Bull. Chem. Soc. Ethiop. **2006**, 20(1), 89-97. ISSN 1011-3924
Printed in Ethiopia

CUMENE CRACKING ON MODIFIED MESOPOROUS MATERIAL TYPE MCM-41

Ahmed Belhakem[1*] and Abdelkader Bengueddach[2]

[1]Laboratory S.E.A.2M/U de Mostaganem, B.P. 1001, 27000 Mostaganem, Algerie
[2]Lababoratory Chimie des Matériaux, Université d'Es-Senia, Oran, Algerie

(Received March 1, 2005; revised July 26, 2005)

ABSTRACT. The effect of ionic exchange degree of aluminated mesoporous materials H(X)-AlMCM-41 materials, the method of its exchange mode and its grains form were investigated for the mesoporous catalytic activity in the cumene (i.e. isopropylbenzene) cracking reaction. Benzene, propylene and xylene derivatives are the main products of this reaction. Olefins like butene and pentene appeared as the products of secondary reactions. No saturated hydrocarbons, except traces of butane, nor ethylbenzene and toluene were formed and seemed to be typical products of secondary reactions obtained with HNaY zeolites. Generally the exchanged H(X)-AlMCM-41 materials by the substitution of Na^+ by NH_4^+ are more active than those exchanged directly with acid solution (substitution of Na^+ by H^+) even if both the two methods used exhibit a comparable content of acid sites within catalysts at a low exchange degrees. However, the first method of exchange has exhibited an important acidity for mesoporous materials when the ionic exchange degree was increased up to 90%; it was probably due not only to the percentage of exchanged degree but also to the distribution of acid sites within the materials.

KEY WORDS: MCM-41 mesoporous, Grains forms, Cumene cracking

INTRODUCTION

The cumene cracking belongs to the largely used catalytic reactions; it has been thoroughly studied on the zeolitic catalysts like ZSM-5 but rarely with mesoporous materials and especially MCM-41.

A series of experiments in which cumene converted were carried out on ZSM-5 zeolites with a different ionic exchange degree [1-3]. Some authors compared the behaviour of some type of zeolites catalysts in cumene conversion and observed distinct differences in the type and the composition of reactions products [4-7].

The aim of the present investigation is to study the catalytic cracking of cumene on H(X)-AlMCM-41 materials for which the acid properties were well characterized [8]. The effects of the exchange mode and the grains forms of the samples were also investigated.

EXPERIMENTAL

The MCM-41 materials, with Si/Al ratio of about 10, were obtained following a method described elsewhere [9]. The parent MCM-41 sample was synthesized using silica source, i.e. Ludox 40 (Fluka), sodium hydroxide (Aldrich), sodium aluminate (Riedle-de Haen 54% Al_2O_3, 41% Na_2O), C_{16}TMAOH (Aldrich, 99%) and deionised water according to the following procedures. First, the C_{16}TMAOH template was dissolved in sodium hydroxide solution with stirring. Secondly, sodium aluminate was added to the above solution followed by Ludox, and the resulting mixture was maintained under constant stirring. The final gel obtained had the following molar composition SiO_2: $0.07Al_2O_3$: $0.5Na_2O$: $0.125C_{16}$TMAOH: $127H_2O$. This gel was then heated at 323 K for 6 days. The product of the synthesis was recovered by filtration,

---

*Corresponding author. Fax: 0021345211018. E-mail: belhakem_ahmed@caramail.com washed with deionised water, dried at 363 K and finally calcined in air at 823 K (heating rate 2 K/min) for 3 h to remove the template used. The samples X-ray diffraction data were collected on a Philips 1830 diffractometer with varied slit using CuK_{α} radiation (λ = 0.1542 nm). Figure 1 shows the main peak of mesoporous phase MCM-41 at d_{100} = 35 Å in the 2θ range from 1° to 10° with a scanning rate of $5°.min^{-1}$. Adsorption measurement was carried out at 77.3 K on an ASAP2010 apparatus (Micromeritics, Norcross, GA, USA). The samples were degassed at 570 K and 10 Pa for 2 h prior to the adsorption measurement. The nitrogen adsorption isotherm was a typical type IV isotherm according to IUPAC classification. The specific surface (S_{BET} = 1000 m^2/g) and pore volume distribution (DPA = 35 Å) were determined by the BET and BJH methods, respectively (see Figures 2a and 2b). After the parent MCM-41 sample was aluminated via the method based on a dry exchange ionic described in detail in literature [10]; the acid forms of AlMCM-41 samples were obtained via two methods separately: first, by exchanging with ammonium nitrate solutions with various concentrations of NH_4OH, after this, samples were subjected to a heat treatment in order to evacuate the NH_3 gas, and second, by treatment with HCl acid solution with varied concentration going from 0.01 N to 0.5 N by exchanging directly Na^+ with H^+. The exchanges carried out via substitution of Na^+ ions with NH_4^+ or by the treatment with acid solution are symbolised NM and AM, respectively.

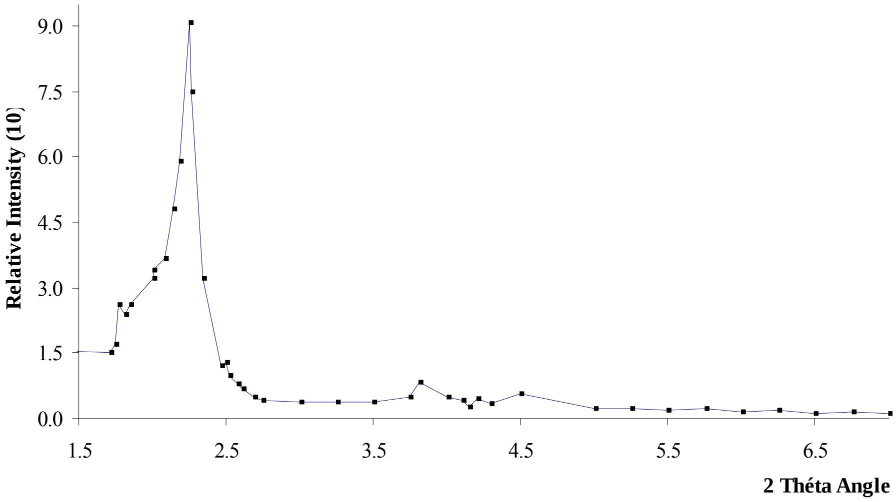

Figure1. X-ray diffraction of parent MCM-41 material.

In order to obtain catalysts with the highest ionic exchange degree the two latter methods were used one after another in different sequences; symbolised by NAM and ANM. The main data characterizing the samples are given in Table 1. The numbers in the symbols of samples give the percentage of ionic exchange. The acid properties of these samples were investigated according to the FTIR method. For the in-situ analysis, the FTIR spectroscopic studies were performed on BIORAD FTS 60A spectrometer at resolution of 2 cm^{-1} using an oven equipped with self supporting wafers, a vacuum and gas-dosing system. The spectra were recorded by accumulating 160 scans which correspond to 1 min time. The integration was carried out using the spectraCalc program as given in literature [11-13]. The decomposition of ammonia during temperature-controlled heating was followed by IR spectroscopy. The ammonia was completely desorbed at 723 K and the IR vibration N-H band had completely disappeared at this temperature which proves the leaving of NH_3 molecules. The IR spectra, of different samples which were exchanged with different method described above, were closely identical and showed a characterized vibration band O-H at 3609 cm^{-1} which shows the presence of strong Brönsted acid centres.

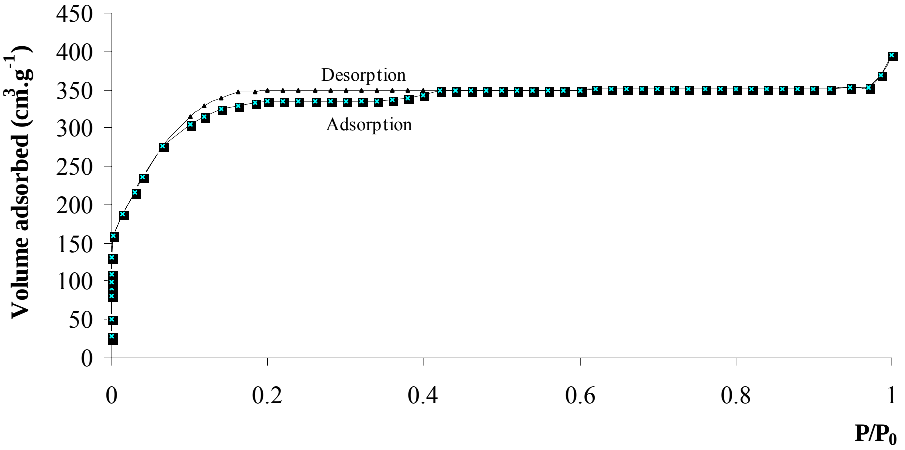

Figure 2a. Isotherm of N_2 adsorption on parent MCM-41 material.

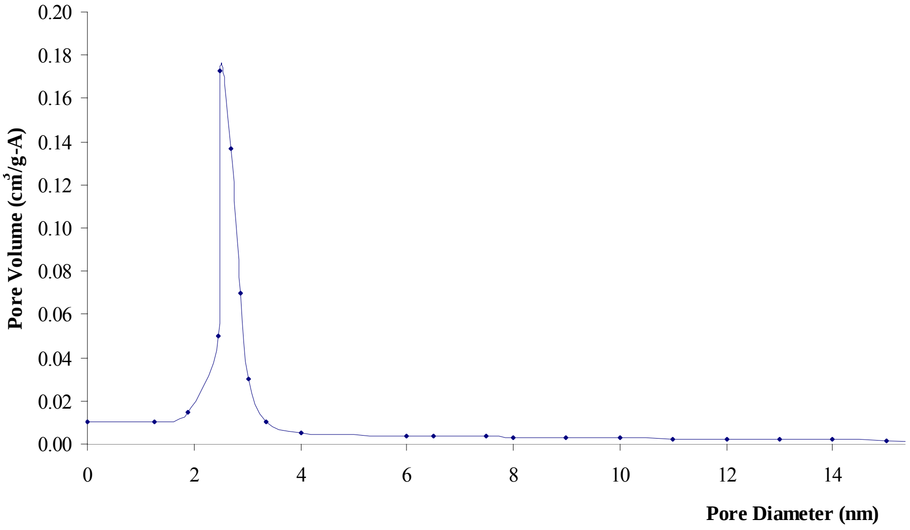

Figure 2b. Average pore distribution (APD) within MCM-41 material determined with BJH method.

Catalytic tests were carried out in a pulse microreactor connected on line with a gas chromatograph; using both samples in which the non extruded one contains crystallites of 1 μm and the other one obtained by grinding the fine crystalline powder and extruding them in the form of pellets and selecting the sieve fraction of grains ranging from 90 to 190 μm. Doses of 3 μL cumene were introduced using helium as a carrier gas with a velocity of 0.35 L.h^{-1}. A quantity of 0.02 g of catalyst diluted in 0.1 g of powdered quartz was activated "in situ" for 3 h at 773 K under helium stream. Pure cumene, obtained from Aldrich, was kept over metallic sodium and distilled before experiments. A Carlo-Erba HRGC 5300 Gas Chromatograph with a programmed heating was used for the analysis of the reaction products; applying a chromatographic column (length 3 m, diameter 4 mm) filled with Chromosorb W covered with 14 % of silicon oil DC 200. The reaction products were then identified using a Mass Spectrometer type LKB9000s. Chromatographs recording were obtained automatically with different samples by collecting data at regular intervals using a valco 6-port valve to calculate the percentage of converted cumene.

Table 1. Characteristics of exchanged MCM-41 samples.

Sample and ionic exchange degree (%)	Apparent activation energy (kJ/mol)		[Acid centre]/unit cell				Rate constant of cumene cracking (min-^{1}) 673 K		633 K	
	Powder	Grains	Strong	Weak	Total	Lewis	Powder	Grains	Powder	Grains
NM-20	64	53	0.30	0.30	0.60	0.09	68	97	29	56
NM-40	58	49	0.50	0.37	0.87	0.16	131	140	81	83
NM-80	53	33	0.88	0.41	1.25	0.19	228	210	138	147
AM-20	60	50	0.34	0.36	0.70	0.14	137	171	67	91
AM-40	42	44	0.84	0.27	1.11	0.19	125	200	72	130
AM-80	37	41	1.06	0.31	1.37	0.15	164	238	120	162
ANM-95	45	42	0.98	0.23	1.21	0.12	110	202	65	134
ANM-80	59	51	1.02	0.20	1.22	0.13	178	272	110	189
NAM-80	80	79	1.00	0.21	1.21	0.15	175	276	116	180
NAM-95	71	68	1.01	0.18	1.18	1.14	172	273	112	175

Catalytic tests were carried out in two stages; first, at constant temperature: the variation of activity and selectivity was investigated using the number of cumene pulses, and second, at different temperatures varying from 550 K to 683 K, and in order to avoid the ageing effect, the cumene was introduced by only one pulse. The rate of cumene conversion was calculated assuming a first order of the reaction.

RESULTS AND DISCUSSIONS

Reaction products

Besides the main reaction products like benzene, propylene and xylene derivatives, obtained on H(X)-AlMCM-41, some amounts of side reactions products were also detected such as butene, pentene and traces of butane. Other authors [6, 14, 15] obtained the same products but with different compositions owing to the catalysts used. Presumably it was due to properties of different products formed inside the catalysts channels and materials structures. In the H(X)-AlMCM-41 materials, the large pores allow the formation of both linear and especially multi-branched oligomers which were transformed, after cracking, into various chain lengths. It would seem that the three-dimensional products formed within mesoporous MCM-41 pores disproportionate into hydrogen rich products like alkanes on one hand and hydrogen deficient products like alkenes on the other hand. These latter products are precursors of the coke formation which are in agreement with previous research [16, 17]

Among the side reaction product, only one aromatic product was detected, i.e. the propylbenzene which is the product of cumene isomerisation. Based on the latter, the reaction under study was occurred via a monomolecular process which characterized by the formation of monomolecular transition complexes. This phenomenon was observed for zeolites with reduced and small pores like Y zeolites. Contrarily to zeolites and in the mesoporous materials, this reaction was occurred via bimolecular process characterized by the formation of bimolecular transition complexes which obviously formed in large pores of H(X)-AlMCM-41 materials which are in agreement with literature [18-21].

Catalysts ageing

The ageing of catalysts was followed at 623 K and 673 K at which a cumene was converted almost totally. A conversion rate versus cumene pulses, as showed on Figures 3a and 3b, had given interesting information about the activation-deactivation process of the catalysts. Although the representative curves, of ANM-80, AM-40 (or NM-40) samples, present a same profile, a less conversion rate was observed for those exchanged at a low ionic degree. The deactivation was then varied slowly with the increasing number of cumene pulses and was distinct for studied temperatures and for different exchanged samples. This could be explained from a part, by a strength and distribution of acidity catalysts and from another part by a rapid desorption process of coke deposited which inhibited catalysts activities. As seen in Figures 3a and 3b and in spite of a slight difference in conversion rate, the grain forms; extruded samples (dashed line) and non-extruded ones (full lines), had no great influence on the catalysts ageing in present study reaction.

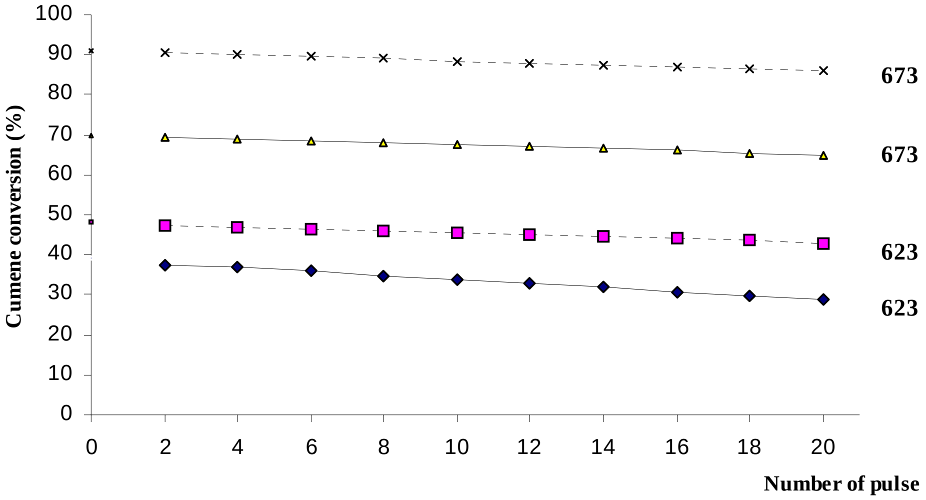

Figure 3a. Cumene conversion versus number of pulses of ANM-80 sample (full line: non-extruded; dashed line: extruded).

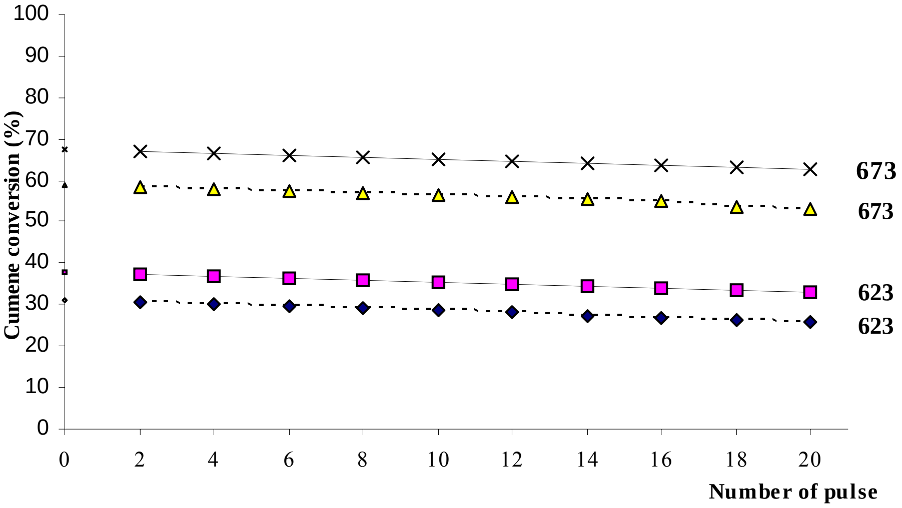

Figure 3b. Cumene conversion versus number of pulse of AM-40 (or NM-40) sample (full line: non-extruded; dashed line: extruded).

Activation-deactivation process, at 623 K and 673 K temperatures, affects enormously the composition of the reaction products. As shown in Figures 4a and 4b, the tendency was closely the same for different catalysts. Moreover, the quantity of benzene in the initial pulses exceeded the sum of quantity of all the other obtained products. The deficit of xylene derivatives could be due to their partially irreversible adsorption resulting in the slow catalyst deactivation and consequently they were obtained with difficulty. Only an amount of xylene derivative was slowly formed out of the catalyst channels. The catalysts deactivation was achieved by a diminishing of the amounts of side reactions products, like olefins, increasing then the quantity of benzene and propylene which are in agreement with literature [2]. Simultaneously an amount of benzene was increased and the total quantity of xylene derivatives was decreased and their molar ratio was exceeded 1:1, thus, the cracking reaction was favoured. Regarding this, the cumene cracking was mainly occured on the acid centres and especially the strongest ones like Brönsted sites which were poisoned at first by coke deposit [22-26].

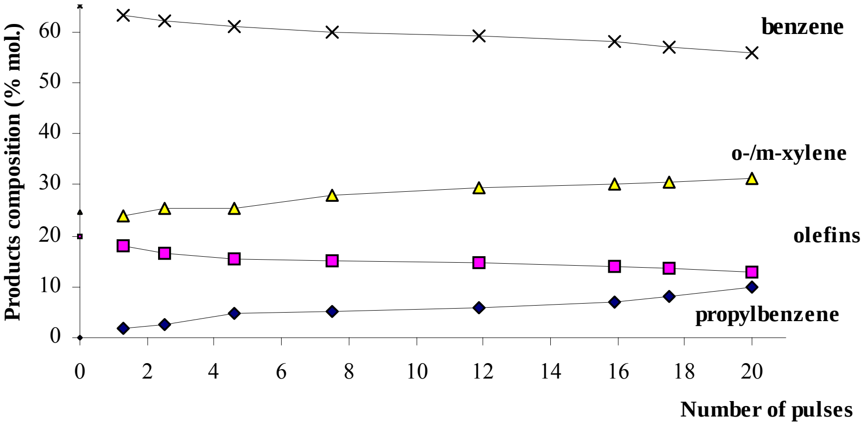

Figure 4a. Composition of the reaction products on non-extruded AM-40 (or NM-40) at 673 K versus number of cumene pluses.

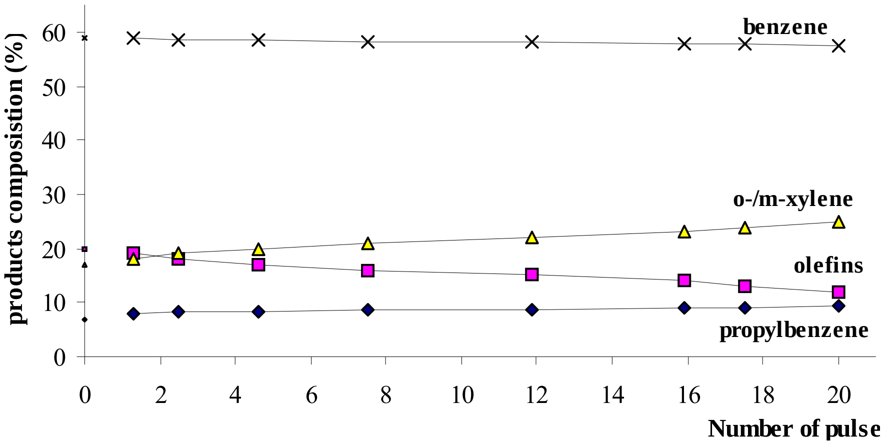

Figure 4b. Composition of the reaction on non-extruded AM-40 (or NM-40) at 623K versus number of cumene pulses.

Effect of ionic exchange degree and deionisation mode

The study of the rate constant versus temperature, obtained with extruded samples at different temperatures, was represented in Figure 5. A comparison of the various samples activities resulted in the following observations:

1. For both series of materials NM and AM the catalytic activity was increased proportionally with ionic exchange degree and also when the acidity increased. The latter was given by the concentration of total acid centres (Brönsted and Lewis).
2. The effect of the deionisation mode could be followed by comparing samples AM-40 and NM-40 with 40 % ionic exchange degree and also samples ANM-80 and NAM-80 with 80 % of ionic exchange. The catalysts activities were similar within the whole range of temperature and the rates constant were increased proportionally with the exchange degree. Except for NM-40 sample which was active only from 600 K temperature and with a rate constant do not exceeding 40 min^{-1}. Despite the fact that this sample presents a good acidity than the AM-40 sample but was remained less active, this is due probably to the distribution of different acid centres within materials. Moreover, a uniform sites distribution was also a primary factor in acid catalysis which is corroborated by literature [17]. The differences in activities were more pronounced and the sequence of catalysts activity was corresponded well to the sequence of the concentration of acid centres especially Brönsted ones. The samples, with important acid centres per unit cell and with a good distribution, were active in this reaction type. These observed differences could be attributed to the higher activity of strongest acid centres which are very catalytically active. The second considered possibility is that for samples with a high exchange degree, on the accessible acid centres, a phenomenon competition could be occurred between different reaction molecules liable to adsorb on these sites.
3. The apparent activation energies of cumene conversion, for different series NM, AM, ANM and NAM are in inverse proportion to ionic exchange degree. The same results were observed for zeolites; e.g. butene isomerisation on NaHY zeolites [18]. Several reasons were considered for this effect; first, the growing number of acid centres, and especially strongest ones, was played an important role and were active in acid catalysis [27, 28]. The presence of these sites was made easier cumene conversion in the inner materials surfaces and therefore the diffusion of different molecules became a determining factor influencing the rate of process. Secondly the increased acid strength of different centres and their uniform distribution inside materials were

induced a lower energy needed for the formation of transition complex. Finally the possible increase of the adsorption heat of the substrate was caused the decrease in the apparent energy of activation even if the true activation energy remains constant.

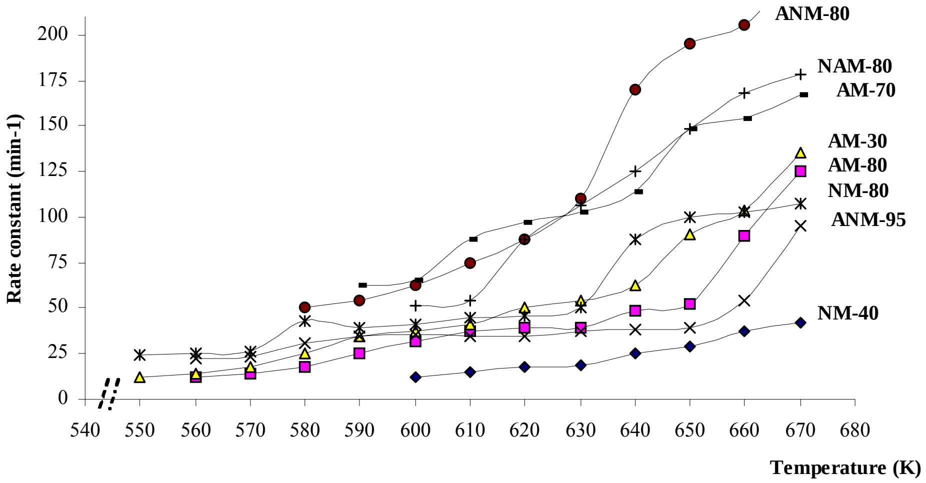

Figure 5. Rate constant of non-extruded catalysts versus temperature.

The effect of sample form is shown in Figure 3. For AM-40 sample which exhibiting a relatively low activity, the effect of extrusion was not pronounced. On the other hand and in the case of highly active sample like ANM-95 sample the conversion on the extruded catalyst was relatively higher. This could be attributed from a part to the fact that the cumene conversion took place not only into the pores (on the inner surface) and also between particular crystallites (on the external surface) and from another part the reagents were remained for a long time in contact with the catalyst. The similar effect was obtained by the prolongation of contact time. The diffusion in the pores of the granule was also one of the reasons of decreasing the apparent activation energy.

CONCLUSION

Benzene and propylene were the main products when the cumene was converted on mesoporous MCM-41 materials at different acid forms and at different temperature. Good performances were observed for NM samples exchanged at high degree. At difference with studies carried out with zeolites like US-Y and ZSM-5 and in addition to the secondary products observed, derivatives of xylene were detected, with a low percentage, in this case of reaction with MCM-41 as catalyst.

REFERENCES

1. Nayak, V.S.; Choudary, V.R. *J. Catal.* **1983**, 81, 26.
2. Kenawi, F.I.; Morsey, A.K. *Hung. J. Ind. Chem.* **1987**, 15, 285.
3. Bautista, F.M.; Campelo, J.M.; Garcia, A.; Luna, D.; Marinas, J.M.; Romero, A.A.; Navio, J.A.; Macias, M. *Catal. Lett.* **1994**, 24, 293.
4. Redey, A.; Sinko, J.; Gardos, G. *Hung. J. Ind. Chem.* **1992,** 19, 13.
5. Lin, H.; Han, M.; Wang, J.; Wang, Z.; Jin, Y. *Chem. Eng. Comm.* **2002**, 189, 1498.
6. Corma, A.; Farag, H.; Wojciechowski, B.W. *Int. J. Chem. Kinetics.* **1981**, 13, 883.

7. McCullen, S.B.; Vartuli, J.C. *U.S. Patent.* **l992**, 5, 156, 829,.
8. Beck, J.S.; Vartulli, J.C.; Leonowicz, M.E.; Schmitt, K.D.; Chu, C.T.W.; Olson, D.H.; Shepard, E.W.; McCullen, S.B.; Higgins, J.B.; Schlenker, J.L. *J. Am. Chem. Soc.* **1992**, 114 10834.
9. Khelifa, K.M.; Khelifa, A.; Belhakem, A.; Marouf, R.; Abdelmalek, F.; Addou, A. *Ads. Sci. Technol.* **2004**, 22, 1.
10. Belhakem, A.; Bengueddach, A. *J. Soc. Alger. Chimie.* **2003,** 13, 215.
11. Mokaya, R.; Jones, W. *Catal. Lett.* **1997**, 49, 87.
12. Mokaya, R.; Jones, W. *J. Mater. Chem.* **1999**, 9**,** 555.
13. Del-Arco, M.; Carriazo, D.; Gutierez, S.; Martin, C.; Rives, V. *Phys. Chem. Chem. Phys.* 2004, 6, 465.
14. Khalil, F.H.; Abo-Lemon, F.S.; Ayad. Z.S. *Hung. J. Ind. Chem.* **1986**, 14, 337.
15. Brei, V.V. *Theor. & Experim. Chem.* **2003**, 39, 70.
16. Watcher, W.A. *U.S. Patent.* **1993,** 5, 221, 648.
17. Corma, A. *Chem. Rev.* **1995**, 95, 559.
18. Guisnet, M.; Andy, P.; Gnep, N.S.; Bennazi, E.; Travers, C. *Oil Gas Sci. Technol.* **1999**, 54, 23.
19. Wojciechowski, B.W.; Corma, A. *Catalytic Cracking. Catalysis, Chemistry and Kinetics*, Marcel Dekker: New York; **1986**.
20. Venuto, P.B. *Microporous Mater.* **1994**, 2, 297.
21. Corma, A. *Chem. Rev.* **1997**, 97, 2373.
22. Xu, M.; Wang, W.; Seiler, M.; Buchholz, A.; Hunger, M. *J. Phys. Chem. B***.** **2002**, 106, 3202.
23. Zhao, D.; Goldfard, D.; in Zeolites; *A Refined Tool for Designing Catalytic Sites*; Bonneviot L.; Kaliguine. S. (Eds.); Elsevier: Amsterdam; **1995**; p 185.
24. Beaumont, R.; Barthomeuf, D. *J. Catal.* **1972**, 27, 45.
25. Parida, K.M.; Acharya, M.; Samantary, S.K.; Mishra, T. *J. Colloid Interface. Sci.* **1999**, 217, 388.
26. Umamaheswari, V.; Palanichamy, M.; Arabindoo, B.; Muresan, V. *Proc. Indian Acad. Sci. (Chem. Sci.)* **2002**, 114, 203.
27. Taouli, A.; Reschetilowski, W. *Stud. Surf. Sci. Catal.* **2002**, 142B, 1315.
28. Inaki, T.; Yoshida, H.; Yoshida, T.; Hattori, T. *J. Phys. Chem B* **2002**, 106, 9098.