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Spontaneous formation and transformation of organic free radical cations upon adsorption of olefins on H-mordenite

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The radical cation of 2,5-dimethyl-2,4-hexadiene is identified by ESR upon adsorption of the parent molecule on activated H-mordenite. The same radical is observed when 2,3-dimethyl-1-butene or 2-methylpropene is adsorbed. This is clear evidence for highly specific dimerisation–fragmentation reactions of the primary radical cations in the zeolite at room temperature.

Keywords: Radical cations; HM zeolite; C–C bond formation

1. Introduction

Organic molecules adsorbed on activated zeolites undergo extensive transformations which have been tailored to important industrial processes in recent years. It is generally accepted that Brønsted acidity is essential in these reactions, whereas the role of Lewis acidity is less clear [1]. It has been possible only in a few cases to directly observe short-lived intermediates. Therefore, the exact mechanisms often remain a matter of speculation. Free radicals have been invoked as intermediates only occasionally [2], although it is known that zeolites

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often change colour when organic molecules are adsorbed, which strongly indicates the presence of open shell species.

Electron spin resonance has served to detect spontaneous radical formation in several cases [3–7], and rearrangements or oligomerisations have been observed [8–11]. The present work continues along these lines with the aim to learn more about intermediates of major processes in heterogeneous catalysis, or of their accompanying side reactions.

2. Experimental

The adsorbates used in this study were 2,5-dimethyl-2,4-hexadiene, 2,3-dimethyl-1-butene, and isobutene, all delivered by FLUKA in a purity $> 98\%$.

0.3 g of H-mordenite (Chemische Fabrik Uetikon, Switzerland; SiO_2/Al_2O_3 ratio 8.9, crystallite size ≈ 1 μm) was predried at 470 K, then placed in a quartz tube of 4 mm i.d. and activated at 870 K in air over-night. This treatment transforms a major fraction of the Brønsted sites into half as many Lewis sites [12,13]. The sample was then evacuated at room temperature to $\leqslant 10^{-5}$ mbar for > 1 h. In carefully exchanged zeolites prepared this way there was no detectable ESR signal prior to adsorption of the olefin.

About 40 mg of adsorbate was degassed by freeze–pump–thaw cycles. The olefin was then deposited from the gas phase on to the zeolite at 77 K. Subsequently, the sample was warmed up and maintained at room temperature for 5 min before it was evacuated again for 5 min to $\approx 10^{-3}$ mbar, and then sealed and immediately measured. The loading obtained in this way was checked and usually found to be 2–5 wt% of the zeolite.

For a comparative radical cation study in a matrix, a solution of a few percent of the olefin in $CFCl_3$ was frozen at 77 K, γ-irradiated using a ^{60}Co source, and then measured at 77 K. Another comparison was made with HZSM-5, which was prepared in an analogous way as the mordenite.

Measurements with zeolites were all performed at room temperature. A solid DPPH crystallite was used as a standard ($g = 2.0037 \pm 0.0002$) [14] for g-value determination. For each adsorbent, two to three samples were prepared in order to ensure reproducibility.

3. Results and discussion

The spectrum obtained after adsorption of 2,5-dimethyl-2,4-hexadiene (DMHD) on H-mordenite (HM) is given in fig. 1 (top). Below, a simulation assuming isotropic conditions and based on two sets of six equivalent protons with 1.06 and 1.31 mT hyperfine coupling constant, two protons with 0.25 mT

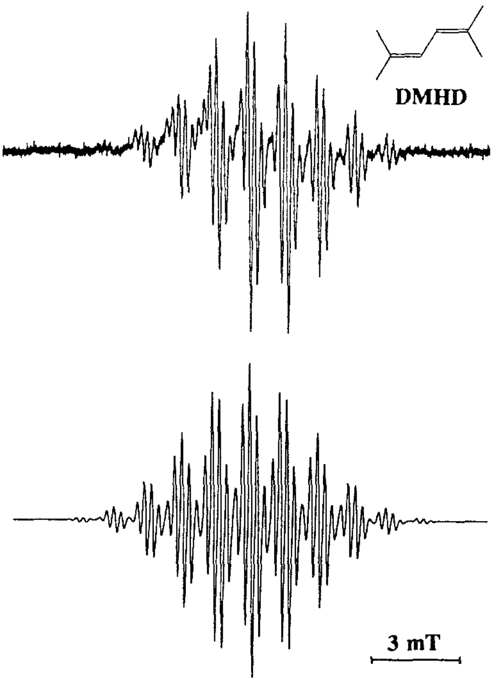

Fig. 1. ESR spectrum recorded 40 min after adsorption of DMHD on HM (top). Simulation of the spectrum assuming isotropic conditions (bottom, see text for parameters).

coupling, and a line width of 0.12 mT is shown. The *g*-factor was determined to be 2.0027. All parameters agree closely with those reported for the radical cation of the same molecule in liquid dichloromethane (1.075, 1.29, and 0.30 mT, $g = 2.0028$) [15]. This is convincing evidence that the species observed is the cation of DMHD in both cases. The deviations between the observed spectrum in the zeolite and its simulation are ascribed to a residual anisotropy which is small enough to leave the spectrum almost liquid-like. It is conceivable that the radicals rotate about their long axis; however, the cylindrical shape of the channels does not permit reorientation about a transverse axis. Anisotropy is much smaller for nuclei in β as compared to α positions. The absence of α protons at the end carbons of the diene system (which carry most of the spin population) therefore furnishes narrow lines. It is expected that the radical cation derived from the unsubstituted butadiene will have considerably broader lines.

It is furthermore obvious that the lines are slightly broader and the spectrum less resolved at the low field side. This is a typical situation which has been encountered previously [11]. Since in the present case there is no evidence that it is due to overlapping spectra it can only mean that the hyperfine and *g* tensors are both anisotropic.

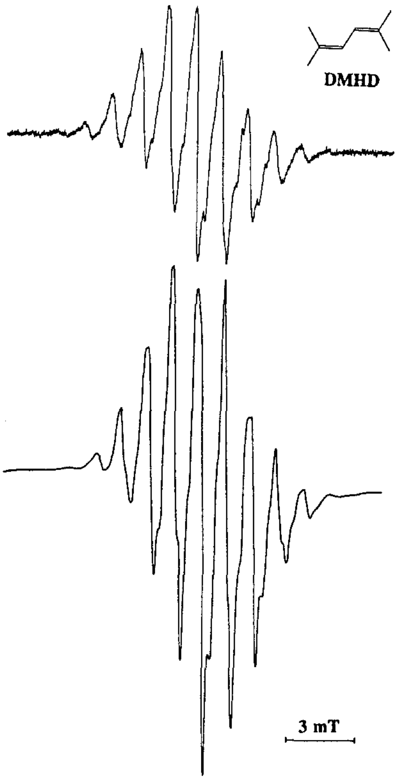

Fig. 2. ESR spectra recorded 65 min after adsorption of DMHD on HZSM-5 (top) and following γ-irradiation of DMHD in a $CFCl_3$ matrix at 77 K (bottom).

The spectrum decayed over a period of several hours at room temperature. All line amplitudes showed the same time dependence, which corroborates that the spectrum belongs to a single species.

For comparison, DMHD was adsorbed on activated HZSM-5, and its radical cation was also generated by γ-irradiation of the parent compound in a freon matrix. The spectra obtained this way are displayed in fig. 2. They are both very similar, consisting of a multiplet of at least 11 lines with a splitting of 1.18 mT (HZSM-5) and 1.16 mT (freon), and a marginally resolved fine structure of 0.32 mT. They represent essentially the envelope of the spectrum given in fig. 1, and there is no indication that they belong to a species other than the radical cation of DMHD. The lower resolution must be a consequence of the more rigid packing in the matrix and the lower mobility in the lower diameter channels (5.6 Å in HZSM-5 as opposed to 7 Å in HM).

Fig. 3 shows the spectrum obtained with 2,3-dimethyl-1-butene (DMB). It is striking and totally unexpected that the spectrum is virtually identical with that of fig. 1. All lines agree in their positions, and there are only minor deviations in some of the relative amplitudes. The latter change in time to some extent which

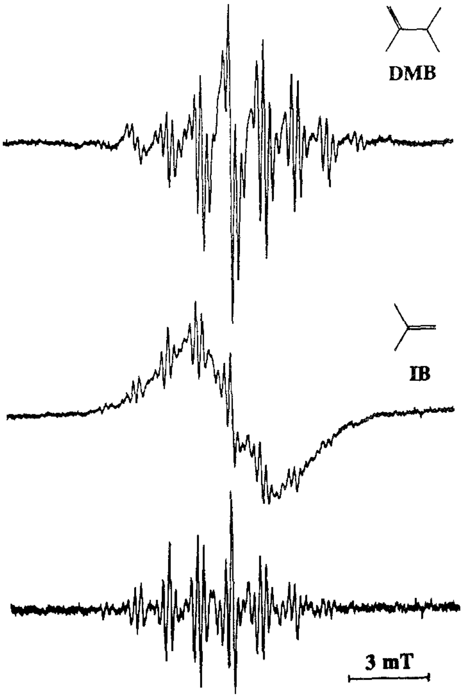

Fig. 3. ESR spectra recorded 130 min after adsorption of DMS (top) and 55 min after adsorption of IB on HM as obtained (middle) and after subtraction of the broad background (bottom).

indicates that the spectrum is contaminated with a second, unidentified species. However, given the high resolution of the spectra there can be no doubt that the major radical is the same in both cases.

The spectrum obtained with isobutene (IB) is also displayed. Its quality is poorer, but it is evident that the same groups of lines appear superimposed on a broad background. The same species is thus formed not only from DMHD but also from DMB and from IB. Preliminary further studies indicate that the DMHD radical cation contributes also to the spectrum obtained following adsorption of 2,3-dimethyl-2-butene, but spectra with a quite different characteristic were obtained when hexa-2,4-diene or different isomers of non-cyclic C_5H_{10} were adsorbed [16].

While it is obvious that the DMHD radical cation is not only formed by ionisation of the parent molecule but also from DMB and from IB, it is not straightforward to suggest a reaction mechanism. IB is imagined to dimerise under loss of H_2, but dimerisation of DMB requires the loss of C_4H_{10} to yield the observed species. This is quite an unusual reaction, and it should certainly be subject to further investigation, in particular with regards to the other cases where the characteristic narrow line spectrum of the DMHD radical cation has not been observed.

Dimerisation and oligomerisation of radical cations has been commonly observed in the condensed phase [15,17], and fragmentation is of course often observed under the energetic and collision-free conditions in a mass spectrometer. Not very specific oligomerisation was interpreted as a step towards coke formation [11]. The present observations show clearly that dimerisation and elimination can both occur in the pores of a zeolite. They demonstrate that Lewis centres are able to oxidise olefins to radical cations, and that this can lead to the formation of new carbon–carbon bonds, which is one of the processes of principle importance in the catalytic activity of a zeolite. The fact that the same species is formed from rather different precursor molecules shows a high specificity of the processes, which is possibly imposed by shape selectivity. The initial steps of "coke formation" thus appear to be well defined processes.

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