

Reaction of Small Olefins on Zeolite H-ZSM-5. A Thermogravimetric Study at Low and Intermediate Temperatures

J. P. VAN DEN BERG, J. P. WOLTHUIZEN, AND J. H. C. VAN HOOFF

Laboratory for Inorganic Chemistry, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

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Oligomerization and cracking reactions of ethene, propene, and isobutene on zeolite H-ZSM-5 ($300 \leq T < 600\text{K}$) were investigated using temperature-programmed adsorption and desorption experiments, high-resolution ^{13}C -NMR spectroscopy, and gas chromatographic product analysis. Evidence is gained that at 300K only the stronger part of the Brønsted-acid sites are active in ethene oligomerization, while at increased temperatures more sites become active. On the contrary, in propene and isobutene oligomerization all sites are already active at 300K. This results in completely analogous products formed upon oligomerization of ethene, propene, and isobutene above 373K. The rate of oligomerization increases sharply with increasing reaction temperatures, resulting in a hindered transport of reactant molecules through the pores due to pore mouth blocking. The reactions on the outer surface become more important, which results in an increased branching of the oligomers formed at higher reaction temperatures. At 400K cracking of the oligomers starts, and at 490K the rate of cracking equals the rate of oligomerization. At this temperature desorption products show considerable branching, while at 573K only highly branched products are desorbed. At temperatures above 500K zeolite H-ZSM-5 becomes a dynamically operating catalytic system in the conversion of small olefins.

INTRODUCTION

In the reaction mechanism for the conversion of methanol into paraffins, olefins, and aromatics on zeolite H-ZSM-5, as we recently proposed (1), ethene and propene are expected to be the primarily formed olefins. The consecutive reactions of these olefins have been the subject of several investigations using conversion measurements (2, 3), thermogravimetry (TG) (4, 5), ir spectroscopy (4), and ^{13}C -NMR spectroscopy (4-8). Important points of discussion that arise from these studies are: (i) the type of active site; (ii) the observed differences in reactivity towards ethene, propene, and isobutene; and (iii) the formation of linear or branched oligomers in low- and medium-temperature reactions of small olefins. We consider these in turn.

(i) *Type of active site.* In order to explain the differences in the reactivity towards ethene, Rajadhyaksha and Anderson (9) proposed that H-ZSM-5 samples, prepared

by HCl treatment, contain different active sites compared to samples prepared by NH_4NO_3 exchange. According to these authors, upon HCl treatment specific sites, obviously strong Lewis-acid sites, are created by dealumination of the crystal lattice. However, our data for ethene conversions on H-ZSM-5 samples subjected to HCl, $\text{HCl-NH}_4\text{Cl}$, and NH_4NO_3 treatment do not show significant differences with respect to the reactivity towards ethene.

Nevertheless, Lewis-acid sites are important in low-temperature reactions of olefins. Kubelkova *et al.* (10, 11) have shown that on H,Na-Y ethene can be oligomerized at 310K only when strong Lewis-acid sites have been formed by dehydroxylation. On the other hand, propene can be oligomerized on Brønsted-acid sites. Karge (12) has shown that on the zeolite H-mordenite (a solid which certainly contains no Lewis-acid sites) ethene can be oligomerized only at 370K and above on Brønsted-acid sites. Recently we reported data (5) that show

that already at room temperature ethene can be oligomerized on Brønsted-acid sites in H-ZSM-5; when, however, Lewis-acid sites are also present the rate of oligomerization is enhanced. Novákova *et al.* (13) also report that on zeolite H-ZSM-5 ethene can be oligomerized on Brønsted-acid sites at room temperature.

(ii) *Reactivity differences.* In conversion experiments on zeolite H-ZSM-5 in which a poor reactivity towards ethene was reported (6, 14), propene and other small olefins could be readily converted. Also our data show (5) that at 300K ethene oligomerizes slowly on zeolite H-ZSM-5, while propene and isobutene react very fast until the pore volume is almost completely filled with reaction products. In this paper new TG experiments will be presented in order to elucidate the temperature dependence of these oligomerization reactions. Furthermore, the differences in the rate of oligomerization of the olefins mentioned will be studied and its consequences for the transport of reactant and product molecules through the intracrystalline pores will be described.

(iii) *Nature of oligomers.* In the preceding paper (8) we report new results obtained by high-resolution solid-state (HRSS) ^{13}C -NMR spectroscopy on the oligomerization of ethene, propene, isobutene, and 2-methyl-butene-1 on zeolite H-ZSM-5. These data give strong evidence that at 300K in all cases only linear oligomers are formed. This result is unique for H-ZSM-5 when compared to the results of analogous oligomerization reactions on H-Y (10, 11) and H-mordenite (12). After oligomeriza-

tion of ethene on H-ZSM-5 at 373K some branched hydrocarbons were observed.

This result, together with the results of some desorption experiments of adsorbed oligomers, will be discussed in the context of the TG experiments mentioned above.

EXPERIMENTAL

Materials. The H-ZSM-5 samples were prepared according to previously described procedures (15) and were characterized by chemical analysis, X-ray diffraction, and $n\text{-C}_4$ adsorption (5). Prior to each experiment the zeolites were calcined in air at 823K during 1 hr. The data are given in Table 1.

Ethene, propene, and isobutene, used in TG experiments, were high-purity reagents (99+%) and were dried by molecular sieves before use. The vector gas He was purified by passing it successively over a BTS, Carbosorb, and molecular sieve column. In the ^{13}C -NMR experiments C_2H_4 -1,2- ^{13}C (90% enriched) from Stohler Isotope Chemicals was used.

TG experiments. A Cahn RG Electrobalance, fitted with a Eurotherm temperature programmer, was used. Prior to each experiment the zeolite samples were dehydrated at 673K in a He flow (200 ml/min). The adsorption experiments were performed in continuous flow. The reactant (40 ml/min) was added to the He flow; at the same time the He flow was decreased proportionally to obtain a constant total gas flow (200 ml/min). In all experiments only chemisorption data are compared, i.e., after adsorption the sample is flushed in a He flow at reaction temperature in order to desorb the physisorbed material.

TABLE I
Chemical Composition and Pore Volume of H-ZSM-5 Samples

Sample	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	SiO ₂ /Al ₂ O ₃ mole ratio	No. B sites (mmol/g)	Pore volume (ml/g)
BII	94.2	3.17	0.07	0.11	50.5	0.59	0.151
GII	88.3	4.48	0.37	0.37	33.5	0.70	0.126

¹³C-NMR experiments. The spectra were obtained at ambient temperature in specially designed 10-mm sample tubes at 22.6 MHz with a Bruker HX-90R spectrometer interfaced with a Digilab FTS-3 NMR pulsing and data system. The bandwidth was 5000 Hz. ²H₆-acetone was used as an external reference.

Prior to adsorption the zeolites were evacuated (0.13 Pa) at 573K for 1 hr. Ethene was adsorbed at 200K and stored overnight at room temperature. After the C₂H₄ resonance in the spectrum had completely disappeared (4, 7) the sample tube was evacuated at 300K. Consecutively the sample tube was closed and the desorption was performed at the temperatures given in the text for 15 min.

RESULTS AND DISCUSSION

It is known (5) that at 300K ethene can be slowly oligomerized on zeolite H-ZSM-5, whereas propene and isobutene react much faster under these conditions. A temperature-programmed adsorption (TPA) of ethene (Fig. 1) shows that at slightly higher

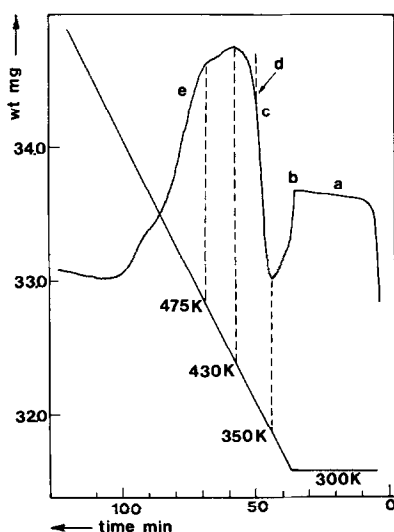


FIG. 1. Thermogravimetric curve of the temperature-programmed adsorption of ethene on zeolite H-ZSM-5. (a) Physisorption + slow chemisorption at 300K. (b) Desorption of physisorbed ethene. (c) Fast chemisorption (oligomerization). (d) Start of cracking of the oligomers. (e) Fast cracking of oligomers.

temperatures the oligomerization of ethene also becomes faster.

In Table 2 TG data are presented of adsorptions of several small olefins on zeolite H-ZSM-5 (sample BII) at different temperatures. From the amounts of adsorbed olefins it can be seen that at 293K more propene and isobutene is adsorbed (about 95% of the pore volume is filled with oligomers) than ethene (only about 75% of the pore volume is filled). High-resolution solid-state (HRSS) ¹³C-NMR spectra of the oligomerization products of ethene, propene, and isobutene on zeolite H-ZSM-5 obtained at room temperature, reported in another paper (8), show that in the case of ethene oligomerization linear paraffins are formed with a high average chain length (about C₂₅), while upon oligomerization of propene and isobutene this average chain length was only C₈-C₁₂. Two points arise from these data: (i) shorter chains are more effective in filling the pore volume, and (ii) the difference in average chain length obtained after oligomerization at room temperature of ethene on the one hand and propene and isobutene on the other indicates that in ethene oligomerization only a small number of sites are active, apparently the most acid ones, whereas in propene and isobutene oligomerization more, if not all, sites may participate under these conditions.

In Fig. 2 the adsorption curves of ethene, propene, and isobutene adsorption at 373K, as well as the temperature-programmed desorption curves of the products formed, are depicted. It is shown that the rate of oligomerization as well as the products formed in these three experiments are similar. This indicates that the differences between ethene oligomerization and the oligomerization of propene and isobutene, observed at 298K, are no longer present at 373K, i.e., at 373K in ethene oligomerization all sites are also active. It can be concluded now that the increase of the rate of oligomerization of ethene at increasing temperatures observed in Fig. 1 is not only due to an increase of the rate constant but also to an

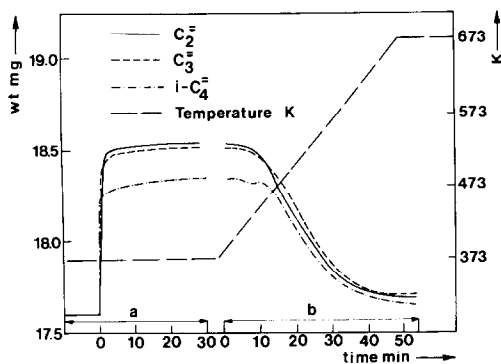


Fig. 2. Adsorption of small olefins at 373K on zeolite H-ZSM-5 and temperature-programmed desorption in a He flow.

increase of the number of sites that participate in the reaction.

The HRSS- ^{13}C -NMR spectrum recorded after adsorption of C_2H_4 at 373K shows that the average chain length has become comparable to the chain length observed upon oligomerization of isobutene at 293K (8). These results support the suggestion that under these conditions all Brønsted sites participate in the oligomerization reactions.

However, the chemisorption data (Table 2) also show that at increased adsorption temperatures the pore volume is less effectively filled by the formed oligomers. Moreover, in the HRSS- ^{13}C -NMR spectrum of the ethene oligomer, formed at 373K, some branched products are observed. This indi-

TABLE 2

Maximum Chemisorption of Small Olefins^a on Zeolite H-ZSM-5^b

Ads. temp. (K)	C_2H_4 (mg/g)	C_3H_6 (mg/g)	Isobutene (mg/g)
293	76 (9.2)	102 (12.3)	103 (12.5)
323		94 (11.4)	
373	81.3 (9.8)	81.2 (9.8)	59.7 (7.2)

^a The number in parentheses represents the average C number of chemisorbed oligomer per ZO H^+ site, calculated as

$$2 \times (\text{C}_2\text{H}_4)_{\text{ads}} (\text{mol/g}) / \text{Al sites} (\text{mol/g}).$$

^b Sample BII.

cates that at increased adsorption temperatures fast oligomerization and isomerization reactions on the outer surface become increasingly important, such that more branched products are formed, but also, and this is even more important, it indicates that the transport of reactant molecules through the intracrystalline pores may become hindered because of pore-mouth blocking. The data of Table 2 indicate that at higher temperatures (373K) the effect of pore-mouth blocking becomes increasingly important in going from ethene to isobutene. This may be due to the fact that in the case of isobutene the initial tertiary carbenium ion can be formed more easily than the initial primary cation in the case of ethene. Especially for isobutene this may result in an increasing rate of oligomerization at the weak acid sites on the outer surface of the zeolite crystallites.

The TPA curve of ethene on zeolite H-ZSM-5 shows that at about 400K (d in Fig. 1) cracking of the initially formed oligomers begins. At about 440K the point is reached where the rate of cracking becomes equal to the rate of oligomerization. At this point the amount of chemisorbed ethene reaches a maximum. These facts are in agreement with the conclusions of Derouane *et al.* (7) that the cracking of the oligomers starts at 413K. GLC analysis of products desorbed at 493K showed mainly linear paraffins although amounts of branched paraffins were present in the mixture. Only small amounts of olefins could be detected.

HRSS- ^{13}C -NMR spectra of the gaseous products desorbed at 493 and 573K, presented in Figs. 3a and b, respectively, clearly show that (i) only paraffins can be detected, and (ii) at 493K linear and branched paraffins are desorbed with an average chain length of C_{4-6} ($\text{CH}_2/\text{CH}_3 \approx 1.7$), while at 573K only very short and highly branched paraffins ($\text{CH}_2/\text{CH}_3 \approx 0.3$) are desorbed. The observation, by GLC as well as by ^{13}C -NMR spectroscopy, that cracking of the oligomerization products results in mainly paraffinic compounds suggests that

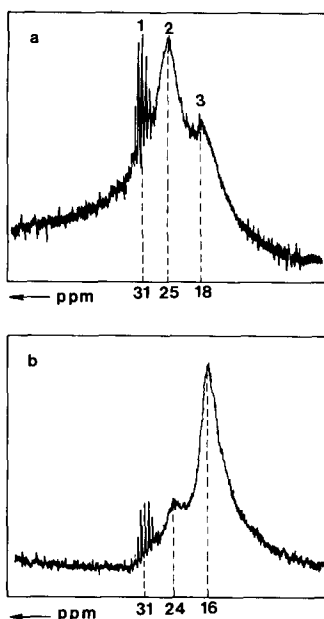


FIG. 3. High-resolution ^{13}C -NMR spectra of decomposition products after cracking of the ethene oligomer. (a) Desorption temperature 493K; (b) desorption temperature 573K. ppm values compared to TMS. 1. $^2\text{H}_6$ -acetone; 2. $-\text{CH}_2-$; 3. $-\text{CH}_3$.

olefins, once formed, are immediately hydrogenated or reoligomerized; this is in agreement with the conclusions of Derouane *et al.* (7).

CONCLUSIONS

Combination of the data reported in this paper and elsewhere (4, 5, 7, 8) shows that small olefins are very reactive towards zeolite H-ZSM-5. In order to understand the temperature dependence of this activity we have to distinguish three temperature regions:

I. $T < 300\text{K}$. Ethene is slowly oligomerized while propene and isobutene are converted rapidly. Only part of the active sites participate in the oligomerization of ethene. The reactions mainly occur inside the intracrystalline pores and consequently only linear oligomers are observed. The oligomerization products are very strongly adsorbed.

II. $300\text{K} < T < 500\text{K}$. The rate of oligomerization per site (turnover number) in-

creases for all reactants. Reactions on the most accessible sites, i.e., sites on the outer surface of the crystallites, are of increasing importance because the intracrystalline transport of reactant molecules may become hindered by pore-mouth blocking. This results in a decreasing maximum chemisorption with increasing temperature. The oligomerization reactions occur to a relatively increasing extent on the outer surface of the crystallites, resulting in the observation of some branched oligomers. Although cracking of the oligomers occurs at $T > 400\text{K}$ the residence time of the oligomerization products on the zeolite surface is long.

III. $T > 500\text{K}$. At these temperatures the rate of cracking of the oligomerization products becomes faster than the rate of oligomerization. Because of this, pore-mouth blocking by oligomers does not occur anymore and the transport of reactant molecules is no longer hindered. The residence time of the products in the zeolite becomes considerably shorter. In fact, starting with this temperature, zeolite H-ZSM-5 becomes a dynamic catalytic operating system in the conversion of small olefins.

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