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Demanding and Structure-Insensitive Nature of Ethane–Deuterium Exchange Reaction

Boudart *et al.* (*1*) were the first to introduce the term "demanding reaction" on the basis of very large differences between the activities of different metals for a given reaction. Later, the principle of "structure-sensitive" reaction was introduced (*2*) based upon the effect of particle size on the activity of a given metal for a given reaction. Recently Frennet *et al.* (*3*) conceptualized the distinction between demanding and structure-sensitive reactions. In this sense structure sensitivity is related to the structure of active sites, i.e., to the arrangement of surface atoms, whereas the demanding character of a reaction is devoted to a hydrogen pressure- and temperature-dependent factor, *G*, derived from the "multiple adsorption site" theory (*4, 5*). This factor includes the coverages in equilibrium with the gas phase and their change may be responsible for the large differences displayed in the activity of the various metals.

According to this classification the demanding reaction may be structure sensitive, such as that for ethane hydrogenolysis on Pt/SiO_2 (*6*), and structure insensitive. The isotope exchange between deuterium gas and alkane, which is considered a demanding reaction (*7, 8*), can be included among the latter, because it does not depend on the change in particle size, as has been found for cyclohexane–D_2 exchange on Pt/SiO_2 catalyst (*6*).

Here, we furnish more evidence for the exchange being structure insensitive in character. Ethane was chosen as a model substance, the hydrogenolysis of which is demanding and structure sensitive while its exchange with deuterium can be expected to be structure insensitive, similarly to cyclohexane exchange.

Platinum was deposited on silica gel (SAS Scientific, England; BET surface area is 560 m^2/g) with very small pores (pore volume below 7 nm is about 0.95 ml measured by hydrogen adsorption) and on Cab-O-Sil HS5 (Cabot Corporation, Mass.; BET surface area is 325 m^2/g and the average particle diameter is 5 nm without pore system) by the ion exchange method (*9*). The catalysts were calcined in oxygen (5 liter/hour) at 573 K for 1 h, and were reduced in a stream of hydrogen at 773 K for 3 h. Between runs the catalyst was treated with 6 kPa oxygen followed by reduction in 6 kPa D_2. The reaction was carried out with a 1 : 10 ethane–deuterium mixture in a static circulation reactor, which was connected to an AEI MS 10 C2 mass spectrometer via a capillary leak. The initial rate of exchange was always calculated and correction was made for the naturally occurring ^{13}C and for fragmentation.

The experimental results are presented in Table 1.

There is fair agreement between N_T values measured on Pt/SiO_2 catalyst of the two dispersions. Regardless of the temperature range used the activation energies, as well as the order of reaction with respect to deuterium, gave the same values. This result undoubtedly proves that the rate of exchange of ethane is not dependent on platinum dispersion similarly to cyclohexane exchange. It can therefore be considered a structure-insensitive reaction.

It is remarkable that the change from silica gel to Cab-O-Sil causes N_T to de-

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TABLE 1

Kinetic Data on Ethane–D_2 Exchange on Pt/SiO_2 and Pt/Cab-O-Sil Catalysts

Catalyst	Dispersion[a]	Temp. range (K)	N_T[b] (at 368 K)	E (kJ mol^{-1})	b[c]
1 wt% Pt/SiO_2	32.5	323–352	3.7×10^{-4}	74.1 ± 2.7	-0.29 ± 0.01
1 wt% Pt/SiO_2	1.0	383–403	3.5×10^{-4}	74.1 ± 2.7	-0.32 ± 0.02
1 wt% Pt/Cab-O-Sil	21.5	383–403	1.2×10^{-5}	71.6 ± 1.1	-0.58 ± 0.01

[a] Measured by hydrogen–oxygen titration.

[b] N_T is the turnover number expressed in mol s^{-1} $site^{-1}$ units.

[c] b is the deuterium exponent in the rate equation, $r = kp^a_{C_2H_6}p^b_{D_2}$.

crease to a value which is 30 times less than that on Pt/SiO_2. Although both supports are silica gel the structure of platinum particles, even at the same dispersion, may be different as far as the deuterium coverage is concerned. According to Frennet's idea the activity revealed in ethane–deuterium exchange is influenced by the deuterium coverage; thus, the different activity should be connected with a different deuterium exponent, which is, indeed, the case (see last column in Table 1). These experiments provide evidence that the terms "demanding" and "structure sensitive" cannot be used interchangeably. However, demanding reactions can be further classified into "structure sensitive" and "structure insensitive." Ethane hydrogenolysis and exchange is a good example for this classification.

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