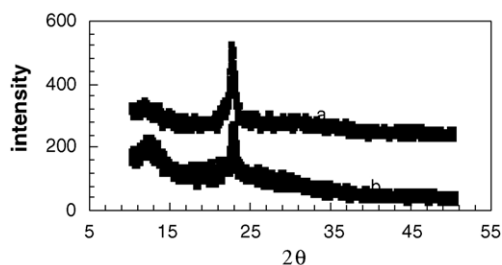


Fig. 2. XRD pattern of zeolite-H β (a) and H β -SnA120 (b).

Powder XRD patterns were recorded using a JEOL JDX-8030 X-ray diffractometer, using Cu K α radiation. There was no significant change in the XRD pattern of H β -SnA120 with respect to parent H β -zeolite (Fig. 2), and the crystallinity of the zeolite was maintained after modifying it with the metal ions.

Solid state ^{119}Sn NMR was recorded using a Bruker MSL-300 NMR spectrometer, ^{119}Sn Larmor frequency = 111.921 MHz, pulse length = 2 μs , recycle delay = 4 s, number of scans = 2000 for SnO $_2$ and 14,000 for zeolite, signal chemical shift in the spectra were with respect to tetramethyl tin [(CH $_3$) $_4$ Sn]. The solid state NMR of Sn modified zeolite and that of SnO $_2$ were taken together to compare the oxidation state and the environment in which Sn was present (Fig. 3). ^{119}Sn NMR showed an isotropic chemical shift at $\delta = -604$ ppm which indicated the presence of Sn in essentially octahedral environment [28].

2.3. Cyclohexylation reaction

The reaction was carried out in a 50 cm 3 round-bottomed two-necked flask attached with a reflux condenser and a CaCl $_2$ guard tube. To the activated catalyst (0.2 g) in the flask, phenol (10 cm 3) and cyclohexanol (1.0 cm 3) were added, and the contents were stirred in an oil bath thermostated at 160 $^\circ\text{C}$. The progress of the reaction was monitored using a

Table 2

The reaction of phenol with cyclohexanol in the presence of different catalysts

Catalyst	Time (min)	C-Mono-alkylated product (%)	Regio-selectivity (%)	
			<i>ortho</i>	<i>para</i>
H β -120	180	93.4	53	47
H β -SnA120	60	87.5	95	5
H β -SbA120	240	88.4	93	7
H β -ZrA120	330	76.2	58	42
H β -AlA120	180	78.6	53	47
H β -TiA120	300	88.1	88	12
H β -FeA120	240	73.4	53	47

Reaction conditions: phenol = 10 mL, cyclohexanol = 10 mmol (1.0 mL), catalyst = 0.2 g, temperature = 160 $^\circ\text{C}$.

gas chromatograph (Chemito 2865) equipped with 10% OV-17 column and FID.

3. Results and discussion

The reaction of phenol (**1a**) with cyclohexanol (**2**) was studied with respect to different parameters. The reaction can give cyclohexyl phenyl ether (**5a**), besides the regioisomers (**3a**) and (**4a**). Dicyclohexylation was found to be negligible.

3.1. Effect of metal cations

To compare the activity of the metal cations, the reaction was carried using the catalysts at 160 $^\circ\text{C}$ (Table 2). In the conversion of cyclohexanol to the C-alkylated product (**3a** + **4a**), cyclohexyl phenyl ether (**5a**) was also formed. **5a** may eventually may converted to **3a** + **4a** by the acidic catalyst. Hence, each reaction was monitored till complete conversion of cyclohexanol as well as cyclohexyl phenyl ether. Although H β -zeolite gave 93% monoalkylated product it displayed only 53% selectivity towards 2-cyclohexylphenol. On the other hand, H β -SnA120 and H β -SbA120 gave 87–88% monoalkylated product and also showed high selectivity of

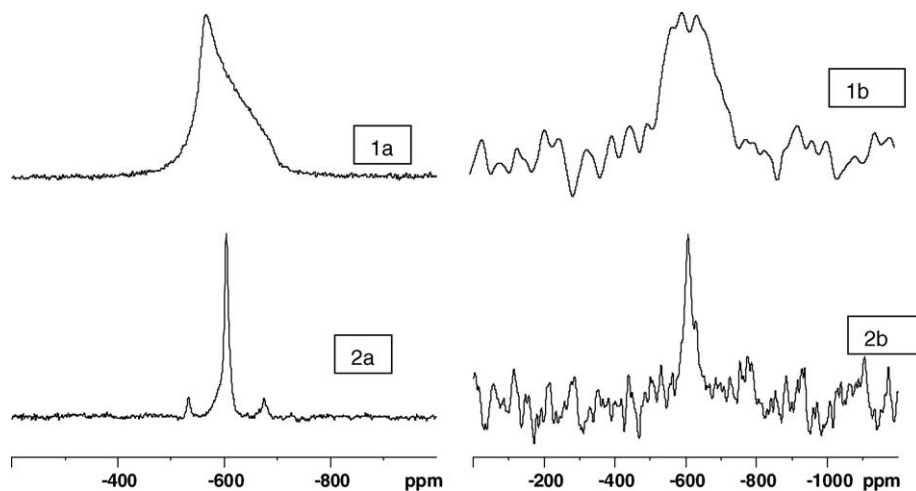


Fig. 3. The static and MAS ^{119}Sn NMR of SnO $_2$ (**1a** and **1b**) and H β -SnA120 (**2a** and **2b**), respectively.

Table 3

The reaction of phenol with cyclohexanol in the presence of different catalysts

Catalyst	Time (min)	C-Mono-alkylated product (%)	Regio-selectivity (%)	
			<i>ortho</i>	<i>para</i>
H β -SnA550	180	85.6	93	7
H β -SbA550	300	88.4	93	7
H β -ZrA550	300	60.8	61	39
H β -AlA550	300	71.1	67	33
H β -TiA550	300	69.5	62.4	37.6
H β -FeA550	300	65.2	54.1	45.9

Reaction conditions: phenol = 10 mL, cyclohexanol = 10 mmol (1.0 mL), catalyst = 0.2 g, temperature = 160 °C.

95 and 93%, respectively, towards 2-cyclohexylphenol with complete conversion of cyclohexanol. The other catalysts did not show such a high selectivity. In the preparation of the Sb catalyst, a large volume of HCl was required and Sb³⁺ cations are toxic in nature. Hence, for further study we used H β -SnA120 catalyst. Among the cations the electronegativity of Sn is 1.93 eV (Pauling scale) which is higher than those of all the other metals with the exception of Sb which has 2.05 eV. This could be the reason of the highest activity and concomitantly selectivity of H β -SnA120.

All these catalysts were also activated at 550 °C to determine the effect of activation temperature. However, the catalysts activated at 550 °C were found to be less active as compared to the catalysts activated at 120 °C (Table 3).

Cseri has reported that the alkylation using alcohols requires Bronsted acidity. However, the Bronsted acidity of the catalyst decreases with increase in activation temperature [29]. Our observations are in agreement with this report.

3.2. Effect of reaction temperature

The effect of temperature was observed in the range of 120–160 °C. The selectivity of the product (approximately *o*:*p*:95:5) was not affected in the range of temperature used, but the rate of the reaction increased with increase in the temperature. In Fig. 4, the combined yield of **3a** and **4a** is plotted against time. Hence, further studies of the reaction were carried out at 160 °C.

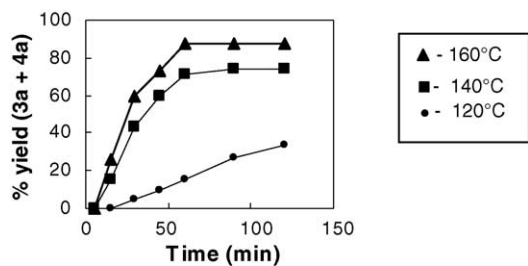


Fig. 4. Effect of temperature on the cyclohexylation of phenol by cyclohexanol in the presence H β -SnA120 catalyst.

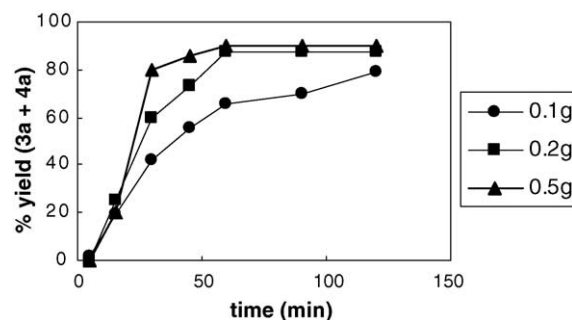


Fig. 5. Effect of catalyst quantity on the cyclohexylation of phenol by cyclohexanol in the presence H β -SnA120 catalyst.

3.3. Effect of catalyst quantity

The effect of catalyst quantity is shown in Fig. 5. As catalyst (H β -SnA120) quantity increased the yield of the product increased, beyond 0.2 g of the catalyst, the increase in the yield was not significant.

3.4. Effect of support

In order to get an idea about the role of the support, different types of catalyst were prepared using K-10 and silica; both of these are common supports for supported reagents. The catalysts, K-10-SnA120 and silica-SnA120 were prepared by same procedure as adopted for H β -SnA120. Some of the basic properties of the supports are given in (Table 4).

The reaction of cyclohexanol with phenol was carried out using K-10-SnA120, silica-SnA120 and that of H β -SnA120. Fig. 6 shows the variation of yield of **3a** + **4a** with time using the three catalysts.

Table 4

Comparison of basic properties of supports

Property	K-10	H β -zeolite	Silica
Surface area (m ² /g)	230	454.4	550
Surface of micropores (m ² /g)	2.5	201.2	–
Micropore volume (cm ³ /g)	0.0011	0.1114	–
Total pore volume (cc/g)	0.320	0.38	0.8
Average pore size (Å)	56	33.5	60
Relative bronsted/Lewis acidity	2.23/1.91	2.51/1.82	–

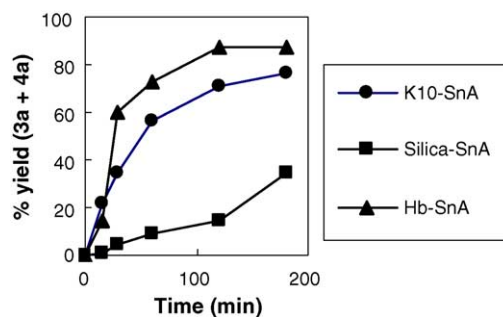
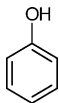
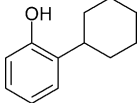
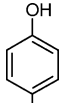
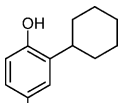
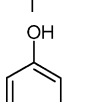
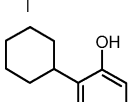
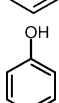
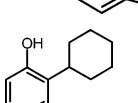


Fig. 6. Effect of support on cyclohexylation of phenol by cyclohexanol using Sn⁴⁺ exchanged catalyst.

Table 5
C-Cyclohexylation of phenols with cyclohexanol in the presence H β -SnA120 catalyst

Entry	Substrate	Product	Time (min)	C-Monoalkylated (%)	<i>o</i> -Selectivity (%)
a			60	87.5	95
b			120	90	100
c			120	95	95
d			300	15	100

Reaction conditions: phenol = 10 mL, cyclohexanol = 10 mmol (1.0 mL), catalyst = 0.2 g, and temperature = 160 °C.

3.5. Leaching experiment

The percentage of Sn loaded on H β -zeolite was analyzed by ICP analysis and found to be 6.77%. Leaching of the metal ion and a possible contribution by the resulting homogeneous catalysis was ruled out by the following experiment. The catalyst was filtered at an early stage of the reaction ($t = 15$ min, 50% yield) and the reaction was allowed to proceed in the filtrate. We observed that the reaction did not proceed further and yield of reaction remained 50%. This proved that there was not enough leaching of the Sn ions to make the reaction homogeneous. Therefore, we concluded that the reaction was truly heterogeneous in nature.

3.6. Formation of intermediate

The conspicuous observation in this reaction was the formation and consequent consumption of cyclohexyl phenyl ether (**5a**), the identity of which was proved by GC–MS. In the case of active catalyst like H β -SnA120, it was not

revealed clearly. However, in the case of H β -AlA120 catalyst this intermediate ether was noticed before attaining the equilibrium; as the reaction was very slow. In Fig. 7, the concentrations of different species in the reaction mixture with respect to time are shown. As the reaction proceeded, the concentration of **5a** increased along with that of **3a** and **4a**, however, after some time it decreased.

The reaction being a Friedel–Crafts alkylation, may proceed through the generation of a potential carbocation from cyclohexanol. The carbocation may produce cyclohexene through H⁺ elimination or the carbocation may undergo nucleophilic attack from the phenolic O end to give cyclohexyl phenyl ether. The formation of this ether has been suggested by Rao [23], but its presence has not been proved. The ether, in turn, may rearrange to C-alkylated product.

3.7. Substrate study

Using the optimised parameters, few phenols were alkylated with cyclohexanol using H β -SnA120 catalyst (Table 5).

4-Chlorophenol and 4-methylphenol showed 100% *ortho* selectivity. The low yield obtained in the case of 4-

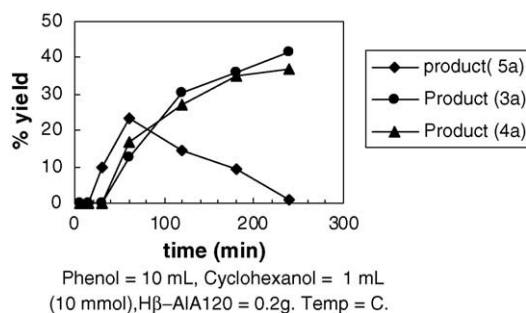


Fig. 7. Alkylation of phenol using cyclohexanol in the presence of H β -AlA120.

Table 6
Recyclability study

Cycle	Time (min)	C-Monoalkylated product (%)	Regio-selectivity (%)	
			<i>ortho</i>	<i>para</i>
1	60	87.5	95	5
2	60	88	95	5
3	60	85	94	6
4	75	85	94	6
5	75	83	93	7

Reaction conditions: phenol = 10 mL, cyclohexanol = 10 mmol (1.0 mL), catalyst = 0.2 g, temperature = 160 °C.

chlorophenol may be due to the deactivating influence of the chloride substituent on the aromatic ring.

3.8. Recyclability study

The catalyst was found to be recyclable. After each cycle the used catalyst was filtered and activated at 120 °C before being used for the next cycle. The activity of the catalyst did not decrease considerably even after five cycles (Table 6).

4. Conclusions

Ti⁴⁺, Sb³⁺, Fe³⁺, Sn⁴⁺, Al³⁺, and Zr⁴⁺ cation exchanged H β -zeolites can function as catalysts for cyclohexylation of phenols using cyclohexanol. Among these catalysts, H β -SnA120 was found to be the best catalyst, and gave 87.5% of the monoalkylated product with 95% *ortho* selectivity, which is highest so far reported. The cyclohexylation of phenols was found to proceed through cyclohexylphenyl ether which may rearrange to *o*-cyclohexyl phenol.

We have developed a highly effective and regio-selective catalyst, H β -SnA120 for the efficient cyclohexylation of phenols with cyclohexanol. The catalyst is recyclable, environmentally benign and thus an attractive alternative to the conventional catalysts, with respect to handling and work-up.

Acknowledgments

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References

- [1] C. Friedel, J.M. Crafts, *Compt. Rend.* 84 (1877) 1392.
- [2] C. Friedel, J.M. Crafts, *Bull. Soc. Chim. Fr.* 27 (1877) 482.
- [3] C. Friedel, J.M. Crafts, *Ann. Chim. Phys.* 1 (1884) 449.
- [4] G.A. Olah, Friedel–Crafts and related reactions, Part 1, vol. 2, Wiley/Interscience, New York, 1964.
- [5] G.A. Olah, R. Krishnamurti, G.K.S. Prakash, in: B.M. Trost, I. Fleming (Eds.), *Comprehensive Organic Synthesis*, vol. 3, Pergamon, Oxford, 1991, p. 293.
- [6] P.B. Venuto, *Micropor. Mater.* 2 (1994) 297.
- [7] M.E. Davis, *Micropor. Mesopor. Mater.* 21 (1998) 173.
- [8] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [9] J.H. Clark, *Green Chem.* 1 (1999) 1.
- [10] R.A. Sheldon, *Appl. Catal. A: Gen.* 189 (1999) 163.
- [11] M. Toba, A. Katayama, G. Takeuchi, F. Mizukimi, S. Niwaans, S. Mitamura, *J. Chem. Soc. Chem. Commun.* (1991) 39.
- [12] S.G. Pai, A.R. Bajpai, A.B. Deshpande, S.D. Samant, *J. Mol. Catal. A: Chem.* 156 (2000) 233.
- [13] S.G. Pai, A.R. Bajpai, A.B. Deshpande, S.D. Samant, *Synth. Commun.* 27 (1997) 2267.
- [14] D.U. Singh, S.D. Samant, *J. Mol. Catal. A: Chem.* 223 (2004) 111.
- [15] S.G. Pai, A.R. Bajpai, A.B. Deshpande, S.D. Samant, *Synth. Commun.* 27 (1997) 379.
- [16] A.B. Deshpande, A.R. Bajpai, S.D. Samant, *Appl. Catal. A: Gen.* 209 (2001) 229.
- [17] J.F. Lorenc, G. Lambeth, W. Scheffer, in: M. Howe-Grant, J.I. Kroschwitz (Eds.), *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 2, Wiley, New York, 1992, p. 113.
- [18] N.S. Kozlov, A.G. Klein, Yu.A. Galishevskii, *Uch. Zap. Perm. Gos. Pedagoginst* 85 (1970) 3; *Chem. Abstr.* 77 139509 (in Russian).
- [19] D.A. Pisanenko, Y.I. Simrnov-Zamnovzh. *Prikl. Khim. (St. Petersburg)* 72 (1999) 1564; *Chem. Abstr.* 132 93065 (in Russian).
- [20] M. Saha, M. Mosbihuzzaman, S. Shaha, *Ind. J. Chem. Technol.* 3 (1996) 292.
- [21] Y.B. Kozlikovskii, V.A. Koshchii, S.A. Butov, A.V. Sokolova, *Zh. Org. Khim.* 23 (1987) 1918; *Chem. Abstr.* 109 6159 (in Russian).
- [22] A. Chakrabarti, M.M. Sharma, *React. Polym.* 17 (1992) 331.
- [23] R. Anand, T. Daniel, R.J. Lahoti, K.V. Shrinivasan, B.S. Rao, *Catal. Lett.* 91 (2002) 241.
- [24] A.R. Abdurasuleva, N. Ismailov, A.V. Kayumov, *Uzbekskii Khim. Zh.* 13 (1969) 50; *Chem. Abstr.* 72:110934 (in Russian).
- [25] N. Ismailov, *Lenina* 379 (1970) 160; *Chem. Abstr.* 81 104900 (in Russian).
- [26] S. Namba, T. Yashima, Y. Itaba, N. Hara, *Stud. Surf. Sci. Catal.* 5 (1980) 105.
- [27] R. Pierantozzi, A.F. Nordquist, *Appl. Catal.* 21 (1986) 263.
- [28] P. Shah, A.V. Ramaswamy, R. Parischa, K. Lazor, V. Ramaswamy, *Proceedings of the 14th International Zeolite Conference*, Cape Town, 2004, p. 870.
- [29] T. Cseri, S. Bekassi, F. Figueras, S. Rizner, *J. Mol. Catal. A: Chem.* 98 (1995) 101.