Catalysis Letters 1 (1988) 311–316

DIRECT OBSERVATION OF TRANSITION STATE SELECTIVITY: LOW TEMPERATURE CYCLIZATION OF DIENES INSIDE H-MORDENITE AND H-ZSM-5 CHANNELS

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Received 16 May 1988; accepted 10 September 1988

The analysis of the ESR-spectra obtained upon the sorption of dienes and olefins on H-mordenite shows that molecules of dienes are not very reactive in oligomerization inside HM-channels. Warming of HM with presorbed 1,4-pentadiene or 1,5-hexadiene results in the selective cyclization of molecules inside the HM channels. In contrast cyclization of dienes does not take place inside the narrower channels of H-ZSM5 in spite of the fact that the nature of both acid and redox sites in these two zeolites is the same. This clearly demonstrates the reality of transition state selectivity.

1. Introduction

Application of electron spin resonance [1–3] to the study of olefin adsorption and conversions on H-mordenite and H-ZSM-5 yields insight into the mechanism of conversion of unsaturated molecules on high-silica zeolites. The majority of radical-forming (redox) sites is linked with acid sites, and these complex centers are located inside the zeolitic channels [1,4]. It therefore follows that the analysis of hyperfine splitting (h.f.s.) in ESR-spectra of radical particles yields information on the structure of molecules and intermediates tightly bonded inside the channels of both HM and H-ZSM5.

The adsorption (at 20 ° C) of C_2–C_8 linear and branched olefins on HM and C_2–C_3 olefins on H-ZSM-5 is accompanied by the formation of the same secondary radical fragment in the oligomeric chain formed rapidly from different monoolefins (see refs. [1,3,5]). On the other hand, the adsorption of cyclopentane and cyclohexane on these two zeolites results in the formation of stable primary radicals from sorbed molecules. The ESR-signal hfs in the case of cycloolefins differs drastically from those registered upon the acyclic monoolefin sorption. The purpose of this work is to explore radical formation consequent upon the sorption of 1,4-pentadiene and 1,5-hexadiene sorption on HM and H-ZSM-5 at temperatures from −78 ° to 100 ° C, and to compare this behaviour with that of earlier studies on cyclic and acyclic monoolefin sorption on the two zeolites.

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2. Experimental

The study was performed on HM sample (Si/Al = 5) and H-ZSM-5 sample (Si/Al = 20) having a decationization degree in excess of 95 percent obtained by thermal decomposition of NH_4-forms in an air stream at 520–550 ° C for 5 h. These very samples were the ones studied earlier [1–3]. X-ray analysis confirms the high crystallinity of the samples.

Prior to each experiment the sample was treated for 2 h at 520 ° C in air to burn off traces of hydrocarbons. Then the ampoule, with sample, was placed in the spectrometer probe and soldered to an adsorption system which permitted evacuation of the sample to 10^{-6} Torr residual pressure and the inlet of the adsorbates from the gas phase. The following sequence of sample treatment in the spectrometer probe then was followed to remove water: (1) heating to 400 ° C and evacuation for 20 min; (2) inlet of pure O_2 at 400 ° C, heating for 10 min and cooling to 20 ° C; (3) evacuation at 20 ° C for 30 min. The hydrocarbons, previously purified to eliminate traces of O_2 and moisture by four freeze-pump-thaw cycles, were introduced at their saturated vapor pressure on the sample cooled to − 78 ° C. The reagent in excess was then pumped out for 10–15 min.

The ESR spectra were taken at − 196 °, and 20 ° C on a reflecting spectrometer ($\lambda = 3.2$ cm) equipped by magnetometer, with a DPPH as a standard.

3. Results and discussion

We investigated the structure of radicals resulting from the interaction of HM and H-ZSM-5 with the following compounds: cyclopentane, 1-methylcyclopentene, cyclohexane, 1,4-pentadiene and 1,5-hexadiene. All ESR-spectra with hfs arising from adsorbate interaction with two zeolites are stable only in the absence of oxygen. Ingress of O_2 at 20 ° C for 1 min results in a reversible disappearance of hfs in ESR signals.

4. Adsorption of cycloolefins

Figure 1 presents isotropic ESR-spectra, taken at − 196 ° C, observed upon cyclopentene adsorption on HM and H-ZSM-5 at − 78 ° C. The hfs of these spectra (taken at − 196 ° C) does not change when the sample is warmed to 20 ° C. The intensity of the signals reduces noticeably as a result of sample treatment at 100 ° C for 30 min but there is no change in hfs (fig. 1). The lack of hfs change upon the heating of the samples from − 78 ° to 100 ° C shows that no chemical change is structure of primary particles formed at low temperature does not occur up to 100 ° C.

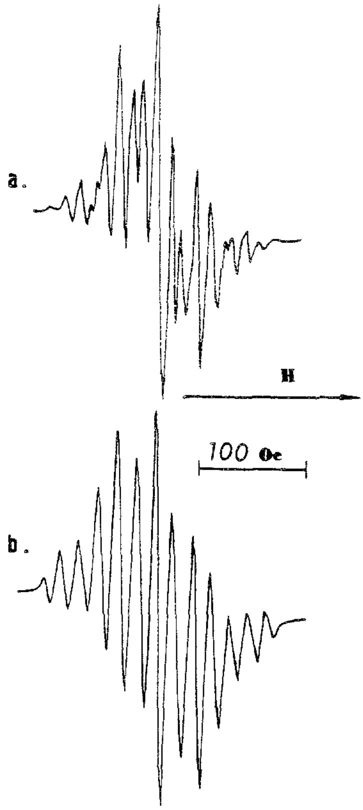

Fig. 1. ESR-spectra, at −196 ° C, of C_5H_8 sorbed at −78 ° C on HM (a) and H-ZSM-5 (b).

It has been noted earlier [1] that the spectrum arising from cyclopentene adsorption on HM is well described in assuming the splitting on two α-protons ($a_{H_1} = 14.5$ Oe) and four β-protons ($a_{H_2} = 37$ Oe). The spectrum with a similar hfs was registered earlier for cyclopentene sorbed on HM at −125 ° C [6]. The total width of the spectrum is quite significant (~ 200 Oe), and it almost coincides with the width of the spectrum obtained upon cyclopentene adsorption on H-ZSM-5 (fig. 1b). The hfs of the spectra in the case of the two zeolites are however rather different. The assumption that $a_{H_1} = 55$ Oe on two α-protons and $a_{H_2} = 18.3$ Oe on six equivalent protons (4β-H + 2γ-H) is necessary to describe the spectrum shown in fig. 1b [13]. It remains to be seen how the density of an unpaired electron is localized on γ-protons of cyclopentene molecule. However, in general it is believed that differences in ESR spectra shown in fig. 1 are due to different localization of molecules in HM and H-ZSM-5 channels a natural consequence of the different structures of the hosts.

Cyclohexane sorption on HM and H-ZSM-5 is accompanied by the appearance of ESR spectra with hfs fully identical to those shown in fig. 1. This was noted earlier [1] for the case of mordenite. So enlargement of the cycle by one carbon atom does not significantly change the unpaired electron distribution in cycloalkanic radical sorbed inside zeolite channels.

1-Methylcyclopentene sorption on HM at −78 °C results in an appearance of an anisotropic ESR spectrum with nonresolved hfs. It may be due to the superposition of signals from radical particles differing by steric restriction of rotation. However, on warming the sample to 20 °C the ESR spectrum develops a well resolved hfs. This spectrum, taken at −196 °C, is fully identical to that shown in fig. 1a. It is clear that the radical particle with a structure of parent α-substituted methylcyclopentene molecule cannot give the signal identical to that from the cyclopentene radical. It may be supposed that isomerization of the sorbed molecules takes place at room temperature and the double bond migration results in the formation of 3-methylcyclopentene molecules. The ESR spectrum of this γ-substituted methylcyclopentene radical in HM must be identical to that of cyclopentene radical. From the formal point of view the enlargement of the cycle with the cyclohexane formation can not be excluded. But double bond migration is a more plausible interpretation.

5. Adsorption of 1,4-pentadiene and 1,5-hexadiene

Adsorption of the dienes on HM at −78 °C is accompanied by a slow appearance of ESR signals with hfs traces. However on warming, sample there is an immediate formation of intensive ESR spectra with well resolved hfs (fig. 2a). The spectra for two dienes are practically identical (fig. 2a); and the hfs of the spectra does not change at 20 °C for 15–20 h. The intensity of the signals reduces slowly upon the sample treatment at 100 °C but no changes in hfs occur.

The ESR spectra of dienes adsorbed on H-ZSM-5 differ drastically from those adsorbed on HM. Adsorption at −78 °C on H-ZSM-5 results in the appearance of very weak ESR-lines without hfs. The sample warming to 20 °C is accompanied by a gradual increase in signal intensities but the hfs in spectra is absent (fig. 2b). Heating the samples at 100 °C is accompanied by a slow fall in signal intensity but no hfs is registered. (Note that the nature of the redox sites in two high silica zeolites is in principle the same. This is evidenced by much similarity in the properties of different-class-radical particles formed in HM and H-ZSM-5 [3].)

For the comparison with dienes, the typical spectrum arising from acyclic monoolefin sorption on HM at 20 °C is given on fig. 2c. It has been shown [1,3] that the adsorption of different C_2–C_8 monoolefins on HM and C_2–C_3 olefins on H-ZSM-5 is accompanied by the appearance of identical ESR spectrum with eleven equidistant lines and $a_H \cong 8$ Oe (fig. 2c). It was assumed that this spectrum is determined by the availability of a secondary radical fragment in the oligomeric chain formed.

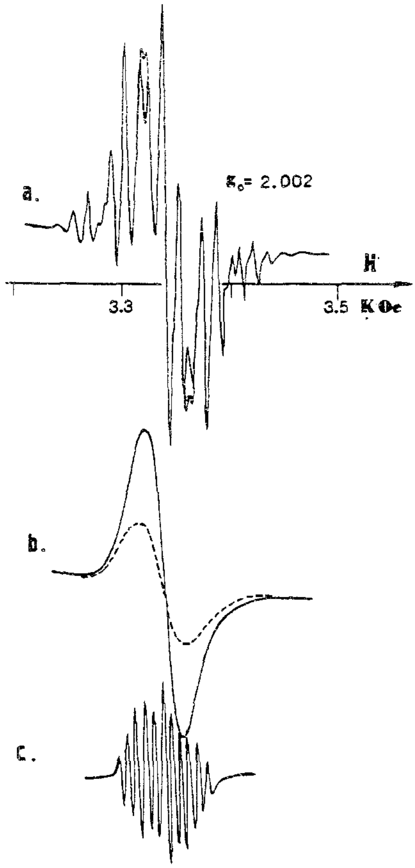

Fig. 2. ESR-spectra of 1,4-pentadiene (unbroken line) and 1.5-hexadiene (dotted line) sorbed at 20 ° C on HM (a) and H-ZSM-5 (b); (c): ESR-spectrum of C_3H_6 sorbed at 20 ° C on HM.

From the comparison of the ESR spectra obtained (figs. 1, 2) it may be safely concluded that the processes of diene and monoolefin transformations inside HM channels differ drastically. ESR spectra of radical particles, formed in HM upon warming the sample with diene presorbed at $-78\,^\circ$C (fig. 2a), are fully identical to those, registered upon the formation of primary cycloalkenic radicals (fig. 1a). At the same time, any lines typical of oligomeric chain formation (fig. 2c) are not registered in the hfs of the signal. So the molecules of nonconjugated 1,4- and 1,5-diene are substructially less reactive in oligomerization inside HM channels than those of monoolefins. The heating of HM with diene presorbed does not lead to oligomer formation but results in a selective cyclization of molecules inside HM channels.

The process of 1,4- and 1,5-diene transformation inside a narrower channel of H-ZSM-5 differs sharply from that found for HM. In spite of the fact that the nature of both acid and redox sites in two zeolites is the same, no selective formation of cycloolefin radical particles in H-ZSM-5 occurs, as shown by the ESR signals without any h.f.s. (fig. 2b).

Different types of selectivity for processes in zeolite pores have been previously discussed, "transition state selectivity" being one of them [8,9]. This type of selectivity is due to the steric restriction imposed on the formation of transient complex in spite of the fact that molecules of both reagent and product are capable of being located inside the void volume of zeolite channel. In our opinion, the results obtained for dienes transformation in HM and H-ZSM-5 clearly demonstrate just this type of selectivity. Those channels that are narrower and with different geometry impose steric restriction on the formation of cyclic molecules from 1,4- and 1,5-dienes in H-ZSM-5.

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