# Acidity study of Nb-containing MCM-41 mesoporous materials. Comparison with that of Al-MCM-41

M. Ziolek * and I. Nowak

*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland*

J.C. Lavalley

*Laboratoire Catalyse et Spectrochimie, URA CNRS 414, ISMRA-Université, 14050 Caen, France*

Received 9 December 1996; accepted 18 March 1997

The acidity of Nb-MCM-41 molecular sieves as well as their hydrogen forms was studied using FTIR spectroscopy with pyridine and 2,6-dimethylpyridine as probe molecules and in test reactions (isopropanol and cumene decomposition). The number of Lewis acid sites (LAS) and Brønsted acid sites (BAS) was estimated from the intensity of IR bands at 1450 and 1549 $cm^{-1}$ respectively. The acidity of niobium-containing materials was compared with that of Al related molecular sieves. The parent Al- and Nb-MCM-41 mesoporous materials studied in this work did not show Brønsted acidity which only appeared after ammonium exchange followed by calcination. The number and the strength of BAS was much higher on H,Al-containing material than that on H,Nb-containing molecular sieves. H,Nb-MCM-41 exhibited a higher concentration of LAS than H,Al related material.

**Keywords:** Nb-MCM-41, Al-MCM-41, hydrogen forms, acidity, FTIR, test reactions

## 1. Introduction

In recent years, a number of extra-large pore materials have been synthesised. Among them MCM-41 molecular sieves, discovered by Mobil Oil Company [1,2], were intensively studied. Efforts are under way to obtain materials with large pores, which would at the same time retain other unique characteristics of zeolites. Acidity of these materials is an important factor in considering their use as catalysts.

In the case of MCM-41 molecular sieves, active sites may be generated by the incorporation of heteroatoms into the electrically neutral purely siliceous framework. Various elements have already been introduced in the MCM-41 framework, for example: aluminium [3–5], gallium [6], titanium [7,8], vanadium [9], iron [10], manganese [11], and chromium [12]. Recently we incorporated niobium into MCM-41 material [13].

The substitution of silica by other metals results in various catalytic activities due to the generation of various active sites. Much effort has been devoted to the introduction of Al into the MCM-41 framework, which gives rise to the formation of Brønsted acid sites. The acidity of aluminosilicate MCM-41 molecular sieves and their proton-exchanged forms has already been studied [8,14–19]. It was stated that the number and strength of acid sites generated are comparable to those of pillared acid-activated clays and lower than those present in a HY zeolite with $Si/Al = 3.65$. Aluminosilicate mesoporous materials appeared to be moderate catalysts for cumene cracking to propene and benzene [19]. The nature of the aluminium source used for the synthesis of MCM-41 sieves influences the acidic properties of the obtained material [16]. Aluminium sulfate was described as a good source to incorporate aluminium into the framework leading to a higher acidity and catalytic activity than when aluminium isopropoxide or pseudo boehmite was used [16]. Therefore, aluminium sulfate was applied to the synthesis of Al-MCM-41 in this work.

The aim of this study was to compare the acidic properties of niobium-containing MCM-41 to aluminium-containing samples.

Niobium compounds and niobium materials have been shown to enhance catalytic properties [20–24]. Datka et al. [25] studied the acidity of niobium oxide supported on various metal oxides and concluded that Brønsted acid sites are generated only when alumina or silica is applied as a support.

Acidity of MCM-41, Al-MCM-41 and Nb-MCM-41 mesoporous materials has been studied in this work using FTIR spectroscopy and pyridine and lutidine (2,6-dimethylpyridine) as probe molecules. In addition, test reactions like isopropanol decomposition and cumene cracking were performed.

## 2. Experimental

### 2.1. Synthesis

Mesoporous silica (MCM-41) and niobium-contain-

---

* To whom correspondence should be addressed.

ing molecular sieves (Nb-MCM-41 with Si/Nb = 16 and 32) were prepared according to the procedure described in our previous paper [13]. Nb-MCM-41 with the Si/Nb = 16 and 32 ratio will be designated in this paper as Nb-MCM-41 (16) and Nb-MCM-41 (32) respectively.

Al-MCM-41 was prepared according to the procedure described for Nb-MCM-41. The source of Al was aluminium sulfate. Diluted $H_2SO_4$ was used for pH adjustment. The bulk Si/Al = 16 ratio was applied.

The templates of the products: MCM-41, Nb-MCM-41 and Al-MCM-41 were finally calcined at 773 K for 6 h in air.

Al- and Nb-silicate molecular sieves contained sodium cations. Hydrogen forms of these materials were obtained via sodium cation exchange with $NH_4^+$ ions and calcination of the modified samples at 673 K. The ion exchange was performed using a conventional method, i.e. stirring of solid in aqua solution of $NH_4Cl$ (0.1 M). The samples after synthesis and before calcination are designed "as-made". The compounds exchanged with $NH_4^+$ cations are denoted by $NH_4$,Al-MCM-41 and $NH_4$,Nb-MCM-41, and those after calcination: H,Al-MCM-41 and H,Nb-MCM-41.

### 2.2. Structure characterisation

The crystallographic structure of the samples was verified by X-ray powder diffraction carried out on a TUR 42 diffractometer using Cu $K_\alpha$ radiation. The calcined samples were contacted with water vapour and after that the XRD studies were performed.

### 2.3. Acidity measurements

Infrared spectra were recorded with a Nicolet 710 FTIR spectrometer using an in situ cell. The samples were pressed, under low pressure, into a thin wafer of $\sim 7.5$ mg $cm^{-2}$ and placed in the cell. The catalysts were evacuated at 673 K during 2 h and pyridine or lutidine was then admitted at RT. After saturation the samples were degassed at RT, 423, 523 and 623 K in vacuum for 30 min.

### 2.4. Catalytic testing

Isopropanol decomposition and cumene cracking were applied as acidity test reactions. Both reactions were performed using a pulse microreactor with a helium flow of 40 $cm^3$/min. The catalyst bed (0.05 g) was first activated for 2 h at 673 K under helium flow. The isopropanol conversion was studied in the temperature range of 523–623 K and the cumene cracking in the range of 623–723 K. The reaction products were analysed using a CHROM-5 gas chromatograph on line with the microreactor.

## 3. Results and discussion

### 3.1. Structure characterisation

XRD patterns of air calcined Nb-MCM-41 and ammonium-exchanged material are shown in figure 1. They are typical of MCM-41 molecular sieves described by Kresge et al. [1]. However, the ammonium form of niobium MCM-41 showed less intensive XRD peaks as compared with the parent material, as was observed earlier for $NH_4$,Al-MCM-41 [19].

### 3.2. Hydroxyl groups

FTIR spectra in the $\nu$(OH) region, recorded after activation of the samples under vacuum, for 2 h at 673 K, are shown in figure 2. Nb-MCM-41 (16) and (32) materials present a sharp band at 3746 $cm^{-1}$ corresponding to silanol groups. This is almost the same as that observed for Si-MCM-41. The width at half height of the IR band recorded for both Nb-MCM-41 samples is about 10 $cm^{-1}$. After $NH_4^+$ exchange of Nb-MCM-41 (32), the intensity of the band at 3744 $cm^{-1}$ is lower than before modification, but the band is much broader (half width 16 $cm^{-1}$ instead of 10 $cm^{-1}$). Moreover, a tail towards lower wavenumbers appears. It is clearly seen that when the material contains more niobium (Si/Nb = 16), the $\nu$(OH) band shows a lower intensity, before or after $NH_4^+$ exchange.

Regarding the Al-MCM-41 mesoporous material, after exchange of sodium with ammonium cations and deammonation, the $\nu$(OH) band becomes also broader (half width 14 $cm^{-1}$); the tail is extended towards lower wavenumber as compared with H,Nb-MCM-41 (16).

Corma et al. [8] and Chen et al. [14] explained the presence of the tail in the low wavenumber range of the IR spectra as due to the interaction of silanol groups with the template. They have shown that this interaction disappeared with the calcination temperature increasing to 773 K. However, in the case of the results presented in this work (figure 2) this explanation cannot be adopted

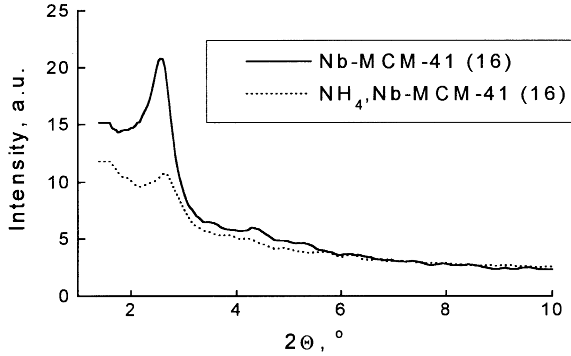


Figure 1. XRD patterns of air calcined Nb-MCM-41 (16) and its ammonium-exchanged form.

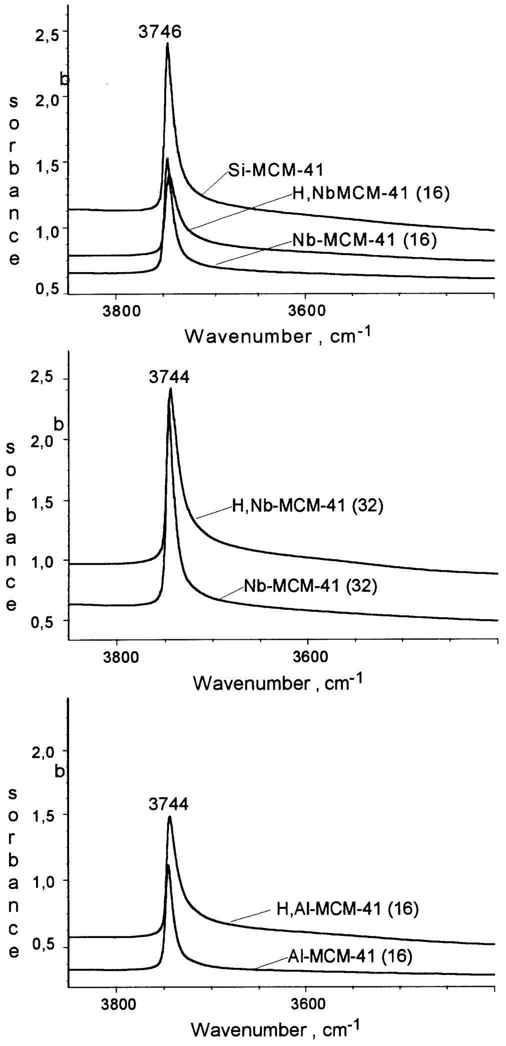


Figure 2. FTIR spectra of the activated compounds in the hydroxyl range (normalised to 10 mg of the calcined sample).

because Nb-MCM-41 materials were calcined at 773 K prior to FTIR study and before the modification with $NH_4^+$. The materials modified with $NH_4^+$ do not contain template and thus, the discussed tail cannot origin from the interaction of silanol groups with template molecules.

To determine if the broad tail could be due to the persistence of a small amount of water, $H_2O$ was adsorbed on the different samples. Generally, a broad band was noticed at about 3480 $cm^{-1}$ accompanied by the $\delta$(HOH) band at 1625 $cm^{-1}$. The latter is characteristic of $H_2O$. On silica samples a band at 1625 $cm^{-1}$ is accompanied by two others at 1965 and 1865 $cm^{-1}$ due to overtones or combination bands. A careful comparison of the intensity of these two bands relative to that at 1625 $cm^{-1}$ does not provide any evidence of water presence in the various samples after $NH_4^+$ exchange and evacuation at 673 K studied in this work. It is possible that this treatment creates additional silanol groups. Increase of their amount would favour their mutual interactions explaining the decrease of the 3745 $cm^{-1}$ band intensity after $NH_4^+$ exchange and the increase of the tail towards lower wavenumbers. It is known that bound vicinal silanols are characterised by a very broad band near 3460–3530 $cm^{-1}$ [26].

IR spectroscopy was not able to detect weak bands characteristic of NbOH, NbOHSi, AlOH or AlOHSi groups in the investigated materials.

### 3.3. Acidity measurements

In order to evaluate the amount and type of acidic sites, infrared spectroscopy (FTIR) of adsorbed bases has been applied. Pyridine ($pK_b = 8.8$) interacts with Lewis acid sites (LAS) giving rise to characteristic IR bands at ~ 1610 ($\nu_{8a}$) and ~ 1450 $cm^{-1}$ ($\nu_{19b}$). The wavenumber of the $\nu_{8a}$ band gives information about the strength of LAS and the intensity of the $\nu_{19b}$ band is related to the number of LAS taking into account that $\varepsilon_{1450} \approx 1.5\ \mu mol^{-1}$ cm [27]. Pyridine interacts also with Brønsted acid sites (BAS) resulting in the appearance of a band near 1550 $cm^{-1}$, which is accompanied by two others near 1640–1620 $cm^{-1}$. $\varepsilon_{1550}$ has been estimated at 1.8 $mol^{-1}$ cm [27]. 2,6-dimethylpyridine (2,6-lutidine, Lu $pK_b = 7.25$) which is a stronger base than pyridine, has been also used in the acidity study. $LuH^+$ species (lutidinium) show IR bands in the 1630–1650 $cm^{-1}$ range characteristic of lutidine adsorption on BAS [28].

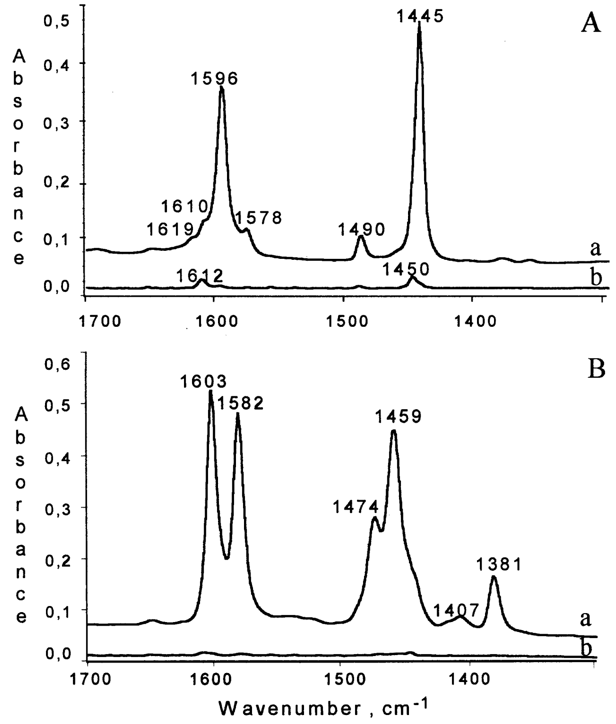


Figure 3. IR spectra after pyridine (A) and lutidine (B) desorption at RT (a) and 423 K (b) on Nb-MCM-41 (16) (normalised to 10 mg of the calcined sample).

Table 1
Number of BAS and LAS calculated per 1 g of the catalysts on the basis of IR bands observed after desorption of pyridine at 423 K and extinction coefficient of pyridine

| Sample | Number of LAS $\times 10^{17}$ | Number of BAS $\times 10^{17}$ | Total number of acid sites $\times 10^{17}$ |
|---|---|---|---|
| Nb-MCM-41 (16) | 147 | – | 147 |
| Nb-MCM-41 (32) | 208 | – | 208 |
| Al-MCM-41 (16) | 307 | – | 307 |
| H,Nb-MCM-41 (16) | 493 | 20 | 513 |
| H,Nb-MCM-41 (32) | 522 | 7 | 529 |
| H,Al-MCM-41 (16) | 353 | 91 | 444 |

### *3.3.1. Nb and Al-MCM-41 samples*

As figure 3A, curve a, shows, the spectrum of Nb-MCM-41 (16) after pyridine (Py) desorption at room temperature (RT) exhibits main bands at 1596, 1578, 1490 and 1445 cm$^{-1}$ which are characteristic of weakly adsorbed Py species. It is important to note the presence of shoulders at about 1619 and 1610 cm$^{-1}$. After evacuation at 423 K (figure 3A, curve b), only two weak bands persist at 1612 and 1450 cm$^{-1}$ characterising the presence of Lewis acid sites. Their intensity does not depend on the Nb content in the sample. The amount of Lewis acid sites can be estimated at $\sim 150 \times 10^{17}$ sites g$^{-1}$ (table 1). In the case of MCM-41 and Al-MCM-41 the spectra after pyridine desorption at RT (not shown here) were almost similar but no shoulder was noted at 1610 cm$^{-1}$.

As for Brønsted acidity, neither pyridine nor lutidine was able to detect it irrespective of the niobium content or the nature of the element (Nb or Al) incorporated into the molecular sieve framework. In particular no IR bands characteristic of LuH$^{+}$ in the 1630–1650 cm$^{-1}$ range were registered in the IR spectra (figure 3B). Note that Jentys et al. [18] reported the presence of both Brønsted and Lewis acid sites on Al-MCM-41 prepared using another aluminium source.

### *3.3.2. H,Nb and H,Al samples*

Figure 4 presents the FTIR spectra obtained on Nb- and Al-containing hydrogen forms of the MCM-41 material after adsorption of pyridine and lutidine and desorption at various temperatures. After pyridine evacuation at RT on H,Nb-MCM-41 (figure 4A, curve a),

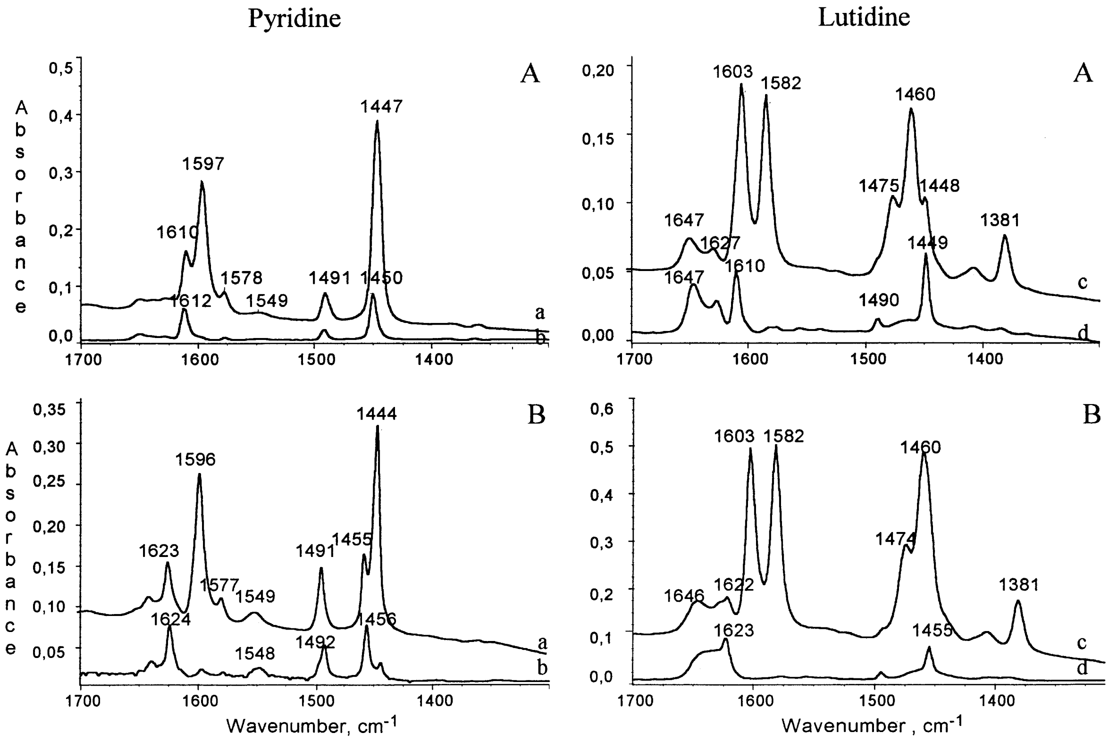


Figure 4. IR spectra after pyridine adsorption and desorption at RT (a), 423 K (b) (left side of the figure); lutidine adsorption and desorption at RT (c), 423 K (d) (right side of the figure) on the following samples: H,Nb-MCM-41 (16) (A) and H,Al-MCM-41 (B) (normalised to 10 mg of the calcined sample).

the spectrum exhibits a well defined band at 1610 cm$^{-1}$ characteristic of pyridine bound to Lewis acid sites and another broad band at 1549 cm$^{-1}$ due to pyridine adsorbed on Brønsted sites. The presence of both sites is confirmed by: (i) pyridine desorption at 423 K (figure 4A, curve b) which well evidences the two bands at 1612 and 1450 cm$^{-1}$ due to Py coordinated to Lewis acid sites, (ii) lutidine adsorption and desorption at RT or 423 K, the spectrum of which presents the very characteristic bands of LuH$^+$ at 1647 and 1627 cm$^{-1}$ (figure 4A, curves c and d).

From the intensity of the PyL species at 1450 cm$^{-1}$ one could estimate the number of Lewis acid sites at 493 and 522 $\times$ $10^{17}$ sites g$^{-1}$ for H,Nb-MCM-41 (16) and (32) respectively (table 1).

Note that the strength of Lewis acid sites, characterised by the 1610 cm$^{-1}$ wavenumber from pyridine adsorption, is the same as observed for Nb$_2$O$_5$ dispersed on silica [25] and that the PyH$^+$ band at 1549 cm$^{-1}$ almost disappeared after evacuation at 423 K showing that the strength of Brønsted acid sites is not very high.

The same experiments performed on the ammonium exchanged H,Al-MCM-41 sample evidenced the presence of Lewis acid sites, characterised by Py bands at 1623 and 1455 cm$^{-1}$ (figure 4B, curves a and b). Their higher wavenumber results from the presence of stronger Lewis sites. Pyridine adsorption also clearly evidences the formation of PyH$^+$ species (the band at 1549 cm$^{-1}$) as a result of the interaction with Brønsted acid sites. The presence of these centres was confirmed by lutidine adsorption (figure 4B, curves c and d). The PyH$^+$ species persists after evacuation at 423 K, showing that the strength of Brønsted acid sites is higher on aluminium than on the niobium containing sample. The amount of Brønsted acid sites in H,Al-MCM-41 is much higher than that observed on both H,Nb-MCM-41 samples since it could be estimated at 91 $\times$ $10^{17}$ sites g$^{-1}$.

### 3.4. Catalytic testing

The test reactions were: (i) isopropanol decomposition which leads to the formation of propene and/or diisopropyl ether on BAS and to dehydrogenation to acetone on basic and/or redox centres [29], and (ii) cracking of cumene which is often used as a test for strong acid sites [30].

Figures 5 and 6 show the results. In both reactions Si-MCM-41 is almost inactive, whereas Al-MCM-41 and Nb-MCM-41 exhibit low activity in the isopropanol conversion. Propene and water were the only products formed. The activity of the Al-MCM-41 sample was higher than that of Nb-MCM-41 at 523 and 573 K. In the cumene cracking both the Nb- and the Al-containing MCM-41 samples were inactive.

Modification of both starting materials (Nb-MCM-41 and Al-MCM-41) with NH$_4^+$ cations followed by deammonation causes the significant increase in the isopropanol conversion. At 523 and 573 K H,Al-MCM-41 (16) presents a higher activity than the H,Nb-MCM-41 (16) while at 623 K both materials show the same 100% conversion. The H,Nb-MCM-41 (32) catalyst, which exhibits a lower number of Brønsted acid centres (table 1) than the material with Si/Nb = 16, shows lower conversion of isopropanol in the whole temperature range studied. In the cumene cracking, which requires the presence of strong acid sites, H,Nb-MCM-41 materi-

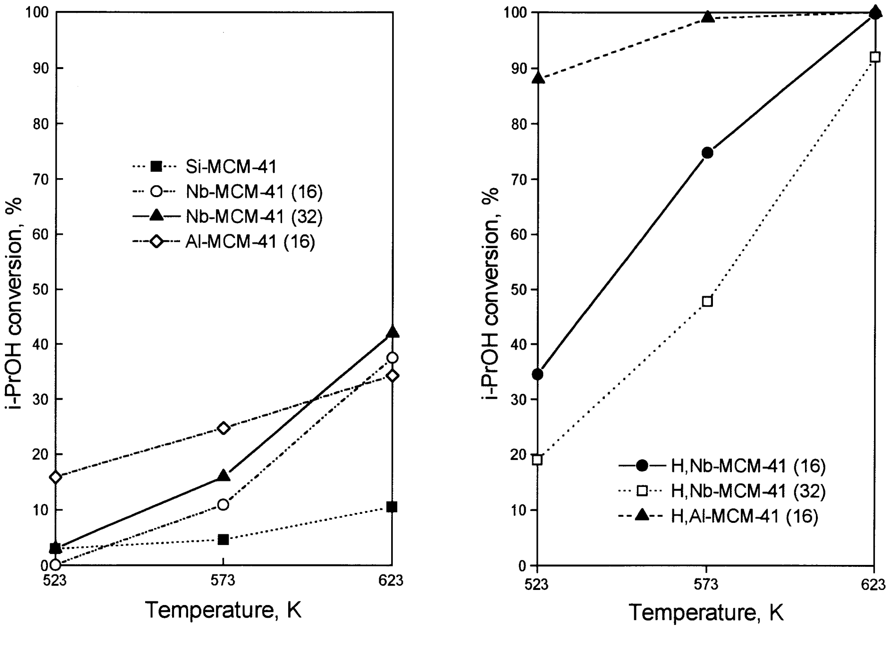


Figure 5. Isopropanol conversion at various temperatures on MCM-41 materials.

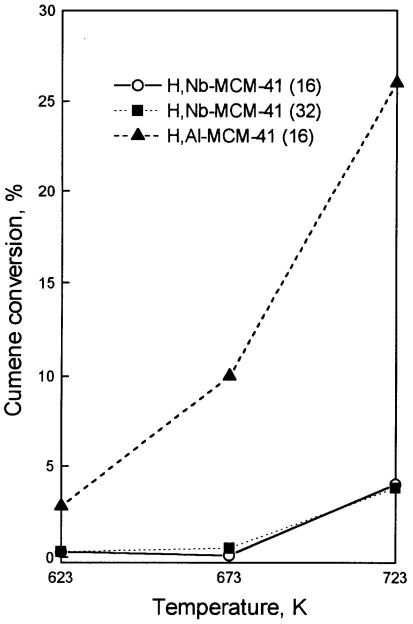


Figure 6. Cumene decomposition at various temperatures on H,Nb- and H,Al-MCM-41.

als do not exhibit any activity at 623 and 673 K and only a slight activity at 723 K. The conversion of cumene on H,Al-MCM-41 varies from 3 to 26% at 623 to 723 K respectively showing that this catalyst exhibits stronger Brønsted acid sites than the hydrogen–niobium samples.

## 4. Conclusions

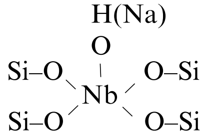
Nb-MCM-41 and Al-MCM-41 materials prepared according to the procedure described in this paper do not show Brønsted acidity after calcination.

The exchange of sodium cations on $NH_4^+$ ions followed by deammonation causes the formation of Brønsted acid sites (BAS) in all samples studied. The number of BAS calculated from the FTIR studies after adsorption and desorption of pyridine is about four times higher on H,Al-MCM-41 (16) than that on H,Nb-MCM-41 (16).

The strength of BAS is higher on the H,Al-sample than on the H,Nb-material, which was concluded on the basis of the pyridine chemisorption strength and the activity in the test reactions. H,Nb-MCM-41 materials were inactive in the cumene cracking which requires the presence of strong BAS, whereas the H,Al-MCM-41 catalyst was active in this reaction.

The appearance of Lewis acid sites on Nb-containing materials is most probably due to the formation of extra-lattice niobium species, as was found for Al-MCM-41 [19]. The lower amount of LAS in Nb-MCM-41 (16) than in Nb-MCM-41 (32) (table 1) can be due to a higher degree of polymerisation of extra niobium species in the sample with the higher amount of Nb (Si/Nb = 16). Ammonium exchange increases the formation of extra-lattice niobium species, which becomes comparable for both Nb-containing materials.

The number of Brønsted acid sites in H,Nb-mesoporous material depends, as expected, on the Si/Nb ratio. However, it is lower than in the H,Al-MCM-41 (16) sample suggesting that the lattice niobium species differs from that in the aluminium sample and/or the number of lattice niobium is lower even if Al/Si and Nb/Si ratio is the same (i.e. 16) for both samples. If the model proposed by Kornatowski et al. [31] for vanadium silicates is adopted for niobium silicates, one can postulate the formation of the following species:



Sodium cations in the Nb-MCM-41 material would be exchangeable contrary to the V–Si sample described earlier [31] and in agreement with the V–Si materials presented in refs. [32,33] explaining why after exchange with $NH_4^+$ cations and deammonation, the samples exhibit a Brønsted acidity not stated for the parent materials.

The fact of a lower acidity of H,Nb-MCM-41 mesoporous materials than that of commonly used H,Al-samples is important in the application of these materials as a support or catalyst. It allowed us to obtain a higher selectivity in the catalytic synthesis of methanethiol from $CH_3OH$ and $H_2S$ on H,Nb-MCM-41 than that observed on H,Al-materials [13].

## Acknowledgement

This work was partially supported by KBN under grants: 3 T09A 099 12 and 3 T09A 098 011.

## References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.
[2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[3] R. Shmidt, D. Akporiaye, M. Stocker and O.H. Ellestad, J. Chem. Soc. Chem Commun. (1992) 1493.
[4] Z.H. Luan, C.F. Cheng, W.Z. Zhou and J. Klinowski, J. Phys. Chem. 99 (1995) 1018.
[5] R.B. Borade and A. Clearfield, Catal. Lett. 32 (1995) 267.
[6] C.F. Cheng and J. Klinowski, J. Chem. Soc. Faraday Trans. 92 (1996) 289.
[7] P.T. Tanev, M. Chibwe and T.J. Pinnavaia, Nature 368 (1994) 321.

[8] A. Corma, M.T. Navarro and J. Perez-Pariente, J. Chem. Soc. Chem. Commun. (1994) 148.
[9] K.M. Reddy, J. Moudrakouski and A. Sayari, J. Chem. Soc. Chem. Commun. (1994) 1059.
[10] Z.Y. Yuan, S.Q. Liu, T.H. Chen, J.Z. Wang and H.X. Li, J. Chem. Soc. Chem. Commun. (1995) 973.
[11] D. Zhao and D. Goldfarb, J. Chem. Soc. Chem. Commun. (1995) 875.
[12] N. Ulagappan and C.N.R. Rao, J. Chem. Soc. Chem. Commun. (1996) 1047.
[13] M. Ziolek and I. Nowak, Zeolites, in press.
[14] J. Chen, Q. Li, R. Xu and F. Xiao, Angew. Chem. Int. Ed. Engl. 34 (1995) 2694.
[15] M. Busio, J. Jänchen, J.H.C. van Hoff, Microporous Mater. 5 (1995) 211.
[16] K. Reddy and Ch. Song, Catal. Lett. 36 (1996) 103.
[17] R. Mokaya and W. Jones, J. Chem. Soc. Chem. Commun. (1996) 983.
[18] A. Jentys, N.H. Phan and H. Vinek, J. Chem. Soc. Faraday Trans. 92 (1996) 3287.
[19] R. Mokaya, W. Jones, Z. Luan, M.D. Alba and J. Klinowski, Catal. Lett. 37 (1996) 113.
[20] A. Morikawa and A. Togashi, Catal. Today 16 (1993) 333.
[21] O. Desponds, R.L. Keiski and G.A. Somorjai, Catal. Lett. 19 (1993) 17.
[22] S. Okazaki and N. Wada, Catal. Today 16 (1993) 349.
[23] J.M. Jehng and I.E. Wachs, Catal. Today 8 (1990) 37.
[24] J.M. Jehng and I.E. Wachs, Catal. Today 16 (1993) 417.
[25] J. Datka, A.M. Turek, J.M. Jehng and I.E. Wachs, J. Catal. 186 (1992) 135.
[26] J.P. Gallas, J.C. Lavalley, A. Burneau and O. Barres, Langmuir 7 (1991) 1235.
[27] S. Khabtou, T. Chevreau and J.C. Lavalley, Microporous Mater. 3 (1994) 133.
[28] P.A. Jacobs and C.F. Heylen, J. Catal. 34 (1974) 267.
[29] C. Lahausse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot and A.M. Le Govic, J. Mol. Catal. 87 (1994) 329.
[30] J.W. Ward, J. Catal. 9 (1967) 225; 11 (1968) 251, 259.
[31] J. Kornatowski, B. Wichterlová, J. Jirkovský, E. Löffler and W. Pilz, J. Chem. Soc. Faraday Trans. 92 (1996) 1067.
[32] P.R. Hari Prasad Rav, A.V. Ramaswamy and P. Ratanasamy, J. Catal. 137 (1972) 225.
[33] B. Sulikowski, Heterogeneous Chem. Rev. 3 (1996) 203.