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Temperature Programmed Surface Reaction of Methylcyclopentane on Pd/NaY and Pd/HY

In previous studies of methylcyclopentane (MCP) conversion over reduced Pd and Pt supported on zeolite Y (*1–6*) it was found that metal sites catalyze the hydrogenolytic ring opening (RO) to *n*-hexane (*n*H), 2-methylpentane (2MP), and 3-methylpentane (3MP), but in the presence of both metal and acid sites ring enlargement (RE) of MCP to cyclohexane (CH) and benzene (Bz) is also observed. Very active RE catalysts are obtained by reducing Pd/HY.

The conventional model of bifunctional catalysis assumes that the addition of protons of high Brønsted acidity to a catalyst exposing Pt or Pd sites opens an additional reaction path without, however, impairing the catalytic activity of the metal. We found, however, that proton-containing samples of Pd in zeolite Y, while catalyzing RE, display a distinctly *lower* turnover frequency (TOF) for RO than proton-free samples. This depression of the TOF for RO was consistently observed also at low conversion, where lowering of the MCP concentration by the prevailing RE reaction would not explain this phenomenon. The question that therefore arises is whether protons also act as *modifiers of metal sites* in zeolites. Previously, Dalla Betta and Boudart (*7*) had shown that Pt in some zeolites becomes "electron-deficient;" accordingly Homeyer *et al.* (*3, 5*) proposed that Pd clusters in zeolites form adducts with protons of the type $[Pd_n–H_z]^{z+}$. While the assumption that such adducts are less active than Pd_n clusters in catalyzing RO of MCP would explain the depression of the TOF for RO in samples with high proton concentration, an alternative explanation would be that one of the RE products, e.g., Bz, is strongly adsorbed on metal sites and therefore lowers the activity for RO. The present study attempts to discriminate between these models by identifying the intrinsic activity for RO of Pd in proton-containing samples in the absence of Bz.

Protons are formed during the reduction of Pd^{2+} ions with H_2; in this note reduced samples will therefore be denoted as Pd/NaHY, to distinguish them from samples where protons were neutralized, e.g., with NaOH. For low loadings of Pd the proton concentration in Pd/NaHY is much lower than in Pd/HY; we therefore speculate that Pd_n clusters and $[Pd_n–H_z]^{z+}$ adducts will coexist in Pd/NaHY, but the adducts will prevail in Pd/HY. Previous tests had shown that the initial RE activity of Pd/HY exceeds that of a physical mixture of Pd/NaY with HY by more than an order of magnitude (*5*).

We have chosen to adsorb MCP on the reduced catalysts, then to increase the temperature in a programmed manner while a gas flow is passed over the sample. The gaseous desorption products of this temperature programmed surface reaction (TPSR) were analyzed. Adsorption of MCP on a clean metal surface will be dissociative; associative desorption of the hexane isomers will require additional hydrogen atoms, in contrast to desorption of CH or Bz. Therefore TPSR studies were done in two modes: either in H_2 on H-covered surfaces, or in He on samples which, after reduction, had been cooled in He.

Pd/NaHY and Pd/HY catalysts were prepared by ion exchange. This was performed by adding a dilute solution (0.01 *M*) of $Pd(NH_3)_4(NO_3)_2$ (Strem Chemical, Lot No. 19167) dropwise to NaY or HY at room

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temperature. The NaY used was Linde LZ-52, of which the approximate unit cell formula is $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$. The HY used was Linde LZ-72, with approximate unit cell formula $H_{44.8}Na_{9.2}(AlO_2)_{54}(SiO_2)_{138}$. The solutions and slurries were prepared using doubly deionized water. This exchange led to a Pd loading on both zeolites of approximately eight Pd ions per unit cell (5 wt%). After being dried in air at room temperature (RT), the samples were calcined under a high flow (180 ml/min) of pure O_2 in a packed bed reactor at 1 bar. The calcination temperature was ramped at 0.5°C/min from RT to 500°C and held at 500°C for 2 h. After calcination, the samples were cooled to RT in helium (UHP, Matheson, USA; 30 ml/min) and reduced in H_2 (UHP, Matheson, USA; 20 ml/min). The reduction temperature was ramped from RT to 350°C at 8°C/min and kept at 350°C for 20 min.

The TPSR experiments were carried out in a flow reactor with an on-line HP 5794 gas chromatograph and an FID detector. After reduction, the 500-mg samples were cooled to RT either in H_2 or in He. Subsequently, MCP was adsorbed by passing a 16/1 H_2/MCP mixture or a 16/1 He/MCP mixture over the catalyst at RT for 20 min. Gaseous and physisorbed MCP were removed by purging with either pure H_2 or pure He at RT for 50 min. TPSR was accomplished by heating either in flowing H_2 or He, slowly raising the temperature from RT to 500°C. A heating rate of 2°C/min and a carrier gas (H_2 or He) flow rate of 20 ml/min were used. The gaseous products were analyzed by GC.

Our previous observations have been confirmed (see Ref. *5*) that a mixture of MCP + H_2 gives predominantly RO products over Pd/NaHY. Not surprisingly, MCP + He shows little hydrogenolytic RO and also a low rate of RE. Over Pd/HY the TOF for RE is very large, but the TOF for RO of the MCP + H_2 mixture is found to be 19 times lower than over Pd/NaHY, which confirms again the negative effect of high proton concentration on the RO activity. The RE/RO ratio on Pd/HY is 35. Remarkably, the TOF for RE over this catalyst is three times larger for MCP + He than for MCP + H_2.

Desorption products of MCP surface reaction in He after adsorption on samples reduced at 350°C and cooled in He show the expected results: with Pd/NaHY only MCP and Bz are desorbed with peak temperatures T_D of 125 and 250°C, respectively. With Pd/HY, however, both RE products are detected; the T_D values are 125°C for MCP, 175°C for CH, and 220°C for Bz. It is conceivable that the large proton concentration favors ring enlargement via carbenium ions, followed by hydride ion transfer, resulting in CH.

Of greater relevance to the problem motivating this study are the TPSR profiles obtained from experiments where H_2 is used after adsorbing MCP on samples that had been cooled in H_2. These profiles are presented in Figs. 1 and 2. With Pd/NaHY all RO products are detected in addition to MCP. Peak integration shows that the products are formed in a ratio of 3MP/2MP/*n*H = 1.0/2.0/2.1 in good agreement with the statistical ratio and the value found by Gault (*8*) for highly dispersed metals. Indeed recent EXAFS results by Zhang *et al.* (*9*) show that the Pd clusters in our Pd/NaHY samples consist of six Pd atoms.

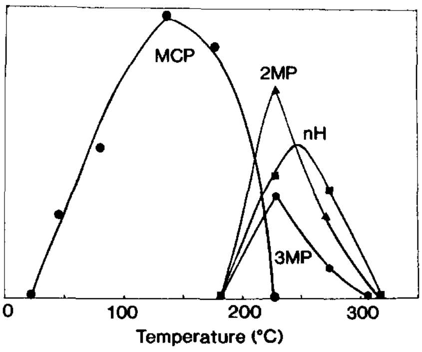

FIG. 1. TPSR profile of MCP on Pd/NaHY in H_2. In comparison to MCP, the intensities of 2MP, 3MP, and *n*H were multiplied by 80.

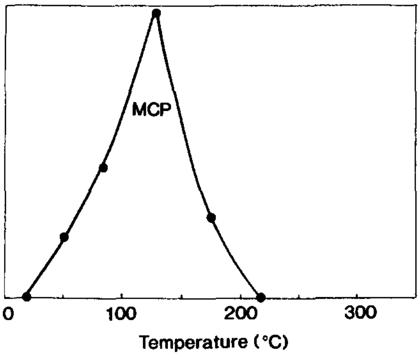

FIG. 2. TPSR profile of MCP on Pd/HY in H_2.

The TPSR profile for Pd/HY in Fig. 2 differs markedly from the profile for Pd/NaHY in Fig. 1: neither RE nor RO products are detectable with Pd/HY.

The absence of RE can be rationalized by accepting that pseudocarbenium ions, that are formed by addition of an olefin to either a proton or a $[Pd_n–H_z]^{z+}$ adduct, will be in equilibrium with the olefin. The concentration of olefins will, however, be much lower in flowing H_2 than in flowing He.

The key observation of this study is the absence of RO products with Pd/HY, in striking contrast to their abundance with Pd/NaHY. This result matches the 19 times lower RO activity of Pd/HY found in the catalytic test. However, in the TPSR test no Bz is present, so that Bz adsorption is eliminated as a possible cause of different RO activity. We therefore have to conclude that the metal sites are modified by the high proton concentration in Pd/HY. This conclusion is consistent with the view that in HY virtually all Pd_n clusters have been transformed into $[Pd_n–H_z]^{z+}$ adducts.

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