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Deuterium-Labeled Methanol in Reactions with HZSM-5 Zeolite

Methanol-d_3 or a mixture of methanol-d_0 and methanol-d_3 were adsorbed at room temperature on HZSM-5 in amounts ranging from 0.2 to 2 equivalents of the amount of zeolite structural hydroxyls. The isotopic composition of products released at various temperatures allowed us to discuss the mobility of the hydrogen of the surface species and the participation of zeolitic hydrogens in the formation of hydrocarbons. © 1986 Academic Press, Inc.

The isotopic exchange of reactants over a catalyst and with a catalyst can often help in the discussion of a reaction mechanism. For example, in the methanol-to-hydrocarbon transformation over HZSM-5, experiments with ^{13}C-labeled dimethyl ether (an assumed intermediate in this reaction) showed that the formation of ethylene at 623 K proceeds through an intermolecular interaction (*1*); assumptions on alkoxide and carbene intermediates were also supported by these experiments (*2*). Deuterated methoxy groups (from the methanol-d_3 plus HZSM-5 reaction) were found to exchange deuterium with hydrogen of the zeolitic hydroxyls above 570 K (*3, 4*). This pointed to the C–H bond weakening within the surface methoxyls which was connected with the formation of hydrocarbons.

By the reaction of methanol with zeolitic OH groups and Al-electron-acceptor centers, surface methoxy groups, $O_{zeol}CH_3$ and $Al_{zeol}OCH_3$, respectively, are formed. This was reported in a previous paper (*4*) on the basis of infrared data. At lower temperatures, these methoxy groups are present along with physisorbed methanol which is gradually removed by heating to 590 K. In this temperature region, dimethyl ether (DME) is released as the main reaction product, formed by the interaction of both species described above. At higher temperatures, the appearance of hydrocarbons in the gas phase is accompanied by the decomposition of methoxy groups; using very low methanol amounts, methane and formaldehyde precede the release of aromatics, while when increasing the methanol amount, alkenes and alkanes precede and accompany the evolution of aromatics. The exchange with the zeolitic groups was mentioned in Ref. (*4*); a more detailed study of the isotopic exchange of the products of methanol-d_3 interactions with the hydrogen of HZSM-5 hydroxyls will be reported here together with the isotopic exchange between methanol-d_3 and methanol-d_0 reaction products over the same zeolite.

Small amounts of methanol (10–100 μmol) were preadsorbed on HZSM-5 (0.1 g) at room temperature. After adsorption for 1 h, the zeolite was heated to 770 K *in vacuo* for 90–180 min, the rate of heating being controlled by the pressure of the released products which was not allowed to exceed 10^{-3} Pa. The products were analyzed with a modified MI 1302 mass spectrometer. HZSM-5 zeolite was prepared in the usual way (*4, 5*) and pretreated *in vacuo* at 670 K for 18 h. Methanol-d_0 (p.a. Lachema) and methanol-d_3 (V/O Izotop, USSR, enrichment 99.8%) were purified by repeating freezing and thawing *in vacuo*. The ratio of the number of preadsorbed methanol molecules to the number of structural hydroxyls of HZSM-5 (determined as reported in Ref. (*4*)) was denoted by the term F, for which the values of 0.25, 0.7, and 2.0, respectively, were used.

The exchange at 295–520 K. No exchange of deuterium of methanol-d_3 with the zeolite is found in this temperature

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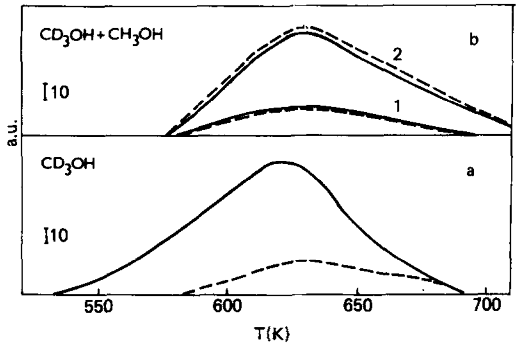

FIG. 1. Deuterium in methane over HZSM-5. (a) From CD_3OH: $F = 0.25$; full line—CD_4, dotted line—CD_3H. (b) From $CD_3OH + CH_3OH$; $F = 0.7$; (1) full line—CD_4, dotted line—CH_4; (2) full line—CD_3H, dotted line—CH_3D.

range. From 370 to 520 K fully deuterated DME is released. It is preceded by some unreacted methanol-d_3 whose amount increases with the increasing value of F. Using the methanol-d_3 and methanol-d_0 mixture (1 : 1), the following labeled DME are observed: $(CH_3)_2O$, $(CD_3)_2O$, and CH_3CD_3O in the ratio 1 : 1 : 2. Although a small amount of methyl hydrogens is exchanged, the major catalytic reaction takes place without the dissociation of the methyl group. This is in character with the previously suggested reaction pathway (*4*): $\text{methanol}_{\text{ads.}}$ reacts with $O_{\text{zeol}}CH_3$ or $Al_{\text{zeol}}OCH_3$ yielding DME.

The exchange at 520–640 K. It has already been shown (*6*) that the characteristic feature of HZSM-5 zeolite in this temperature range is the production of methane and formaldehyde when $F < 1$. Using methanol-d_3, fully deuterated methane (and formaldehyde, not shown here) appears below 600 K as can be seen in Fig. 1a. This implies, therefore, that this reaction takes place via hydrogen transfer between methoxy groups without the participation of the zeolitic hydrogen. Indeed, when the mixture of methanol-d_3 and methanol-d_0 is preadsorbed on HZSM-5, the equimolecular amounts of CD_3H and CH_3D exceeding the equimolecular amounts of CD_4 and CH_4 appear in the gas phase (Fig. 1b). The determination of the concentration of CD_2H_2 lacks accuracy because of the overlapping of its molecular peak with the molecular peak of water. Above 600 K some CD_3H is formed from methanol-d_3 (Fig. 1a) reflecting thus the starting isotopic exchange with hydrogen of zeolitic hydroxyls.

In experiments with a higher methanol concentration, $F = 2$, no methane and formaldehyde are observed in the gas phase, but lower alkenes and alkanes appear instead. These products contain hydrogen from the hydroxyl groups; the mechanism of their formation is probably the same as that described below.

The exchange at 640–750 K. In this temperature range, aromatics (and also alkenes and alkanes, when $F > 1$) appear in the gas phase. Compounds with the highest amount of light hydrogen are released from methanol-d_3 at first, and then the amount of deuterium in these products increases. This is demonstrated in Figs. 2a–c by toluene; higher aromatics (up to C_9) and aliphatic hydrocarbons behave in the same way. When increasing the value of F, the final concentration of deuterium in the desorbed

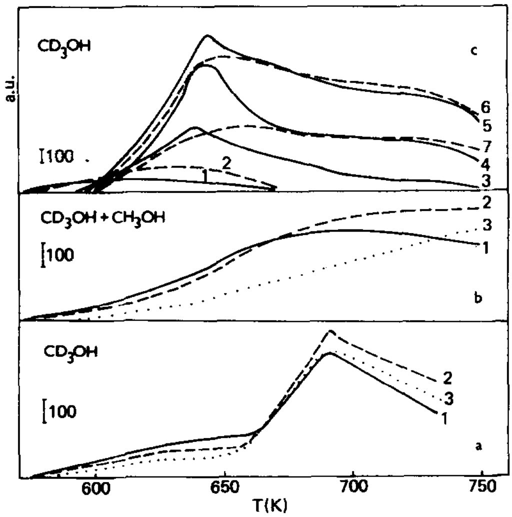

FIG. 2. Deuterium in toluene over HZSM-5. (a) From CD_3OH; $F = 0.25$; (b) from $CD_3OH + CH_3OH$; $F = 0.7$; (c) from CD_3OH; $F = 2.0$: (1) toluene-d_0, (2) toluene-d_1, (3) toluene-d_2, (4) toluene-d_3, (5) toluene-d_4, (6) toluene-d_5, (7) toluene-d_6.

products increases. This implies that the surface species must undergo extensive isotopic exchange with hydrogen of the remaining free hydroxyl groups (proved in Refs. (*3*, *4*)) whose number greatly exceeds the number of methoxy groups (*4*). Hydrogen of OH groups thus apparently takes part in the formation of hydrocarbons from methanol. This reaction has to involve splitting of C–H as well as $(OH)_{zeol}$ bonds, accompanied by rapid H-transfer; it can occur via various mechanisms (*7*).

Conclusions. From the above experiments the following can be concluded.

(i) In the temperature range where the formation of DME prevails, the C–H bonds in methyl groups are not weakened enough to be dissociated. The elimination mechanisms of water involving hydrogen transfer between hydroxyl groups of methanol and those of the zeolite probably govern this reaction (*7*).

(ii) At 520–600 K, when a very low amount of methanol is preadsorbed, methane and formaldehyde are formed by the mutual interaction of the most active methoxy groups, probably with the participation of the less stable $Al_{zeol}OCH_3$ (*4*).

(iii) Above 670 K, and in the case of a higher concentration of surface species even at lower temperatures, hydrocarbons ($C \geq 3$) are formed. This is accompanied by the cleavage of C–H bonds in methoxy groups and rapid deuterium exchange between intermediates and hydroxyl groups. This points to the direct involvement of hydrogen of OH groups in the reaction, the hydrogen transfer being facilitated by the zeolite framework.

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