# Investigation of Coke Deposits on Al-MCM-41

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Carbonaceous compounds deposited on aluminosilicate mesoporous molecular sieves of the MCM-41 type during conversion of cyclohexene at various temperatures were investigated using TGA; DRIFT, UV−vis, and $^{13}C$ solid state NMR spectroscopies; and a sorption technique. The chemical composition of the deposits is not significantly affected by the Al content of Al-MCM-41 and depends mainly on the temperature and the duration of the reaction. At lower applied temperatures, both aliphatic and aromatic compounds are formed; they are relatively weakly bound to the surface of the material. After a longer reaction period, some deposits appear that are strongly bound to the surface. At higher temperatures, a fraction of the coke migrates out of the pores. Then, part of the coke (most likely aliphatics) desorbs and moves away, while the other part (presumably aromatics) adsorbs on the external surface of the sieve. The coke remaining both in the pores and on the external surface mostly forms multilayered polyaromatic structures that are strongly bound to the surface of the material. The water sorption capacity of the studied materials decreases with the content of the deposits.

## Introduction

Aluminum-containing MCM-41 materials are potential catalysts or catalyst supports for acidic, basic, and redox catalysis because of their acidity, high specific surface area, and porosity.[1−12] The high surface area also makes these materials active adsorbents.

During catalytic conversion of organic compounds, carbonaceous deposits are usually formed, which is the most frequent cause for deactivation of solid catalysts.[13] The deposits occur in the pores and/or on the outer surface of the catalysts, and their composition depends to a great extent on the reaction temperature. The products retained on the catalysts can be polyaromatic and/or nonpolyaromatic, and they form mainly at higher and lower temperatures, respectively. Both types of retained products are designated here as "coke". An interesting procedure for characterizing the carbonaceous compounds was developed by Guisnet and co-workers.[13] The method consists of removing the catalyst matrix with hydrofluoric acid and subsequently analyzing the carbonaceous compounds with various techniques.

In the recent years, considerable efforts have been made to arrive at a possibly full understanding of the factors responsible for the formation of coke in the intracrystalline channels or on the external surfaces of microporous molecular sieves.[14−16] Despite the vast amount of data accumulated during the last two decades, many questions still remain open or controversial. Investigations carried out up to now have mainly focused on zeolites, including the most commonly used ZSM-5.[17−19] The wide-porous zeolites, like mordenite or zeolite Y, have been studied relatively infrequently and mostly for comparative purposes.[20−22] Carbonaceous

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† Nicholas Copernicus University.
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(1) Reddy, K. M.; Mondrakovski, I. L.; Sayari, A. *J. Chem. Soc., Chem. Commun.* **1994,** 1059.
(2) Corma, A.; Navarro, M. T.; Perez-Pariente, J. *J. Chem. Soc., Chem. Commun.* **1994,** 147.
(3) Tanev, P. T.; Chibwe, M.; Pinnavaia, T. J. *Nature* **1994,** *368,* 321.
(4) Sayari, A.; Reddy, K. M.; Mondrakovski, I. L. *Stud. Surf. Sci. Catal.* **1995,** *98,* 19.
(5) Sayari, A.; Danumah, C.; Mondrakovski, I. L. *Chem. Mater.* **1995,** *7,* 813.
(6) Sayari, A.; Mondrakovski, I. L.; Danumah, C.; Ratcliffe, C. I.; Ripmeester, J. A.; Preston, K. F. *J. Phys. Chem.* **1995,** *99,* 16373.
(7) Cheng, C.-F.; He, H.; Zhou, W.; Klinowski, J.; Goncalves, J. A. S.; Gladden, L. F. *J. Phys. Chem.* **1996,** *100,* 390.
(8) Sayari, A. *Chem. Mater.* **1996,** *8,* 1840.
(9) Sayari, A. In *Recent Advances and New Horizons in Zeolite Science and Technology*; Chon, H., Woo, S. I., Park, S.-E., Eds.; Elsevier: Amsterdam, 1996; Chapter 1.
(10) Carvalho, W. A.; Varaldo, P. B.; Wallau, M.; Schuchardt, U. *Zeolites* **1997,** *18,* 408.
(11) Kosslick, H.; Lischke, G.; Walther, G.; Storek, W.; Martin, A.; Fricke, R. *Microporous Mater.* **1997,** *9,* 13.
(12) Mokaya, R. *J. Catal.* **1999,** *186,* 470.
(13) Guisnet, M. In *Handbook on Heterogeneous Catalysis*; Ertl, G., Knoezinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, Germany, 1997; Vol. 2, pp 626−632.
(14) Karge, H. G.; Lange, J. P.; Gutsze, A.; Laniecki, M. *J. Catal.* **1988,** *114,* 144.
(15) Nováková, J.; Kubelková, L. *Stud. Surf. Sci. Catal.* **1991,** *65,* 405.
(16) Moljord, K.; Magnoux, P.; Guisnet, M. *Appl. Catal. A* **1995,** *122,* 21.
(17) Vedrine, J. C.; Dejaifve, P.; Grabowski, E. *Stud. Surf. Sci. Catal.* **1980,** *5,* 29.
(18) Dejaifve, P.; Vedrine, J. C.; Bolis, V.; Derouane, E. G. *J. Catal.* **1980,** *63,* 331.
(19) Gielen, B.; Palikar, M. G. *Zeolites* **1989,** *9,* 208.
(20) Moljord, K.; Magnoux, P.; Guisnet, M. *Appl. Catal.* **1995,** *121,* 245.

deposits formed during the conversion of methanol over zeolite Y have been studied with different techniques such as thermogravimetric analysis (TGA);[23,24] gas chromatography (GC);[25] coke combustion combined with GC;[23,24] and spectroscopic methods including UV–vis,[26,27] IR,[23–25] ESR,[26] and ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si NMR.[26,27] It has been concluded that the temperature of the reaction and the pore structure of the zeolite have essential effects on the nature and amount of carbonaceous deposits formed in a particular system.[28] As has been found, three different types of the deposits can be distinguished depending on the reaction temperature. The first type comprises the deposits obtained at temperatures below 523 K. They arise inside the pores and are probably aliphatic, of low molecular mass, and weakly bound to the zeolite surface, and they can easily be removed by heating. Deposits of another type are produced within the temperature range of 523–593 K. They form inside the pores as well and are blocked there. They are presumably mostly aromatic species of a relatively low molecular mass. When separated from the zeolite framework, they are soluble in organic solvents. The third type of deposits includes those obtained at temperatures above 593 K. In this case, coke forms not only inside the pores but also on the external surface of the zeolite crystallites. The constituent compounds are highly aromatic and of a high molecular mass.

In the present work, we report on investigations of the carbonaceous deposits formed during conversion of cyclohexene over aluminosilicate mesoporous molecular sieves of the MCM-41 type at different temperatures. The studies have been performed using TGA; DRIFT, UV–vis, and ^{13}C solid-state NMR spectroscopies; and a sorption technique.

## Experimental Section

**Samples.** The parent Al–MCM-41 samples were prepared as described previously.[29] The Si/Al molar ratios in the reaction mixtures were chosen to be 15, 30, and 60. These ratios in the calcined products, as determined by AAS, equaled 12.2, 19.9, and 36.8, respectively. The conversion of cyclohexene was carried out within the temperature range of 483–663 K for 12 or 55 h.[29] The contents of carbonaceous deposits in the coked samples were determined as a function of time-on-stream according to the modified procedure by Bibby et al.[29–32] At certain time intervals, the reaction was stopped, the bed was

**Table 1. Contents of Carbonaceous Deposits in the Al-MCM-41 Materials Determined after the 12-h Reactions at Different Temperatures**

| sample | coke content (wt %)[a] | | |
|---|---|---|---|
| | calcination (oxygen) | TGA (air) | TGA (helium) |
| Al−MCM-41(15)+C483 | 48.81 | 44.93 | 45.98 |
| Al−MCM-41(15)+C513 | 33.80 | 30.72 | 27.74 |
| Al−MCM-41(15)+C543 | 23.24 | 23.68 | 23.46 |
| Al−MCM-41(15)+C573 | 28.38 | 29.87 | 24.75 |
| Al−MCM-41(15)+C573[b] | 60.17 | 62.60 | 30.21 |
| Al−MCM-41(15)+C603 | 18.85 | 20.12 | 16.96 |
| Al−MCM-41(15)+C633 | 21.12 | 21.21 | 20.48 |
| Al−MCM-41(15)+C663 | 13.46 | 16.76 | 14.94 |
| Al−MCM-41(30)+C573 | 13.54 | 12.36 | 12.99 |
| Al−MCM-41(60)+C573 | 6.92 | 6.72 | 6.38 |

[a] Calculated as (g of deposits)/(g of calcined sample) × 100%.
[b] 55-h reaction.

purged with pure helium for about 30 min, and 50-mg samples were transferred from the reactor directly into weighed glass containers equipped with Teflon stoppers. The amount of coke in each sample was evaluated from the difference between the sample mass after the reaction and that after regeneration performed by calcination under oxygen at 773 K for 5 h. The parent and coked samples are referred to as Al–MCM-41($x$) and Al–MCM-41($x$)+C$T_c$, respectively, where $x$ stands for the Si/Al molar ratio in the reaction mixture, C for coking, and $T_c$ for the reaction temperature (in Kelvin). The coked and subsequently calcined samples are referred to as regenerated.

**Methods.** Thermogravimetric analyses (TGA) were carried out with an OD-102 MOM (Hungary) derivatograph on 100-mg samples under both air and helium within the temperature range of 293–1273 K and at a heating rate of 5 K/min. The samples used in these determinations had been purged with helium overnight while being cooled to room temperature after reaction.

Diffuse-reflectance infrared Fourier transform (DRIFT) spectra were recorded with a Perkin-Elmer FT-IR 2000 instrument within the range of 450–3800 cm^{−1}. UV–vis spectra were measured with a Carl Zeiss Jena Specord M-40 spectrophotometer.

^{13}C solid-state NMR spectra were obtained with a Bruker AMX300 WB spectrometer employing the techniques of cross polarization, high-power proton decoupling, magic-angle spinning, and total suppression of sidebands. A contact time of 1 ms, a recycle time of 5 s, and a 7-mm-o.d. zirconia rotor spun at 4.5 kHz were used.

The water sorption capacities of the samples (298.2 K, 79% relative humidity) were determined as a function of time-on-stream or of the reaction time analogously to the procedure described earlier.[23] The samples taken at certain time intervals from the reactor and transferred directly into weighed glass containers (cf. above) were weighed, placed over the saturated NH₄Cl solution for 24 h, and then weighed again.

## Results and Discussion

**Content of Coke and Sorption Capacity for Water.** The results of calcination (Table 1) show that the amount of coke formed in the Al–MCM-41 materials during the conversion of cyclohexene depends on both the temperature of the reaction and the Si/Al molar ratio of the sample. The general tendency is that the higher the reaction temperature, the lower the coke amount (e.g., about 49 and 13.5 wt % at 483 and 663 K,

(21) Karge, H. G.; Boldingh, E. *Catal. Today* **1988**, *3*, 379.
(22) Lange, J. P.; Gutsze, A.; Karge, H. G. *J. Catal.* **1988**, *114*, 136.
(23) Rozwadowski, M.; Wloch, J.; Erdmann, K.; Kornatowski, J. *Collect. Czech. Chem. Commun.* **1992**, *57*, 959.
(24) Rozwadowski, M.; Wloch, J.; Erdmann, K.; Kornatowski, J. *Bull. Soc. Chim. Belg.* **1992**, *101*, 463.
(25) Wloch, J.; Rozwadowski, M.; Erdmann, K. In *Proceedings of the 2nd Polish–German Zeolite Colloquium*; Rozwadowski, M., Ed.; Nicholas Copernicus University Press: Toruń, Poland, 1995; p 69.
(26) Rozwadowski, M.; Wloch, J.; Kornatowski, J.; Pruski, M.; Lang, D. In *Proceedings of the Symposium: Characterization and Properties of Zeolitic Materials*; Rozwadowski, M., Ed.; Nicholas Copernicus University Press: Toruń, Poland, 1994; p 89.
(27) Wloch, J.; Rozwadowski, M.; Erdmann, K.; Bludziñska, J. In *Proceedings of the 2nd Polish–German Zeolite Colloquium*; Rozwadowski, M., Ed.; Nicholas Copernicus University Press: Toruń, Poland, 1995; p 141.
(28) Wloch, J.; Rozwadowski, M.; Erdmann, K. In *Proceedings of the 3rd Polish–German Zeolite Colloquium*; Rozwadowski, M., Ed.; Nicholas Copernicus University Press: Toruń, Poland, 1998; p 255.
(29) Rozwadowski, M.; Lezanska, M.; Wloch, J.; Erdmann, K.; Golembiewski, R.; Kornatowski, J. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5510.

(30) Rozwadowski, M.; Lezanska, M.; Wloch, J.; Erdmann, K.; Golembiewski, R.; Kornatowski, J. *Langmuir*, in press.
(31) Bibby, D. M.; Milestone, N. B.; Patterson, J. E.; Aldridge, L. P. *J. Catal.* **1986**, *97*, 493.
(32) Bibby, D. M.; Howe, R. F.; McLellan, G. D. *Appl. Catal.* **1992**, *93*, 1.
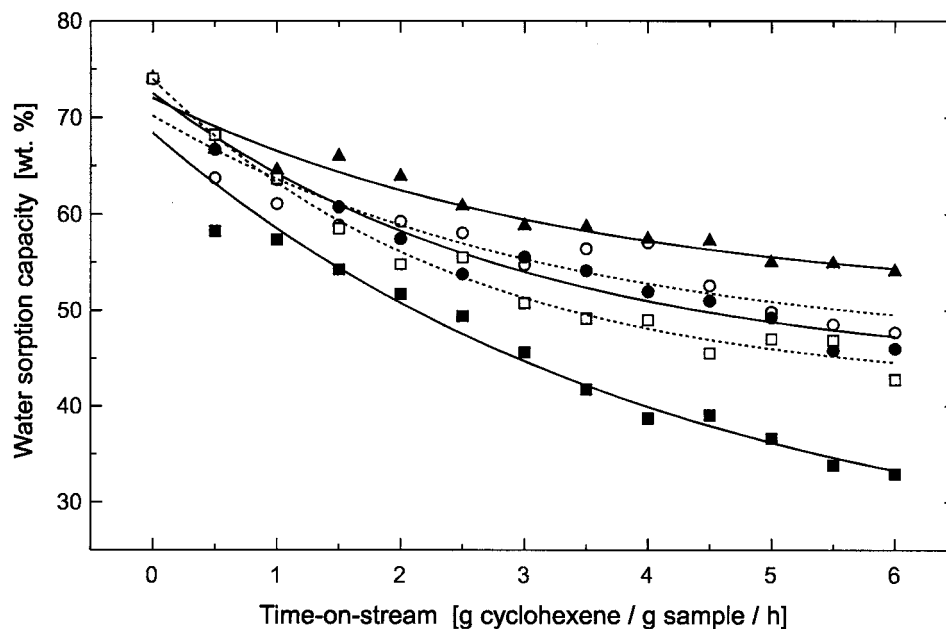
**Figure 1.** Water sorption capacities of Al−MCM-41(15) after the reactions at 483 (■), 513 (●), 573 (□), 633 (○) and 663 K (▲), as functions of time-on-stream.

respectively, for the 12-h reaction). It has also been found that, for the conversion at 573 K, the amount of coke increases with both the Al content and the reaction time (Table 1). The latter effect is obvious, and the former effect can be explained as follows: with decreasing Al content in the materials, the acidic centers become more and more separated from one another, and thus, formation of higher amounts of coke is hindered.

The coke contents were also determined from the TG curves obtained as a result of TGA. The data (Table 1) can be compared with those from calcination. In the analysis of the TG curves, the mass loss due to removal of the adsorbed water, i.e., that below ca. 423 K, was subtracted from the total mass loss.

The determinations of the coke content from calcination were done with an accuracy of ca. ±1.5%, i.e., within the limits of an analytical determination. The accuracy of the results from the TG curves (especially those under helium) was somewhat lower, mainly because of the technical limitations of this method. Nevertheless, the data obtained from calcination and from thermogravimetry under air are close to one another, generally within the accuracy of ±1.5%. An exception is the Al−MCM-41(15)+C663 sample, which shows a coke content from calcination that is clearly lower than those from TGA under both air and helium (Table 1), indicating a higher error in this case. For the reaction temperatures of 483 and 513 K, the TGA values are distinctly lower (by more than 3 wt %) than those from calcination. Probably, the carbonaceous compounds formed at these relatively low temperatures were weakly bound to the surface and were partially removed when the reactor bed was purged with helium (cf. explanation to Figure 6 below). The amounts of coke obtained from TGA under helium are generally slightly smaller than those obtained from TGA under air or from calcination (Table 1). This indicates that oxygen is necessary for the complete removal of the carbonaceous deposits. For the Al−MCM-41(15) sample subjected to the reaction at 573 K for 55 h, the difference between the TGA

results under air and helium is greater. This indicates that an extended reaction time leads to the formation of deposits that are more strongly bound to the surface and cannot be removed during TGA under helium. Deposits of this type constitute about one-half of the whole coke. Thus, the color of this sample after the analysis is still gray, whereas all of the other samples become white.

The variations in the coke content correspond well with the sorption capacities for water of the coked Al-MCM-41(15) materials. The sorption capacity decreases with decreasing reaction temperature, i.e., with increasing amount of coke (Figure 1), and the changes generally proceed similarly to those for benzene and nitrogen.[30] This suggests that the hydrophobicities of coke and the MCM-41 surface are similar to each other. Thus, the reason for the decrease in the sorption capacity is a lowering of free space available to water molecules because of coke deposition. This conclusion is also supported by the shapes of the plots of the coke contents and of the water sorption capacities of Al−MCM-41-(15)+C573, presented as functions of the reaction time (Figure 2), which are almost mirror images of each other. This similarity points out that the two parameters are mutually closely connected. The substantial reduction of the sorption capacity (e.g., by 20 and 40 wt % after the 12-h reactions at 663 and 483 K, respectively) indicates that the carbonaceous deposits not only form a layer on the pore surface but also fill the pore volume. The maximum level of the coke content, i.e., about 60 wt %, is attained after the reaction time of ca. 35 h (Figure 2). The lack of both further increase in the coke amount and a decrease in the sorption capacity for water indicates that, starting from this point of the reaction, the pore volume around the Al centers of the material is probably completely filled with carbonaceous deposits.

The sorption capacities of the regenerated samples remain roughly at a constant level (Figure 2). The observed irregular deviations can likely be explained by
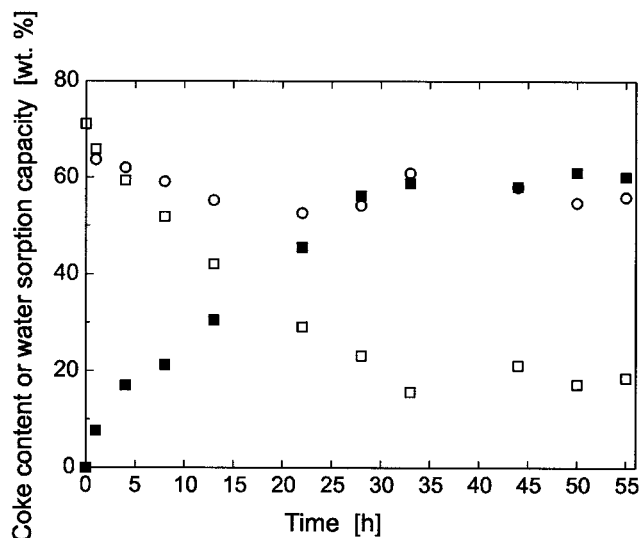
**Figure 2.** Water sorption capacities (□) and coke contents (■) for Al−MCM-41(15)+C573 and water sorption capacities (○) for the regenerated sample, as functions of the reaction time.
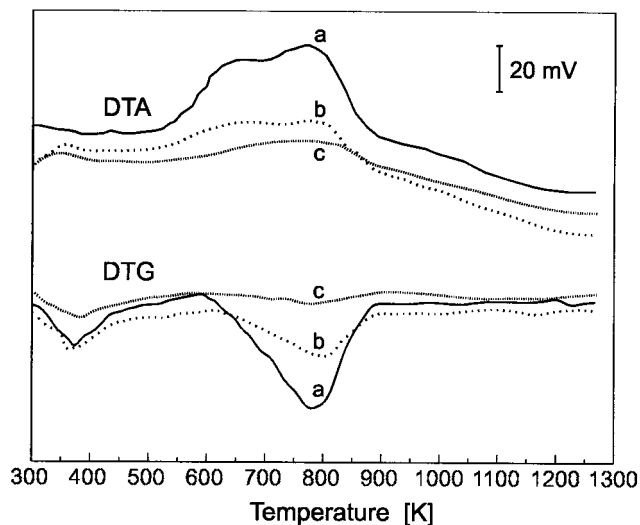


**Figure 3.** DTG and DTA plots for Al−MCM-41 with the Si/Al ratio equal to (a) 15, (b) 30, and (c) 60. Samples after the 12-h reaction at 573 K; analyses performed under air.

random differences between particular samples.

**Character of the Deposits.** Deposition of coke and regeneration do not cause any major changes in the structure of Al−MCM-41, as seen by XRD.[29]

The thermogravimetric analysis shows that the effects connected with the removal of coke occur in the temperature range above ca. 423 K (Figures 3−6). Therefore, the initial parts of the DTG and DTA curves, showing some minor effects below ca. 423 K, were not considered.

The curves of DTG under air confirm the results shown in Table 1 that the amount of coke decreases with both the sample Si/Al ratio (Figure 3) and the reaction temperature (Figure 4).

The plots of DTA under air (Figure 5) reveal two main peaks in the temperature range of 473−873 K, indicating the presence of at least two types of carbonaceous deposits in a series of the Al−MCM-41(15) samples subjected to the reactions at different temperatures for 12 h and at 573 K for 55 h. The intensity ratio of the
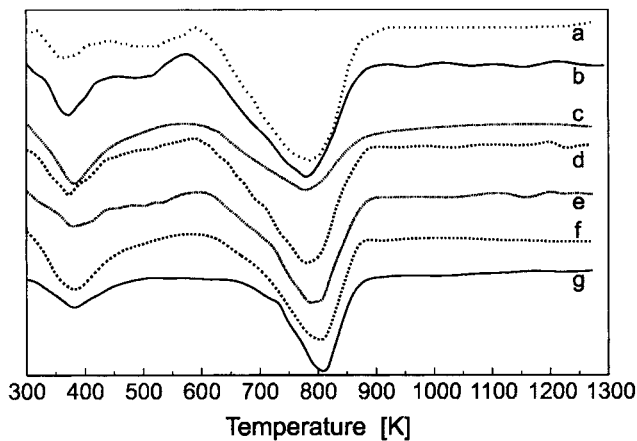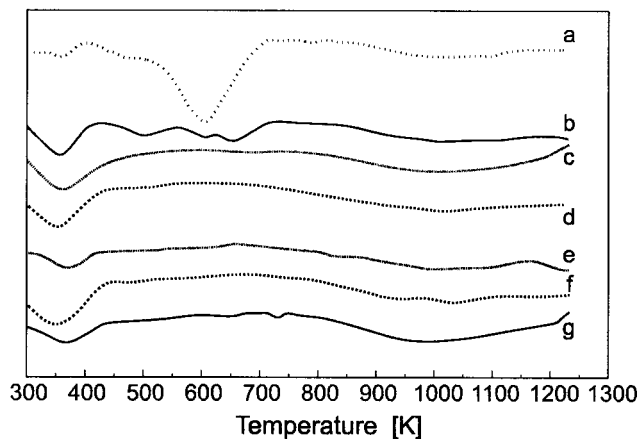


**Figure 4.** DTG plots for Al−MCM-41(15) after the 12-h reactions at (a) 483, (b) 513, (c) 543, (d) 573, (e) 603, (f) 633, and (g) 663 K. Analyses under air.
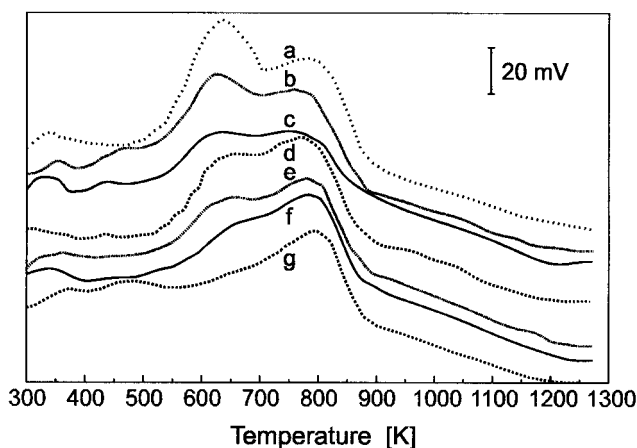


**Figure 5.** DTA plots for Al−MCM-41(15) after the 12-h reactions at (a) 483, (b) 513, (c) 543, (d) 573, (e) 603, (f) 633, and (g) 663 K. Analyses under air.

low- to high-temperature peaks decreases with the reaction temperature. The curves of DTG under air (Figure 4) show that the temperature corresponding to the maximum rate of mass loss increases slightly with reaction temperature. These tendencies suggest that the low-temperature peak corresponds to a more aliphatic-type coke and the high-temperature one to a more aromatic-type coke. The carbonaceous compounds that are removed within the temperature range of 473−703 K can then be termed volatile, while those eliminated within the range of 703−873 K can be considered nonvolatile (Figure 5).

As mentioned above, the carbonaceous compounds that formed at relatively low temperatures (483 and 513 K) were probably partially removed when the reactor bed was purged with helium. This conclusion is confirmed by the results of DTG under helium (Figure 6): a distinct loss of mass is observed for Al−MCM-41-(15)+C483 and Al−MCM-41(15)+C513 within the temperature range of 473−703 K. Thus, the deposits formed at these temperatures (483 and 513 K) desorb mainly up to ca. 703 K. The deposits formed at 543 K and above desorb at higher temperatures, with the maximum rate of mass loss at ca. 1000 K. These data give a good illustration of the volatility of the products. Interestingly, these results agree quite well with earlier findings for carbonaceous deposits on acidic zeolites, which

**Figure 6.** DTG plots for Al−MCM-41(15) after the 12-h reactions at (a) 483, (b) 513, (c) 543, (d) 573, (e) 603, (f) 633, and (g) 663 K. Analyses under helium.
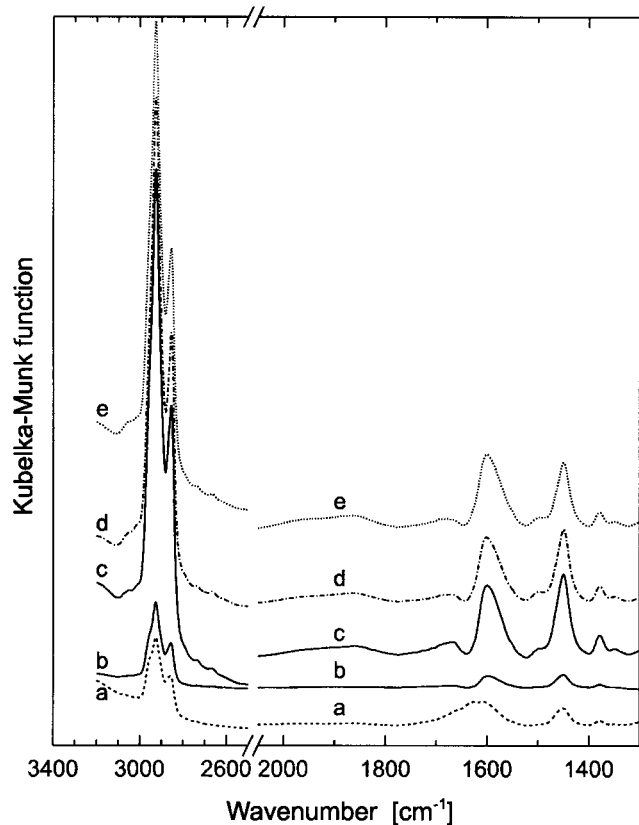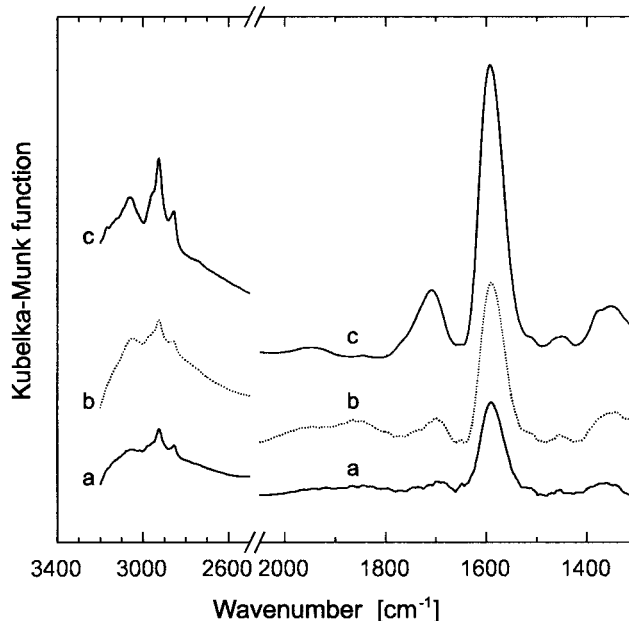


**Figure 7.** DRIFT spectra of Al−MCM-41(15) after the reaction at 483 K for (a) 2, (b) 4, (c) 6, (d) 10, and (e) 12 h.
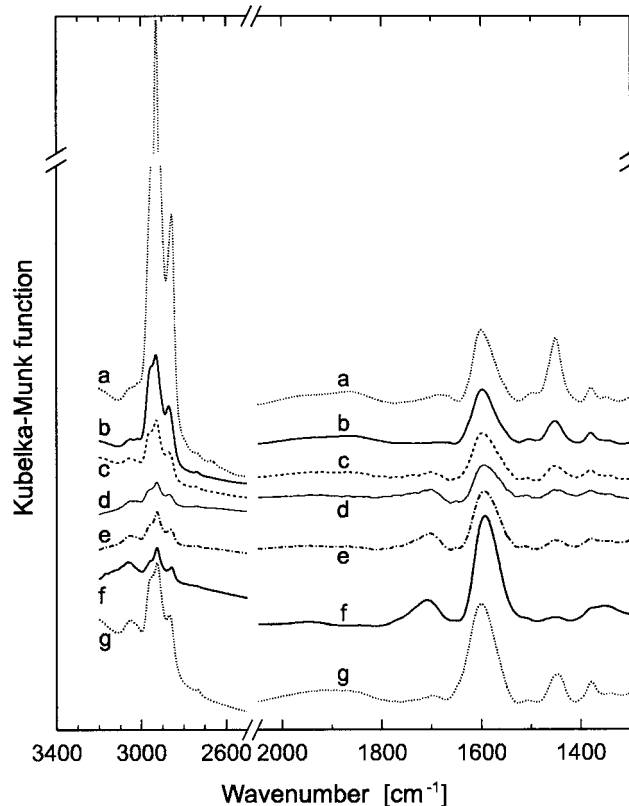


**Figure 8.** DRIFT spectra of Al−MCM-41(15) after the reaction at 663 K for (a) 4, (b) 8, and (c) 12 h.



**Figure 9.** DRIFT spectra of Al−MCM-41(15) after the 12-h reactions at (a) 483, (b) 513, (c) 543, (d) 573, (e) 633, and (f) 663 K and (g) after the 55-h reaction at 573 K.

suggest that a low-temperature coke (formed at temperatures below 500 K) and a high-temperature coke (formed above 500 K) can be distinguished.[33] In our case, the low-temperature coke would correspond to that formed at 483 and 513 K, whereas the high-temperature coke would correspond to that formed at temperatures above 513 K.

IR spectroscopy provides more detailed information on the character of the deposits. In Figures 7−9, the DRIFT spectra of the coked Al−MCM-41(15) samples are presented. The spectra have been plotted assuming the model of Kubelka and Munk for diffuse reflectance,

with the Kubelka−Munk function being analogous to absorbance.[34] Two main frequency regions in which the detected bands occur (2800−3000 and 1300−1500 cm$^{-1}$) and an intense broad band (at ca. 1600 cm$^{-1}$) can be distinguished. The two regions contain paraffinic and/ or olefinic bands,[33,35] and the 1600 cm$^{-1}$ band is known

(33) Lange, J.-P.; Gutsze, A.; Allgeier, J.; Karge, H. G. *Appl. Catal.* **1988**, *45*, 345.

(34) Paweewan, B.; Barrie, P. J.; Gladden, L. F. *Appl. Catal. A: Gen.* **1999**, *185*, 259.

as the coke band.[36] Single bands at ca. 3070, 1700, 1670, and 1510 $cm^{-1}$ are observed in the presented spectra as well.

In the range of the C−H stretching vibrations in alkanes (2800−3000 $cm^{-1}$), the bands occurring at 2870, 2926, and 2955 $cm^{-1}$ are assigned to the symmetric vibrations of $CH_2$ and $CH_3$, the asymmetric vibration of $CH_2$, and the asymmetric vibration of $CH_3$, respectively.[35,37] The band at 2926 $cm^{-1}$ increases in intensity at the expense of the 2955 $cm^{-1}$ band with both the reaction time (Figure 7) and the temperature (Figure 9). This fact suggests that the number of $CH_2$ groups increases in relation to the number of $CH_3$ groups, i.e., the branching of the aliphatic substituents decreases. This is observed especially for the reaction temperature of 483 K (Figure 7), whereas for 663 K (Figure 8), this feature is not as evident as all of these bands are of low intensity (although they increase slightly in intensity with reaction time). The 3070 $cm^{-1}$ band is probably due to the stretching vibration of C−H in polyalkenes or in aromatics.[34,35]

For the coking temperature of 483 K (Figure 7), the bands in the range of 1300−1700 $cm^{-1}$ stop increasing in intensity with reaction time already after 6 h. The band at ca. 1670 $cm^{-1}$ is attributed to the stretching vibration of C=C in alkenes.[35] The bands at ca. 1600 and 1350 $cm^{-1}$, also found for ground graphite, carbon blacks, and activated carbons,[38] are assigned to coke.[39] In particular, the former band is attributed to the stretching vibration of C=C in microcrystalline graphitic structures, which are present in polycyclic aromatic compounds and might also constitute the carbonaceous deposits.[40] The band at 1495 $cm^{-1}$ probably originates from the bending vibration of C−H in carbocations (>$C^+H$ or >$C^+H_2$).[41,42] The bands at 1450 and 1380 $cm^{-1}$ are ascribed, respectively, to the asymmetric and symmetric bending vibrations of $CH_3$.[35] It is to be expected that the band due to the in-plane bending vibration of $CH_2$ (at 1465 $cm^{-1}$)[35] is also present, but it might overlap with the 1450 $cm^{-1}$ band.

The spectra of Al−MCM-41(15) subjected to the reaction at 663 K (Figure 8) differ considerably in band intensities from those discussed above (Figure 7): the paraffinic bands (2800−3000 $cm^{-1}$) are significantly less intense in relation to the coke band (ca. 1600 $cm^{-1}$) (cf. explanation to Figure 9 below). In addition, two bands change somewhat in position: instead of the bands at 1670 and 1495 $cm^{-1}$ occurring in the spectrum shown in Figure 7, the bands at ca. 1700 and 1510 $cm^{-1}$ are observed in the spectrum in Figure 8. The band at 1700 $cm^{-1}$, the intensity of which increases with the reaction time, presumably originates from vibrations of tetrasubstituted C=C in olefinic compounds[43] (traces of C=

O might also be present). The 1510 $cm^{-1}$ band might correspond to vibrations of aromatic rings as the bands between 1500 and 1525 $cm^{-1}$ usually arise when simple aromatics are converted to a mixture of more complex aromatics, perhaps para-substituted ones.[44] Note that a band for a simple aromatic compound, e.g., toluene, adsorbed on zeolite Y occurs at 1495 $cm^{-1}$.[45] The assignment of the 1510 $cm^{-1}$ band is supported by the presence of the band centered at about 3070 $cm^{-1}$ (cf. above). As mentioned earlier, the bands at 1450 and 1380 $cm^{-1}$ are due, respectively, to the asymmetric and symmetric bending vibrations of $CH_3$. In contrast to the spectra shown in Figure 7, the latter band is more intense than the former. As suggested elsewhere,[44] when aromatics are formed, the oligomer $CH_2$ band at 1465 $cm^{-1}$ is replaced by a band at 1442 $cm^{-1}$ that originates from aliphatic groups attached to aromatic rings; a double bond next to $CH_2$ lowers this frequency to about 1440 $cm^{-1}$. A relatively small band at ca. 1450 $cm^{-1}$ (Figure 8) suggests that aliphatic groups connected with aromatic rings are present in a comparatively low amount. The 1350 $cm^{-1}$ band is relatively more intense than in the case of the reaction at 483 K, indicating that more graphitic structures form at 663 K.

The results presented above (Figures 7 and 8) conform to the spectra of Al−MCM-41(15) subjected to the reactions at different temperatures for 12 h and at 573 K for 55 h (Figure 9). The bands within the ranges of 2800−3100 and 1300−1500 $cm^{-1}$ generally increase in intensity with the coke content, i.e., with decreasing reaction temperature and increasing reaction time. The superposition of the bands assigned to vibrations of C=C in alkenes and in aromatics makes the interpretation of the spectra ambiguous to some extent. However, the variations of the band intensities in the high-frequency region (the stretching vibration of C−H) with the reaction temperature indicate formation of paraffinic and olefinic compounds at lower temperatures and mostly aromatic and some olefinic compounds at higher temperatures. The shift of the band at 1600 $cm^{-1}$ (Figure 9a) to 1590 $cm^{-1}$ (Figure 9f) with the reaction temperature (also observed by others),[36] connected probably with delocalization of the $\pi$ bond, supports that conclusion. The same applies to the band at 1495 $cm^{-1}$, which shifts to ca. 1510 $cm^{-1}$. Moreover, the intensity of the band at 1590 $cm^{-1}$ (Figure 9f) is almost twice that at 1600 $cm^{-1}$ (Figure 9a), although the coke contents are 13.5 and 48.8 wt %, respectively. In addition, the former band is not accompanied by bands of considerable intensity in the region of 1370−1480 $cm^{-1}$ corresponding to the bending vibrations of C−H in paraffinic and olefinic compounds.

The UV−vis spectra confirm the IR findings. The spectra of Al−MCM-41(15) subjected to reactions at 483, 573, and 663 K for 4 and 12 h without subsequent purging of the material bed with helium (Figure 10) are largely similar to each other, i.e., the types of deposits are alike, although the relative intensities of the individual bands vary. In the range of 200−270 nm, two distinct bands are observed. That at ca. 230 nm most probably indicates the presence of olefins, and that at

(35) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998.

(36) Eberly, P. E. Jr. *J. Phys. Chem.* **1967**, *71*, 1717.

(37) Paweewan, B.; Barrie, P. J.; Gladden, L. F. *Appl. Catal. A: Gen.* **1998**, *167*, 353.

(38) Friedel, R. A.; Carlson, G. L. *Fuel* **1972**, *51*, 194.

(39) Ghosh, A. K.; Kydd, R. A. *J. Catal.* **1986**, *100*, 185.

(40) Haldeman, R. G.; Botty, M. C. *J. Phys. Chem.* **1959**, *63*, 489.

(41) Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360.

(42) Avram, M.; Mateescu, C. D. *Infrared Spectroscopy, Application in Organic Chemistry*; Wiley-Interscience: New York, 1972.

(43) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen & Co.: London, 1966.

(44) Colthup, N. B.; Daly, L. H.; Wiberly, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1975.

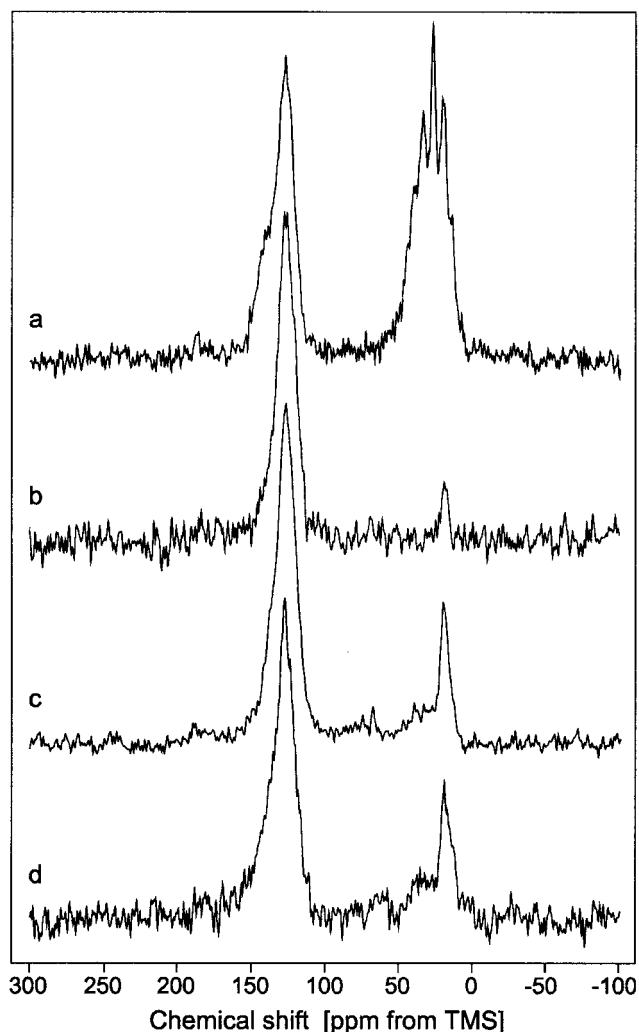(45) Datka, J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 511.

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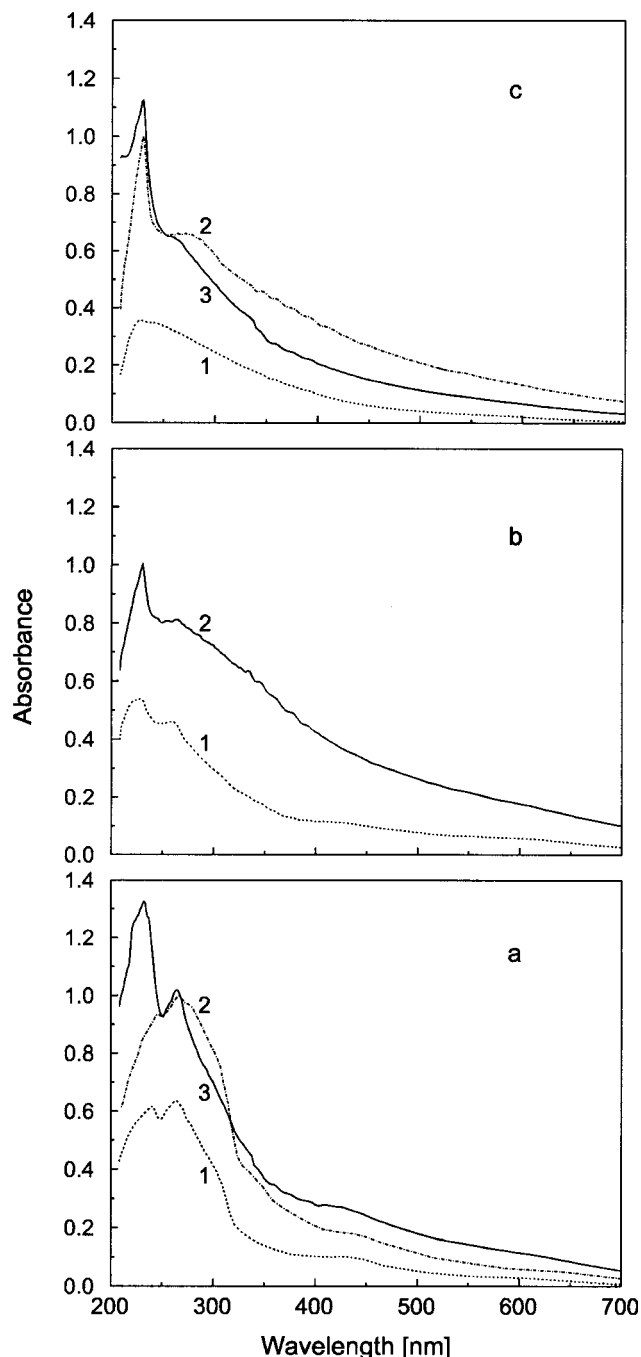


**Figure 10.** UV–vis spectra of Al–MCM-41(15) after the reactions at (a) 483, (b) 573, and (c) 663 K for (1) 4 h, (2) 12 h, and (3) 12 h with subsequent purging with helium during cooling to room-temperature overnight.

270 nm is associated with phenyl groups.[35] The latter band can also be ascribed to cyclic dienes with two double bonds in a ring.[46] Weak bands in the range of 360–385 nm are assigned to polyenylic carbocations.[47] In the case of the spectra of the sample subjected to the reaction at 483 K, a weak band at ca. 430 nm is attributed to condensed aromatic rings typical of carbonaceous deposits.[27] Interestingly, purging of this sample with helium leads to a significant change in the



**Figure 11.** $^{13}$C solid-state NMR spectra of (a) Al–MCM-41-(15)+C483, (b) Al–MCM-41(15)+C663, (c) Al–MCM-41-(15)+C573, and (d) Al–MCM-41(60)+C573.

spectrum: the 230 nm band increases dramatically in intensity (Figure 10). This is probably caused by the diffusion of some carbonaceous compounds from the pores to the external surface of the material. These compounds form structures similar to the surface deposits obtained at higher temperatures. The change in the spectrum of the sample subjected to the reaction at 663 K is relatively small.

Results from the $^{13}$C solid-state NMR spectra (Figure 11) correspond to those from IR and UV–vis spectra. The spectra of Al–MCM-41(15) subjected to the reactions at 483, 573, and 663 K (a, c, and b, respectively) and of Al–MCM-41(60) at 573 K (d), all for a reaction time of 12 h, show resonances in two regions of the chemical shift corresponding to aromatics and olefins (115–150 ppm) and to paraffins (5–60 ppm).[35] The main downfield peak, centered at ca. 127 ppm, originates from aromatic CH groups,[35,48] and the shoulder at ca. 140 ppm (spectrum a) can be assigned to substituted aromatic carbons, olefinic CH groups, or olefinic carbocations.[48,49] The occurrence of several single peaks in the paraffinic region (14, 19, 21, 27, 34, 40, and 44 ppm;

(46) Szafran, M. *Structure Determination of Organic Compounds with Spectroscopic Methods*; PWN: Warsaw, Poland, 1988 (in Polish).
(47) Karge, H. G.; Laniecki, M.; Ziolek, M.; Onyestyak, G.; Kiss, A.; Kleinschmit, P.; Siray, M. *Stud. Surf. Sci. Catal.* **1989**, *49*, 1327.

(48) Weitkamp, J.; Maixner, S. *Zeolites* **1987**, *7*, 6.
(49) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229.

spectrum a) suggests that the CH$_3$, CH$_2$, and CH groups in the Al−MCM-41(15)+C483 sample are in a number of distinctly different surroundings. The peak at 14 ppm can be assigned to the methyl groups in paraffins.[35,48] The 19 ppm peak is probably associated with the methyl groups attached to polyaromatics.[35,48,50] This peak predominates in the paraffinic region of the spectra for the carbonaceous compounds deposited at medium (573 K) and high (663 K) temperatures. The peak at 21 ppm is presumably due to the methyl groups connected to olefinic carbons.[48] The 27 ppm peak can be assigned to the α-methylene groups in paraffins and in alkyl substituents of olefins, and that at 34 ppm to the internal methylene groups in paraffins and olefins.[35] The peaks at 40 and 44 ppm probably originate from tertiary paraffinic carbons present in different surroundings.[35,48]

Moreover, it can be concluded from spectra a, c, and d (Figure 11) that the higher the reaction temperature, the lower the content and variety of paraffins. The Al content of Al−MCM-41 does not noticeably affect the chemical composition of the carbonaceous deposits, at least for the reaction temperature of 573 K (spectra c and d).

## Conclusions

As expected, the formation of coke on Al−MCM-41 catalysts during the conversion of cyclohexene causes a decrease in their sorption capacity for water. It was found that the lower the reaction temperature, the higher the coke content and the lower the sorption capacity. The amount of coke increases with the reaction time as well. The maximum coke content and the minimum sorption capacity are attained after ca. 35 h (for the reaction at 573 K).

(50) Pradhan, A. R.; Wu, J. F.; Jong, S. J.; Tsai, T. C.; Liu, S. B. *Appl. Catal. A: Gen.* **1997**, *165*, 489.

The results from TGA and IR and UV−vis spectroscopy show that the chemical nature of the carbonaceous compounds deposited on the studied catalysts depends mainly on the temperature of the reaction. Both aliphatic and aromatic compounds are formed in this process. However, the higher the reaction temperature, the higher the content of aromatic deposits. At lower applied temperatures, the deposits remain on the inner surface (i.e., in the pores) of the examined materials. Part of the deposits is relatively weakly bound to the surface and is removed after the reaction when the coked material is purged with helium. A longer reaction time (55 h) leads to the formation of some deposits that are either strongly bound to the surface or blocked in the pores and that cannot be removed upon heating even to 1273 K under helium (TGA results). At higher reaction temperatures, a fraction of the coke migrates out of the pores. Then, this fraction (most probably aliphatics) partially desorbs and moves away, while the other part (presumably aromatics) adsorbs on the external surface of the sieve. The carbonaceous compounds remaining both in the pores and on the external surface mostly form multilayered polyaromatic structures that are strongly bound to the surface of the material.

The NMR data support the findings that the reaction temperature influences the chemical composition of the coke and indicate that the Al content of Al−MCM-41 does not noticeably affect this composition.

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