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Isopropylation of Ethyl Benzene Using MCM-41 and Metals Substituted MCM-41

S. SELVAKUMAR*, S. STANLY and BANUMATHI ARABINDOO†
Department of Applied Chemistry, Sri Venkateswara College of Engineering,
Pennalur, Sriperumbudur-602 105, India
E-mail: sselva@svce.ac.in

Mesoporous MCM-41, Al-MCM-41, Fe-MCM-41, Mg-MCM-41 and Mn-MCM-41 were synthesized by hydrothermal process for catalytic applications. Tetradecyl trimethyl ammonium bromide was used as the structure directing template. Sodium silicate and salts of aluminium, iron, magnesium and manganese were the sources of silicon, aluminium, iron, magnesium and manganese, respectively. All the synthesised materials were characterised by BET, XRD and FTIR techniques. The XRD patterns of all the samples showed an intense signal at an angle of about 2º (2θ) due to (100) plane of hexagonal mesophase. The patterns due to other planes were less intense. BET surface area of all the materials were in the range from 772-1273 m^2/g and the pore diameter varies from 2.546-2.663 nm. The catalytic performance of these materials has been tested for isopropylation of ethyl benzene. The influence of temperature, feed ratio and weight hourly space velocity (WHSV) were studied for all the aforesaid reactions for maximum conversion and product selectivity. In addition to *p*-isopropylethylbenzene, a commercially valuable compound diisopropyl ether was also obtained from isopropyl alcohol.

Key Words: Isopropylation, Ethylbenzene, MCM-41, *p*-Isopropylethylbenzene, Diisopropyl ether.

INTRODUCTION

Alkylation of aromatic hydrocarbons is a wide range of synthesis reaction in chemical industry. The well known Friedel-Crafts reaction is an important method for the introduction of alkyl substituents to an aromatic ring[1]. This reaction is catalyzed by Lewis-acids such as $AlCl_3$ or protic acids, such as H_2SO_4. But it involves corrosive liquids, pose problems like difficulty in handling, safety, corrosion, waste disposal and product separation. It can be seen once again that when working with reactants of smaller size, the zeolite is the most active catalyst.

However when the size of the reactants increases, the diffusional restrictions imposed by the zeolite pores strongly decreases the observed rate of reaction, while in the case of the MCM-41 catalyst the ratio remains very close, regardless of the size of the reactant. This makes the ordered mesoporous acid catalyst a very convenient

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†Department of Chemistry, Anna University, Chennai-600 025, India.

one for carrying out alkylation reactions, especially when bulky reactants and products are involved. The mild acidity combined with the large pores in MCM-41 has been especially useful for carrying out reactions such as alkylations, acetylations, isomerization, Beckman rearrangements, glycosidation and aldol condensation. In addition, MCM-41 can provide similar special environment for the reactants in the channels as that in homogeneous solution phase thus aiding the formation of products which are largely kinetic controlled.

Good selectivities have been reported for Al-MCM-41 in the liquid phase alkylation of benzene with propylene compared to the traditional amorphous silica-alumina[2,3].

EXPERIMENTAL

Chemicals for the synthesis of MCM-41 and metal substituted MCM-41 such as tetradecyl trimethyl ammonium bromide, sodium silicate, aluminium sulphate and the respective metal salts were purchased from E-merck (Germany). Ethyl benzene and isopropyl alcohol were purchased from SD fine chemicals.

Synthesis of mesoporous MCM-41 and metal incorporated MCM-41 molecular sieves: Siliceous metal containing MCM-41 materials were synthesized using tetradecyl trimethyl ammonium bromide as described[4]. The following gel composition was used for Si-MCM-41 materials: $10SiO_2$: 5.4 $C_nH_{2n+1}(CH_3)_3NBr$: 4.25 Na_2O: $1.3H_2SO_4$: 480 H_2O. Tetradecyl trimethyl ammonium bromide (32 g) and water (115 g) were mixed and stirred for 0.5 h. Sodium silicate solution (37.4 g in 100 g of water) was added dropwise to the surfactant solution under vigorous stirring for another 0.5 h. Then 2.4 g H_2SO_4 in 10 g of water was added to the above mixture and the stirring was continued for another 0.5 h. The resulting gel was transferred into a polypropylene bottle and kept in an oven at 100 °C for 24 h. After cooling to room temperature, the resultant solid was recovered by filtration, washed with distilled water and dried in an oven at 100 °C for 6 h. Finally the material was calcined in a muffle furnace at 540 °C for 10 h.

The synthesis of metals incorporated MCM-41 (Me-MCM-41) materials were carried out analogous to the synthesis of Si-MCM-41 samples. A solution containing desired amount of metal salt in 5 mL of water was added after the addition of silicon source. The n_{Si}/n_{Me} ratio was fixed at 20 which resulted in the following gel composition: $10SiO_2$:$5.4C_nH_{2n+1}(CH_3)_3NBr$: $0.25Me_2O_3$: $3.27Na_2O$: $1.3H_2SO_4$: 480 H_2O.

Characterization of catalyst

Nitrogen sorption studies: Surface area, pore volume and pore size distribution of the sampled were measured by nitrogen sorption at 77 K with ASAP-2010 porosimeter from micrometrics corporation (Norcross, GA). Before the analysis, the samples were degassed overnight at 623 K at 10^{-5} torr. The mesopore volume was estimated from the volume of nitrogen adsorbed against the relative pressure by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distributions were estimated using Barrett, Joyner and Haleda (BJH) algorithm (ASAP 2010 built-in software from Micrometrics).

X-Ray diffraction: XRD patterns of all the samples were recorded in a stereoscan diffractometer using Phillips 1051, nickel filteres CuK_α radiation (λ = 1.5405 Å) and liquid nitrogen cooled germanium solid state detector. The samples were scanned from 1-40° (2θ) in steps of 0.02° with the count time of 10 s at each point. The peaks were identified with reference to compilation of simulated XRD powder patterns.

FTIR Spectroscopy: Mid-infrared spectrum of the MCM-41 and Me-MCM-41 were recorded on a Nicolet 360 instrument using KBr pellet technique. About 10 mg of the sample was ground finely with about 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 spectra in the range 4000-400 cm^{-1}.

Catalytic reactor studies for isopropylation of ethyl benzene: The schematic diagram of the reactor set-up used in the present study is presented in Fig. 1. The reactor system was fixed-bed, vertical, downward flow reactor made up of quartz tube of 40 cm length and 2 cm internal diameter. The quartz reactor was heated to the requisite temperature with the help ofa tubular furnace controlled by digital temperature controller cum indicator. The chromel-alumel thermo couple was used to measure the temperature of the catalyst bed. About 0.5 g of the catalyst was placed in the reactor and supported on either side with a thin layer of quartz wool and ceramic beads. The top portion of the reactor was connected to a glass bulb having two inlets. Reactants were fed into the reactor through one inlet by a syringe infusion pump that can be operated at different flow rates. The bottom of the reactor was connected to a coiled condenser and receiver in which the products were collected.

The influence of temperature (200, 250, 300, 350 and 400 °C), feed ratio (1:1, 1:2 and 1:3) and WHSV (2.46, 3.28 and 4.92 h^{-1}) was studied to optimize the reaction parameters. The catalytic activities of all the synthesized catalysts were compared in order to understand the effect of metal substituted catalysts and correlate the nature of the substituent with conversion and selectivity for all the aforesaid reactions.

The liquid products during the first 15 min of each run were discarded and analysis was made only for the products collected after this time. This was done to ensure that attainment of steady state for the reaction over the catalyst and also to allow any temperature fluctuation due to the starting of the reaction. After each catalytic run, the catalyst was regenerated by passing air free from both moisture and carbon dioxide through the reactor at 540 °C for 6 h. In the case of transition metal substituted samples during the regeneration they may be oxidized to higher oxidation state. Hence, before the catalytic run, these transition metal incorporated catalysts were reduced to their original oxidation states by passing pure hydrogen

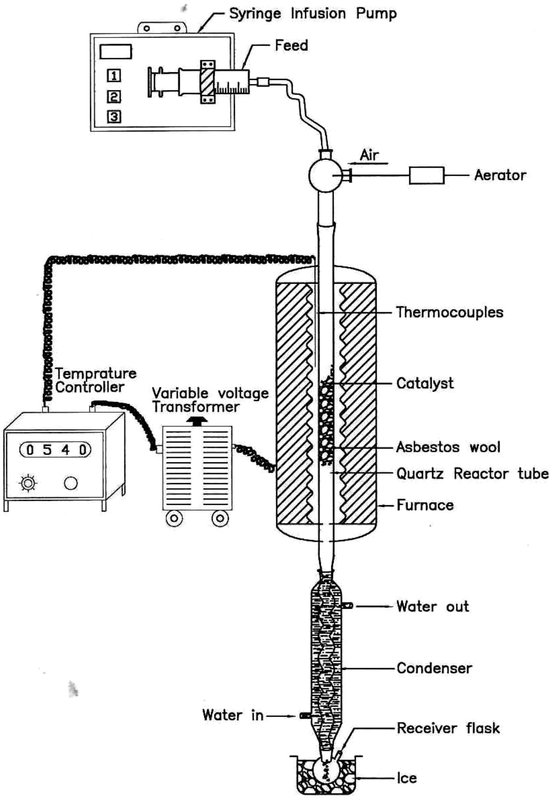

Fig. 1. Schematic diagram of the reactor set-up

for a period of 1 h at the reaction temperature. The liquid products were analyzed by Netel Micro 9100 series GC fitted with a flame ionization detector (FID) and OV 101/carbowax/C-30 column. Nitrogen was used as the carrier gas at a flow rate of 30 mL/min.

RESULTS AND DISCUSSION

Nitrogen sorption studies: Adsorption isotherms of nitrogen on MCM-41, Al-MCM-41, Fe-MCM-41, Mg-MCM-41 and Mn-MCM-41 samples at 77 K showed type IV character. The adsorbed amount increased gradually with increasing relative pressure due to multilayer adsorption. A steep rise in the adsorbed amount was observed at a relative pressure of 0.2-0.4, being caused by capillary condensation of nitrogen in the mesoporous of 2-3 nm diameter. This rise became more gentle and is shifted to lower relative pressure with metal incorporation, which suggests that the pore size was narrowed and distributed. The desorption branch of the isotherm of each sample coincided with the adsorption branch.

Curves show an increase in the adsorption capacity of N_2 with time for the samples synthesized under hydrothermal condition, indicating improvement in the order of the mesopore phase. However, as it has been observed from XRD pattern, the MCM-41 phase is formed more readily under autogenic pressure, showing a small dependence with synthesis time.

The specific surface area (S_{BET}), mean diameter of the mesoporous (d_{mp}) and total volume of pores (V_t) obtained are shown in Table-1. The S_{BET} was 1273 m^2/g for MCM-41 and it ranged between 772 and 934 m^2/g for Me-MCM-41.

TABLE-1
SURFACE AREA, PORE SIZE AND XRD ANALYSIS OF THE CATALYSTS

Catalyst	Surface area and Pore analysis			XRD	
	BET (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	d_{100} (Å)	a_0 (Å)
MCM-41	1273.0	0.8400	2.663	36.31	41.92
Al-MCM-41	934.0	0.6150	2.621	36.01	41.58
Fe-MCM-41	772.6	0.5010	2.596	38.69	44.68
Mg-MCM-41	812.0	0.5358	2.546	38.02	43.91
Mn-MCM-41	872.8	0.5624	2.578	36.75	42.44

X-Ray diffraction: The X-ray diffraction patterns of all the calcined MCM-41 and Me-MCM-41 such as Al-MCM-41, Fe-MCM-41, Mg-MCM-41 and Mn-MCM-41 (Si/Me ratio fixed to be 20) materials are shown in Fig. 2. The samples exhibit an intense bragg peak at about 2θ = 2.3° due to [100] plane and weak signals pertaining to [110], [200] and [210] planes between 4 and 6° (2θ). These peaks can be assigned to a hexagonal mesophase as already observed by the nitrogen adsorption isotherm[5]. These clear peaks indicated that the long-range order structure is achieved and the regular mesoporous structure is retained after the introduction of metals. These Bragg peaks broadened and shifted slightly to higher angle in the case of metal substituted mesoporous with respect to MCM-41, although the hexagonal structure still remained intact. This result suggests that the regularity of the mesoporous structure decreased and the pore size became slightly narrower with the introduction of metals.

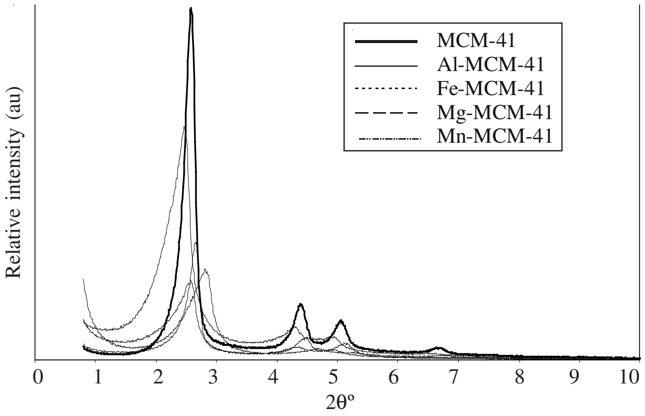

Fig. 2. XRD spectra of the MCM-41 catalysts

The d_{100} spacing and lattice parameter (a_0) (Table-1) shows that the samples possess well defined pore structure due to condensation of Si-OH groups[6-8].

Infrared spectra: The infrared spectra of calcined MCM-41 and Me-MCM-41 such as Al-MCM-41, Fe-MCM-41, Mg-MCM-41 and Mn-MCM-41 are shown in Fig. 3. The broad envelope around 3450 cm^{-1} is due to O-H stretching of water, surface hydroxyl groups and bridged hydroxyl groups. The peaks between 500 and 1200 cm^{-1} are assigned to framework vibrations. The asymmetric stretching of Si-O-Si groups produce peaks around 1633 and 1096 cm^{-1}. The peak at 968 cm^{-1} assigned to the presence of defective Si-OH groups in the materials. The symmetric stretching modes of Si-O-Si groups are observed around 800 cm^{-1} and the peak of 468 cm^{-1} is due to the bending mode of Si-O-Si.

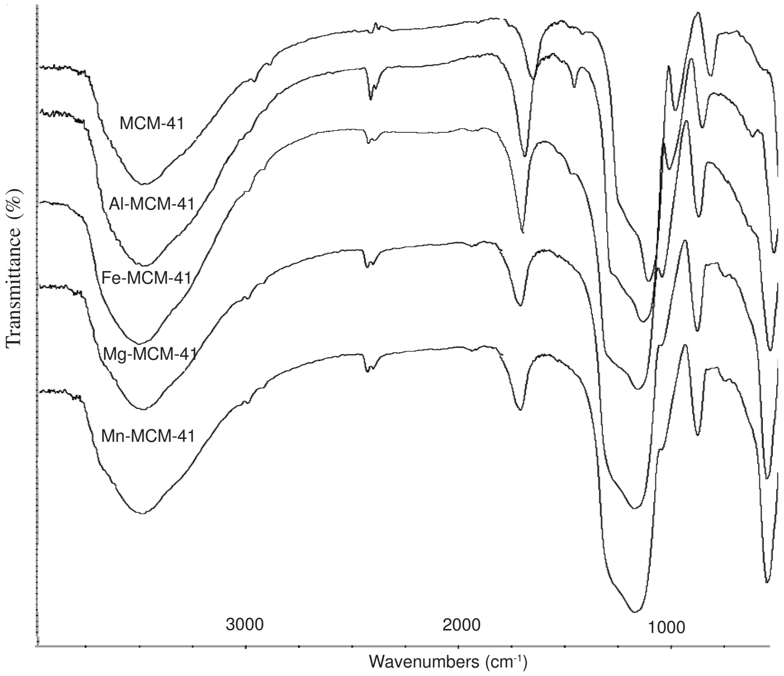

Fig. 3. FTIR spectra of the MCM-41 catalysts

Isopropylation of ethyl benzene with isopropyl alcohol: Isopropylation of ethylbenzene with isopropyl alcohol was studied over MCM-41, Al-MCM-41, Fe-MCM-41, Mg-MCM-41 and Mn-MCM-41 at 200, 250, 300, 350 and 400 °C for the feed ratios 1:1, 1:2 and 1:3 with WHSV = 2.46, 3.28 and 4.92 h^{-1}. Only two products namely *p*-isopropyl ethyl benzene (*p*-IPEB) and di-isopropyl ether (DIPE) were obtained (Fig. 4). An important observation in the study is high selectivity to *p*-isopropyl ethyl benzene. Although the ethyl group in ethyl benzene is *ortho-para* directing, avoidance of *ortho*-isopropylation might be due to steric hindrance. In the *para*-position the steric force substitution occurred exclusively.

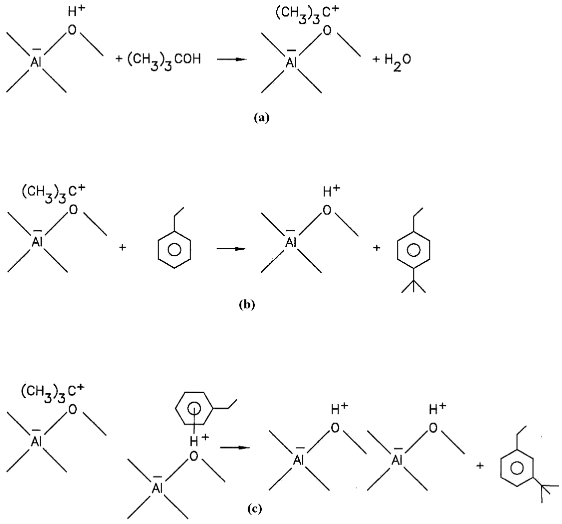

Fig. 4. Mechanism of the isopropylation of ethyl benzene with isopropyl alcohol

Effect of feed ratio: The results obtained over MCM-41 and Me-MCM-41 for the feed ratios 1:1, 1:2 and 1:3 at 300 °C with WHSV = 2.46 h^{-1} are presented in Table-2. The conversion was more for the feed ratio 1:3 than either 1:1 or 1:2. At the feed ratios 1:1 and 1:2 ethyl benzene could be competing with isopropyl alcohol for chemisorption on the Bronsted acid sites and led to less conversion. But at the feed ratio 1:3 isopropyl alcohol could be more chemisorbed than ethyl benzene

TABLE-2
EFFECT OF MOLE RATIO ON ISOPROPYLATION OF ETHYL BENZENE WITH ISOPROPYL ALCOHOL
Temperature = 300 °C, WHSV = 2.46 h^{-1}

Catalyst	Mole ratio	Ethyl benzene conversion (%)	Selectivity of products (%)	
			p-isopropyl ethyl benzene	di-isopropyl ether
MCM-41	1:1	23.4	100.0	
	1:2	31.4	95.6	4.4
	1:3	33.2	93.1	6.9
Al-MCM-41	1:1	31.4	100.0	
	1:2	36.2	100.0	
	1:3	39.1	100.0	
Fe-MCM-41	1:1	2.8	100.0	
	1:2	3.2	100.0	
	1:3	5.5	100.0	
Mg-MCM-41	1:1	8.4	100.0	
	1:2	8.8	100.0	
	1:3	11.7	100.0	
Mn-MCM-41	1:1	6.8	100.0	
	1:2	7.6	100.0	
	1:3	9.2	100.0	

resulted thus more conversion. In MCM-41, the feed ratio 1:3 gave slightly increased selectivity to ether as there would be more amount of isopropyl alcohol in the vapour phase in addition to those chemisorbed. For Me-MCM-41 catalysts selectivity is 100 % for *p*-isopropyl ethyl benzene.

Effect of temperature: Effect of temperature in the conversion percentage of isopropyl alcohol is presented in Table-3. Conversion of ethyl benzene in all the catalyst increased with increase in temperature up to 350 °C but it slightly decreased at 400 °C. At high temperature (above 300 °C) 100 % selectivity was obtained for the product *p*-isopropyl ethyl benzene, but not less than 80 % even at low temperatures. The second product, di-isopropyl ether was only observed at low temperatures (below 300 °C). Even at low temperature range, the selectivity of di-isopropyl ether decreased with increase in temperature. Similar observations were also reported by the Balasubramanian *et al.*[9], Kannan *et al.*[10] and Umamaheswari *et al.*[11].

TABLE-3
EFFECT OF TEMPERATURE ON ISOPROPYLATION OF ETHYL BENZENE WITH ISOPROPYL ALCOHOL
WHSV= 2.46 h^{-1}, mole ratio: 1:3

Catalyst	Temperature (ºC)	Ethyl benzene conversion (%)	Selectivity of products (%)	
			p-isopropyl ethyl benzene	di-isopropyl ether
MCM-41	200	22.6	88.6	11.4
	250	23.6	89.2	10.8
	300	33.2	93.1	6.9
	350	38.9	100	
	400	31.1	100	
Al-MCM-41	200	29.4	81.6	18.4
	250	29.8	82.5	17.5
	300	39.1	100	
	350	43.8	100	
	400	43.6	100	
Fe-MCM-41	200	1.8	100	
	250	4.7	100	
	300	5.5	100	
	350	5.8	100	
	400	3.3	100	
Mg-MCM-41	200	4.8	89.8	10.2
	250	10.3	90.4	9.6
	300	11.7	100	
	350	11.9	100	
	400	8.5	100	
Mn-MCM-41	200	6.8	100	
	250	9.4	100	
	300	12.5	100	
	350	12.8	100	
	400	9.8	100	

Effect of WHSV: Table-4 presents the comparison of conversion with respect to WHSV 2.46, 3.28 and 4.92 h^{-1}, it shows the conversion is maximum for WHSV = 3.28 h^{-1}. Generally decrease in conversion is expected for increase in flow rate. But increase in conversion from 2.46-3.28 h^{-1} suggests less blocking of active sites in 3.28 h^{-1} than with 2.46 h^{-1}, whereas blocking sites increases when WHSV increased from 3.28-4.92 h^{-1}, which decreases the conversion percentage. The selectivity of di-isopropyl ether was more for the WHSV 3.28 h^{-1}.

TABLE-4
EFFECT OF SPACE VELOCITY ON ISOPROPYLATION OF ETHYL BENZENE WITH ISOPROPYL ALCOHOL
Temp = 300 °C, Mole ratio: 1:3

Catalyst	WHSV (h^{-1})	Ethyl benzene conversion (%)	Selectivity of products (%)	
			p-isopropyl ethyl benzene	di-isopropyl ether
MCM-41	2.46	33.2	93.1	6.9
	3.28	49.4	79.8	20.2
	4.92	44.4	89.6	10.4
Al-MCM-41	2.46	39.1	100	
	3.28	53.9	67.7	32.3
	4.92	50.8	87.5	12.5
Fe-MCM-41	2.46	5.5	100	
	3.28	17.3	100	
	4.92	7.2	100	
Mg-MCM-41	2.46	11.7	100	
	3.28	28.1	86.6	13.4
	4.92	16.8	88.8	11.2
Mn-MCM-41	2.46	9.2	100	
	3.28	11.0	100	
	4.92	10.7	100	

Effect of the catalyst: Conversion was very less over Fe-MCM-41 over other catalysts due to rapid diffusion. Similar observations over Mg-MCM-41 and Mn-MCM-41 also attributable to fast diffusion of the reactants. Ether was not observed over this catalyst as the strong Bronsted acid sites were less. Depending upon the conditions MCM-41, Al-MCM-41, Mg-MCM-41 yielded both *p*-isopropyl ethyl benzene and di-isopropyl ether while Fe-MCM-41 and Mn-MCM-41 yielded only *p*-isopropyl ethyl benzene irrespective of the variation factor. The selectivity to *p*-isopropyl ethyl benzene was high for both the catalysts. Conversion of ethyl benzene over Al-MCM-41 was more than that of any other Me-MCM-41 for all the feed ratios, WSHV and temperatures due to more density of acid sites in Al-MCM-41. Conversion was less than 10 % for all the feed ratios illustrating insufficient number of Bronsted acid sites due to framework leaching of metal ions.

Conclusion

MCM-41 and Al-MCM-41 are found to be more active catalysts for isopropylation of ethyl benzene. Conversion was more at 350 °C, but was less at 400 °C due to coke formation. An important observation in the study is 100 % selectivity to *p*-isopropyl ethyl benzene at higher temperatures. Increase in WHSV = 2.46-3.28 h^{-1} led to increase in conversion and it was attributed to less deactivation of catalysts as coke formation at the latter flow rate was to be less. Only with WHSV = 4.92 h^{-1} decrease in conversion was observed due to fast diffusion. Study of time on stream illustrates decrease in conversion with increase in stream due to gradual blocking of active sites. Transition metal substituted catalysts undergo deactivation readily above 300 °C due to coke formation.

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