CATALYTIC PROPERTIES AND ACIDITY OF MODIFIED MCM-41 MESOPOROUS MATERIALS WITH LOW Si/Al RATIO: HEPTANE ISOMERISATION

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

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

ABSTRACT. The catalytic properties and acidity of modified MCM-41 with a low Si/Al ratio and 0-95% NH_4^+ exchange were investigated. The samples were characterised by X-ray diffraction, scanning and transmission electron microscopy, and nitrogen adsorption. The acidity was studied by pyridine adsorption, temperature programmed desorption (TPD) of ammonia, and infrared (IR) spectroscopy. Adsorption of pyridine and IR spectroscopy indicated various types of Lewis and Brönsted acid sites. The density distribution of acid sites was determined by TPD. Both Lewis and Brönsted acid sites were found to be active in the heptane isomerisation. The presence of aluminium (low Si/Al) combined to the ionic exchange between Na^+ and NH_4^+ increases the acidity of MCM-41 materials. A close correlation between acidity and isomerisation was observed. Coke deposition, which reduces the activity, was also studied.

KEY WORDS: MCM-41 materials, Catalytic properties, Acid strength, Heptane isomerisation

INTRODUCTION

Recently, several new types of large-pore molecular sieves have been reported [1, 2]. Their structure and texture confer to these materials important catalytic and adsorptive properties [3]. Potential applications of these mesoporous molecular sieves are as exciting as their discovery. In earlier work mesoporous materials were used as catalysts relating to their above characteristics [3, 4]. Catalytic reactions with MCM-41, one of a family of mesoporous materials with regular well-defined 15-100 Å channels, in acid medium were tested with good results [5].

Interesting studies have been geared toward acid-catalysed reactions of large molecules [6]. Hence the relationship between the acidity and catalytic behaviour of these materials is of great interest. The isomerisation is an acid-catalyzed reaction type [7]. So, it is important that the isomerisation catalysts hold both Brönsted and Lewis acid sites. The heptane isomerisation was facilitated by large pores of MCM-41 combined with adequate acidity. It seems that the activity of MCM-41 is not due only to the large concentration of Brönsted and Lewis acid sites, but also to their regular density distribution within MCM-41 materials. According to the acidity and IR studies, H(X)-AlMCM-41 materials, in which X indicates the degree of replacement of sodium ions by NH_4^+, reveal the existence of both Brönsted and Lewis acidity [8-10].

Hydrocarbon conversions over mesoporous catalysts often lead to carbonaceous deposits [11]. Their formation is a complicated process depending on the nature of the reactants, products, temperature and time. Moreover, such as zeolites, for MCM-41 catalyst pore structure, number, location and strength of the acid sites affect enormously the coking behaviour [12, 13]. Isomerisation over mesoporous materials was generally performed at temperature about 623 K where aliphatic coke was formed initially [14, 15]. This temperature was higher than that reported for reactions on catalysts like Pt/zeolites or sulfated zirconias [16, 17], which were able to operate at a low temperature but were quickly deactivated [18, 19]. Among important

_____

*Corresponding author. Fax: 0021345211018, E-mail: belhakem_ahmed@caramail.com

catalytic and adsorptive studies which carried out on exchanged MCM-41, the heptane hydroconversion and VOCs (volatile organics compounds) respectively, can be mentioned [20, 21].

The aim of this work was to study the acidity and the isomerisation of heptane on the exchanged forms of MCM-41 materials and consequently to establish close relationship between them.

EXPERIMENTAL

Preparation of materials

MCM-41 with a low Si/Al ratio of about 10, synthesised by the procedure described by Schmidt [22], was used as starting material. Samples of H(0-95)%-AlMCM-41 were obtained by exchange with ammonium nitrate solution with various concentrations of NH_4OH. In order to obtain H-form catalysts, samples were heated to remove the NH_3 gas.

Catalytic tests

The catalysis operations were carried out in a flow fixed-bed reactor at atmospheric pressure, connected to a Perkin-Elmer gas phase chromatograph equipped with a flame ionisation detector and Perkin-Elmer integrator. The products were analysed by use of a 3 m column packed with Bentone-3,4-didecyl phthalate and silicon oil A on chromosorb W [23]. The stainless-steel electrically heated reactor was packed with 0.1 g of 0.2-0.3 mm catalyst grains mixed with 0.1 g of quartz. Additional amounts of quartz were loaded below and above the catalyst charge. Prior to the reaction, the samples were heated in a dry argon stream at 623 K for 3 h. Under a hydrogen atmosphere, at various temperatures and degrees of exchange, the activities of H(X)-AlMCM-41 were studied with 20 mL/g catalyst/hour W.H.S.V. (weight hourly space velocity) defined as the ratio of inlet heptane per hour to the weight of catalyst used.

Acidity study

The acid properties of MCM-41 materials were studied in situ by pyridine adsorption in a temperature range 423 K to 823 K and followed by infrared analysis. These require the preparation of thin wafers of MCM-41 by pressure and outgassed in situ at 623 K for 1 h. Recording spectra were obtained on a Specord 75IR spectrometer working on line with a P.C. equipped with IR software. However, two constant intensity bands were detected at 1548 cm^{-1} and 1450 cm^{-1} related to acid sites PyH^+ and PyL, respectively. The concentrations of relatively weak Brönsted and Lewis acid sites per unit cell and their corresponding integrated extinction coefficients (I.E.C.) were determined from the intensities of the two previous detected bands. The strong Brönsted acid sites were estimated by the A_{850}/A_0 ratio which represents the concentration of OH groups absorbing at 3609 cm^{-1} that hold pyridine after desorption at 850 K. The A_0 and A_{850} factors were calculated from the O-H IR intensity bands. The I.E.C. study showed on one hand that the values of the acid strength were similar to those founded by pyridine adsorption and on the other hand confirms the presence of two kinds of acidity: Brönsted and Lewis sites [24], which were also shown by IR studies.

The following methods were used to study the type and the density of various acidic sites. First, a small amount of pyridine was adsorbed on to materials until a constant intensity of the pyridinium bands at 1548 cm^{-1} was reached. Secondly, the infrared cell was connected to a liquid nitrogen trap and heated at various temperatures (523-1023 K). After each desorption step, the infrared cell was cooled to 423 K and the IR spectra were recorded. The pyridine

molecules neutralising Lewis and weak Brönsted acid sites, absorbing at 1450 cm^{-1} and 1548 cm^{-1}, were removed at low temperatures and consequently the total number of acidic sites decreases. At high temperatures, the pyridine molecules were removed from strong Brönsted sites absorbing at 3609 cm^{-1}. The removed species by desorption at low temperatures correspond to the concentration of both PyL and PyH^{+} acid sites and the remaining concentration of the sites correspond to the Brönsted strong with IR band at 3609 cm^{-1}.

The global distribution density of acid sites within MCM-41 materials was determined by ammonia TPD which was adsorbed on the material at different temperatures from 423 to 823 K. The quantity adsorbed at each temperature was determined by back titration with HCl solution.

RESULTS AND DISCUSSION

Catalyst characterisation

Powder X-ray diffraction patterns were collected on a Philips 1830 diffractometer with Cu$_{K\alpha}$ radiation (λ = 0.1542 nm). The 2θ range was from 1° to 10° and the scanning rate 5°.min^{-1} (Figure 1). Only one peak was detected for MCM-41 around 2θ = 1.5°, which is not sufficient to characterise this material. Because of their semi-amorphous structure, other methods were used for complementary characterisation [23, 43]. Nitrogen adsorption was measured at 77.3 K on an ASAP2010 apparatus (Micromeritics, Norcross, GA, USA), samples were then degassed at 570 K and 10 Pa for 2 h. The adsorption was described by a typical type IV isotherm. The specific surface area (S_{BET} = 1000 m^2.g^{-1}) and pore volume distribution (DPA = 35 Å) were determined by the BET (Brunaur-Emmet-Teller) and BJH (Barret-Joyner-Halenda) methods, respectively (Figures 2a and 2b). In order to confirm the existence of mesopores, crystallites morphologies were examined by scanning and transmission electron microscopy using a Hitachi H-600 apparatus (Figures 3a and 3b). The obtained results confirm the cylindrical form of the materials and the openings corresponding to the mesopores (Table 1).
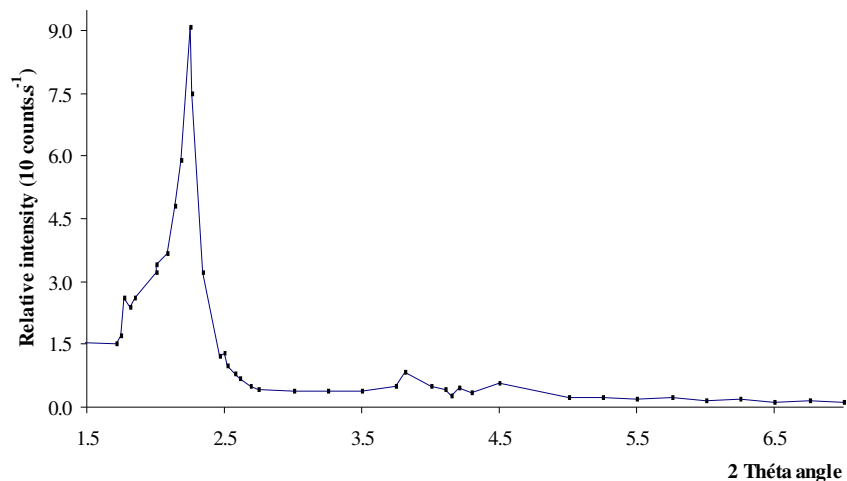

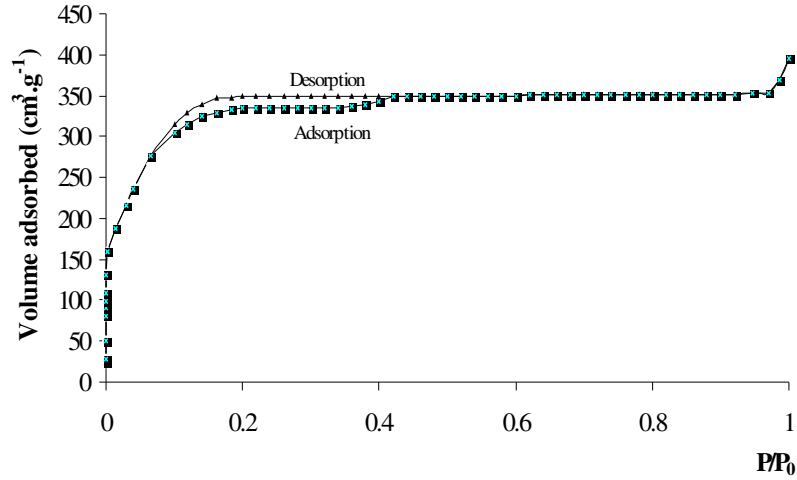Figure 1. X-ray diffraction of parent MCM-41 material.

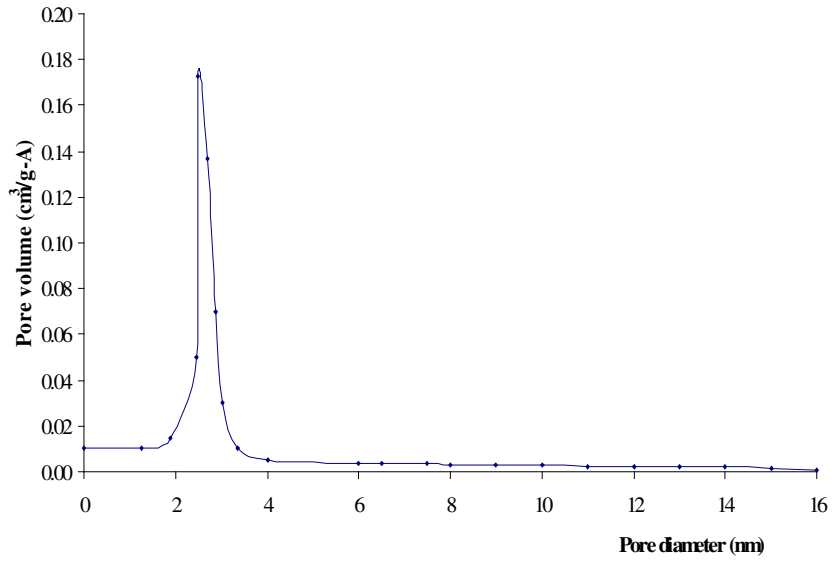Figure 2a. Isotherm of N_2 adsorption on parent MCM-41 material.

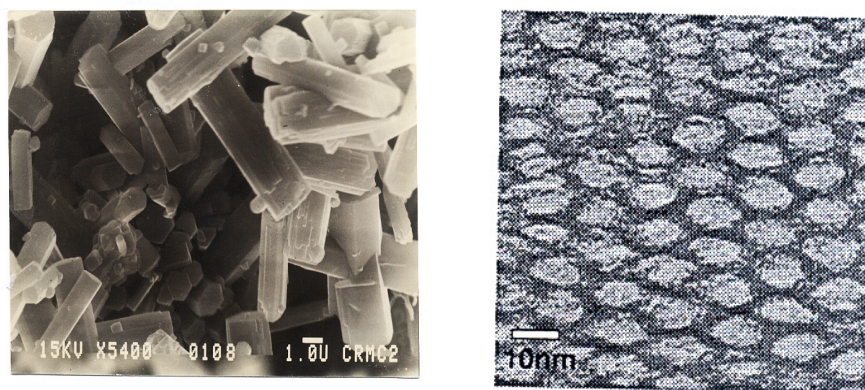Figure 2b. Average pore distribution (APD) within MCM-41 material determined with BJH method.

Figure 3. Scanning and transmission electron micrograph of parent MCM-41.

Table 1. Textural properties of exchanged H(X)-AlMCM-41.

Samples	BET surfaces area $(m^2.g^{-1})$			Pore volume $(cm^3.g^{-1})$			APD (nm)
	Micro pore	Meso pore	Total	Micro pore	Meso pore	Total	
MCM-41 parent	0	990	990	0	0.54	0.54	3.3
0.15 NH$_4$-MCM-41	0	980	980	0	0.60	0.60	4.6
0.30 NH$_4$-MCM-41	0	981	981	0	0.61	0.61	4.5
0.45 NH$_4$-MCM-41	0	975	975	0	0.64	0.64	4.8
0.60 NH$_4$-MCM-41	0	960	960	0	0.70	0.70	5.1
0.75 NH$_4$-MCM-41	0	965	965	0	0.68	0.68	5.0
0.95 NH$_4$-MCM-41	0	976	976	0	0.63	0.63	4.8

The characteristics of the exchanged samples are listed in Table 2. The parent material (Si/Al $\approx$ 10) is designated NaMCM-41, despite the fact that a small number of acid sites were detected by IR spectroscopy.

Table 2. Characteristics of (NH$_4^+$, Na$^+$)-AlMCM-41 materials (Si/Al $\approx$ 10).

Materials	NH$_4^+$ (D.E.)	Unit composition	B+2L/U.C.	Al-Na/U.C.
Na-MCM-41	0	Na$_{9.8}$H$_{1.9}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	02.3	01.9
0.15 NH$_4$-MCM-41	15	Na$_{7.8}$H$_{1.9}$(NH$_4$)$_{1.9}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	03.7	03.9
0.30 NH$_4$-MCM-41	30	Na$_{5.1}$H$_{1.9}$(NH$_4$)$_{4.2}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	05.9	06.4
0.45 NH$_4$-MCM-41	45	Na$_{3.4}$H$_{1.9}$(NH$_4$)$_{6.3}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	09.4	08.4
0.60 NH$_4$-MCM-41	60	Na$_{2.1}$H$_{1.9}$(NH$_4$)$_{7.6}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	15.0	09.5
0.75 NH$_4$-MCM-41	75	Na$_{1.5}$H$_{1.9}$(NH$_4$)$_{8.2}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	24.0	10.1
0.95 NH$_4$-MCM-41	95	Na$_{0.8}$H$_{1.9}$(NH$_4$)$_{9.1}$(AlO$_2$)$_{11.7}$(SiO$_2$)$_{99.5}$	38.4	10.8

D.E.: Degree exchange, U.C.: unit composition, B: Bronsted acid sites, L: Lewis acid sites.

Acid properties of MCM-41

As shown on Figure 4, when the exchange degree increases, the total acid number of acid sites also increases especially Brönsted ones. However, Lewis acid sites number remains relatively low and increases slightly with the degree of exchange indicating that the degree of dehydroxylation is reduced under the activation conditions. This observation is corroborated by previous conclusions [25, 26].
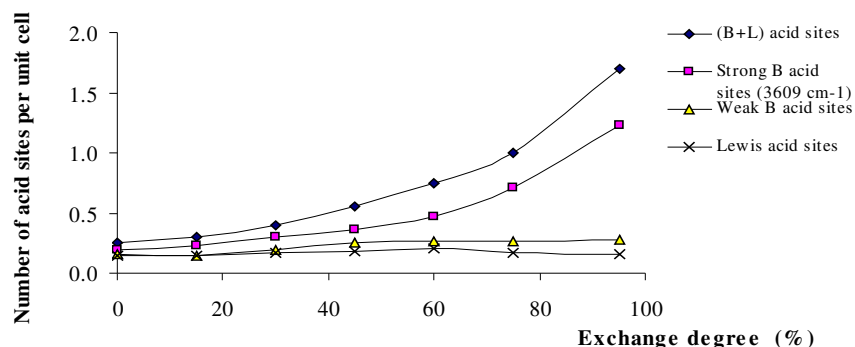

Figure 4. Acid sites number, per unit cell, within H,NaMCM-41 materials versus exchange degree.

The number of acid sites determined by IR spectroscopy was compared to those calculated from chemical analysis (Tables 2 and 3). When the Si/Al ratio is of about 10, it can be supposed that each Lewis acid site was formed by dehydroxylation process. Therefore Stoichiometrically, the creation of two Brönsted sites generates one Lewis site [27, 28] which can be explained by the departure of structural water. The factor $B+2L$, (B and L stand, respectively, for Brönsted and Lewis sites), is the concentration of protonic sites subsequent to the decomposition of ammonium ions and prior the dehydroxylation. Results in Table 2 suggest that the various values of ($B+2L$) are comparable to the proton content calculated from the difference between the aluminium and sodium contents.

Table 3. IR intensity of the pyridine absorption bands at different exchanged degree.

Sample	Desorption temperature			Sample	Desorption temperature		
	Bronsted acidity B sites				Lewis acidity L sites		
	423 K	523 K	623 K		423 K	523 K	623 K
MCM-41(0)	-	-	-	MCM-41(0)	22	17	10
MCM-41(15)	02.0	01.5	0.0	MCM-41(15)	25	20	12
MCM-41(30)	03.0	02.0	01.0	MCM-41(30)	31	23	15
MCM-41(45)	05.5	03.0	02.0	MCM-41(45)	37	27	17
MCM-41(60)	06.0	04.0	02.0	MCM-41(60)	43	30	20
MCM-41(75)	08.0	05.0	02.0	MCM-41(75)	45	32	22
MCM-41(95)	12.0	06.0	03.0	MCM-41(95)	47	34	24

Furthermore, it was established that the concentration O-H groups, which absorb at 3609 cm^{-1}, was proportional to the exchange degree of MCM-41 materials. Thus the variation of A_{850}/A_0 ratio versus exchange degree (Figure 5b) emphasized the proportional relationship between the exchange degree and the concentration of strong Brönsted sites from where the

retained pyridine was desorbed at high temperature around 850 K. It seems that the non-homogeneous distribution of aluminium in MCM-41 was responsible for the increase of OH acid strength. Considering the data represented in Figures 5a and 5b, it is possible to infer that the distance between Al atoms decreases with the increase of the exchange of Na^+ by NH_4^+ inside mesoporous materials. This phenomenon can cause the increase of polarisation of neighbouring OH groups which in agreement with others studies [23]. The heterogeneity of these groups can be explained as follows: the ions, introduced first into the MCM-41 materials, form less acidic groups with the structural oxygen in a larger quantity, than the ions introduced later at a high exchange degree.
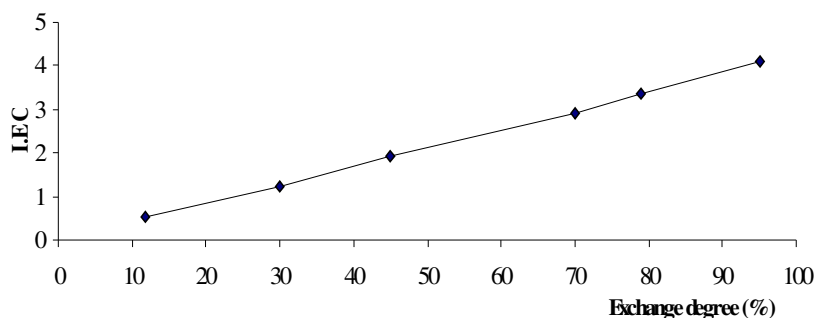

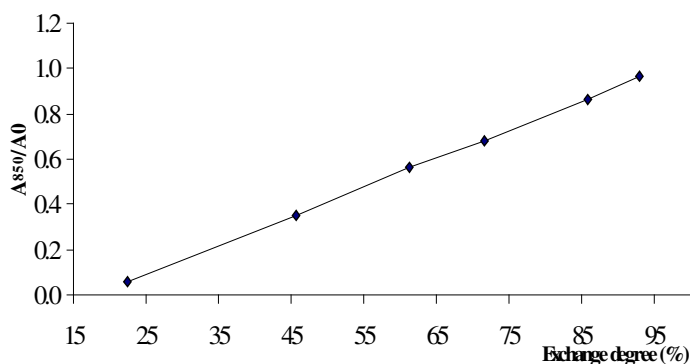Figure 5a. MCM-41 integrated extinction coefficient versus exchange degree.

Figure 5b. Factor A_{850}/A_0 versus exchange degree.

Both pyridine adsorption and IR analysis methods have revealed, on one hand the existence of different acid sites and their corresponding strengths (Figure 6a and Table 3) and on the other hand the effective adsorption of pyridine highlighted by the appearance of bands ascribed to pyridinium ions at 1548 cm^{-1} and 1450 cm^{-1} (Figure 6b).

The ammonia TPD method also has showed the distribution of the different acidic sites in MCM-41 materials. Data represented in Figure 7 show the same profile with a slight growth in acidity for all the exchanged material. Hence, the acidity distribution in these materials, with a low Si/Al ratio, is homogeneous and comparable to the distribution in zeolites. The density distribution for acid sites for H(X)-AlMCM-41 have samples shown two acidity maxima for temperatures of about 473 and 623 K. This indicates the range where the acidity is important and consequently the materials are active in catalysis.

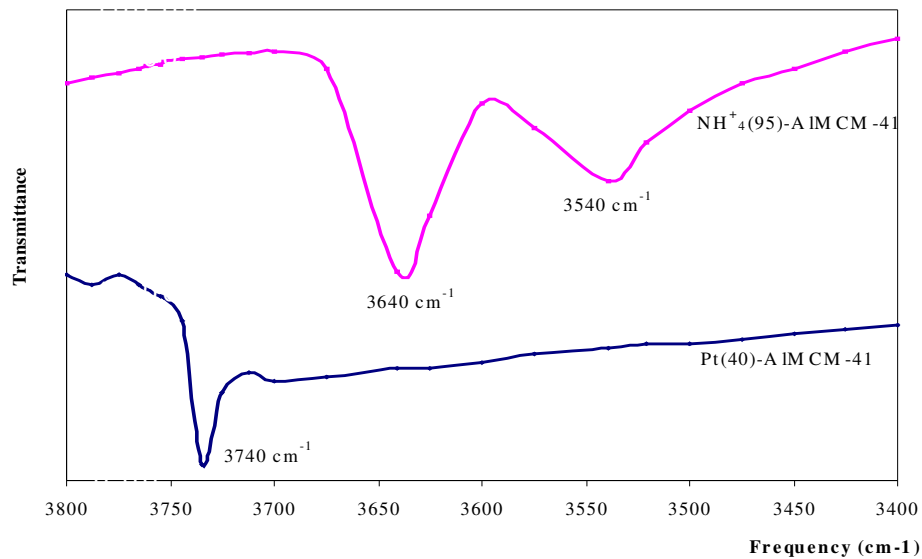Ahmed Belhakem and Abdelkader Bengueddach.

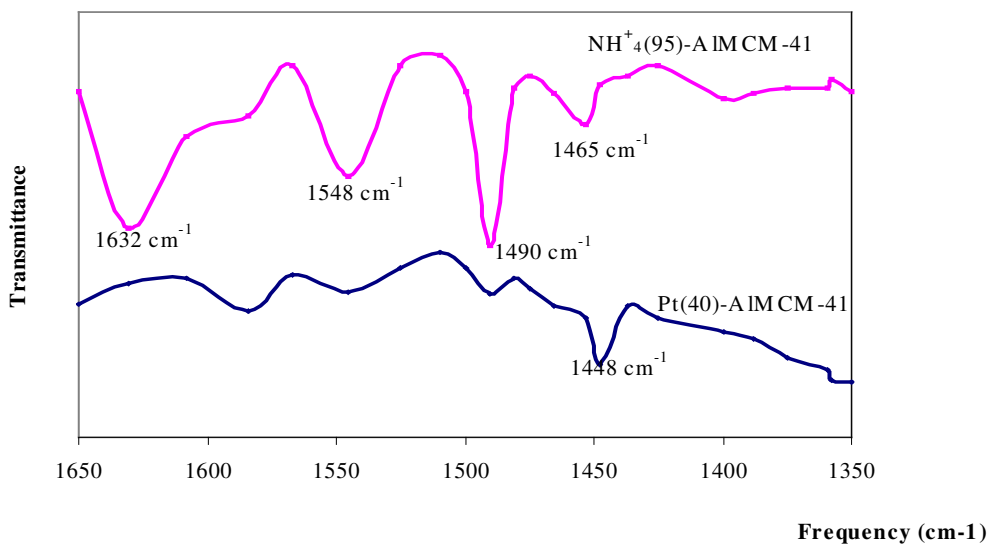Figure 6a. IR spectra of dealuminated MCM-41 at 473 K.

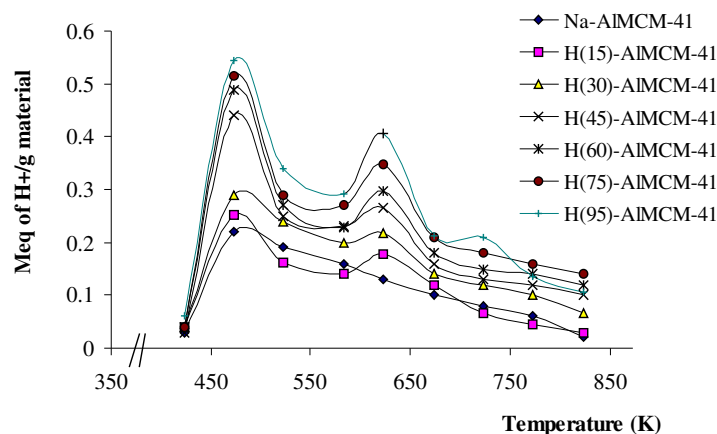Figure 6b. IR spectra of pyridine adsorption within MCM-41 material.

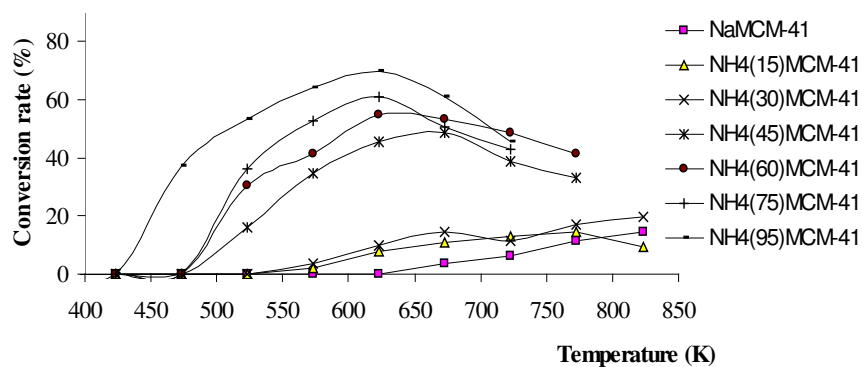Figure 7. Density distribution of acidity within MCM-41.

Figure 8. Conversion of n-heptane as a function of temperature at different degree exchange.

Catalytic properties of MCM-41 materials

Figure 8 represents the variation of catalytic activities for heptane isomerisation versus temperatures, and at temperatures less than 423 K, no activity was noticed for the exchanged materials even for those with a high exchange degree. Moreover, authors have observed a catalytic activity for some catalysts, at low temperature, but only in homogenous catalysis [23, 43]. Contrarily to the studied catalysts in present work, the homogenous catalysts were rapidly deactivated and were not easily regenerated. Materials with a high exchange degree of NH_4^+ exhibit higher catalytic activities where an optimum was around 623 K which was due mainly to the creation of more acidic sites. Above 623 K, the activity begins to decrease because the pores volumes were blocked by coke deposition. The Na-AlMCM-41, H(15)-AlMCM-41 and H(30)-AlMCM-41 samples were not active in isomerisation reaction. This is due probably to the low acidity as shown on figure 7, which did not exceed 0.3 Meq of H^+/g and hence the acidity of these catalysts were not sufficient to catalyze this type of reaction According to the results of acidity studies, samples active in isomerisation must, on one hand, contain the two types of acid

sites and especially Brönsted ones, and on the other hand have a good acid site density distribution.

The increase of the exchange degree and the creation of extra-framework aluminum by dehydroxylation (departure of structural water) results in a sharp raise in catalytic activity with an optimum at 623 K. Hence, it is clear that heptane isomerisation requires the two kinds of acid sites (Figure 9). These results are in agreement with previous findings [29-32].
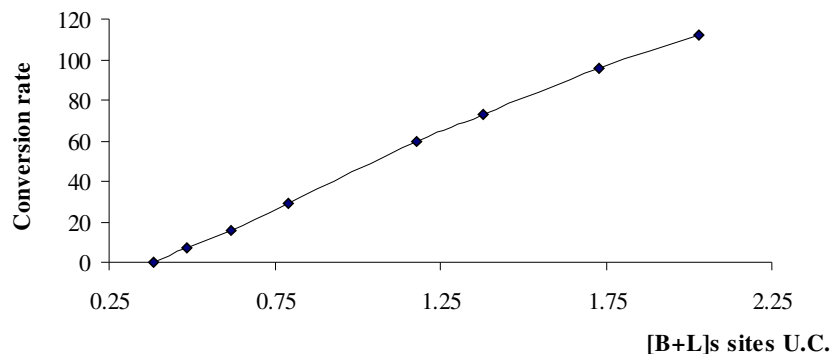

Figure 9. Conversion rate of MCM-41 versus [B+L] sites/U.C.
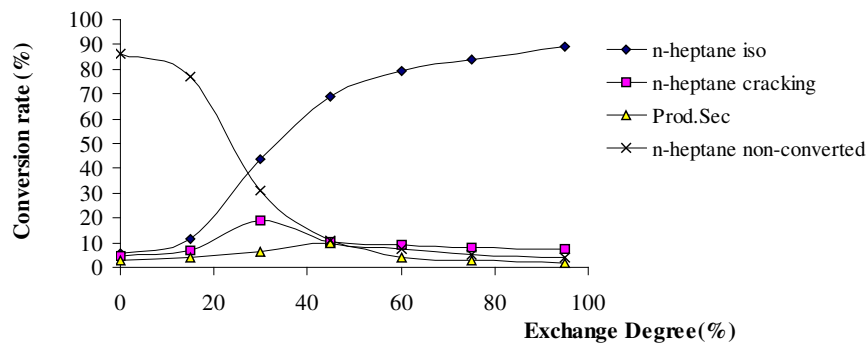

Figure 10. Conversion rate of heptane as a function of exchange degree for H(95)-AlMCM-41.

The conversion rate versus exchange degree (Figure 10) shows that the increase of exchange degree causes an increase in catalytic activity and that the highest activity was observed for the H(95)MCM-41. Similar results were observed for materials exchanged with some noble metals such as platinum or palladium. As reported in literature [33-35], the introduction of these metals, even at low degree exchange, generates good catalysts acidity and consequently a good catalytic activity. Contrarily to H(X)-AlMCM-41 materials used in this work, the materials exchanged with noble metals present some disadvantages such as high cost of platinum or palladium, rapid catalysts deactivation and their difficult regenerateability. However, these studies permitted to understand that in isomerisation reaction, hydrogenation/dehydrogenation process was an important intermediate. Thus, in our study this process was allowed by the presence of aluminium which is responsible for the creation of acid sites. However, the

isomerisation process was occurred on the inner surface catalysts on both Lewis and Brönsted acid sites asrepresented on the following scheme [7].
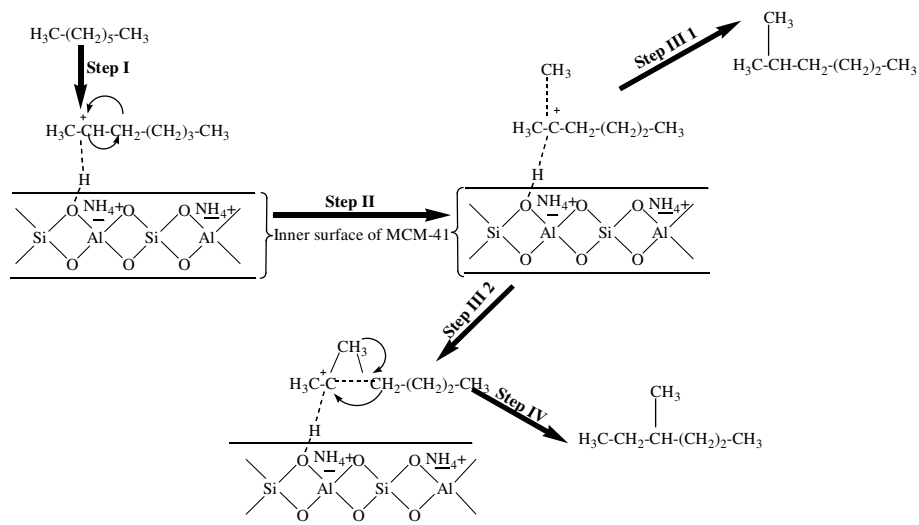
Scheme 1. Schematic representation of heptane isomerisation reaction over MCM-41 catalysts.

A close correlation was established between acidity and catalytic performances. The results of the experiments with pyridine adsorption (Figure 4) and the comparison with the integrated extinction coefficients (I.E.C. Figure 5a) showed that the acidity increases with the exchange degree and these acid solid materials were active in this type of reaction. For H(30)-AlMCM-41 exchange degree and less, the acidity strength is the lowest and for this, they are too weak to catalyse the reaction investigated in the present study.

When the exchange degree was higher than 30%, the isomerisation of heptane increases proportionally with the number of strong Brönsted acid sites (Figures 5a and 5b). As noticed for some studied catalysts [22, 36], a linear relationship between catalytic activity and acidity of mesoporous materials was founded. These results indicate a found threshold for the acid strength where beneath it; the acidic strength has no effect on the catalytic activity. The present study suggests that only when the degree of exchange was higher than 30%, the exchanged MCM-41 materials can give satisfactory results for heptane isomerisation.

Irrespective of the reaction mechanisms, the isomerisation of heptane by Brönsted and Lewis sites results in coke formation. As mentioned in previous studies [14, 37], these two types of acidity as well as their acidic strength affected the catalytic activity of MCM-41 materials and the initial rate of coke formation.

Data in Table 4 revealed that at a high exchange degree of H(X)Al-MCM-41 material with its high surface area could achieve a good dispersion of extra-framework aluminum species created by structural dehydroxylation which is corroborated by literature [38, 39]. Unlike to what usually happen with zeolites, with MCM-41 materials the catalytic reaction and particularly the isomerisation was occurred only on the inner surface because the external walls are amorphous and consequently diffusion problems do not arise [40] and therefore, isomerisation is enhanced compared with cracking reaction [35]. A variation in mono-/di-branched ratio was noticed for all studied exchanged materials. This selectivity was related to

regularity and pores size, the nature and type of cations introduced within the materials. Moreover, an increase of mono-branched isomers was observed with the increase of the exchange degree, while a maximum was remarked for di-branched isomers neighboring 70% of heptane rate conversion. This is due probably on one hand to the uniform dispersion of extra-framework aluminum which favors the formation of mono-branched isomer and on the other hand to the hindrance effect caused by juxtaposition of di-branched molecules as also observed [35]. Less coke-formation was obtained for materials that contained a lower number of NH_4^+ groups. From this observation it can be supposed that the density of acid sites affects the contact-time of the products. Short contact-time of catalysts results in a higher selectivity for mono-branched isomers, though the variation of O-H groups amounts. The isomer yield in skeletal isomerisation was linearly proportional to the concentration of Brönsted and Lewis acid sites. Both the density of acid sites and their strength have a significant impact on the formation of coke. The acid strength affects both activity and selectivity in heptane isomerisation and has a significant effect on coke formation in agreement with literature [41, 42]. Due to the high number of acid sites pores are very sensitive by carbonaceous deposits blockage. The number, nature, location and density distribution of various acid sites are crucial factors [13]. Coke formation is thus, a decisive factor in determining the scope of the isomerisation.

Table 4. Characteristics of (NH_4^+, Na^+)-AlMCM-41 materials (Si/Al $\approx$ 10) with WHSV = 0.2 h^{-1} and at 623 K.

Materials	Exchange degree (%)	Total conversion	Cracking products (%)	MBI (%)		DBI (%)
				Methyl	Ethyl	Dimethyl
Na-MCM-41	00	08.7	4.5	01.3	01.1	00.9
0.15 NH$_4$-MCM-41	15	14.8	7.3	02.5	02.1	01.9
0.30 NH$_4$-MCM-41	30	29	19.1	03.9	03.2	02.5
0.45 NH$_4$-MCM-41	45	90.6	11.8	21.4	26.0	27.8
0.60 NH$_4$-MCM-41	60	94.5	11.2	23.7	29.1	31.0
0.75 NH$_4$-MCM-41	75	98	10.9	26.0	31.0	32.0
0.95 NH$_4$-MCM-41	95	91	10.7	28.1	36.8	16.3

D.E.: degree exchange, WHSV: space velocity, MBI: mono-branched isomers, DBI: di-branched isomers.
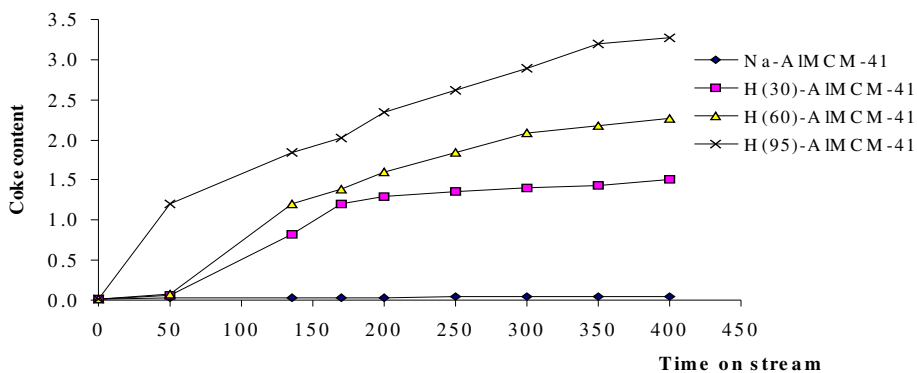

Figure 11. Coke content *vs* time on stream for exchanged MCM-41.

Study of the variation of the catalyst weight, versus time, has shown that two different deposition mechanisms were operating. The initial blockage of the internal surface was followed by a much slower filling of the channels. The transition from one mechanism to the other depends subtly on temperature.

To characterize the amount of carbon deposits on catalysts and their activities, a method described elsewhere was used [12, 43]. The amount of carbon on the catalyst was estimated after each reaction. The profiles of deposited carbon on catalysts after 400 min reaction at 623 K are shown in Figure 11.

CONCLUSIONS

On the basis of these results, both Lewis and Brönsted acid sites in MCM-41 materials could be determined simultaneously by IR spectroscopy and adsorption of pyridine. In the H(X)-AlMCM-41 materials with a low Si/Al ratio, the acid sites were generated directly by exchange with ammonium salts solutions and then heating to evacuate the NH_3. The acid sites characterised by pyridine adsorption and detected by IR spectroscopy were absorbed at 1450 cm^{-1}, 1548 cm^{-1} and 3609 cm^{-1} bands which correspond to Lewis, weak and strong sites, respectively. In contrast to the strong sites, the number of both weak Brönsted and Lewis sites were relatively low and increased slightly with temperature treatment.

In the studied reaction, the maximum of rate conversion was obtained for temperature about 623 K where the contribution of Lewis sites, compared with Brönsted sites, were almost negligible. The distribution of acid sites within the H(X)-AlMCM-41 was also an important factor which have indicated minimum of acidity (0.3 meq.g^{-1}) below it, the exchanged materials have no catalytic effect on the isomerisation.

Thus, The materials Na-AlMCM-41, H(15)-AlMCM-41 and H(30)-AlMCM-41 show lower acidity which was not sufficient to catalyse the reaction under the conditions used. So in this study the catalytic activity was not affected for this threshold level of the acidity and was depended directly on the two types of acidity generated within the materials and their different properties such as distribution and strength.

Finally, the study of heptane isomerisation and the use of H(X)-AlMCM-41 have revealed a good of isomerisation catalysts characteristics. These materials are active and practically non-selective for the isomerisation reaction of heptane. The non-selectivity was due to the large pore size and the distribution of different species within the mesoporous material. This behaviour distinguishes the MCM-41 materials from zeolites.

REFERENCES

1. Kresge, C.T.; Leonowicz, M.E.; Roth, W.J.; Vartuli, J.C.; Beck, J.S. *Nature* **1992**, 359, 710.
2. 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.
3. Kinski, I.; Gies, H.; Marlow, F. *Zeolites* **1997**, 19, 375.
4. Beck, J.S.; Vartuli, J.C. *Solid State Mater. Sci.* **1996**, 1, 76.
5. Aguado, I.; Serrano, D.P.; Romero, M.D.; Escola, J.M. *Chem. Soc. Chem. Commun.* **1996**, 725.
6. Zhao, D.; Nie, C.; Zhou, Y.; Xia, S.; Huang, L.; Li, Q. *Catal. Today* **2001**, 68, 11.
7. Allinger, N.L.; Cava, M.P.; Dejongh, D.C.; Johnson, C.R.; Lebel, N.A.; Stevens, C.L. in *Chimie Organique Tome II: Réactions*, 8th ed., McGraw-Hill: New York; **1984**.
8. Armor, J.N. *Appl. catal. A* **1994**, 121, 113.

9. Reddy. K.M.; Song, C. *J. Catal.* **1997**, 172, 211.
10. Zhang, Z.; Han, Y.; Zhu, L.; Wang, R.; Yu, Y.; Qui, S.; Zhao, D.; Xiao, F.S. *Agew. Chem. Int.* Ed., **2002**, 41, 2226.
11. Jungie, B.; Jing, L.; Xiangsheng, W.; Xiumei, L.; Xinhe, B. *Mat. Chem. Phys.* **2002**, 77, 406.
12. Guisnet, M.; Magnoux, P. *Appl. Catal.* **1989**, 54, 1.
13. Mokaya, R.; Jones, W. *J. Mat. Chem.* **1999**, 9**,** 555.
14. Doka Nassionou, G.A.; Magnoux, P.; Guisnet, M. *J. Chim. Phys.* **1999**, 96, 303.
15. Groten, W.A.; Wojciechowski, B.W.; Hunter, B.K. *J. Catal.* **1990**, 125**,** 311.
16. Tran, M.T.; Gnep, N.S.; Guisnet, M.; Nascimento, P. *Catal. Lett.* **1997**, 47**,** 57.
17. Centeno, M.A.; Grange, P. *J. Phys. Chem. B* **1999**, 103, 2431.
18. Ganapati, D.Y.; Ambareesh, D.M. *Adv. Synt. Catal.* **2004**, 346, 389.
19. Mokaya, R.; Jones, W.; Moreno, S.; Poncelet, G. *Catal. Lett.* **1997**, 49, 87.
20. Zhao, X.S.; Lu, G.Q.; Millar, G.J.; Li, X.S. *Catal. Lett.* **1996**, 38, 33.
21. Luan, Z.; Cheng, C.F.; He, H.; Klinowski, J. *J. Phys. Chem.* **1995**, 99, 10590.
22. Song, S.X.; Pilko, M.; Kydd, R.A. *Catal. Lett.* **1998**, 55, 97.
23. Corma, A. *Chem. Rev.* **1997**, 97, 2373.
24. Xu, M.; Wang, W.; Seiler, M.; Buchholz, A.; Hunger, M. *J. Phys. Chem. B* **2002**, 106**,** 3202.
25. A. Taouli, A.; Reschetilowski, W. *Stud. Surf. Sci. Catal.* **2002**, 142B, 1315.
26. Halliche, D.; Cherifi, O.; Auroux, A. *J. Therm. Anal. Calorim.* **2002**, 68, 997.
27. Borade; R.B.; Clearfield, A. *Chem. Ind. Ser.* **1997**, 69, 431.
28. Magnoux, P.; Joly, G.; Brimaud, S.; Ragil, K. *Oil Gas Sci. Tech.* **2003**, 558, 343.
29. Bhore, N.A.; Johnson, I.D.; Keville, K.M.; Le, Q.N.; Yokomizo, G.H. *U.S. Patent* **1993,** 5, 260, 501.
30. Höchtl, M.; Jentys, A.; Vinek, H. *Micro. Mesop. Mat.* **1999**, 31, 271.
31. Figueras, F.; Kochkar, H.; Caldarelli, S. *Micro. Mesop. Mat*. **2000**, 39, 249.
32. Kosslick, H.; Lischke, G.; Parlitz, B.; Storek, W.; Frike, R. *Appl. Catal. A*: *General* **1999**, 184, 49.
33. Borade, R.B.; Zhang, B.; Clearfield, A. *Catal. Lett.* 1997, 45, 233.
34. Hynek, B.; Roman, H.; Naezda, Z.J.C. *Catal. Lett.* **2004**, 97, 25.
35. Corma, A.; Martinez, A.; Pergher, S.; Paratello, S.; Perego, C.; G. Bellusi, G. *Appl. Catal. A* **1997**, 152, 107.
36. Guisnet, M. *Polish J. Chem.* **2003**, 77**,** 637.
37. Wang, S.; Murata; K.; Hayakawa; T.; Hamakawa, S.; K. Suzuki, K. *Catal. Lett.* **2000**, 66, 13.
38. Uytterhoven, J.B.; Christner, L.G.; Hall, W.K. *J. Phys. Chem.* **1965**, 69**,** 2117.
39. Koninsberger, D.C.; De Graaf, J.; Mojet, B.L.; Ramaker, D.E.; J.T. Miller, J.T. *Appl. Catal. A* **2000**, 191**,** 205.
40. Siriporn, J.; Paneeya, S.; Thirasak, R.; Somchai, O.; E.R. Daniel, E.R. *J. Catal.* **2003**, 218**,** 1.
41. Narendra, K.; Ville, N.; Lars, E.L.; Tapio, S.; Dmitry, Y.M.; Ensio, L.; Teemu, H. *Catal. Lett*. **2002**, 78**,** 105.
42. Armengol, E.; Corma, A.; Gracia, H.; Primo, *J. Appl. Catal. A*: *General* **1997**, 149, 411.
43. Corma, A. *Chem. Rev.* **1995**, 95, 559.