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Chemisorption of Neopentane in Zeolites Studied by UV–Vis Spectroscopy

Alkenyl carbocations formed from hydrocarbons in zeolites can be detected by UV–Vis spectroscopy (*1–3*). During the course of an investigation of the nature and transformation of the alkenyl carbenium ions generated from various hydrocarbons and their derivatives, UV–Vis spectroscopic investigations were also carried out on the interaction of neopentane with zeolites. Preliminary results of this study have been reported elsewhere (*4, 5*).

Protolytic cleavage of neopentane as the primary reaction step over acidic zeolites was proposed by Lombardo *et al.* in order to explain the initial reaction in the catalytic cracking of neopentane (*6*). The tertiary butyl ion formed exclusively in this first step was regarded as playing a role in the propagation of the cracking process. As hydrogen was not found in the products, the formation of the isopentyl carbocation was disregarded. The importance of Lewis acid sites for the generation of carbenium ions by hydride ion abstraction was questioned, although these ions should be capable of inducing cracking.

In this Note chemisorption of neopentane on zeolites of different structures and acidities, i.e., different proton contents and different ratios of Brønsted to Lewis acid sites, is reported in order to yield more insight into the conversion of neopentane over the H forms of zeolites.

Zeolites HNaY-FAU, HNaM-MOR, and HNaZSM-5 were used for the measurements. The concentration of Brønsted centers was varied by the degree of NH_4^+ ion exchange, while the ratio of Brønsted to Lewis sites was adjusted by the pretreatment temperature. The acidity of the samples was evaluated from the amount of adsorbed pyridine determined by the intensities of its IR bands. The unit cell compositions and the ratios of Brønsted to Lewis acid sites Bpy/Lpy are listed in Table 1. Self-supporting wafers of the zeolites were outgassed for 12 h between 670 and 870 K under high vacuum. The experimental setup has been described in detail previously (*7*). The UV–Vis spectra of the zeolites exposed to neopentane (Matheson, 99.96%) were recorded in transmission on a Cary 17 spectrometer under computer control.

Immediately after neopentane admission into the optical cell at room temperature, absorptions arose at 310–320 nm and at higher wavelengths (see Figs. 1–3). In Figs. 2 and 3 the location of a second band at about 380 nm becomes more definite. According to Ref (*2*) they were attributed to mono- and dienyl carbenium ions. First the band at 310–320 nm emerges, followed by that near 380 nm.

The intensities of the bands varied with the proton contents of the samples. On zeolite NaY-FAU, where no Brønsted acidity and only traces of Lewis acidity were detectable, no enylic carbocations were formed. With increasing Brønsted content of the zeolites the bands developed with increasing intensity, as can be seen from Fig. 1. It was found that the higher the Bpy/Lpy ratio of the HNaY-FAU sample, exchanged by NH_4^+ to the same extent, the less pronounced was the development of the 380 nm band (see Fig. 2).

Independently of the type of zeolite the formation of alkenyl carbenium ions was found to be similar; i.e., the band positions were nearly the same in the case of faujasite, mordenite, and ZSM-5, even though

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TABLE 1

Unit Cell Compositions, Ratios of Brønsted to Lewis Acid Sites, and Pretreatment Temperatures of the Zeolite Samples

Sample No.	Composition	Bpy/Lpy	Pretreatment temperature (K)
1	$Na_{58}Al_{58}Si_{134}O_{384}$	—	770
2	$(NH_4)_5Na_{53}Al_{58}Si_{134}O_{384}$	6.00	670
3	$(NH_4)_{32}Na_{26}Al_{58}Si_{134}O_{384}$	2.96	670
4	$(NH_4)_{42}Na_{16}Al_{58}Si_{134}O_{384}$	5.37	670
5	$(NH_4)_{42}Na_{16}Al_{58}Si_{134}O_{384}$	0.19	770
6	$(NH_4)_{42}Na_{16}Al_{58}Si_{134}O_{384}$	0.05	870
7	$(NH_4)_{6.3}Na_{0.2}Al_{6.5}Si_{41.5}O_{959}$	0.46	770
8	$(NH_4)_{1.02}Na_{0.06}Al_{1.08}Si_{94.9}O_{192}$	2.15	770

the intensities and the widths of the bands were different (Fig. 3). The latter is not very surprising as the diffusion of the molecules in the channels of the zeolites and the transformations of simple carbenium ions into oligomers are influenced by the pore diameter and the concentration of acid sites, correlating with the Al/Si ratio. These properties were rather different in the samples under study.

Dynamic UV–Vis spectral measurements showed that formation and transformation of the carbocations proceed with measurable rate even at room temperature.

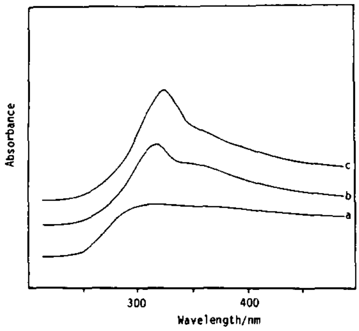

FIG. 1. Transmission electronic spectra recorded after 1 h of contact time at room temperature of 1.33 kPa neopentane adsorbed in faujasites of different ammonium contents pretreated *in vacuo* at 670 K for 12 h (sample Nos. 2, 3, and 4).

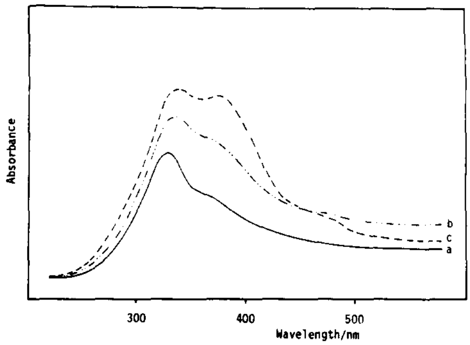

FIG. 2. Transmission electronic spectra of HNaY-FAU zeolites with different Bpy/Lpy ratios, 5.37 (a), 0.19 (b), and 0.05 (c), after loading with 1.33 kPa neopentane for 1 h at room temperature (sample Nos. 4, 5, and 6).

The results may be discussed as follows. Alkenyl carbenium ions can be generated from neopentane only by secondary transformation of primarily formed alkyl carbenium ions like neopentyl, isopentyl, and isobutyl carbocations. Olah *et al.* (*8*) studied the ion formation from neopentane in superacid solutions and found that two types, isopentyl and isobutyl ions, developed depending on the temperature and acidity of the solution. At 253 K neopentane lost a primary hydrogen in FSO_3H–SbF_5–SO_2ClF solution, rearranging the

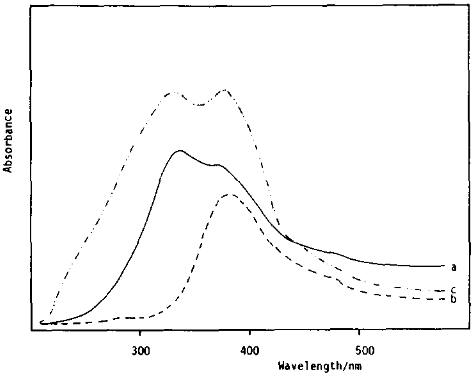

FIG. 3. Transmission electronic spectra after 1 h of contact time at room temperature of 1.33 kPa neopentane adsorbed on zeolites HNaY-FAU (a, No. 5), HNaM-MOR (b, No. 7), and HNaZSM-5 (c, No. 8) pretreated at 770 K *in vacuo*.

neopentyl into a *t*-amyl ion. At 298 K in FSO_3H-SbF_5 solution the *t*-butyl cation was exclusively formed while simultaneously methane was released. It was stated that protolytic cleavage of neopentane depends strongly on the temperature and acidity of the superacidic solution: "Thus at higher temperatures abstraction of methide ion giving the *t*-butyl cation is favored over hydride ion abstraction" (*9*). To a first approximation, the heat of formation can be used for the comparison of carbocation stability. In this way the following order of stability of carbenium ions can be established: neopentyl < *t*-butyl < *t*-pentyl (*10, 11*). This sequence clearly shows that if hydride ion abstraction occurs from neopentane, e.g., by Lewis acid sites of the zeolites, the primarily formed neopentyl ion should isomerize, probably immediately, to the most stable *t*-pentyl ion, as was also stated by Olah *et al.* This means that under certain conditions the formation of *t*-pentyl carbenium ions from the primary product of the transformation of neopentane in acidic media cannot be excluded.

In our reactor experiments carried out under the same conditions as those in the spectroscopic studies no decomposition of neopentane was found by GC analysis up to 473 K and a pronounced methane formation could be established only for temperatures higher than 550 K. Thus, for the first reaction step during interaction of neopentane with zeolites at room temperature not the protolytic cleavage to methane and isobutyl carbenium ions but rather a protolytic cleavage to the *t*-pentyl ion or hydride ion abstraction on Lewis acid sites may be assumed. These ions may take part in further transformations leading to enylic and polyenylic carbenium ions detected by UV–Vis spectroscopy.

As zeolites are solid acids and they contain superacidic sites as well (*12, 13*), they can behave analogously to superacidic solutions in hydrocarbon transformations. These similarities found in the capability of hydrocarbons for ion formation and the applicability of the Sorensen equation, which proves to be valid for the identification of alkenyl carbocations in superacids as well as in zeolites (*14, 15*), support this statement.

Consequently, transformation of neopentane over zeolites takes place via *t*-pentyl carbenium ions at room temperature while at higher temperatures it proceeds with participation of *t*-butyl carbenium ions in agreement with our results and those of Lombardo *et al.* (*6*), respectively, as well as those found by Olah *et al.* (*8, 9*) in superacids.

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