

Cumene Cracking on Modified Mesoporous Material Type MCM-41

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The effect of ionic exchange degree of H(X)-AIMCM-41 materials, the method of its exchange and its grain form were investigated for mesoporous catalytic activity in the cumene 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, which are typical products of secondary reactions obtained with HNaY zeolites, were formed, except for traces of butane. Generally the exchanged H(X)-AIMCM-41 materials by the substitution of Na⁺ by NH₄⁺ are more active than those exchanged directly with acid solution (substitution of Na⁺ by H⁺) even if both the methods used exhibit a comparable content of acid sites within catalysts at a low exchange degree. However, the first method of exchange exhibited significant 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

Cumene cracking is a commonly used catalytic reaction; it has been thoroughly studied on zeolitic catalysts like ZSM-5 but rarely with mesoporous materials and especially MCM-41.

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

The aim of the present investigation was to study the catalytic cracking of cumene on H(X)-AIMCM-41 materials for which the acid properties were well characterized. The effects of the exchange mode and the grain forms of the samples were also investigated.

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Experimental

The MCM-41 materials, with a Si/Al ratio of about 10, were obtained using a method described elsewhere^{8,9}. The parent MCM-41 sample was synthesized using a silica source, i.e. Ludox 40 (Fluka), sodium hydroxide (Aldrich), sodium aluminate (Riedle-de Haen 54% Al₂O₃, 41% Na₂O), C₁₆TMAOH (Aldrich, 99%) and deionized water according to the following procedures. First, the C₁₆TMAOH 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 SiO₂:0.07 Al₂O₃:0.5 Na₂O:0.125 C₁₆TMAOH:127 H₂O. This gel was then heated at 323 K for 6 days. The product of the synthesis was recovered by filtration, washed with deionized 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 a varied slit using CuK_α radiation ($\lambda = 0.1542$ nm). Figure 1 shows the main peak of the 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 was measured 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 ($S_{BET} = 1000$ m²/g) and pore volume distribution (DPA = 35 Å) were determined by the BET and BJH methods respectively (see Figures 2a and 2b). After that, the parent MCM-41 sample was aluminated via the method based on a dry exchange ionic described in detail in the literature¹⁰. The acid forms of AlMCM-41 samples were obtained via 2 methods separately. The first was by exchanging with ammonium nitrate solutions with various concentrations of NH₄OH; after this, samples were subjected to heat treatment in order to evacuate the NH₃ gas. The second was by treatment with HCl acid solution with varied concentration of 0.01 to 0.5 N by exchanging directly Na⁺ with H⁺. The exchanges carried out via substitution of Na⁺ ions with NH₄⁺ or by treatment with acid solution are termed NM and AM, respectively.

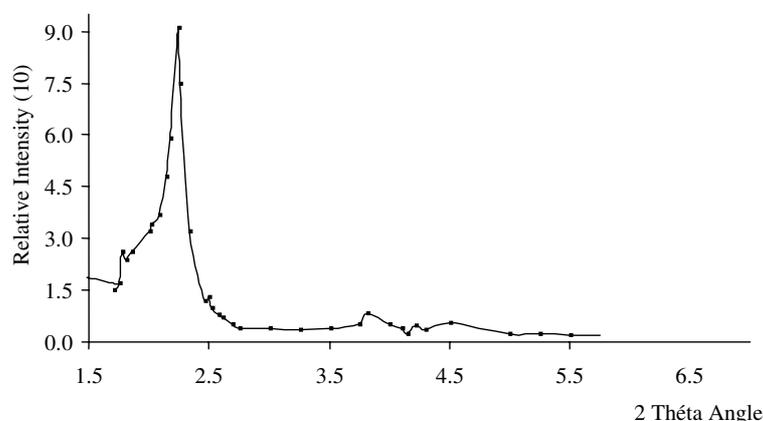


Figure 1. X-ray diffraction of parent MCM-41 material.

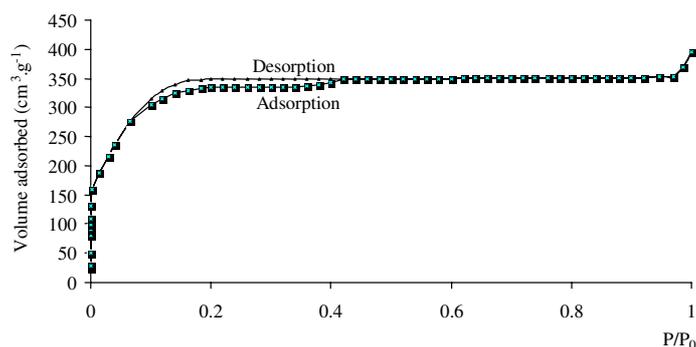


Figure 2a. Isotherm of N_2 adsorption on parent MCM-41 material.

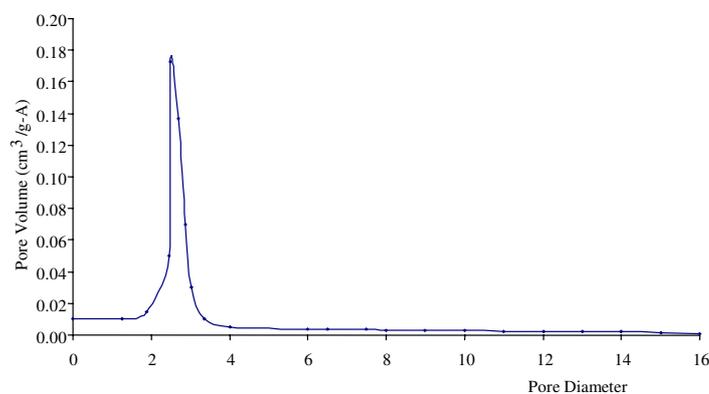


Figure 2b. Average pore distribution (APD) within MCM-41 material determined with BJH method.

In order to obtain catalysts with the highest ionic exchange degree the 2 latter methods were used one after another in different sequences, termed NAM and ANM. The main data characterizing the samples are given in the Table. 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 as described in the literature^{11–13}. For the in situ analysis, FTIR spectroscopic studies were performed on a BIORAD FTS 60A spectrometer at a resolution of 2 cm^{-1} using an oven equipped with self-supporting wafers, a vacuum and a gas-dosing system. The spectra were recorded by accumulating 160 scans, corresponding to 1 min of time. The integration was carried out using the spectraCalc program^{14–18}. 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 a different method described above, were identical and showed a characterized vibration band O-H at 3609 cm^{-1} , which shows the presence of strong Brönsted acid centers.

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 $1\ \mu\text{m}$ and the other one is 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 $190\ \mu\text{m}$. Doses of $3\ \mu\text{l}$ cumene were introduced using helium as a carrier gas with a velocity of 0.35 L.h^{-1} . Then 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 the experiments. A Carlo-Erba HRGC 5300 Gas Chromatograph with

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. Chromatograph recordings 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 ^{4,19,20}.

Table. Characteristics of exchanged MCM-41 samples.

Sample and ionic exchange degree (%)	apparent energy activation KJ/mol		[acid center]/unit cell				Rate Constant of cracking cumene min ⁻¹			
	powder	grains	strong	weak	total	Lewis	673 powder	673 grains	633 powder	633 grains
NM-20	64	42	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	40	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 2 stages. First, at constant temperature, the variation of activity and selectivity was investigated using a number of cumene pulses. Second, at different temperatures varying from 573 to 673 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 Discussion

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 ^{6,21,22} obtained the same products but with different compositions owing to the catalysts used. Presumably it was due to the different properties of the different products formed inside the catalysts' channels and materials' structures. In the H(X)-AlMCM-41 material, 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, in agreement with previous research ^{23,24}.

Among the side reactions, only one aromatic product was detected, i.e. propylbenzene, which is the product of cumene isomerization. Based on the latter, the reaction under study occurred via a monomolecular process characterized by the formation of monomolecular transition complexes. This phenomenon was observed for zeolites with reduced and small pores like Y zeolites. In contrast to zeolites and in the

mesoporous materials, this reaction occurred via a bimolecular process characterized by the formation of bimolecular transition complexes, which obviously formed in large pores of H(X)-AlMCM-41 materials, in agreement with the literature^{25–28}.

Catalyst ageing

The ageing of the catalysts was followed at 623 and 673 K, at which cumene was converted almost totally. A conversion rate versus cumene pulses, as shown in Figures 3a and 3b, gave interesting information about the activation-deactivation process of the catalysts. Although the representative curves of ANM-80 and AM-40 (or NM-40) samples present the same profile, a lower 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 partly by the strength of acidity catalysts and partly by a rapid desorption process of coke deposited, which inhibited catalyst activities. As seen in Figures 3a and 3b and in spite of a slight difference in the conversion rate, the grain forms—extruded samples (dashed lines) and non-extruded ones (solid lines)—had no great influence on catalyst ageing in the present study reaction.

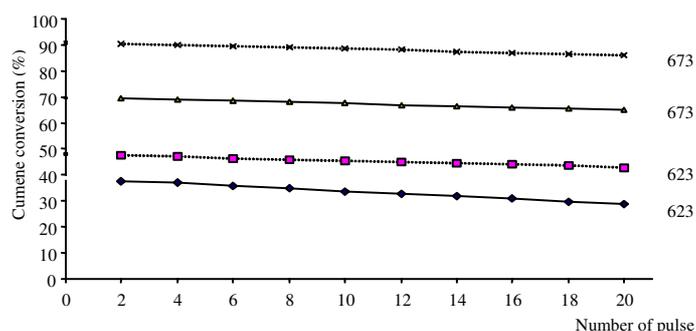


Figure 3a. Cumene conversion versus number of pulses of ANM-80 sample Solid line: non-extruded; dashed line: extruded.

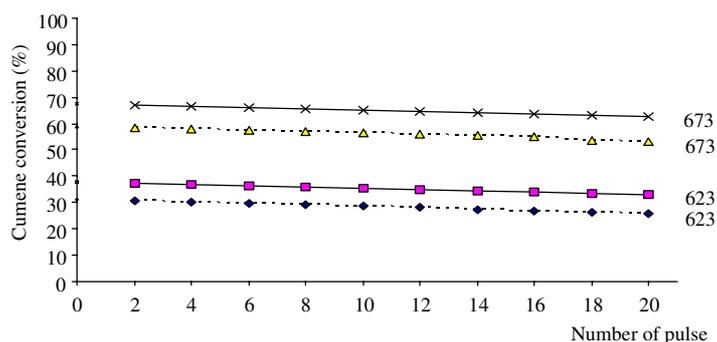


Figure 3b. Cumene conversion versus number of pulse of AM-40 (or NM-40) sample full line: non-extruded; dashed line: extruded.

The activation-deactivation process, at 623 and 673 K, affects enormously the composition of the reaction products. As shown in Figures 4a and 4b, the tendency was very similar for different catalysts. Moreover, the quantity of benzene in the initial pulses exceeded the sum of quantities 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 diminishing the amounts of side reaction products, like olefins, and increasing then the quantity of benzene and propylene, in agreement with the literature ². Simultaneously the amount of benzene was increased and the total quantity of xylene derivatives was decreased and their molar ratio exceeded 1:1, thus, the cracking reaction was favored. Regarding this, the cumene cracking mainly occurred on the acid centers and especially the strongest ones like Brönsted sites, which were poisoned at first by coke deposits.

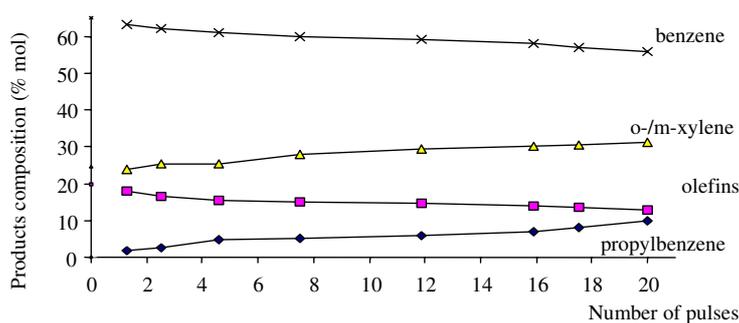


Figure 4a. Composition of the reaction products on non-extruded AM-40 (or NM-40) at 673K versus number of cumene pulses.

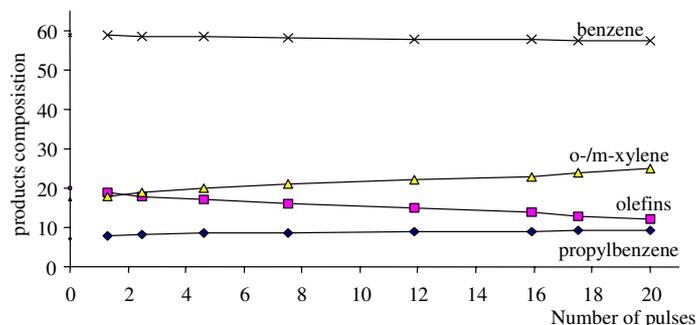


Figure 4b. Composition of the reaction on non-extruded AM-40 (or NM-40) at 623K versus number of cumene pulses.

Effect of ionic exchange degree and deionization mode

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

1. For both series of materials NM and AM the catalytic activity was increased proportionally with ionic exchange degree and when the acidity increased. The latter was given by the concentration of total acid centers (Brönsted and Lewis).

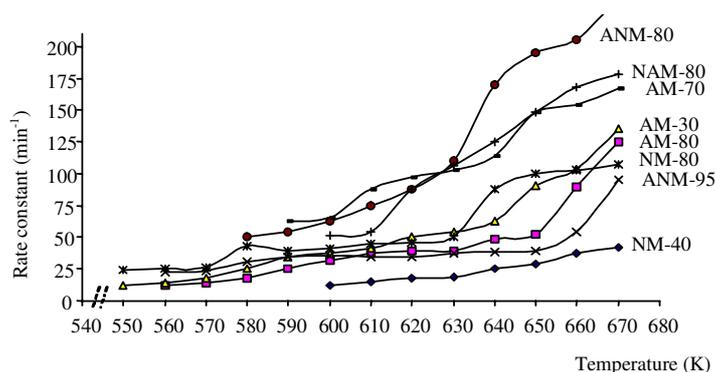


Figure 5. Rate constant of non-extruded catalysts versus temperature.

2. The effect of the deionization mode could be followed by comparing samples AM-40 and NM-40 with 40% ionic exchange and on the samples ANM-80 and NAM-80 with 80% ionic exchange. The catalysts' activities were similar within the whole range of temperature and the rate constants increased proportionally with the exchange degree, except for the NM-40 sample, which was active only from 600 K and with a rate constant not exceeding 40 min^{-1} . Despite the fact that this sample presents a better acidity than the AM-40 sample it remained less active. This is due probably to the distribution of different acid centers within materials. Moreover, a uniform site distribution was also a primordial factor in acid catalysis, which is corroborated by the literature ²⁴. The differences in activities were more pronounced and the sequence of catalysts activity was corresponded well to the sequence of the concentration of acid centers especially Brönsted sites. The samples, with important acid centers 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 the strongest acid centers, which are very catalytically active. The second considered possibility is that for samples with a high exchange degree on the accessible acid centers competition could occur 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 were in inverse proportion to the ionic exchange degree. The same results were observed for zeolites, e.g., butene isomerization on NaHY zeolites ²⁵. Several reasons were considered for this effect. Firstly, the growing number of acid centers, and especially the strongest ones, played an important role and were active in acid catalysis. The presence of these sites made cumene conversion easier in the inner materials' surfaces and therefore the diffusion of different molecules became a determining factor influencing the rate of the process. Secondly, the increased acid strength of different centers and their uniform distribution inside materials induced a lower energy needed for the formation of transition complex. Finally, the possible increase in the adsorption heat of the substrate caused the decrease in the apparent energy of activation even if the true activation energy remained constant.

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

Conclusion

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

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