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EPR investigation, before and after adsorption of naphtalene, of mordenite containing Fe^{3+} and Cr^{5+} ions as impurities

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During the study of mordenite with the EPR technique, three EPR signals centered at $g = 4.3$; $g = 2.4$ and $g = 1.98$ were evidenced. The first two were attributed to Fe^{3+} ions (signal at $g = 4.3$ typical to isolated framework iron species, signal at $g = 2.4$ characteristic to agglomerated non-framework ones). The signal at $g = 1.98$ was assigned to Cr^{5+} ions. All these cations are present in the solid as impurities. Furthermore, under certain conditions the Cr^{5+} ions can be in interaction with two equivalent ^{27}Al nuclei according to a formation of a superhyperfine structure in the EPR signals. After adsorption of naphtalene on the mordenite samples, organic π-radicals are formed via secondary reactions of primary cation-radicals nearby the aluminum atoms of the mordenite framework. The formation of radicals seems to be correlated to the presence of impurities in the solids. Thus not only acidity but also content of transition metals may be an important factor in the formation of radicals.

KEY WORDS: EPR; mordenite; aluminum; iron; chromium; naphtalene.

1. Introduction

The growing demand for 2,6-diisopropylnaphtalene, an important monomer in the synthesis of advanced polymer materials, promoted intense investigation of shape selective alkylation of naphthalene over zeolite catalysts. Among the systems studied, mordenites seem to be the most promising microporous catalysts due to the optimal pore size dimension for para-selective alkylation of condensed aromatics. Corresponding referencing on this subject may be found e.g., in a recent review [1]. Nevertheless, deactivation by accumulation of alkylated naphthalene derivatives and coke is in the pores a major drawback. Coking occurs comparatively fast under the reaction conditions e.g., Kim *et al.* shown coking of mordenites after 1 h of catalytic run [2]. Positive effect of mordenite dealumination is reported for naphthalene alkylation with olefin. Dealumination improves catalyst longevity due to the lower density of acid sites, creation of a secondary (meso)porous network and thus lowering the probability of coking [3].

Formation of coke deposits proceeds via non-selective oligomerization and dehydrogenation-cracking reactions of adsorbed organic molecules on external and internal surface of zeolites. Non-selective side-reactions are often initiated by the oxidative centers existing on zeolites (and in particular, mordenites [4]) capable of one-electron abstraction from the adsorbed molecules of unsaturated hydrocarbons. Lewis acid centers [5] as well as inevitable iron impurities in zeolites [6] (or a combination of both [7]) are believed to be the main candidates for redox centers though the question is still under a debate. Oxygen may also be an important agent for the radical formation [8]. Extensive information on this subject may be found in a number of reviews [9,10].

Formation of radical species stabilized in zeolite is a starting point in the coke formation and thus deactivation as was shown by Karge *et al.* [11]. Since deactivation due to the non-specific side-reactions is a key factor in the catalyst selection, we monitored radicals formed upon naphthalene adsorption together with the signals of iron species on a series of mordenite catalysts and correlated these data with the catalytic activity.

EPR is widely used to investigate paramagnetic species having one or more unpaired electrons either in the bulk or on the surface of various solids. The high sensitivity of this technique as compared to other spectroscopic tools (XPS, IR, Raman, etc.) is perhaps its best known advantage and makes it well suited to the investigation and characterization of low-abundance active sites at catalyst surfaces.

Mordenites can be studied using EPR spectroscopy when a paramagnetic species is present into the lattice either as a catalytic site (transition ions) or as an impurity. The presence of such unexpected impurities could affect the catalytic properties of solids in the case

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where they not previously evidenced. Numerous types of zeolite have been already used in catalysis without taking into consideration if impurities were present in these solids.

The purpose of this work is to evidence with the EPR technique, how in mordenite catalysts certain metal ions present in the solids as impurities can change their chemical properties towards on certain adsorbed organic molecules.

2. Experimental

The starting mordenite (HMOR) with Si/Al = 7.6 was supplied by Zeolyst. About 0.1 g of mordenite was placed into the EPR tube equipped with a greaseless stopcock. The sample was evacuated at 773 K for 1 h and oxidized under 700 Torr of oxygen at 773 K (HMOR-773) or 1023 K (HMOR-1023) for 2 h and cooled in oxygen down to a room temperature. After this, the sample was evacuated for 5 min and reference EPR spectrum was recordered.

Two milligrams of naphthalene were introduced into the tube under N_2 atmosphere using glove box. After brief evacuation EPR spectra were recordered. Then the samples were heated up to 373 and 523 K for 30 min. After each heating step the sample was cooled down to a room temperature and the EPR spectra were recordered.

The electron paramagnetic resonance (EPR) measurements were performed at 295 and 77 K on EMX Bruker spectrometer. A cavity operating with a frequency of 9.3 GHz (X-band) was used with a frequency modulation at 100 kHz. Precise g values are determined from simultaneous precise frequency and magnetic field values.

3. Results and discussion

3.1. Characterization of paramagnetic centers

HMOR-773 and HMOR-1023 samples exhibited complex EPR spectra at room temperature and at 77 K constituted by several signals: narrow signal centered at $g = 4.3$, wide signal with approximate center position at $g = 2.4$ and narrow almost isotropic signal at $g = 1.98$ (Figure 1). Compared to that obtained on the HMOR-773 sample, the signal centered at $g = 2.4$ was very weak in intensity on HMOR-1023. Apparently and after literature data, these signals can be typical to iron impurities in zeolites. Despite a very long (more than three decades) history of research on iron species in zeolites there is still a continuing debate on the possibility of correct attribution of each signal. Established tradition (following a number of benchmarking papers) attributes the signal at $g = 4.3$ to the framework iron (i.e., Fe^{3+} ions in tetrahedral positions of the lattice) started by McNicol and Pott [12]. Broad signals around $g = 2.4$ were interpreted as ordered spin system e.g., ferrimagnetic Fe_3O_4 phase [12,13]. At the same time absence of the signal at $g = 4.3$ does not rule out the presence of the framework iron in the zeolite and, moreover, Fe^{3+} ions in the framework positions may produce signals at $g \sim 2.0$ as well [14]. Clear existence of a number of pros and contras of certain assignments of iron signals in zeolites was rationalized recently on the basis of the inhomogeneity of zero field splitting interactions in Fe–ZSM5 zeolites [15,16]. This inhomogeneity explains the absence of one-to-one correspondence of spectral and structural features on one hand, and on another – computational treatment [15] based on this idea permitted good reproduction of experimental spectra in a broad range of frequencies.

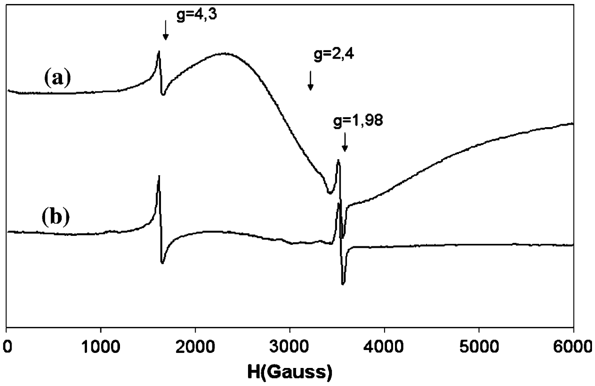

Figure 1. EPR spectra, recorded at room temperature, of (a) HMOR-773 and (b) HMOR-1023 samples.

In conclusion, the signal centered at $g = 4.3$ was attributed to isolated Fe^{3+} ions located in the framework of the mordenite lattice whereas that centered at $g = 2.4$ was assigned to Fe^{3+} agglomorates. These particulates are undetectable with the EPR when they are large. This can explain why this signal was very weak in intensity on HMOR-1023 sample.

Narrow ($\Delta H_{pp} = 50$ G) signal at $g = 1.98$ was reported earlier for the Fe-ZSM-5 and attributed to Fe^{3+} sites [17], though an assignment of the narrow signals at $g < 2.0$ to iron is not supported by the majority of works on paramagnetic iron centers in zeolites. Quite unexpectedly about 15 components of superhyperfine structure were resolved for the narrow signal at $g = 1.98$ in case of HMOR-773 sample (Figure 2a). This structure disappeared when the sample was calcined at 1023 K, but narrow signal with $g = 1.98$ was preserved (Figure 2b). Compared to the HMOR-773 sample, the intensity of the narrow signal was decreased.

Superhyperfine structure for Fe^{3+} signals in zeolites was never reported before in literature, indeed, similar EPR signals attributed to a single electron in interaction with two aluminum atoms ($I = 5/2$) have already been observed in different conditions: (i) after γ-irradiation, at 300 K, of dealuminated Y-type zeolite, already treated

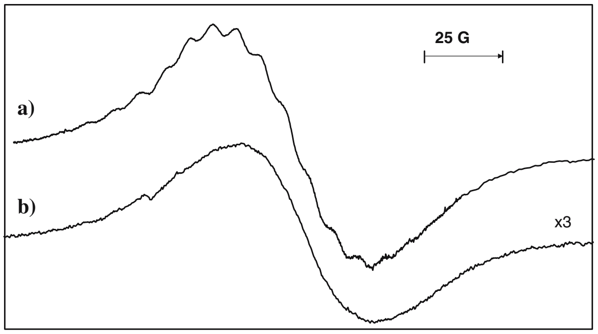

Figure 2. EPR signals ($g = 1.98$) obtained on (a) HMOR-773 and (b) HMOR-1023 samples.

at 873 K under vacuum where a hole of an electron trapped on an oxygen atom bonding two nearby ^{27}Al atoms [18]; (ii) after adorption on the alumina surface of certain specific probe organic molecules and formation of the corresponding radicals bonding two aluminum atoms [19] and (iii) after reduction some transition ions, present in certain matrices containning alumina, into d^1 electron configuration (Mo^{5+}, V^{4+}, Cr^{5+}) wich interacts with two aluminum atoms [20–25]. In this latter condition, the usual interpretation of the visible structure is based on the spin density interaction with a nearby lattice ^{27}Al nuclei ($I = 5/2$, 100% abundance) with a corresponding formation of *shf* structure. At least 15 components of the *shf* structure observed on Figure 2 also corroborate the earlier data – 15 *shf* lines are clearly seen for Cr-doped ZSM5 at X band [22,23].

Taking into account rather broad *shf* features of this signal on one hand and possible anisotropy of powder spectrum on another hand, computer simulation was performed assuming that *shf* structure appears due to two equivalent ^{27}Al nuclei. Experimental signal was reproduced with good quality. The corresponding 15 *shf* lines can be attributed to 11 hyperfine structure split by a rhombic anisotrpy of g as indicated in the Figure 3. The EPR parameter values are $g_{xx} = 1.9652$, $g_{yy} = 1.9782$, $g_{zz} = 1.9887$ and $g_{iso} = 1.9774$ and $A_{xx} = 7.65$ G, $A_{yy} = 7.45$, $A_{zz} = 7.40$ and $A_{iso} = 7.50$.

Since multiple EPR works on Fe-containing zeolites never reported signals with *shf* structure, and considering almost identical signal shape reported for Cr-doped ZSM-5 [22,23], one should have a strong feeling that the signal with *shf* structure at $g = 1.98$ is produced not by iron but by chromium species. We conducted chemical analysis of our samples using ICP. For non-leached zeolite Cr content was about 210 ppm i.e., enough for the production of the detectable EPR signals. Therefore, narrow signals at $g = 1.98$ sometimes detected in zeolites may be produced by the chromium impurities.

The disappearence of the *shf* structure of the narrow signal when the HMOR-773 sample is calcined at 1023 K can be explained by a simple moving of Cr^{5+} cations away from the two ^{27}Al nuclei. Indeed, this *shf* structure disappeared when the mordenite sample was dealuminated by leaching with methanesulfonic or oxalic acids. This confirms that the aluminum atoms are responsible of this structure.

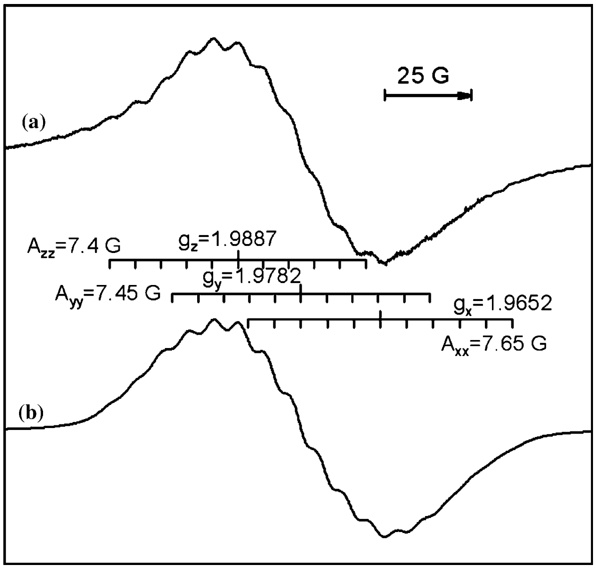

Figure 3. (a) Experimental and (b) calculated EPR signals ($g = 1.98$) obtained on HMOR-773.

In mordenite one can find four possible positions for framework aluminum usually marked as T1–T4. According to *ab initio* DFT calculations of Demuth *et al.* [26] aluminum occupy only T3 and T4 positions, solid-state NMR measurements performed earlier by Bodart *et al.* [27] also favored aluminum occupancy of T3 and T4 sites. Earlier Monte Carlo and energy minimization work on aluminium in mordenite [28] suggested the following probabilities of occupation: $T_3 > T_4 > T_1 = T_2$. Therefore Cr(V) species are probably localized close to T3 and T4 positions and therefore, either in the main channels formed by 12-membered rings or smaller channels formed by 8-membered rings (Figure 4).

3.2. *Formation of radicals upon adsorption of naphthalene*

Naphthalene adsorption onto HMOR-773 and HMOR-1023 samples leads to the progressive disappearance of signals already attributed to Fe^{3+} and Cr^{5+} ions with the time and with the calcination temperature and the formation of a new narrow signal (ΔH_{pp} less than 10 G) centered at $g = 2.0045$ (figure 5–6). Formation of this signal correlates with the change of color from white to faint-blue and rose-blue. From the EPR parameter values of the narrow new signal, it is unambigously due to a certain adsorbed hydrocarbon radical on the mordenite surfaces.

Either on the HMOR-773 or on the HMOR-1023 sample, the signal obtained immediately after 5 min of naphtalene adsorption at room temperature was formed

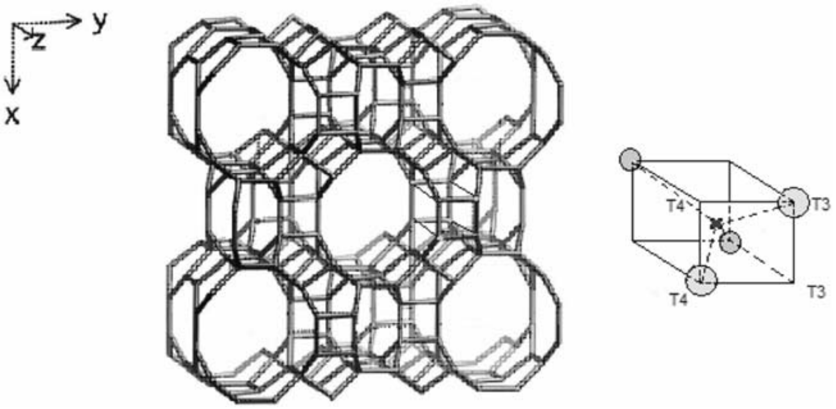

Figure 4. Left: Mordenite backbone showing only tetrahedral positions. Right: Exploded view of a square prim formed by T3 and T4 positions. Aluminum positions are represented by balls, probable position for Cr^{5+} is presented by a square in the center of the prim.

by six hyperfine structure lines. This result indicates that the radical formed is in interaction with one ^{27}Al nuclei of the framework structure of mordenite. Since the hyperfin splitting constant was 6 G for the signal obtained on the first solid and 3 G for the second one (Figure 5A–B), these values suggest that the interaction of the radical with the modernite surface is more important for the first sample. This difference in the interaction can be due either to the difference in the the acidic properties of the both solids or to the nature of naphtalene adsorption sites. Indeed, the intensity of the new narrow signal decreased with the dealumination of mordenite by acids, this indicates that the acidic properties of aluminum atoms of the framework lattice are responsible of the formation of such a radical on the modernite surface [29].

In parallel, the *shf* of the Cr^{5+} signal observed on HMOR-773 sample disappeared and its intensity decreased after naphtalene adsorption. This result can indicate that the Cr^{5+} ions present in mordenite as impurities can play a role to form the corresponding radical.

The six hyperfine structure lines of the new narrow signal obtained on HMOR-773 or/and HMOR-1023 samples completely disappeared either after 2 days of naphtalene adsorption at room temperature or after heating the sample at 373 K to finally give a simple symmetric signal. This disappearence can be due to the high concentration of adsorbed naphtalene. In addition, the intensity of the symmetric signal increased with the calcination temperature to reach a maximum at 373 K and decreased for high calcination temperatures. This decrease is probably due to an oxidation of hydrocarbon radicals.

In parallel, the intensity of the signal already attributed to Cr^{5+} ions decreased with time and with calcination temperature after adsorption of naphtalene and completely disappeared at 523 K of calcination. This

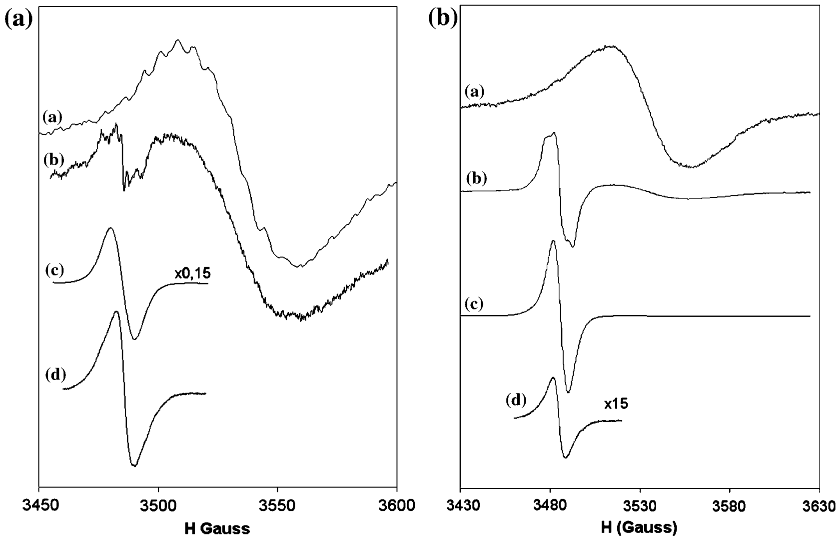

Figure 5. Variation of the EPR signal centered at $g = 1.98$ after naphthalene adsorption onto HMOR-773 (A) and HMOR-1023 (B) samples: (a) after 30 min at room temperature; (b) after 2 days at room temperature; (c) after 30 min at 373 K; (d) after 30 min at 523 K.

disappearance can be explained by the soft naphtalene reduction of Cr^{5+} into Cr^{4+} ions. This latter species is difficult to detect with the EPR technique.

Furthermore, the Fe^{3+} ions present in the both solids in the form of isolated and particulates interact after adsorption of naphtalene but less important than the Cr^{5+} ions. Indeed, the two EPR signals already attributed to isolated and particulate Fe^{3+} ions decreased in intensities with the time and with the calcination temperature but slower than in the case of Cr^{5+} ions. In fact, the iron signals remain detectable after a calcination temperature at 523 K (Figure 6A–B). The diminution in the intensities of the Fe^{3+} ion signals is due to the reduction by naphtalene these latter species into Fe^{2+} ions.

Characteristic *g*-value and the way of formation suggest that these centers should be attributed to aromatic π-radicals formed via secondary reactions of naphthalene cation-radicals that are supposed to be primary radical species formed upon adsorption of naphthalene onto the mordenites [30,31]. Despite rather mild conditions of naphthalene adsorption we were unable to find signals typical for naphthalene cation-radicals on zeolites. Probably this may be explained by the high local concentration of naphthalene, since usually dilute solutions of aromatics are used for the formation of cation-radicals. This is somewhat supported by the old results of Zhavoronkov *et al.* [32] on the formation of radicals upon adsorption of anthracene from the solutions having different concentration. If adsorption was performed from the 0.04 M solution then singlet signal was observed. For the dilute solutions (0.001 M) more complex signal shape was observed.

4. Conclusion

Transition metal ion impurities present in commercial mordenite samples were manifested by the characteristic EPR signals at $g = 4.3$, 2.4 and 1.98. The first two signals are usually assigned to inevitable Fe^{3+} impurity, but an observation of superhyperfine structure of narrow signal at $g = 1.98$ and results of chemical analysis

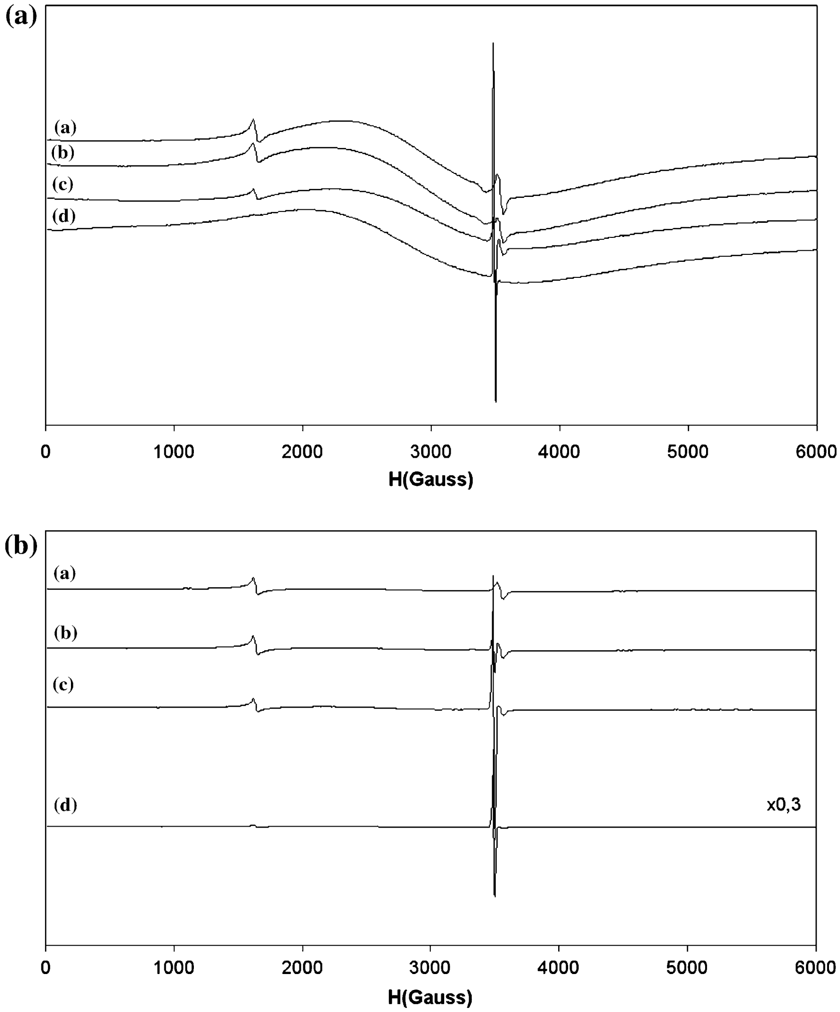

Figure 6. Variation of the EPR spectrum after naphthalene adsorption onto HMOR-773 (A) and HMOR-1023 (B) samples: (a) after 30 min at room temperature; (b) after 2 days at room temperature; (c) after 30 min at 373 K; (d) after 30 min at 523 K.

provided grounds for existence of Cr(V) impurity. *Shf* structure was adequately confirmed by simulation and attributed the interaction of Cr(V) center with two equivalent ^{27}Al nuclei. Thus presence of these impurities may have some consequences in redox chemistry of mordenites though this statement requires further investigation.

Adsorption of naphthalene on the mordenite led to the formation of organic radicals under ambient conditions or slightly elevated temperatures. The highest concentration of radicals was observed on samples heated at 373 K. The radical formed seems to be localized near an aluminum of the mordenite framework and its formation seems to be correlated to the presence of Fe^{3+} and Cr^{5+} impurities in the mordenite.

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