

Preparation of highly ordered mesoporous AISBA-15 and its application to isopropylation of *m*-cresol

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Abstract

Aluminum incorporated SBA-15 mesoporous molecular sieves with different $n_{\text{Si}}/n_{\text{Al}}$ ratios have been hydrothermally synthesized by adjusting the synthesis gel pH below the isoelectric point of silica ($\text{pH} \sim 2$) using nonionic surfactant as the structure directing agent. All the samples were characterized by X-ray diffraction, N_2 adsorption to determine specific pore volume, pore size and specific surface area, FT-IR, TGA-TPD to determine the acid sites and ^{27}Al magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR). Vapor phase alkylation of *m*-cresol with isopropanol was carried out over large pore AISBA-15 catalysts with different $n_{\text{Si}}/n_{\text{Al}}$ ratios. The influence of various reaction parameters such as reaction temperature, reactant feed ratio and space velocity affecting the activity and selectivity of AISBA-15, were studied. 2-Isopropyl-5-methylphenol (2I-5MP) was obtained as a major product with high selectivity. AISBA-15 (45) was found to be the most active catalyst in this study. It showed 73.5% *m*-cresol conversion and a selectivity of 45.68% for 2I-5MP under the optimized reaction conditions. Further, large pore AISBA-15 (45) catalyst was not deactivated when the reaction was carried out for several hours of reaction time.

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1. Introduction

Microporous zeolites with uniform pores have been widely used as industrial catalysts. However, they cannot catalyze reactions of large molecules due to limitation of micropore size. The discovery of mesoporous materials, such as MCM-41 has attracted much attention because of their potential use as catalyst and catalyst support for the conversion of large molecules [1]. However, as compared with conventional zeolites, these mesostructured materials have relatively low acidity and hydrothermal stability that limit their extensive use [2,3]. Many attempts have been made to

improve the stability of MCM-41 [4–7] or to prepare other stable mesoporous materials [5,8,9]. SBA-15, a new type of mesoporous silica with tunable pore diameter, thicker walls and much higher hydrothermal stability than MCM-41, has been prepared using tri-block copolymer as template [9]. Pure siliceous materials have electrically neutral framework and consequently no Brønsted acidity. However, it is very difficult to prepare SBA-15 containing heteroatoms in the framework because of the strong acidic synthesis conditions. Recently, many efforts have been made to incorporate of Al, Ti and V into the framework of SBA-15, by post-synthesis grafting procedures [10–12] and direct synthesis [13,14]. The post-synthesis method always needs a complex experimental condition and the metal oxides tend to appear in the channels or external surface of the catalysts, which would block the channels [15]. Yue et al. tried to incorporate aluminum

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directly into the framework of SBA-15 through direct synthesis, but the product contains extra framework aluminum species and post-synthetic method is necessary to remove the extra framework aluminum [13].

Alkylation of phenol is an industrially important reaction because many alkyl phenols have been used in the manufacture of drugs, pharmaceuticals, dyestuffs, pesticides, paints and plastics [16]. Catalytic alkylation of phenol using zeolites and mesoporous catalysts may be very promising way for their synthesis considering their activity, selectivity and reusability and the increasing demand for eco and environmentally harmonized routes in the chemical industry. There has been lot of work done concerning the isopropylation of phenol over solid acid catalysts. It has been found that the *meta*-, *para*-, and *ortho*-isopropylphenols have been selectively produced in phenol alkylation with 2-propanol or propylene over different solid acid catalysts, where *ortho* position alkylation could be obtained over large pore zeolite H-beta and H-ZSM-12 [17–19]. However, medium pore opening H-ZSM-5 gave only production of *para*-isopropylphenol. Velu and Swamy studied alkylation of phenol with 1-propanol and 2-propanol over hydrotalcites and found that the reaction of phenol and 1-propanol proceeded without skeletal isomerization of the propyl moiety, suggesting an S_N^2 type mechanism [20]. Yoo et al. studied the acidity effect on the catalytic properties for phenol isopropylation and found that the pore size and Brønsted acid sites of the zeolite controls the conversion of phenol and selectivity for *ortho*- and *para*-isopropylphenol [21].

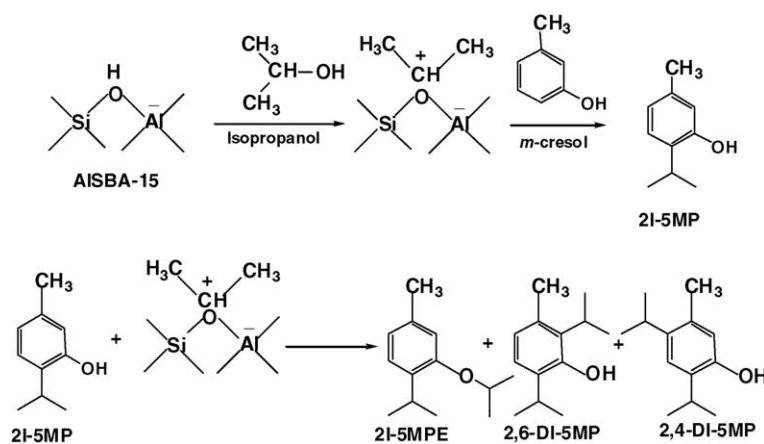
Among the several alkylated products, the *m*-cresol-derived 2-isopropyl-5-methylphenol (thymol) is the most important because it is a precursor of menthol [22]. Menthol has been used in the manufacture of antiseptic agents, local anesthetics, antibacterial agents, antifungicidal agents, flavors, fragrances, cooling agents, and preservatives [23]. Thymol exhibits activity in protecting low-density lipoproteins [24] and shows high antioxidant effectiveness [25–27]. Thymol has been prepared by liquid phase alkylation of *m*-cresol with

propylene over acidic catalyst [28], and gas phase alkylation of *m*-cresol with propylene in the presence of supported metal sulphates [29], wide- and medium-pore zeolites [30] and γ -alumina [31,32]. Recently, we have reported the vapor phase alkylation of *m*-cresol with isopropanol over AIMCM-41 catalysts with different n_{Si}/n_{Al} ratio [33]. Very recently, Vinu et al. have reported the direct incorporation of high amount of Al in the SBA-15 framework by simply adjusting the molar water to hydrochloric acid ratio of the synthesis medium, and also studied the influence of aluminum sources on the extent of metal incorporation [34]. They also found that pore diameter of the AISBA-15 materials can easily be controlled by changing the synthesis temperature. In this work, we report the results of vapor phase isopropylation of *m*-cresol over AISBA-15 catalysts with various n_{Si}/n_{Al} ratios. AISBA-15 materials with different n_{Si}/n_{Al} ratios were successfully synthesized by hydrothermal process using tri-block copolymer as template and characterized by XRD, AAS, N_2 adsorption, TGA-TPD and ^{27}Al MAS NMR spectroscopy and as their catalytic activity were tested in the isopropylation of *m*-cresol (Scheme 1). It has been found that AISBA-15 (45) catalyst shows 74% *m*-cresol conversion which is significantly higher and achieved at low temperature as compared to AIMCM-41 under optimized conditions.

2. Experimental

2.1. Materials

Aluminum isopropoxide and tetraethyl *ortho*-silicate (Merck) were used as the source for aluminum and silicon respectively. Tri-block copolymer poly (ethylene glycol)-*block*-poly (propylene glycol)-*block*-poly (ethylene glycol) (Pluronic P123, molecular weight = 5800, EO₂₀PO₇₀EO₂₀) (Aldrich) was used as the source for structure directing template. *m*-Cresol and isopropanol were purchased from Merck and used without further purification.



Scheme 1. Alkylation products of *m*-cresol with isopropyl alcohol over AISBA-15.

2.2. Preparation of the catalysts

AlSBA-15 samples with different $n_{\text{Si}}/n_{\text{Al}}$ ratios were synthesized using tri-block copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) as a structure directing agent with the following molar gel composition – TEOS: 0.02–0.15, Al_2O_3 : 0.016, P123: 0.46, HCl: 127, H_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. About 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 *ortho*-silicate and required amount of aluminum source were added and the resulting mixture was stirred for 24 h at 313 K and finally heated to 373 K for 48 h. 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 813 K to remove the template.

2.3. Characterization

The powder X-ray diffraction patterns of AlSBA-15 materials were collected on Siemens D5005 diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.154$ nm) radiation. The diffractograms were recorded in the 2θ range of 0.8 – 10° with a 2θ step size of 0.01° and a step time of 10 s. Nitrogen adsorption and desorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 sorption analyzer. The samples were outgassed for 3 h at 250°C under vacuum in the degas port of the adsorption analyzer. The specific surface area was calculated using the BET model. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) method.

Solid state ^{27}Al MAS NMR experiments were performed at room temperature on a BRUKER MSL 500 NMR spectrometer with a resonance frequency of 130.32 MHz, applying a short 2.1 μs pulse and a recycle delay of 100 ms. Typical rotation frequency was at about 10 kHz using a 4 mm diameter zirconia rotor. About 12500 scans were necessary to obtain a well resolved spectrum. Mid-infrared spectra of AlSBA-15 molecular sieves were recorded on a Nicolet (Avatar 360) instrument by KBr pellet technique. About 4 mg of the sample was ground with 200 mg of spectral grade KBr to form a mixture, which was then made into a pellet using a hydraulic press. This pellet was used to record the infrared spectra in the range 4000 – 400 cm^{-1} . Elementary analysis was done using an Analyst AA 300 spectrometer. The density and strength of acid sites of different AlSBA-15 materi-

als were determined by temperature-programmed-desorption (TPD) of pyridine. About 100 mg of the materials were evacuated for 3 h at 523 K under vacuum ($p < 10^{-5}$ h Pa). Thereafter, the samples were cooled to room temperature under dry nitrogen followed by exposure to a stream of pyridine in nitrogen for 30 min. Subsequently, the physisorbed pyridine was removed by heating the sample to 393 K for 2 h in a nitrogen flow. The temperature-programmed desorption (TPD) of pyridine was performed by heating the sample in a nitrogen flow (50 ml/min) from 393 to 973 K at a rate of 10 K/min using a high-resolution thermogravimetric analyzer (SETARAM setsys 16 MS). The observed weight loss was used to quantify the number of acid sites assuming that each mole of pyridine corresponds to one mole of protons.

2.4. Catalytic studies

The isopropylation of *m*-cresol was carried out in a fixed-bed flow-type reactor made up of a borosil glass tube with a length of 40 cm and an internal diameter of 2 cm. About 0.5 g of catalyst was placed in the reactor and supported on either side with a thin layer of quartz wool and ceramic beds. The reactor was heated to the reaction temperature with the help of a tubular furnace controlled by a digital temperature controller. The catalyst was activated in air at 773 K for 6 h prior to the catalytic runs. Reactants were fed into the reactor using a syringe infusion pump. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products obtained in the first 10 min were discarded, and the product collected after different time-on-stream was analyzed for identification. The liquid products were analyzed by a Shimadzu gas chromatograph GC-17A using a DB-5 capillary column. Product identification was achieved by co-injection and GC-MS Hewlett Packard HP 6810 series equipped with HP 5973 mass detector. The conversion of *m*-cresol was calculated on the basis of *m*-cresol converted.

3. Results and discussion

3.1. Characterization

Elemental composition of AlSBA-15 materials is presented in Table 1. In all cases, the $n_{\text{Si}}/n_{\text{Al}}$ ratio of the calcined materials is higher than $n_{\text{Si}}/n_{\text{Al}}$ ratio in the synthesis gel. This could be due to the high solubility of aluminum source in the

Table 1
Textural parameters of AlSBA-15 samples prepared at different $n_{\text{Si}}/n_{\text{Al}}$ ratios

Sample	a_0 (nm)	$n_{\text{Si}}/n_{\text{Al}}$		A_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter, $d_{\text{p,ads}}$ (nm)
		Gel	Product			
AlSBA-15 (45)	11.3	7	45	930	1.4	9.7
AlSBA-15 (136)	10.2	14	136	1025	1.4	9.6
AlSBA-15 (215)	9.6	27	215	1035	1.3	8.9

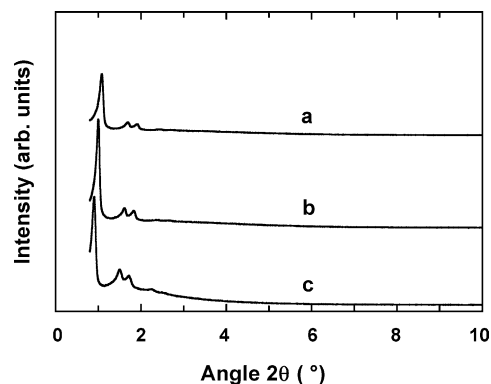


Fig. 1. XRD powder patterns of AISBA-15 materials prepared with different $n_{\text{Si}}/n_{\text{Al}}$ ratios: (a) AISBA-15 (215), (b) AISBA-15 (136) and (c) AISBA-15 (45).

acidic medium. Fig. 1 shows the XRD pattern of AISBA-15 samples synthesized using aluminum isopropoxide as the aluminum source with different $n_{\text{Si}}/n_{\text{Al}}$ ratios. All the samples show all the four well resolved peaks, which are indexed to (100), (110), (200) and (210) reflections of ordered hexagonal mesophase. Interestingly, the intensity of the lines increased with decreasing $n_{\text{Si}}/n_{\text{Al}}$ ratio. This indicates improved structural order with the aluminum incorporation in the framework. It is interesting to note that the unit cell parameter increases significantly with the increase of aluminum content in the synthesis gel (Table 1), which could suggest that the presence of aluminum in the SBA-15 walls.

Fig. 2 shows the nitrogen adsorption isotherms of AISBA-15 samples synthesized with different $n_{\text{Si}}/n_{\text{Al}}$ ratio. All isotherms show a steep rise in the high relative pressure in the range of 0.63–0.9, which is a good indication of large mesopore size of the materials. It can also be seen that the capillary condensation step was shifted to high relative pressure with the increase of aluminum content in the product. This could be attributed to the increase of pore diameter as the aluminum content increases. Moreover, incorporation of aluminum has a consequential impact on the BET specific surface area, specific pore volume and pore size of the materials (Table 1). It has been found that the pore size of AISBA-15 can be con-

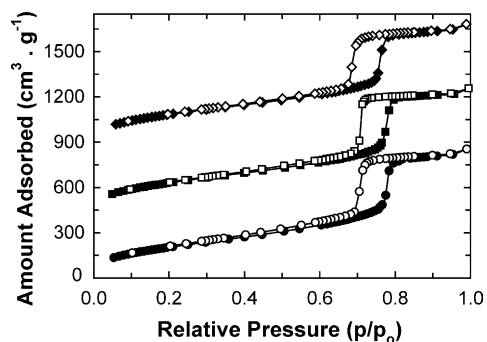


Fig. 2. Nitrogen adsorption isotherms of AISBA-15 materials prepared with different $n_{\text{Si}}/n_{\text{Al}}$ ratios (closed symbols: adsorption; open symbols: desorption): (♦) AISBA-15 (215), (■) AISBA-15 (136) and (●) AISBA-15 (45).

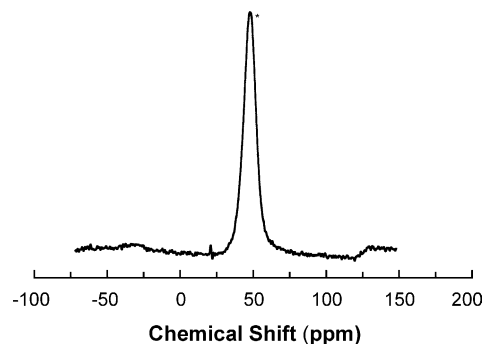


Fig. 3. ^{27}Al MAS NMR spectra of AISBA-15 (45).

trolled while perpetuating the long range structural order by varying the $n_{\text{Si}}/n_{\text{Al}}$ ratio of the synthesis gel. It can be seen from Table 1 that while increasing the Al content, the pore diameter increases from 8.9 to 9.7 nm and the specific surface area decreases from 1033 to 930 m^2/g . It is an acclaimed fact that for materials having cylindrical type pores, the surface area is inversely proportional to the pore diameter of the materials. However, the specific pore volume increases from 1.31 to 1.35 cm^3/g as the $n_{\text{Si}}/n_{\text{Al}}$ ratio decreases to 45. The increase of specific pore volume and pore diameter with increasing aluminum content might suggest the absence of aluminum oxide species inside the mesopores of AISBA-15. ^{27}Al MAS NMR spectrum of the calcined AISBA-15 (45) is shown in Fig. 3. There is only one sharp peak centered around 53 ppm which can be attributed to the presence of aluminum only in tetrahedral coordination.

The infrared spectra of the as-synthesized and calcined AISBA-15 (45) molecular sieves are shown in Fig. 4. The broad envelope around 3500 cm^{-1} is due to O–H stretch of water, surface hydroxyl groups and bridged hydroxyl groups. There are less intense peaks in the spectra of the as-synthesized samples (Fig. 4) just below 3000 cm^{-1} which are assigned to symmetric and asymmetric stretching modes of $-\text{CH}_2$ group of the locked-in template. Their corresponding bending mode is observed at 1400 cm^{-1} . The peaks between 500 and 1200 cm^{-1} are assigned to framework vibrations. The peaks around 1232 and 1083 cm^{-1} are attributed to the

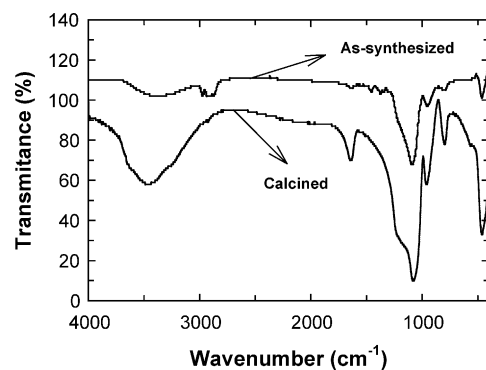


Fig. 4. FT-IR spectra of as-synthesized and calcined AISBA-15 (45) samples.

Table 2
Density and strength of acid sites of AISBA-15 catalysts with different $n_{\text{Si}}/n_{\text{Al}}$ ratios

Catalyst	Acid sites (mmol/g)			Theoretical ^a
	Weak (393–623 K)	Medium (623–723 K)	Strong (>723 K)	
AISBA-15 (45)	0.42	0.18	0.26	0.36
AISBA-15 (136)	0.47	0.11	0.16	0.12
AISBA-15 (215)	0.48	0.04	0.07	0.08
AIMCM-41 (25)	0.75	0.09	0.27	0.69

^a Theoretical amount of acid sites generated by introduction of aluminum if Al is exclusively in tetrahedral coordination and all Brønsted sites formed are accessible to pyridine.

asymmetric stretching modes of T–O–T groups. The symmetric stretching modes of T–O–T groups are observed at 805 and 540 cm^{-1} , and the peak at 460 cm^{-1} is attributed to the bending mode of T–O–T. The peaks at 963 and 460 cm^{-1} is assigned to the presence of defective Si–OH groups. It is to be noted that symmetric and asymmetric stretching modes of the $-\text{CH}_2$ group of the template are absent in the spectra of calcined samples (Fig. 4).

The density and strength of the acid sites were determined using temperature-programmed-desorption (TPD) of pyridine and the data are presented in Table 2. Weak (weight loss between 393 and 623 K), moderate (623–723 K) and strong (723–873 K) are found in all samples. The weak acid sites are attributed to surface hydroxyl groups, and the medium and strong acid sites originate from the incorporation of aluminum atoms into the SBA-15 walls. It is very interesting to note that, as $n_{\text{Si}}/n_{\text{Al}}$ ratio increases, the number of weak acids sites which comes from the weakly held hydrogen-bonded pyridine on terminal silanol group increases. This is consistent with the fact that the concentration of terminal silanol groups per fixed weight of samples is expected to increase with $n_{\text{Si}}/n_{\text{Al}}$ ratio. However, the medium acid sites decreases with increase of $n_{\text{Si}}/n_{\text{Al}}$ ratio. However, the number of acid sites calculated theoretically is lower than those determined for the catalysts by TPD of pyridine. Hence, it

has to be assumed that some of the surface silanol groups on the surface are also responsible for the medium acid sites. It should be noted that the number of strong acid sites in AISBA-15 increases with decreasing $n_{\text{Si}}/n_{\text{Al}}$ ratio. The total number of acid sites increases in the following order: AISBA-15 (215) < AISBA-15 (136) < AISBA-15 (45).

3.2. Catalytic activity

Isopropylation of *m*-cresol with isopropyl alcohol over AISBA-15 ($n_{\text{Si}}/n_{\text{Al}} = 45, 136$ and 215) was studied at 200, 250, 300, 350 and 400 °C with the feed ratio $n_{\text{isopropanol}}/n_{\text{m-cresol}}$ 3 and WHSV 3.5 h^{-1} . The products of the reaction were found to be 2-isopropyl-5-methylphenol (2I-5MP), 2,6-diisopropyl-5-methyl phenol (2,6-DI-5MP), 2,4-diisopropyl-5-methyl phenol (2,4-DI-5MP) and 2-isopropyl-5-methylphenylether (2I-5MPE). There were also unidentified products formed in significant amount with increase in temperature and their selectivity also increased with increase in temperature. The reaction results are presented in Table 3. Conversion of *m*-cresol and selectivity of 2-isopropyl-5-methylphenol (2I-5MP) as a function of reaction temperature are shown in Figs. 5 and 6, respectively. The data indicate a nonlinear response of conversion with increase in temperature. Conversion at lower temperatures is

Table 3
Catalytic activity of AISBA-15 (45, 136 and 215) for isopropylation of *m*-cresol

Catalyst	Temperature (°C)	<i>m</i> -Cresol conversion (%)	Products selectivity (%)				
			2I-5MP	2,6-DI-5MP	2,4-DI-5MP	2I-5MPE	Others
AISBA-15 (45)	200	37.5	47.5	3.3	8.6	28.5	12.1
	250	58.2	50.8	17.2	9.0	18.7	4.4
	300	48.2	38.6	46.1	7.0	2.2	6.1
	350	31.1	32.8	54.8	7.0	–	5.4
	400	17.3	15.2	39.5	–	–	45.3
AISBA-15 (136)	200	34.5	56.4	–	11.1	18.6	13.9
	250	35.9	66.2	12.0	12.1	9.7	–
	300	24.3	56.6	32.5	10.9	–	–
	350	14.8	40.6	51.7	7.7	–	–
	400	5.6	33.7	66.3	–	–	–
AISBA-15 (215)	200	1.4	61.6	38.4	–	–	–
	250	6.8	81.9	18.1	–	–	–
	300	4.6	100	–	–	–	–
	350	3.4	100	–	–	–	–
	400	1.7	100	–	–	–	–

WHSV = 3.5 h^{-1} ; $n_{\text{isopropanol}}/n_{\text{m-cresol}} = 3$.

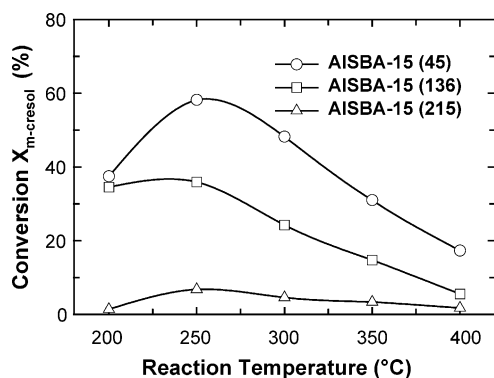


Fig. 5. Conversion of *m*-cresol over AISBA-15 with different $n_{\text{Si}}/n_{\text{Al}}$ ratios as a function of reaction temperature (WHSV = 3.5 h^{-1} , $n_{\text{isopropanol}}/n_{m\text{-cresol}} = 3$); (○) AISBA-15 (45), (□) AISBA-15 (136) and (△) AISBA-15 (215).

higher than at higher temperatures. The less conversion at higher temperature is due to coke formation [35]. The order of activity of the catalysts is AISBA-15 (45) > AISBA-15 (136) > AISBA-15 (215) based on the conversion at all the temperatures (Fig. 5). It is also the order of the acidity of the catalysts. Generally alkylation of phenol over zeolites and AIMCM-41 molecular sieves occurs by electrophilic reaction between alkyl cation on the catalyst surface and *m*-cresol in the vapor phase or in the chemisorbed state. As the $n_{\text{isopropanol}}/n_{m\text{-cresol}}$ ratio is 3, alcohol may have more probability for chemisorption than *m*-cresol. Hence the former type of electrophilic reaction may be predominant. If conversion over AISBA-15 (45) and AISBA-15 (136) are compared, the magnitude of decrease in conversion over AISBA-15 (45) is more than AISBA-15 (136) above 250 °C. It is due to rapid blocking of active sites by coke over AISBA-15 (45) due to its more density of acid sites. As the pore diameter is large, many molecules of alcohol can be chemisorbed to produce the alkyl cations. Hence, when *m*-cresol diffuses through the pores it can readily undergo multialkylation to form coke. As the acid sites are well scattered in AISBA-15 (136), the repeated alkylation to produce coke formation in it is to be comparatively less probable thus accounting less rate of de-

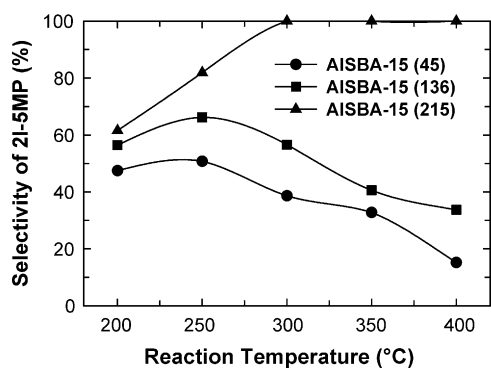


Fig. 6. Selectivity of 2I-5MP over AISBA-15 with different $n_{\text{Si}}/n_{\text{Al}}$ ratios as a function of reaction temperature (WHSV = 3.5 h^{-1} , $n_{\text{isopropanol}}/n_{m\text{-cresol}} = 3$); (●) AISBA-15 (45), (■) AISBA-15 (136) and (▲) AISBA-15 (215).

crease in conversion with increase in temperature. If conversion at 250 °C is compared for AISBA-15 (45) and AISBA-15 (136), the former shows 21% increase in conversion but the latter just 1%. This can be attributed to the partial blocking of the active sites by *m*-cresol at 200 °C in AISBA-15 (45) and less at 250 °C, thus providing enhanced chemisorption of isopropanol to give more conversion. The acid sites are less in AISBA-15 (136) (Table 2) and so there can be less competition for alcohol for chemisorption at 200 °C. Hence, there cannot be enhanced chemisorption of alcohol in order to give increased conversion at 250 °C.

The selectivity to 2I-5MP increases from 200 to 250 °C but above this temperature it decreases for all the catalysts (Fig. 6 and Table 3). Although the 2nd, 4th and 6th positions in *m*-cresol are susceptible to electrophilic attack, 2nd and 4th positions are sterically crowded compared to 6th position, as the –OH group is not offering steric hindrance. Thus 2I-5MP is formed with higher selectivity at 200 °C over AISBA-15 (45). At 250 °C, there is an increase in the selectivity, but the increase is not much, and above 250 °C the selectivity gradually decreases. Although the conversion is high at 250 °C compared to 200 °C, the less selectivity to 2I-5MP at 250 °C is attributed to its conversion to 2,6-DI-5MP. The selectivity of 2,6-DI-5MP, which increases from 200 to 350 °C, clearly demonstrates the requirement of high activation energy for consecutive alkylation of *m*-cresol. The selectivity to 2,6-DI-5MP is higher than the other two 2I-5MP dependent products, namely, 2,4-DI-5MP and 2I-5MPE. The selectivity to 2,4-DI-5MP is not much altered up to 350 °C. This illustrates that the transition state that provides this product is less stable and its probability is also not much changed from 200 to 250 °C. Its complete disappearance at 400 °C suggests blocking of the active sites that are necessary to produce the transition state for these products. At 200 °C, next to 2I-5MP the one with more selectivity is 2I-5MPE. The selectivity of the latter decreases from 200 to 300 °C, and reaches zero above this temperature. At higher temperatures the selectivity to 2,6-DI-5MP is higher than 2,4-DI-5MP. Now it is clearly evident that large decrease in the selectivity of 2I-5MP at 400 °C is not due to its prevention from formation but due to its high conversion to 2,6-DI-5MP. Similar selectivity features are reflected over AISBA-15 (136). The selectivity to 2I-5MP increases from 200 to 250 °C and above this temperature it decreases as observed over AISBA-15 (45). If the magnitude of selectivity of 2I-5MP is compared for AISBA-15 (45) and AISBA-15 (136), the latter gives more selectivity than the former. It clearly indicates the presence of less density of acid sites on the surface of AISBA-15 (136), which will not encourage bi-alkylation or ether formation as much as that of AISBA-15 (45) (Table 2). The absence of unidentified products above 250 °C once again supports less density of acid sites due to which all these unidentified products are absent. It is very well evident by comparing these data with those of AISBA-15 (45). Comparison of selectivity to 2,4-DI-5MP over AISBA-15 (45) and AISBA-15 (136) reveals nearly same values but more selectivity at 200, 250 and 300 °C for

Table 4
Effect of feed ratio on isopropylation of *m*-cresol over AISBA-15 (45)

Catalyst	WHSV (h ⁻¹)	<i>n</i> _{isopropanol} / <i>n</i> _{<i>m</i>-cresol} ratio	<i>m</i> -Cresol conversion (%)	Products selectivity (%)				
				2I-5MP	2,6-DI-5MP	2,4-DI-5MP	2I-5MPE	Others
AISBA-15 (45)	3.5	3	58.2	50.8	17.2	9.0	18.7	4.4
	3.4	5	73.5	45.7	20.1	7.4	20.8	6.0
	3.3	7	63.1	51.9	20.2	9.0	17.2	1.8
	3.8	0.5	28.3	66.9	14.5	12.7	6.0	–
	3.9	0.25	15.6	68.0	16.7	12.4	3.0	–
	3.9	0.16	10.8	64.1	20.1	13.6	2.3	–

Temperature = 250 °C.

the latter. The high selectivity of 2,4-DI-5MP at 200 °C over AISBA-15 (136) is due to absence of 2,6-DI-5MP at this temperature. Hence it is suggested that 2,4-DI-5MP is formed at the expense of 2,6-DI-5MP. The complete absence of the other products at 400 °C over this catalyst suggests they all depend on density of the acid sites of the catalysts. Based on this one can suggest that they may be polyalkylated *m*-cresol and or polypropenic oligomers.

The results over AISBA-15 (215) indicate 100% selectivity at higher temperature and higher selectivity at 200 and 250 °C than the previous catalysts (Table 3). Although the results are interesting, the conversion obtained for this catalyst is less than 7%. The absence of 2,4-DI-5MP, 2I-5MPE and other products once again proves the importance of density of acid sites for their formation (Table 2). It is also applicable to 2,6-DI-5MP, which completely disappears at 300 °C and above. So, based on conversion, 250 °C may be taken as the optimum temperature for both AISBA-15 (45) and AISBA-15 (136).

The effect of feed ratio on the reaction was studied over AISBA-15 (45) at 250 °C with a WHSV 3.5 h⁻¹ and *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.16, 0.25, 0.5, 3, 5 and 7. The results are presented in Table 4. The *n*_{isopropanol}/*n*_{*m*-cresol} ratio 5 gives higher conversion than 7 and 3. The higher conversion at the *n*_{isopropanol}/*n*_{*m*-cresol} ratio of 5 than 3 is due to more adsorption of isopropanol on the active sites of the catalyst. It also shows more adsorption of *m*-cresol on the catalyst surface at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 3. But the less conversion at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 7 might be due to more dilution of *m*-cresol in the vapor phase. In order to confirm more adsorption of *m*-cresol than isopropanol on the active sites at the *n*_{isopropanol}/*n*_{*m*-cresol} ratio 3, the *n*_{isopropanol}/*n*_{*m*-cresol} ratios 0.5, 0.25 and 0.16 were employed. The results of these feed ratios are also given in Table 4. With increase in the *m*-cresol content in the feed, conversion decreases thus confirming our view of more adsorption of *m*-cresol at the *n*_{isopropanol}/*n*_{*m*-cresol} ratio 3. Although *m*-cresol can be preferentially adsorbed at *n*_{isopropanol}/*n*_{*m*-cresol} ratios 0.16, 0.25 and 0.5, adsorption of isopropanol is not avoided, as there is significant conversion of *m*-cresol for all these three feed ratios. *m*-Cresol can react with isopropyl cation by remaining in the vapor phase or in the chemisorbed state on the catalyst surface. The exclusive reaction between chemisorbed *m*-cresol and isopropyl cation can be confirmed by the conversion at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.5 at which free *m*-cresol content could be almost nil

compared to the *n*_{isopropanol}/*n*_{*m*-cresol} ratios 0.25 and 0.16. But chemisorbed *m*-cresol can give mono- and di-ring alkylation but not *O*-alkylation. If there is *O*-alkylation it could be due to the reaction between 2I-5MP and isopropyl cation on the catalyst surface. The selectivity of 2I-5MP is more at the *n*_{isopropanol}/*n*_{*m*-cresol} ratio of 3 and less at 5. But at *n*_{isopropanol}/*n*_{*m*-cresol} ratio of 7, it again increases. The decrease in selectivity of 2I-5MP at *n*_{isopropanol}/*n*_{*m*-cresol} ratio of 5 compared to 3 is attributed to more conversion of 2I-5MP into its dependent products due to enhanced availability of isopropyl cation. But the selectivity of 2I-5MP at the *n*_{isopropanol}/*n*_{*m*-cresol} ratio 7 gives an increase of nearly 6% compared to *n*_{isopropanol}/*n*_{*m*-cresol} ratio 5. This illustrates the prevention of 2I-5MP for further alkylation with isopropyl cation by dilution. As a result, the selectivity of the dependent products instead of enhancement, remains equal to that at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 5. The selectivity of 2I-5MP increases when the *n*_{isopropanol}/*n*_{*m*-cresol} ratio is changed from 0.25 to 0.5, but at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.16, there is a decrease in its selectivity. Similar to the previous argument the increase in the selectivity of 2I-5MP from *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25–0.5 can be due to prevention of 2I-5MP from reacting with isopropyl cation. The selectivity to 2I-5MP is observed to be the same at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25 and 0.5. But the selectivity to 2I-5MP at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25 is expected to be higher than at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.5, as free *m*-cresol in the vapor state is more in the former than the latter. But it is observed that the selectivity to 2,6-DI-5MP is more at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25 than at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.5. This observation clearly illustrates conversion of more amount of 2I-5MP to 2,6-DI-5MP at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25 equalising thus its selectivity to 0.5. The selectivity of 2I-5MPE is slightly more at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.5 than at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25. Generally adsorption of 2I-5MP on the catalyst surface is important to produce more *O*-alkylation. Since at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.5 there should be more adsorbed 2I-5MP the selectivity to ether is higher at this feed ratio than at *n*_{isopropanol}/*n*_{*m*-cresol} ratio 0.25.

The effect of WHSV on *m*-cresol conversion and products selectivity over AISBA-15 (45) at 250 °C with the *n*_{isopropanol}/*n*_{*m*-cresol} ratio of 5 is shown Fig. 7. Conversion increases from 68 to 74% when WHSV is increased from 1.7 to 3.4 h⁻¹. But at WHSV 5.0 h⁻¹ the conversion is decreased to 53%. At lower WHSV, *m*-cresol may be adequately ad-

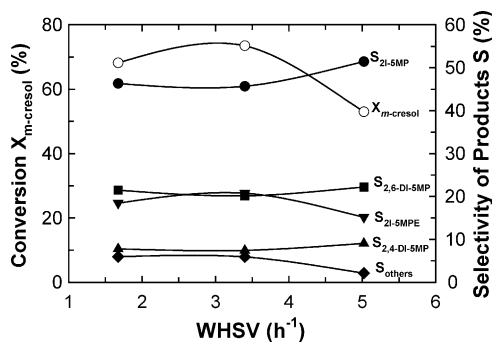


Fig. 7. Effect of WHSV on the *m*-cresol conversion and selectivity of products over AISBA-15 (45) at 250 °C, $n_{\text{isopropanol}}/n_{m\text{-cresol}} = 5$; (○) *m*-cresol conversion, (●) S_{2I-5MP} , (■) $S_{2,6-DI-5MP}$, (▲) $S_{2,4-DI-5MP}$, (▼) $S_{2I-5MPE}$ and (◆) S_{others} .

sorbed on the active sites producing less conversion. But at WHSV 3.4 h^{-1} due to little enhancement in the velocity of the feed, *m*-cresol may be slightly prevented from adsorption. So there is more conversion at this WHSV than at 1.7 h^{-1} . But the increase in WHSV is not expected to suppress adsorption of isopropanol, though it becomes more important at WHSV 5.0 h^{-1} as the conversion is less. It is also reflected in the selectivity of 2I-5MP. At WHSV 5.0 h^{-1} , the selectivity of 2I-5MP is high, as it would escape without producing the time dependent dialkylated products. But, if the selectivity to 2,6-DI-5MP and 2,4-DI-5MP is examined, the values are nearly the same at all WHSV. Hence, the increase in WHSV does not alter the selectivity of these two compounds. If the selectivity of 2I-5MP and 2I-5MPE is compared, one can understand that the selectivity to 2I-5MPE is more dependent on the change in WHSV.

Therefore the optimum conditions for the reaction are temperature = 250 °C, $n_{\text{isopropanol}}/n_{m\text{-cresol}}$ ratio = 5 and WHSV = 3.5 h^{-1} . Under the same conditions the reaction was also carried out over AIMCM-41 (25) and H-beta zeolite and the results are shown in Table 5. The results reveal that AISBA-15 (45) is more active than other catalysts. The activity of the catalysts increases in the order: AISBA-15 (45) > AIMCM-41 (25) \approx H-beta zeolite. This order is not in accordance with the acidity of the catalysts as reported in Table 2. Hence acidity alone is not the controlling factor in deciding the difference in the activity of the catalyst. In this context the hydrophobic property of the catalysts may be a better parameter to account for the difference in their activity. AISBA-15 (45) is to be more hydrophobic than AIMCM-41 (25) and zeolite, hence isopropyl alcohol which is partly hydrophobic can be better attracted and chemisorbed on the

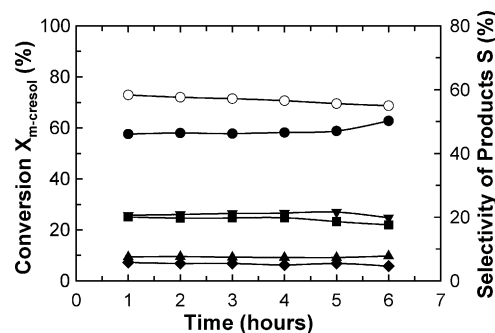


Fig. 8. Effect of time-on-stream on the *m*-cresol conversion and selectivity of products over AISBA-15 (45) at 250 °C, WHSV = 3.5 h^{-1} , $n_{\text{isopropanol}}/n_{m\text{-cresol}} = 5$; (○) *m*-cresol conversion, (●) S_{2I-5MP} , (■) $S_{2,6-DI-5MP}$, (▲) $S_{2,4-DI-5MP}$, (▼) $S_{2I-5MPE}$ and (◆) S_{others} .

surface of AISBA-15 (45), thus accounting for its high conversion. In addition the high surface area and pore volume are also important to account for its high conversion.

To study the sustainability and activity of AISBA-15 (45) the effect of time on stream was carried out at 200, 250, 300, 350 and 400 °C at the optimized $n_{\text{isopropanol}}/n_{m\text{-cresol}}$ of 5 and WHSV 3.5 h^{-1} . The results are presented in Table 6. At 200 °C the conversion decreases with increase in time on stream. The maximum decrease in conversion after 6 h of time on stream is about 6% only. This observation clearly suggests that catalyst is stable and its activity is retained. The selectivity to the products nearly remains the same. The large open space and less temperature might be the cause for the sustainability and same activity of the catalyst.

The effect of time on stream at 250 °C over the same catalyst illustrates similar trend as that at 200 °C, but the values are higher than at 200 °C. Hence the reaction is suggested to be activation energy demanding. The high activation energy required for this reaction may be understood based on the formation of molecular clusters of isopropanol on the catalyst surface, which requires high energy for chemisorption. Fig. 8 illustrates *m*-cresol conversions, and selectivity of the products nearly remains the same. This reveals the avoidance of coke formation on the catalyst surface and same mechanism prevails for the entire time on stream. At 300 °C the conversion decreases with increase in time on stream but it is less than at 250 °C, thus revealing blocking of active sites by coke. Although the conversion matches with 200 °C there is difference in selectivity of the products. The selectivity to 2I-5MP is comparable to that at 200 °C but selectivity of 2,6-DI-5MP becomes higher than at 200 °C. The selectivity to 2I-5MPE is low at 200 °C.

Table 5

Comparison of AISBA-15 (45), AIMCM-41 (25) and H-beta zeolite – temperature = 250 °C; WHSV = 3.5 h^{-1} ; $n_{\text{isopropanol}}/n_{m\text{-cresol}} = 5$

Catalyst	<i>m</i> -Cresol conversion (%)	Products selectivity (%)				
		2I-5MP	2,6-DI-5MP	2,4-DI-5MP	2I-5MPE	Others
AISBA-15 (45)	73.5	45.7	20.1	7.4	20.8	6.0
AIMCM-41 (25)	59.6	46.0	16.3	8.0	21.8	8.0
H-beta (15)	59.7	46.8	17.2	8.6	23.0	4.5

Table 6
Effect of time on stream at different reaction temperature, WHSV = 3.5 h⁻¹, $n_{\text{isopropanol}}/n_{m\text{-cresol}} = 5$

Temperature (°C)	Time (h)	<i>m</i> -Cresol conversion (%)	Products selectivity (%)				
			2I-5MP	2,6-DI-5MP	2,4-DI-5MP	2I-5MPE	Others
200	1	53.5	42.1	2.1	9.4	32.6	13.8
	2	52.6	42.1	2.1	9.5	32.9	13.5
	3	50.9	44.2	1.8	9.5	30.2	14.3
	4	49.8	44.4	1.6	9.5	30.3	14.2
	5	48.5	45.1	1.6	9.7	29.0	14.6
	6	47.9	45.6	1.6	9.6	28.2	14.9
250	1	73.0	46.1	20.0	7.5	20.6	5.8
	2	72.0	46.4	19.7	7.6	20.8	5.5
	3	71.5	46.2	19.7	7.4	21.2	5.5
	4	70.7	46.6	19.8	7.4	21.3	5.0
	5	69.5	47.0	18.6	7.3	21.6	5.5
	6	68.7	50.2	17.6	7.8	19.8	4.6
300	1	53.9	40.2	43.0	7.1	3.5	6.2
	2	52.4	45.4	40.5	7.5	3.9	2.8
	3	49.1	49.4	36.0	8.0	4.1	2.6
	4	49.8	47.1	39.7	7.6	3.6	2.1
	5	46.2	49.6	35.2	8.1	4.1	3.1
	6	45.9	45.3	41.6	7.8	3.4	1.9
350	1	26.4	34.7	51.9	6.2	–	7.2
	2	25.5	35.5	50.4	6.7	–	7.4
	3	25.0	37.2	50.6	7.6	–	4.6
	4	24.0	42.5	45.9	7.5	–	4.2
	5	23.5	40.3	47.6	7.3	–	4.8
	6	23.2	40.0	46.8	7.8	–	5.3
400	1	21.6	5.1	9.5	–	–	85.4
	2	20.9	4.7	7.9	–	–	87.4
	3	19.8	5.8	13.5	–	–	80.7
	4	19.0	5.1	10.1	–	–	84.8
	5	18.4	6.3	21.4	–	–	72.4
	6	18.0	9.6	7.4	–	–	83.0

At 350 and 400 °C there is a large decrease in conversion. If the magnitude of decrease is compared at each temperature there is not much variation. Hence there must be more blocking of the active sites even at the end of first hour of the time on stream. The selectivity to 2I-5MP and 2,6-DI-5MP is higher than 2,4-DI-5MP. 2I-5MPE is not formed at the entire hours of time on stream. At 400 °C the selectivity to polyalkylated *m*-cresol and olefinic products is found to be more predominating than either 2I-5MP or 2,6-DI-5MP.

From this time on stream study it is concluded that 250 °C might be the optimum temperature for high conversion with high selectivity to 2I-5MP. At lower temperatures the catalytic activity is retained throughout the stream. But at higher temperatures the initial less activity as a result of coke formation is nearly retained for the entire stream. Hence the large pore diameter of the catalyst is observed to be advantageous to give high conversion without loss in activity due to coke formation.

4. Conclusions

The large pore AISBA-15 molecular sieves with $n_{\text{Si}}/n_{\text{Al}}$ ratios 45, 136 and 215 were synthesized and characterized

by physico-chemical methods such as XRD, N₂ adsorption, AAS, TGA-TPD and ²⁷Al MAS NMR spectroscopy. N₂ adsorption study shows that the specific pore volume and pore diameter increase with increasing aluminum content in the samples. ²⁷Al MAS NMR spectra confirm that aluminum is exclusively in tetrahedral coordination, which imparts Brønsted acidity. The catalytic activity of the AISBA-15 samples was tested in the acid-catalyzed isopropylation of *m*-cresol using isopropanol as the alkylating agent. Among the three catalysts studied, AISBA-15 (45) was found to be the most active catalyst and showing ca. 74% *m*-cresol conversion, which is significantly higher compared to AIMCM-41 (25) catalyst under optimized reaction conditions. It has also been found that large pore AISBA-15 (45) catalyst was not deactivated when the reaction was carried out for several hours of reaction time.

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References

- [1] A. Corma, Chem. Rev. 97 (1997) 2373.
- [2] Z. Tuel, Zeolites 15 (1995) 236.
- [3] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 352 (1992) 710.
- [4] J.M. Kim, S. Jun, R. Ryoo, J. Phys. Chem. B 103 (1999) 6200.
- [5] K.R. Kloetstra, H. van Bekkum, J.C. Jansen, Chem. Comm. (1999) 2281.
- [6] R. Mokaya, W. Jones, Chem. Comm. (1997) 2185.
- [7] R. Mokaya, Angew. Chem. 111 (1999) 3079.
- [8] S.S. Kim, W. Zhang, J.T. Pinnavaia, Science 282 (1998) 1032.
- [9] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
- [10] Z. Luan, M. Hartmann, D. Zhao, W. Zhou, L. Kevan, Chem. Mater. 11 (1999) 1621.
- [11] M.S. Morey, S. O'Brien, S. Schwarz, G.D. Stucky, Chem. Mater. 12 (2000) 898.
- [12] Z. Luan, J.Y. Bae, C. Kevan, Chem. Mater. 12 (2000) 3202.
- [13] Y. Yue, A. Gedeon, J.L. Bonardet, N. Melosh, J.B. D'Espinose, J. Fraissard, Chem. Comm. (1999) 1697.
- [14] L.N. Bharat, O. Johnson, K. Sridhar, Chem. Mater. 13 (2001) 552.
- [15] R. Murugavel, H.W. Roesky, Angew. Chem. Int. Ed. Engl. 109 (1997) 4491.
- [16] H. Fiege, in: W. Gehartz (Ed.), ULMANN's Encyclopedia of Industrial Chemistry, VCH, Weinheim, 1987, pp. 324–332.
- [17] M.M. Wu, US Patent 4 391 998 (1983).
- [18] G.E. Stead, L.B. Young, US Patent 4 405 818 (1983).
- [19] C.D. Chang, S.D. Hellring, US Patent 5 175 375 (1992).
- [20] S. Velu, C.S. Swamy, Catal. Lett. 40 (1996) 265.
- [21] J.W. Yoo, C.W. Lee, B. Wang, S.E. Park, Bull. Korean Chem. Soc. 22 (2001) 263.
- [22] J.C. Leffingwell, R.E. Shackelford, Cosmetics Perfumery 89 (1974) 69.
- [23] R. Hopp, Recent Adv. Tobacco Sci. 19 (1993) 46.
- [24] P.L. Teissedre, A.L. Waterhouse, J. Agric. Food Chem. 48 (2000) 3801.
- [25] E.L. Krause, W. Ternes, Eur. Food Res. Technol. 209 (1999) 140.
- [26] N.V. Yanishlieva, E.M. Marinova, M.H. Gordon, V.G. Raneva, Food Chem. 64 (1999) 59.
- [27] M. Milos, J. Mastelic, I. Jerkovic, Food Chem. 71 (2000) 79.
- [28] T. Yamanaka, Bull. Chem. Soc. Jpn. 49 (1976) 2669.
- [29] M. Nitta, K. Yamaguchi, K. Aomura, Bull. Chem. Soc. Jpn. 47 (1974) 2897.
- [30] P. Wimmer, H.-J. Buysch, L. Puppe, US Patent 5 030 770 (1991).
- [31] M. Nitta, K. Aomura, K. Yamaguchi, Bull. Chem. Soc. Jpn. 47 (1974) 2360.
- [32] W. Biedermann, H. Koller, K. Wedemeyer, US Patent 4 086 283 (1978).
- [33] V. Umamaheswari, M. Palanichamy, V. Murugesan, J. Catal. 210 (2002) 367.
- [34] A. Vinu, V. Murugesan, W. Böhlmann, M. Hartmann, J. Phys. Chem. B 108 (2004) 11496.
- [35] M. Selvaraj, A. Pandurangan, K.S. Seshadri, P.K. Sinha, V. Krishnasamy, K.B. Lal, J. Mol. Catal. A: Chem. 186 (2002) 173.