

## Primary Reaction Steps in the Methanol-to-Olefin Transformation on Zeolites

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The interaction of methanol with HZSM-5 and dealuminated HY zeolites was studied by temperature-programmed desorption/mass spectrometric detection and infrared spectroscopy of surface compounds. The increased amount of preadsorbed methanol and/or methanol added during the thermal desorption at 250–400°C changed the composition of gaseous products over HZSM-5 from methane and formaldehyde to C<sub>2-5</sub> aliphatic compounds, mainly ethylene and propylene, while over dealuminated HY only the latter products appeared. The reaction of gaseous methanol with very reactive surface C<sub>1</sub> species is assumed to be responsible for the formation of the first C–C bonds on both zeolite types. © 1987 Academic Press, Inc.

### INTRODUCTION

Methanol transformation over zeolites to olefins and gasoline has become an important industrial process. For this reaction, numerous mechanisms were proposed (1). The present paper was written to contribute information on the primary reaction steps of the interaction of methanol with zeolites by temperature-programmed desorption/mass spectrometric detection (TPD/MS) of the products of small preadsorbed amounts of methanol and by infrared (IR) spectral analysis of surface compounds. Recently, using these techniques, we have observed a difference between the compositions of the gaseous products obtained over dealuminated HY (HY-deal) and the HZSM-5 zeolite. Before the release of aromatics, light olefins were evolved from HY-deal, while methane and formaldehyde were obtained from HZSM-5 (2, 3). In this paper, we study this difference in more detail and suggest a mechanism of the first C–C bond formation.

### EXPERIMENTAL

**Zeolites.** HZSM-5 was synthesized according to the patent (4) using tetrapropyl-

ammonium bromide as a template. The product was calcinated at 550°C in an oxygen stream. The Si/Al ratio was 13.6, the number of strong Brønsted acid sites was 1.1 mmol g<sup>-1</sup> (obtained by IR measurements of pyridine adsorption), and the sorption capacity measured with Ar at -196°C was 5.0 mmol g<sup>-1</sup>. HY-deal was prepared from NaY by dealumination with SiCl<sub>4</sub> (5), followed by washing with water. NaY was supplied by Vurup, Czechoslovakia. The Si/Al ratio in the lattice (determined from skeletal vibrations) was 12.0, the number of strong acid sites was 0.8 mmol g<sup>-1</sup>, and the sorption capacity was 9.2 mmol g<sup>-1</sup>. Prior to the experiments, zeolites were NH<sub>4</sub><sup>+</sup> exchanged at 80°C and deammoniated *in vacuo* (10<sup>-4</sup> Pa) overnight.

**Reactants.** Methanol was of A grade purity (Lachema, Czechoslovakia), dried with KA zeolite, and degassed by repeated freezing and thawing. The same procedure was employed for benzene used as a chemical trap for surface species; the other chemical traps, methane, ethane, and propane, were supplied by Mattheson and used without further treatment.

**IR measurements.** IR spectra were recorded at room temperature on a Nicolet

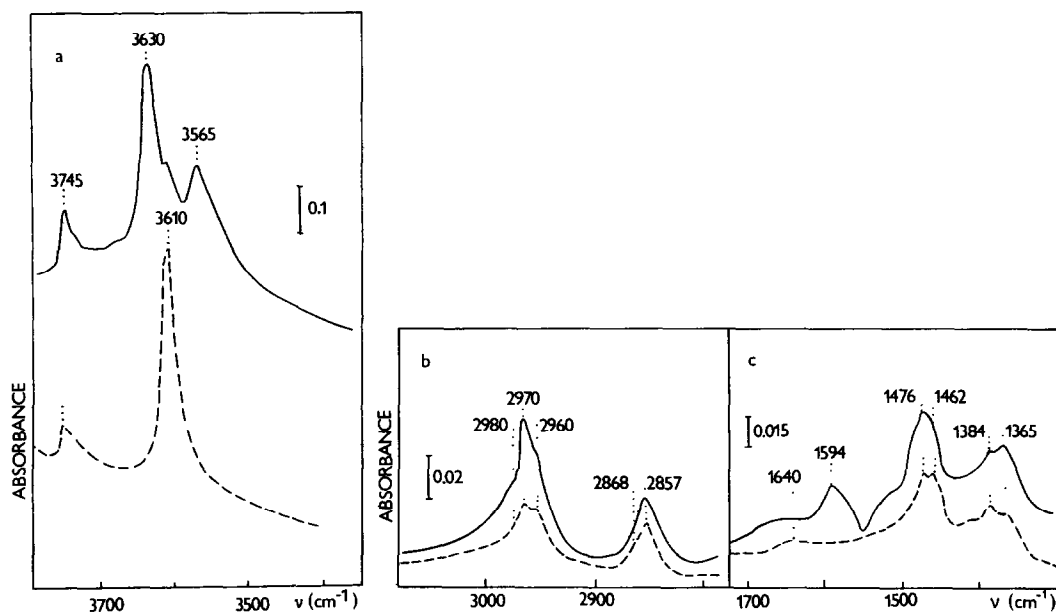


FIG. 1. IR spectra of HZSM-5 and HY-deal. (a) OH groups before methanol adsorption; (b) methoxy groups after methanol desorption up to 200°C; (c) methoxy groups, formates, and carbonates after methanol desorption up to 300°C. In (b) and (c), 4 mmol g<sup>-1</sup> of methanol preadsorbed, (—) HY-deal, (---) HZSM-5.

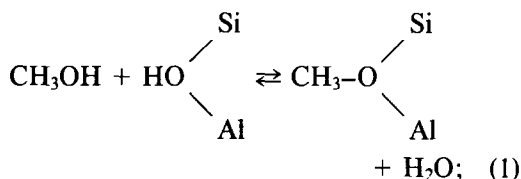
MX-1E Fourier transform infrared spectrometer on self-supported zeolite pellets (7–9 mg cm<sup>-2</sup>). The spectra of OH groups and surface species were measured before and after methanol adsorption and thermal desorption.

**TPD/MS measurements.** Zeolite (0.1 g, in some cases 0.01 g) was allowed to adsorb methanol vapor (0.03–0.6 mmol g<sup>-1</sup>) at room temperature for 30 min. Then TPD was started with a heating rate of 10°C min<sup>-1</sup>. The released gaseous products were directly analyzed by a mass spectrometer (MI 1302, USSR).

## RESULTS AND DISCUSSION

The IR spectra of hydroxyl groups characterizing both zeolite types before the interaction with methanol are depicted in Fig. 1a and those of methyl groups remaining on HY-deal and HZSM-5 after methanol desorption up to 200°C in Fig. 1b. The latter spectra indicate the presence of (i)

skeletal methoxy groups, CH<sub>3</sub>-O<sub>zeol</sub>, formed by the interaction of methanol with skeletal hydroxyls according to scheme



(ii) methoxyls bound to the Al electron-accepting sites, CH<sub>3</sub>O-Al; and (iii) CH<sub>3</sub>O-Si methoxyls (formed by the reaction of methanol with silanol groups vibrating at 3745 cm<sup>-1</sup>) and some remaining physisorbed methanol. The characteristic bands of these compounds are found at 2980, 2970, and 2960 cm<sup>-1</sup>, respectively (2). Their thermal stability increases in the sequence CH<sub>3</sub>OH < CH<sub>3</sub>O-Al < CH<sub>3</sub>-O<sub>zeol</sub> = CH<sub>3</sub>O-Si. The decomposition of CH<sub>3</sub>-O<sub>zeol</sub> leads to the reformation of framework hydroxyls.

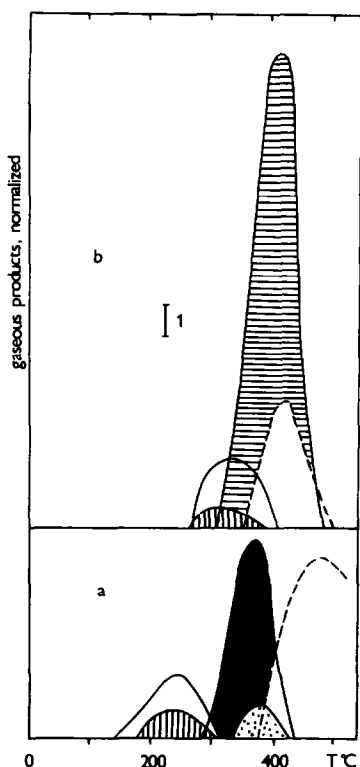


FIG. 2. TPD of methanol from HZSM-5 (a) and HY-deal (b). Methanol preadsorbed ( $0.12 \text{ mmol g}^{-1}$ ), ( $\square$ ) unreacted methanol, ( $\text{▨}$ ), DME, ( $\blacksquare$ ) methane, ( $\square$ ) formaldehyde, ( $\text{▤}$ ) aliphatics  $\text{C}_{2-5}$ , (---) aromatics  $\text{C}_{7-11}$  ( $\text{C}_{7-9}$  on HZSM-5); scales in all of the following figures are related to the abscissa in (b).

After desorption above  $200^\circ\text{C}$ , bands at  $1365$ – $1386$ ,  $1460$ – $1490$ , near  $1590$ , and  $1650 \text{ cm}^{-1}$  are clearly visible in the region  $1200$ – $2000 \text{ cm}^{-1}$  (Fig. 1c). The bands at  $1460$ – $1490 \text{ cm}^{-1}$  can be assigned to the deformation vibrations of methyl groups; the other bands are most probably connected with the formation of formates and carbonate-like species. These latter species are very stable and are observable even after desorption at  $400^\circ\text{C}$ ; their amount is far higher on HY-deal than on HZSM-5.

TPD curves are depicted in Figs. 2a and 2b for HZSM-5 when the preadsorbed methanol amount is lower than about one-third of the number of structural hydroxyls. It follows from Fig. 2 that (i) the release of

unreacted methanol and of the first reaction product, dimethylether (DME), starts and also ends at lower temperatures with HZSM-5 than with HY-deal; (ii) the adsorption of unreacted (or more probably re-formed) methanol over HY-deal cannot be separated from the release of aliphatics  $\text{C}_{2-5}$  (mainly ethylene and propylene) which takes place at  $300$ – $400^\circ\text{C}$ . HZSM-5 yields mainly methane and formaldehyde in the same temperature range; (iii) the conversion of surface species to methane and formaldehyde on HZSM-5 is lower than that to aliphatics on HY-deal. On the other hand,  $\text{C}_{7-9}$  aromatics appear over HZSM-5 in a greater amount than  $\text{C}_{7-11}$  aromatics over HY-deal. On HZSM-5, the release of aromatics is accompanied by the evolution of carbon monoxide, carbon dioxide, and hydrogen.

As the formation of the first C–C bonds occurs at  $250$ – $350^\circ\text{C}$ , this temperature range will be of special interest here. To simulate the conditions of TPD over HY-deal, where some methanol always accompanies the evolution of olefins, we added methanol to the reaction vessel in which TPD on HZSM-5 was taking place. The effect of this addition is depicted in Figs. 3a–3c: while a small amount of added vapors only increases the yield of methane and formaldehyde (the latter compound is not depicted in this and the following figures for simplicity, its ratio to methane is usually  $<1$ ), a larger amount of methanol results in the appearance of olefins and in a decrease in the yield of methane and formaldehyde. This can be due to the formation of olefins via a reaction of methanol vapor with surface species. As the added methanol can increase the concentration of methoxyls (Scheme (1)), the formation of olefins might also proceed via their mutual reaction as was assumed in (6). For this reason, we investigated the effect of the amount of preadsorbed methanol on the composition of the products. No qualitative change occurred over HY-deal and olefins were formed even when the preadsorbed dose

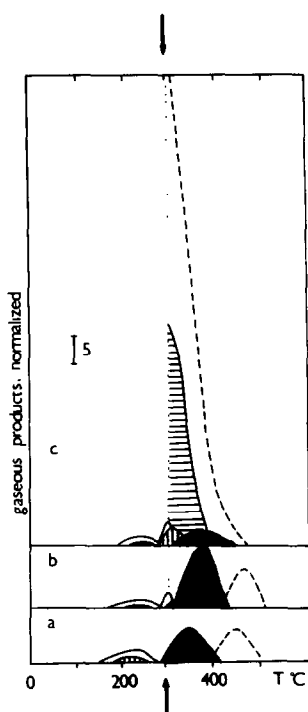


FIG. 3. Effect of methanol added at 300°C on TPD methanol from HZSM-5. Methanol preadsorbed (0.12 mmol g<sup>-1</sup>), (a) 0, (b) 0.08, (c) 0.6 mmol g<sup>-1</sup> of methanol added at 300°C; (□) unreacted methanol, (▨) DME, (■) methane, (▤) aliphatics C<sub>2-5</sub>, (---) aromatics C<sub>7-9</sub>.

was as low as 0.03 mmol g<sup>-1</sup>. In contrast, the amount of preadsorbed methanol on HZSM-5 substantially changed the composition of the released products. From Figs. 4a–4d it follows that when increasing the preadsorbed methanol amount from 0.03 to 0.12 mmol g<sup>-1</sup>, only the yield of methane and formaldehyde increases. A higher preadsorbed methanol amount (0.38 mmol g<sup>-1</sup>) results in the appearance of olefins together with the latter products, while the highest methanol dose (0.6 mmol g<sup>-1</sup>) leads to a suppression of the methane and formaldehyde yield and to the increased yield of olefins (and aromatics). In this case, the release of unreacted methanol and of DME is very high (in Fig. 4d depicted in 4× diminished scale) and cannot be completely evacuated below the temperature of the

release of olefins. This particular unreacted methanol (and/or DME formed) could react with surface methoxyls. Therefore, two TPD experiments were conducted with the same amount of methanol per gram of HZSM-5 (0.6 mmol g<sup>-1</sup>), but using samples with 0.01 (a) and 0.1 g weight (b), respectively. The absolute amount of methanol in the two cases was different by one order of magnitude, thus enabling rapid evacuation of unreacted methanol above the sample (a). As follows from Fig. 5, olefins appear only in case (b), corresponding to a higher partial methanol pressure (and/or DME; both compounds are diminished 2× in Fig. 5b).

All the above experiments support the assumption that gaseous methanol participates in the formation of primary C–C bonds, e.g.,

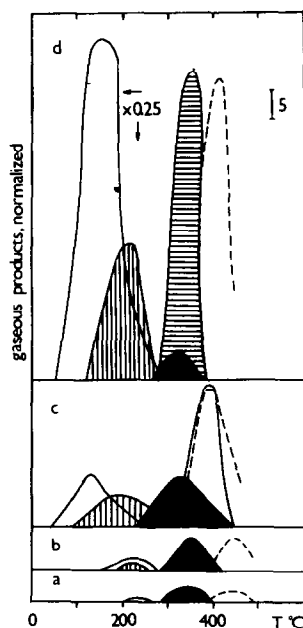
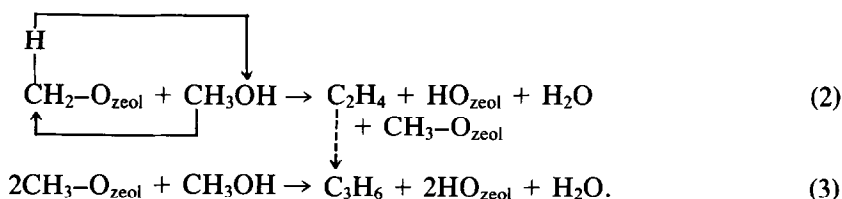


FIG. 4. Effect of the amount of preadsorbed methanol on TPD from HZSM-5. Methanol preadsorbed in millimoles per gram: (a) 0.03, (b) 0.12, (c) 0.38, (d) 0.6 (values of CH<sub>3</sub>OH and DME are 4× diminished in (d)); (□) unreacted methanol, (▨) DME, (■) methane, (▤) aliphatics C<sub>2-5</sub>, (---) aromatics C<sub>7-9</sub>.



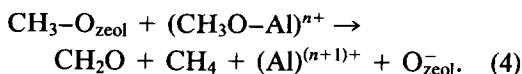
Similar reactions can be written for the interaction of methoxyls with DME whose conversion over zeolites yields the same products as that of methanol; for this reason, we cannot exclude that the reactions (2), (3) proceed with DME which was formed previously from methanol. The reaction of DME with methoxyls yielding propylene was postulated in Ref. (8) and reaction of methanol or DME with methyl carbonium ions formed from methoxyls was assumed in Ref. (9).

The essential condition of the C-C bond formation via (2), (3) is the weakening of C-H bonds in skeletal methoxyls (7) lead-

ing to the proton transfer between strongly polarized methoxyls and methanol or DME with the participation of skeletal oxygens.

DME is also formed at lower temperatures by Eley-Rideal attack of methoxyls with methanol. However, in this case only hydrogen of the OH group of methanol substitutes the surface methyl group whose C-H bonds are strong. This follows from the experiments conducted with the mixture of CH<sub>3</sub>OH and CD<sub>3</sub>OH which yielded (CH<sub>3</sub>)<sub>2</sub>O, (CD<sub>3</sub>)<sub>2</sub>O, and CH<sub>3</sub>CD<sub>3</sub>O only (7, 10).

If no gaseous methanol is present over HZSM-5, methoxyls most probably form methane and formaldehyde via disproportionation, e.g.,



Participation of CH<sub>3</sub>O-Al methoxyls in this reaction seems quite probable, since the incorporation of zeolitic oxygen into the product could hardly occur at 300°C. Moreover, the above reaction of methanol to methane and formaldehyde is known to take place over alumina (11).

If the assumption of the reaction path sub (2), (3), and (4) is correct then it is not clear why HY-deal does not also yield methane and formaldehyde similarly to HZSM-5. HY-deal has a considerably larger amount of nonskeletal Al than HZSM-5 and therefore also a larger amount of CH<sub>3</sub>O-Al methoxyls; consequently, reaction path sub (4) can be expected to be operative. Indeed, a higher concentration of surface formates and carbonates is observed on HY-deal (Fig. 1c) and under favorable conditions a small fraction of methane is recorded in the gaseous products. Thus we assume that

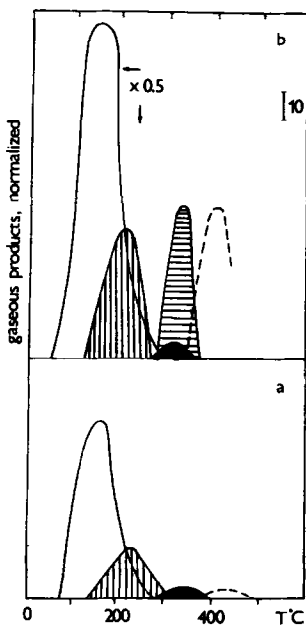
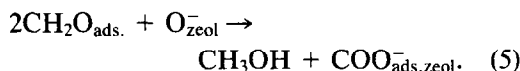


FIG. 5. Effect of absolute methanol amount of TPD from HZSM-5: (a) 0.006 mmol g<sup>-1</sup>/0.01 g, (b) 0.06 mmol/0.1 g (values of CH<sub>3</sub>OH and DME are 2× diminished in (b)); (□) unreacted methanol, (▨) DME, (■) methane, (▤) aliphatics C<sub>2-5</sub>, (---) aromatics C<sub>7-9</sub>.

reaction (4) takes place on HY-deal, however, without release of formaldehyde. This may be due to a reaction of the Cannizzaro-like type:



Such a reaction would yield the methanol needed for the formation of olefins (Schemes (2) and (3)) and also surface formates or carbonate-like species. Naturally, some other reactions of formaldehyde cannot be excluded, e.g., condensation or formation of methylal. Formaldehyde as well as methylal, when they are preadsorbed in small amounts on HZSM-5, yield the same products as those of methanol during TPD.

Since there was a possibility that the difference in the products over HZSM-5 and HY-deal could be a result of the different pore sizes of these two zeolite types, TPD over H-erionite was also measured. Similarly to HZSM-5, methane and formaldehyde appear in the gaseous phase. It follows that the pore size may also play a role in the earliest steps of methanol interaction with zeolites.

Special experiments carried out with chemical traps point to the identical nature and almost equal number of surface species formed from methanol on HZSM-5 and HY-deal at 300°C. As far as the nature of the surface species is concerned, they are of C<sub>1</sub> composition, easily methylate benzene, and are incorporated into ethane and propane, but not into the C–H bonds of methane. This behavior can be characteristic of strongly polarized methoxyls which were observed by IR or of protonated formaldehyde-like species, which can serve as precursors of carbene-like intermediates. The formation of these species was found to be possible theoretically (12).

## CONCLUSIONS

Formation of the first C–C bond in ethylene and propylene during methanol transformation over zeolites is assumed to occur via the reaction of gaseous methanol (or DME) with C<sub>1</sub> species whose C–H bonds are strongly weakened. These species are probably polarized methoxyls or protonated formaldehyde which could also yield species of carbene-like character.

On HZSM-5, the lack of methanol in the gas phase leads to disproportionation of methoxyls to methane and formaldehyde. This is not observed on HY-deal probably due to the supply of methanol by the decomposed surface species.

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