

Catalytic performance of Al-MCM-41 materials in the *N*-alkylation of aniline

Rafael Luque*, Juan Manuel Campelo, Diego Luna,
Jose Maria Marinas, Antonio Angel Romero

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Córdoba, Campus Universitario de Rabanales, Edificio Marie Curie, E-14014 Córdoba, Spain

Received 16 November 2006; received in revised form 9 January 2007; accepted 14 January 2007

Available online 20 January 2007

Abstract

Al-MCM-41 mesoporous molecular sieves with Si/Al ratio ranging from 40 to 15 were synthesized and characterized as previously reported. Materials were tested in the *N*-methylation of aniline with methanol. The aniline methylation was a pseudo-first-order process with respect to aniline concentration. *N*-Methylation products [*N*-methylaniline (NMA) and *N,N*-dimethylaniline (NNDMA)] were predominant with a 65–80% selectivity to NMA at 573 K. Low reaction temperatures favoured the *N*-alkylation pathway whereas high temperatures produced higher quantities of *C*-alkylated products. Aniline conversion and selectivity to NNDMA decreased whereas selectivity to NMA continuously increased with time on stream. Selectivity to NMA remained almost the same, irrespective of the aniline conversion, aluminum content and acidity. On the other hand, the re-used Al-MCM-41 catalysts would be described as amorphous aluminosilicates because of their structural deterioration with the water produced in the reaction as a by-product.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Mesoporous materials; Al-MCM-41; Heterogeneous catalysis; Aniline alkylation

1. Introduction

Alkylations are among the most important reactions in organic chemistry. Aniline alkylation is an industrially important reaction due to the fact that alkyl-anilines are basic raw materials for synthesis of organic chemicals, chemical intermediates and/or additives in dyes, synthetic rubbers, explosives, herbicides and pharmaceuticals [1]. Vapor-phase aniline alkylation over environmentally safe solid catalysts is the answer to the conventional method of liquid phase alkylation using mineral acids and Friedel–Crafts type catalysts [2]. Although it provides higher yield [3] than vapor phase alkylation, this process is restricted due to disadvantages such as high capital cost, corrosion problems and formation of by-products that cannot be recycled. With the increasing awareness of environmental issues,

a wide variety of solid acid catalysts and alkylating reagents have been employed in this process. Recently, progresses in the application of acid catalysts for aniline alkylation have been reviewed [4]. AlPO_4 , $\text{AlPO}_4\text{-Al}_2\text{O}_3$ and CrPO_4 , $\text{CrPO}_4\text{-AlPO}_4$ and magnesium phosphates catalysts [5] have been reported by our group as highly effective and selective materials for this alkylation reaction. Similarly, several solid acids have been reported in the aniline alkylation reaction, including zeolites [6], modified clays [7] and different vanadium [8] and iron oxides [9]. Acid–base properties (amount of active sites and strength) and shape-selectivity in the solid catalyst as well as the experimental conditions (temperature, composition and feed rate) are the major factors influencing the activity and selectivity (*N*-and/or *C*-alkylation). Small quantities of basic sites have been proved to enhance the materials' catalytic activity but a further basicity increase rendered materials that experienced a rapid deactivation [10]. However, basic properties are not as critical as acid properties, in terms of the materials' performance in the alkylation reaction, since the alkylation reaction do not occur on basic sites. On the other hand, as has been demonstrated [10,11], the use of strong solid acids with high concentration of Brønsted

* Corresponding author. Present address: Department of Chemistry, Green Chemistry Centre of Excellence, The University of York, York YO10 5DD, UK. Tel.: +44 1904432568; fax: +44 1904432705.

E-mail addresses: rla3@york.ac.uk (R. Luque), qo1capej@uco.es (J.M. Campelo).

acid sites may not be very suitable for this reaction. The surface strong acid sites can be neutralised and poisoned since a strong base such as aniline can be adsorbed on these acid centres. Moreover, depending on the conditions, the aniline may protonate, also reducing the effective reagent concentration for the reaction. Weak to moderate strength acid sites have been agreed to be involved in the reaction mechanism, the process being favoured by the presence of Lewis acid sites. Therefore, the design and development of materials with tunable surface and acid properties may potentially extend the scope of this reaction. We have previously reported the synthesis, characterisation and catalytic activity of acidic Al-MCM-41 with tunable acid properties depending on the aluminum content in samples and a post-treatment in a NH_4F solution [12]. Materials were shown to be highly active in the cracking of isopropylbenzene, in which moderate to strong acid sites appear to be involved. So, in order to extend the applicability of the mesoporous Al-MCM-41 in acid catalysed reactions, the materials' activities were investigated in the gas phase alkylation of aniline with methanol and compared to those of commercial zeolites including the H-Y, H-ZSM-5, H-mordenite and H- β materials.

2. Experimental

Al-MCM-41 materials have been prepared as previously reported [12] and in this manuscript they have been named accordingly: XAl-40 or XAl-40-F where F refers to NH_4F post-treatment and $X=40, 30, 20$ and 15 were the Si/Al ratio in the synthesis gel and 40 stands for the degree of exchange (mol%) of hydroxide for bromide ion in the surfactant [12a]. Similarly, materials obtained using a 23% hydroxide exchange degree in the surfactant were denoted Al-X and Al-F-X, where $X=40, 30, 20, 15$ were also the Si/Al ratios in the synthesis gel [12b]. Commercial zeolites were purchased from Zeolyst Inc.

Thermal analysis was performed by simultaneous TG-DTA measurement using the Setaram thermobalance Setsys 12. Samples were heated in the temperature range 293–1173 K at a heating rate of 10 K min^{-1} , in air.

Temperature programmed-mass spectrometry measurements (TP-MS) were performed in a continuous flow reactor coupled to a quadrupole mass spectrometer (VG GAS Prolab) operating in the multiple ion monitoring (MIM) mode. The experimental conditions were similar to those of the thermal analysis [heating rate, 10 K min^{-1} , 323–1023 K temperature range, 50 mL min^{-1} flow rate (N_2 or air)].

Diffuse reflectance Fourier-Transform infrared (DRIFT) spectra were recorded on a Bomem MB series instrument equipped with an “environmental chamber” (Spectra Tech, P/N 0030-100) placed in the diffuse reflectance attachment (Spectra Tech, Collector). The resolution was 8 cm^{-1} , and 256 scans were averaged to obtain spectra in the $4000\text{--}400 \text{ cm}^{-1}$ range. Samples were dried at 423 K for 24 h, mixed with KBr to 15 wt%, placed in an environmental chamber cell with a 20 mL min^{-1} flow of air, heated to 573 K, and held at this temperature for 1 h prior to measuring the spectrum.

Surface acidity was measured in a dynamic mode by means of a pulse chromatographic technique of gas-phase (573 K)

adsorption of PY (sum of Brønsted and Lewis acid sites) and 2,6-dimethylpyridine (DMPY, Brønsted sites) as probe molecules, using a method previously described [12]. Very small volumes of solutes were injected so as to approach conditions of gas-chromatography linearity.

The aniline alkylation was carried out in a tubular stainless-steel, continuous flow mixed-bed microreactor (6 mm i.d.) surrounded by an electric heater. An iron constantan thermocouple was placed in the middle of the catalyst bed, and the unit was operated at atmospheric pressure. The substrate (an aniline 2 M solution in methanol) was delivered at a set flow rate ($40 \mu\text{L min}^{-1}$) with a Gilson 307 Piston-Pump system and was vaporised before it was passed through the catalyst bed in the presence of a nitrogen flow as carrier (3 L g^{-1}). The catalyst charges (W), typically ca. 0.03 g, were held by quartz wool at the centre of the reactor. Reaction temperature was in the 573–673 K range. Blank runs confirmed that under the experimental conditions, thermal effects were negligible. Reaction products, analysed in a FISON GC 8000 series and characterized by GC-MS, were *N*-methylaniline and *N,N*-dimethylaniline as well as minor amounts of *N,N*-dimethyl-4-methylaniline (less than 2%) that were not considered in the selectivity values. Interestingly, no *C*-alkylated products were obtained under the reaction conditions.

3. Results and discussion

Aniline alkylation is a sequential reaction process, in which methylation of aniline produces *N*-methylaniline (NMA), then *N,N*-dimethylaniline (NNDMA) and subsequently *N,N*-dimethyltoluidines (NN-DMT, *p*->*o*-). Low reaction temperatures favour the *N*-alkylation pathway whereas high temperatures produce higher quantities of *C*-alkylated products according to previously reported results [7]. Al-MCM-41 surface acidity titration values (against PY and DMPY) are shown in Table 1. Reaction rate constants (k) and catalytic performance (total conversion and selectivity) of Al-M41S materials are summarised in Table 2. The acidity of the Al-MCM-41 (Table 1) increased with aluminum content (decreasing Si/Al ratio, Table 1), and so did the aniline total conversion, although this relationship was not linear, having a maximum for ratios Si/Al 20 and 30, depending on the materials [12]. Furthermore, the incorporation of F to Al-MCM-41 samples led to an enhancement of the acid surface sites, increasing, in general, both Brønsted and Lewis sites [12].

Surprisingly, the materials' acidity enhancement did not provide an improved performance in the alkylation reaction, as the catalytic activity between fluorinated and non-fluorinated materials did not significantly change with the NH_4F treatment. In fact, most of the fluorinated materials exhibited a lower catalytic activity and reaction rate constants than non-fluorinated materials, irrespective of the Si/Al ratio. This effect seemed to be related to the different aluminum major environments (Al_{td} and Al_{oh}) present in the solid acids, in good agreement with previously reported results on the Al^{3+} atoms extraction from the mesoporous network [12]. The different Al environment in fluorinated and non-fluorinated materials

Table 1

Al-MCM-41 surface acidity using pyridine (PY, $\mu\text{mol g}^{-1}$ and $\mu\text{mol m}^{-2}$) and 2,6-dimethyl pyridine (DMPY, $\mu\text{mol g}^{-1}$ and $\mu\text{mol m}^{-2}$) as titrating probe molecules (T_{ads} : 573 K)

Material	PY ($\mu\text{mol g}^{-1}$)	PY ($\mu\text{mol m}^{-2}$)	DMPY ($\mu\text{mol g}^{-1}$)	DMPY ($\mu\text{mol m}^{-2}$)
40Al-40	164	0.13	39	0.03
30Al-40	183	0.14	83	0.06
20Al-40	125	0.11	47	0.04
15Al-40	172	0.17	40	0.04
40Al-40-F	120	0.12	69	0.07
30Al-40-F	183	0.17	97	0.09
20Al-40-F	190	0.19	104	0.10
15Al-40-F	218	0.23	100	0.10
Al-40	152	0.11	39	0.03
Al-30	177	0.14	50	0.04
Al-20	212	0.17	53	0.04
Al-15	188	0.17	68	0.06
Al-F-40	173	0.19	33	0.04
Al-F-30	245	0.26	84	0.09
Al-F-20	192	0.19	120	0.12
Al-F-15	195	0.20	100	0.10

resulted in an unexpected catalytic performance for fluorinated samples, also in terms of deactivation, as we will see later on. Al-MCM-41 displayed a better catalytic performance in the aniline alkylation than some commercial zeolites including H-Y, H-ZSM-5 and H-Mor, despite their higher acidities compared to our mesoporous materials. Certainly, in zeolitic materials, diffusional and shape selectivity constraints are often the main drawbacks for catalytic applications.

The difference in conversion, due to the materials' varying acidity [Brønsted (DMPY data) and Lewis (PY-DMPY data)

acid sites], cannot be explained with surface acidity values of catalysts since there is not a simple relationship between aniline alkylation activity and acidity as measured by PY and DMPY adsorption at 573 K (Tables 1 and 2).

In terms of selectivity, the alkylation reaction was found to be 100% selective to the *N*-alkylation process. No *C*-alkylated products were detected under the reaction conditions. In general, materials exhibited a preferential selectivity to *N*-monoalkylated products. NMA selectivity continuously increased with time on stream whereas NNDMA and aniline conversion decreased as a result of the acid sites deactivation. Interestingly, neither the NH_4F post-treatment nor the aluminum content (acidity) of materials did have a pronounce effect in the selectivity to NMA. It remained almost unchanged (70–80%) for all the solid acids prepared. These results are in good agreement with previously reported Al-HMS [10b], AlPO_4 [13], $\text{CrPO}_4\text{-AlPO}_4$ and $\text{AlPO}_4\text{-oxides}$ [5]. Table 3 summarises a comparison in catalytic activity of different materials employed in the *N*-methylation of aniline, confirming the outstanding activities of our Al-MCM-41 materials at extremely low catalyst loadings (typically 0.03 g).

Deactivation curves of NH_4F treated and untreated Al-MCM-41 mesoporous materials are shown in Fig. 1. Al-MCM-41 endured a slight deactivation with time on stream (approximately 20–30% of the initial activity) that can be attributed to the deactivation and poisoning of the active acid sites as well as to the adsorption and subsequent coking of the aniline molecules over the catalyst surface. However, although selectivity to NMA and conversion values were found to be similar between fluorinated and non-fluorinated materials, the F incorporation in Al-MCM-41 provided highly stable materials that did not deactivate, appreciably, with time on stream (less than 10% after

Table 2

Total aniline conversion (X_{AN} , mol%), reaction rate constant (k , $\text{mol g}^{-1} \text{s}^{-1}$) and *N*-methylaniline selectivity (S_{NMA} , mol%), at different reaction times, in the aniline alkylation with methanol using Al-M41S materials^a

Catalyst	4 h reaction			8 h reaction			16 h reaction		
	X_{AN}	k ($\times 10^6$)	S_{NMA}	X_{AN}	k ($\times 10^6$)	S_{NMA}	X_{AN}	k ($\times 10^6$)	S_{NMA}
40Al-40	14.9	7.1	67.7	12.9	6.1	71.9	10.5	4.9	75.4
30Al-40	16.1	7.8	66.0	14.1	6.7	69.2	12.6	5.9	72.6
20Al-40	19.0	9.3	71.8	17.7	8.6	73.2	16.3	7.9	78.4
15Al-40	20.8	10.3	65.2	18.4	9.8	68.0	17.0	8.2	70.9
40Al-40-F	9.3	4.3	74.7	8.9	4.1	76.1	8.5	3.9	76.2
30Al-40-F	17.8	8.7	73.0	17.0	8.3	77.6	16.3	7.9	78.9
20Al-40-F	19.3	9.6	68.7	18.7	9.3	69.6	18.1	8.9	71.3
15Al-40-F	19.4	9.5	64.6	18.9	9.3	64.8	17.8	8.7	67.6
Al-40	12.7	6.1	76.5	12.2	5.8	78.9	10.5	4.9	82.6
Al-30	19.7	9.8	65.1	18.4	9.1	68.3	16.7	8.1	72.3
Al-20	16.3	8.0	71.8	15.4	7.4	72.3	14.3	6.8	74.0
Al-15	17.0	8.3	76.0	15.9	7.7	77.6	14.2	6.8	81.1
Al-F-40	11.8	5.6	78.7	11.6	5.5	79.8	11.1	5.2	80.7
Al-F-30	16.7	8.2	76.2	16.5	8.1	77.9	15.6	7.7	80.9
Al-F-20	11.1	5.2	76.1	10.9	5.1	77.2	10.5	4.9	77.9
Al-F-15	12.4	5.9	77.8	11.9	5.6	79.3	11.6	5.5	79.2
H- β -25	42.4	24.1	73.8	40.4	22.4	70.6	30.8	16.1	76.1
H-Mor-20	0.6	0.3	100.0	–	–	–	–	–	–
H-Y-30	1.4	0.6	100.0	1.3	0.6	100.0	1.1	0.5	100.0
H-ZSM5-30	10.9	5.1	80.8	8.6	4.0	83.1	6.7	3.1	85.0

^a $T = 573 \text{ K}$; $F = 1.34 \times 10^{-6} \text{ mol s}^{-1}$; $\text{WHSV} = 14.8 \text{ h}^{-1}$; 2 M aniline solution in methanol.

Table 3
Catalytic activity comparison of different materials in the *N*-methylation of aniline with methanol

Catalyst (best)	Temperature (K)	Catalyst amount (g)	Time (h)	Aniline conversion (mol%)	NMA selectivity (mol%)
APAI-A-15-773 [5a] ^{a,b}	523	0.15	2.0	20.3	76.7
CrP-PA-923 [5b] ^{a,b}	673	0.15	2.0	10.0	92.7
MgPPc [5c] ^{c,d}	773	0.18	1.7	47.6	58.0
Cr _{0.8} Mn _{0.2} Fe ₂ O ₄ [9a] ^e	623	0.50	2.0	58.5	100.0
ZCF-X [9b] ^{c,d}	573	3.00	1.0	55.8	97.0
15Al-40 ^{c,f}	573	0.03	2.0	25.0	64.9

^a Methanol to aniline 3:1 molar ratio.

^b WHSV = 2 h⁻¹.

^c Methanol to aniline 6:1 molar ratio.

^d WHSV = 9.5 h⁻¹.

^e WHSV = 14.8 h⁻¹.

^f Methanol to aniline 5:1 molar ratio.

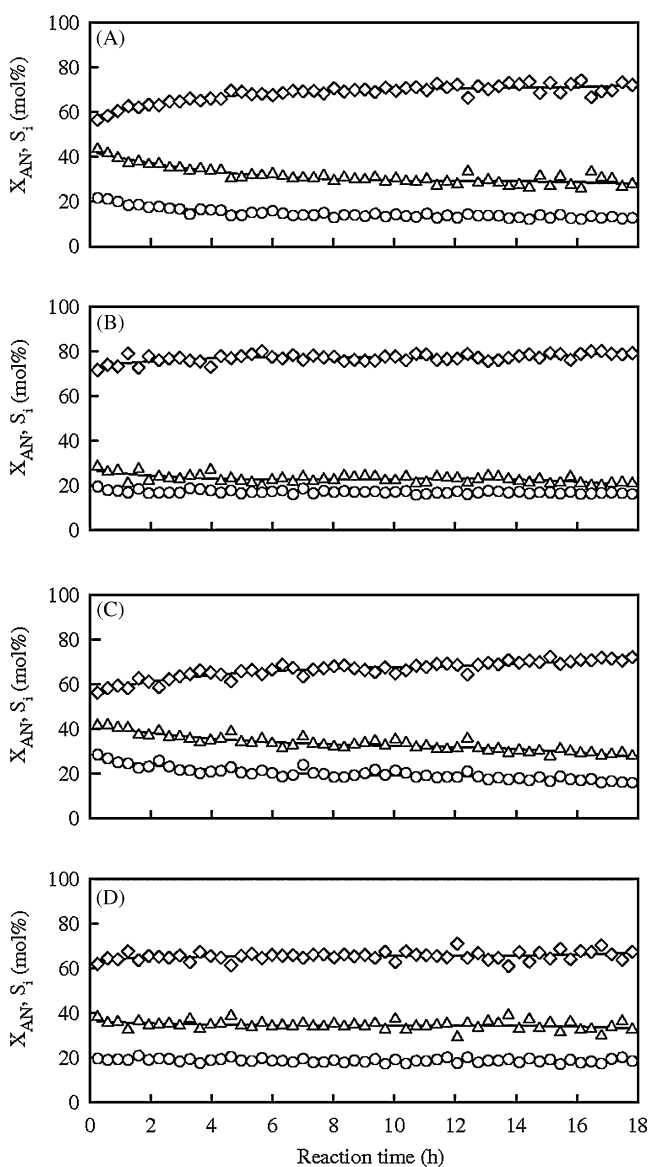


Fig. 1. Deactivation curves [total aniline conversion (\circ , X_{AN}) and selectivities (S_i) to *N*-methylaniline (\diamond , S_{NMA}) and *N,N*-dimethylaniline (Δ , S_{NDMA})], in the aniline alkylation with methanol at 573 K over Al-MCM-41 materials: (A) 30-41Al-40; (B) 30-41Al-40-F; (C) 15Al-40; (D) 15Al-40-F.

16 h of reaction). Fluorinated materials exhibited an improved hydrothermal stability (taking into account that water is generated in the alkylation process as by-product) as demonstrated on previous publications [12] and possibly a higher tolerance to the carbonaceous deposits over the materials surface. These facts can be explained in view of the different acid sites environments in NH_4F materials, after Al^{3+} extraction from the mesoporous network, compared to non-fluorinated ones in which the framework tetrahedral aluminum appeared to be more affected by the deactivation phenomenon.

The effect of the temperature was also studied. Three different reaction temperatures (573, 623 and 673 K) were screened in the alkylation of aniline with methanol. Results are summarised in Table 4. Both treated and untreated materials increased their respective catalytic activities with a temperature increase, irrespective of the aluminum content. This activity increase (up to a 60–65% depending on the solid acids) was at the expense of the *N*-methylaniline selectivity which was severely reduced at higher temperatures. The di-alkylation process, affording the *N,N*-dimethylamine as major product, was the main process at temperatures higher than 623 K. Nevertheless, the NMA selectivity increases with time of reaction in a similar way as has been pointed out before. In terms of stability, the materials proved to be very stable even at high temperatures, experiencing a similar deactivation to that at low temperatures (in any case less than 30% of the initial activity).

3.1. Materials regeneration experiments

Preliminary studies regarding the effect and evolution of the aniline and/or carbonaceous species adsorbed on the catalysts surface were carried out prior to the material regeneration. TG-DTA, TP-MS and DRIFT experiments were obtained for deactivated 20Al-40. Results are shown in Figs. 2–4.

TG-DTA curves (323–1123 K, 10 K min⁻¹) of partially deactivated 20Al-40 pointed out that the desorption and/or decomposition process of adsorbed and deposited carbonaceous species on the catalysts surface consisted of three different steps (Fig. 2): (1) in the first step ($T < 413$ K), the desorption of physisorbed water, generated as by-product in the alkylation reaction [14], took place. The mass loss is approximately 1–2%. (2) The ongoing water removal as well as the beginning

Table 4
Total aniline conversion (X_{AN} , mol%), reaction rate constant (k , $\text{mol g}^{-1} \text{s}^{-1}$) and selectivity to *N*-methylaniline (S_{NMA} , mol%) of 20-41Al-40, 20-41Al-40-F, 30-41Al-25 and 30-41Al-25-F materials at different temperatures and reaction times^a

Catalyst	4 h reaction			8 h reaction			16 h reaction		
	X_{AN}	$k (\times 10^6)$	S_{NMA}	X_{AN}	$k (\times 10^6)$	S_{NMA}	X_{AN}	$k (\times 10^6)$	S_{NMA}
20Al-40-573 K	19.0	9.3	71.8	17.7	8.6	73.2	16.3	7.9	78.4
20Al-40-623 K	43.9	25.6	46.2	41.9	24.1	51.5	34.3	18.6	56.8
20Al-40-673 K	59.4	39.8	36.9	57.5	36.6	39.2	53.5	33.7	43.3
20Al-40-F-573 K	19.3	9.6	68.7	18.7	9.3	69.6	18.1	8.9	71.3
20Al-40-F-623 K	37.3	20.7	54.4	36.3	20.0	56.3	32.3	17.3	56.2
20Al-40-F-673 K	65.9	47.5	33.2	63.8	44.9	32.8	60.3	40.8	34.3
Al-30-573 K	19.7	9.8	65.1	18.4	9.1	68.3	16.7	8.1	72.3
Al-30-623 K	39.4	23.8	51.0	36.6	20.2	54.3	34.0	18.5	56.1
Al-30-673 K	61.1	40.6	30.8	58.7	38.8	33.9	54.9	34.9	36.8
Al-F-30-573 K	16.7	8.2	76.2	16.5	8.1	77.9	15.6	7.7	80.9
Al-F-30-623 K	35.8	19.5	59.3	34.7	18.8	54.0	33.0	17.6	58.7
Al-F-30-673 K	59.5	40.2	36.6	57.2	38.0	40.0	50.8	31.5	41.4

^a $T = 573 \text{ K}$; $F = 1.34 \times 10^{-6} \text{ mol s}^{-1}$; WHSV = 14.8 h^{-1} .

of the carbonaceous and/or organic compounds desorption (exothermic peak at 567 K, Fig. 2B) occurred in the second step (413–643 K), contributing to a 2% of mass loss. On a mesostructure containing adsorbed water, the co-adsorption of organic compounds, including aniline, can occur by weak hydrogen bonding through surface water molecules [15]. (3) Finally, ATD curves exhibited one (643–923 K, Fig. 2A) or several sharp exothermic peaks (773–823 K, Fig. 2B) which can be attributed to the removal of carbonaceous species (coke and/or organic basic molecules), confirming data from TP-MS and DRIFT experiments (Figs. 3 and 4).

The low-temperature peak has been suggested to be related to a more aliphatic-type coke while a more aromatic-type coke seemed to be responsible for the higher temperature peak [16], in good agreement with earlier findings for carbonaceous deposits in zeolites [17].

TP-MS spectra of deactivated samples comprised of several m/z signals (Fig. 3)—(m/z): 18 (H_2O), 28 (CO) and 44 (CO_2).

Results demonstrated the desorbed water came from both the physisorbed water (350–360 K peak) and the decomposition of

the adsorbed organic compounds (approximately 590 K in air). The latter came along with a CO_2 peak (Fig. 3 and step 2 in the TG-DTA experiments) indicative of the partial decomposition of these compounds related to H_2O and CO_2 loss. The complete removal of carbonaceous species took place at temperatures higher than 873 K (CO_2 and H_2O signals in the 873–973 K range). Interestingly, neither aniline desorption peaks ($m/z = 93$) nor *N*-methyl ($m/z = 106$) or *N,N*-dimethylaniline ($m/z = 122$) were detected in the TP-MS spectra. Thus, the materials activity

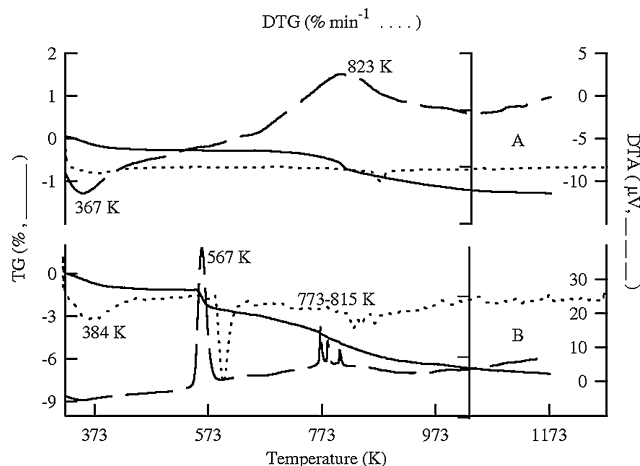


Fig. 2. TG, DTG and DTA curves of deactivated 20Al-40: (A) inert atmosphere (Ar); (B) oxidant atmosphere (air).

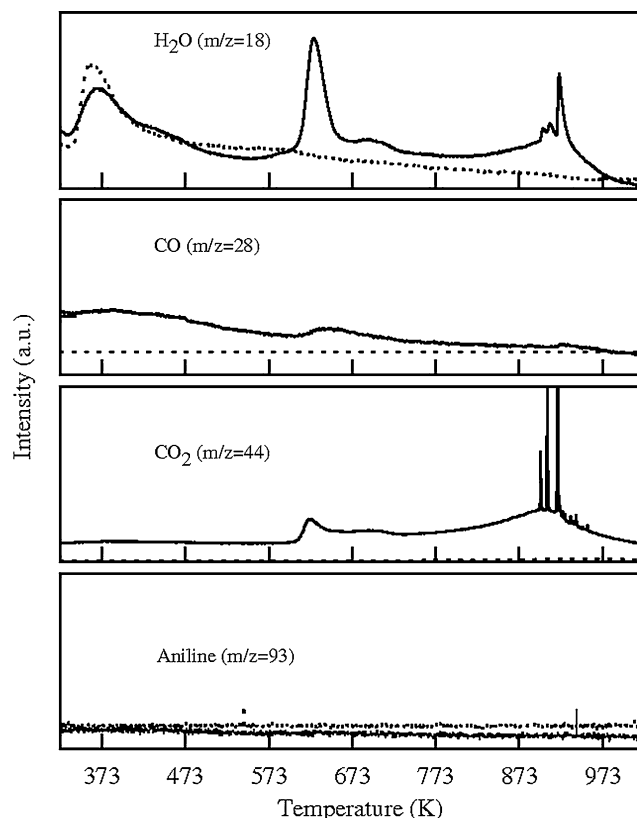


Fig. 3. Deactivated 20Al-40 TP-MS spectra (carrier 50 mL min^{-1}): (—) in air; (···) in Ar.

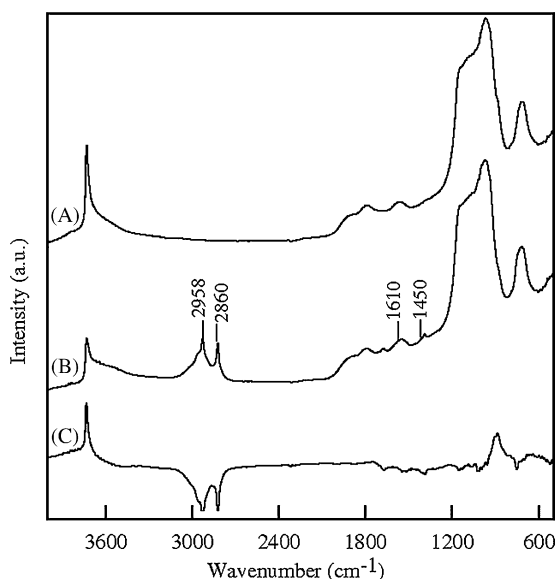


Fig. 4. Aluminosilicate 20-48Al-40 DRIFT spectra: (A) fresh material; (B) deactivated sample (573 K, 12 h of reaction); (C) differential fresh/deactivated sample spectrum.

should not be strongly influenced by the adsorption of these basic molecules.

Furthermore, DRIFT measurements were in good agreement with TG-DTA and TP-MS results as shown in Fig. 4. Eimer et al. [15] and Rozwadowski et al. [16] reported two different regions in the IR range ((A) 3000–2800 cm^{-1} and (B) 1800–1350 cm^{-1}) where several bands, that can be attributed to different organic compounds (including alkanes, alkenes and/or aromatics) and (C) [17], are to be present in deactivated samples. Characteristic and sharp peaks at 3050 and 2940 cm^{-1} , respectively, may be assigned to the symmetric and asymmetric stretching vibrations of CH_2 and CH_3 , respectively [18,19]. Moreover, the 1610 cm^{-1} peak has been attributed to polyalkenes and polyaromatic species, being a good indicator of the presence of coke [16,19]. Finally, peaks at 1450 and 1380 cm^{-1} (can be seen by peak enhancement), remarkably less intense than those due to the stretching vibrations, were ascribed to the asymmetric and symmetric bending vibrations of CH_3 .

Materials reactivation studies were conducted after partial catalysts deactivation (typically after 16 h of reaction). Regeneration experiments comprised of three key steps: (a) a quick thermal treatment (573–823 K) in nitrogen (100 mL min^{-1}); (b) proper thermal activation under either inert (N_2 , 100 mL min^{-1}), reductive (H_2 , 100 mL min^{-1}) or oxidant (air, 50 and 100 mL min^{-1}) atmosphere; (c) samples were cooled down, using N_2 as carrier gas, to the reaction temperature (573 K).

Thermal reactivation of Al-MCM-41 was deeply influenced by the nature of the carrier gas (inert, reductive or oxidant atmosphere) as well as by its flow employed during the reactivation procedure. Reactivation using N_2 or H_2 as carriers did not contribute to any increase in the catalytic activity of the materials, whereas the oxidative treatment rendered materials that preserved up to 80% of their initial activity (typ-

ically 10–15% conversion) after three reuses. However, XRD diffraction measurements verified the Al-MCM-41 hexagonal characteristic diffraction lines disappeared after the catalytic reaction (results not shown), irrespective of the atmosphere employed in the regeneration process. Al-MCM-41 materials structure was irreversibly deteriorated as a result of the water produced in the aniline alkylation. Therefore, no additional reactivation experiments were conducted since the re-used Al-MCM-41, even though they remain highly active, should be denoted as amorphous aluminosilicates. Regenerated materials were found to experience a similar deactivation to that obtained for the fresh catalysts, irrespective of the NH_4F treatment in the materials.

4. Conclusions

Al-MCM-41 samples were active catalysts in aniline alkylation. Samples treated with NH_4F showed a structure improvement, an enhancement in surface acid properties and a better *N*-methylaniline selectivity as well as a lower catalyst deactivation compared to that of untreated materials. In the present reaction conditions, only *N*-alkylated products (*N*-methylaniline and *N,N*-dimethylaniline) were obtained with a total conversion of aniline between 10 and 20% and a NMA selectivity higher than 70%. Strong acid sites are not required for the *N*-methylation of aniline whereas weak to moderate acid sites seemed to be responsible for the reaction. The difference in conversion, due to the materials various acidity, cannot be explained with surface acidity values of catalysts. In this reaction, the increase in acidity not only did not result in an increase of activity, but also decreased X_{AN} , confirming the fact that there is not a simple relationship between aniline alkylation activity and acidity as measured by pyridine and 2,6-dimethylpyridine adsorption at 573 K. Weak to moderate acid sites were shown to be sufficient for the *N*-alkylation, whereas strong acid sites are prerequisite for *C*-alkylation.

Acknowledgments

This research was subsidized by grants from Dirección General de Investigación (Project CTQ2005-04080), Ministerio de Educación y Ciencia, FEDER Funds and Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Project FQM-191).

References

- [1] (a) S. Sunwanprasop, T. Nhujak, S. Roengsumran, A. Petsom, *Ind. Eng. Chem. Res.* 43 (2004) 4973; (b) S.R. Stauffer, J.F. Hartwig, *J. Am. Chem. Soc.* 125 (2003) 6977; (c) J.S. Kim, O.J. Shon, J.A. Rim, S.K. Kim, J. Yoon, *J. Org. Chem.* 67 (2002) 2348; (d) M. Negwer, *Organic-Chemical Drugs and their Synonyms*, 7th ed., Akademie Verlag GmbH, Berlin, 1994 (an international survey).
- [2] A.K. Bhattacharya, D.K. Nandi, *Ind. Eng. Chem. Prod. Res. Dev.* 14 (1975) 162.
- [3] L.K. Doraiswamy, G.R.W. Krishnan, S.P. Mukherjee, *Chem. Eng.* 88 (1981) 78.
- [4] S. Narayanan, K. Deshpande, *Appl. Catal. A* 199 (2000) 1.

- [5] (a) F.M. Bautista, J.M. Campelo, A. García, D. Luna, J.M. Marinas, A.A. Romero, *Appl. Catal. A* 39 (1998) 166;
(b) F.M. Bautista, J.M. Campelo, A. García, D. Luna, J.M. Marinas, A.A. Romero, M.R. Urbano, *J. Catal.* 172 (1997) 103;
(c) M.A. Aramendia, V. Borau, C. Jiménez, J.M. Marinas, F.J. Romero, *Appl. Catal. A* 183 (1999) 73.
- [6] (a) R. Anand, S.S. Khaire, R. Maheswari, K.U. Gore, V.R. Chumbhale, *Appl. Catal. A* 242 (2003) 171;
(b) I.I. Ivanova, E.B. Pomakhina, A.I. Rebrov, M. Hunger, Y.G. Kolyagin, J. Weitkamp, *J. Catal.* 203 (2001) 375;
(c) S. Narayanan, A. Sultana, *Appl. Catal. A* 167 (1998) 103.
- [7] (a) G.D. Yadav, N.S. Doshi, *J. Mol. Catal. A* 194 (2003) 195;
(b) S. Narayanan, K. Deshpande, *Appl. Catal. A* 135 (1996) 125;
(c) K. Sreekumar, S. Sugunan, *Appl. Catal. A* 230 (2002) 245.
- [8] (a) S. Narayanan, K. Deshpande, *J. Mol. Catal. A* 104 (1995) L109;
(b) S. Narayanan, B.P. Prasad, *J. Mol. Catal. A* 96 (1995) 57.
- [9] (a) K. Nishamol, K.S. Rahna, S. Sugunan, *J. Mol. Catal. A* 209 (2004) 89;
(b) K. Sreekumar, T. Mathew, S.P. Mirajkar, S. Sugunan, B.S. Rao, *Appl. Catal. A* 201 (2000) L1.
- [10] (a) I.K. Park, K.Y. Park, S.I. Woo, *Catal. Lett.* 26 (1994) 169;
(b) S.I. Woo, J.K. Lee, B.S. Hong, Y.K. Park, Y.S. Uh, *Stud. Surf. Sci. Catal.* 49B (1989) 1095;
(c) P.Y. Chen, M.C. Chen, H.Y. Chu, N.S. Chang, T.K. Chuang, *Stud. Surf. Sci. Catal.* 28 (1986) 739.
- [11] J.M. Campelo, F. Lafont, J.M. Marinas, *Zeolites* 15 (1995) 97.
- [12] (a) R. Luque, J.M. Campelo, D. Luna, J.M. Marinas, A.A. Romero, *Micropor. Mesopor. Mater.* 84 (2005) 11;
(b) J.M. Campelo, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, J.J. Calvino, M.P. Rodríguez-Luque, *J. Catal.* 230 (2005) 327.
- [13] F.M. Bautista, J.M. Campelo, A. García, D. Luna, J.M. Marinas, A.A. Romero, *Stud. Surf. Sci. Catal.* 108 (1997) 123.
- [14] T. Kugita, M. Ezawa, T. Owada, Y. Tomita, S. Namba, N. Hashimoto, M. Onaka, *Micropor. Mesopor. Mater.* 44–45 (2001) 531.
- [15] G.A. Eimer, M.B. Gomez Costa, L.B. Pierella, O.A. Anunziata, *J. Colloid Interface Sci.* 263 (2003) 400.
- [16] M. Rozwadowski, M. Lezanska, J. Wloch, K. Erdmann, R. Golembiewski, J. Kornatowski, *Chem. Mater.* 13 (2001) 1609.
- [17] J.P. Lange, A. Gutsze, J. Allgeier, H.G. Karge, *Appl. Catal. A* 45 (1988) 345.
- [18] R.M. Silverstein, F.X. Webster, *Spectroscopic Identification of Organic Compounds*, Wiley, New York, 1998.
- [19] B. Paweewan, P.J. Barrie, L.F. Gladden, *Appl. Catal. A* 167 (1998) 353.