Heats of Adsorption of Propylene and Oxygen on a Bi–Mo/SiO_2 Oxide Catalyst

In two recent articles on Bi–Mo and Bi–Mo/SiO_2 oxide catalysts (*1*, *2*), we determined the amount of adsorption of propylene and oxygen and the heats of adsorption. We have now repeated certain measurements in more detail, especially those which were estimated by the calorimetric method at 170°C when the adsorption of propylene is followed by its slow oxidation. Heats evolved during adsorption in our earlier work (*2*) were determined for relatively large doses so that in the case of their dependence on surface coverage they would represent mean values. In the new work reported here, we have studied the changes of these heats for proplene and oxygen with the coverage (reduction or reoxidation) of the surface.

The determination was performed at 170°C by means of a calorimeter of the Wittig type (*3*) connected to a volumetric adsorption apparatus. The equipment and method, including the catalyst and the gases employed were as described earlier (*2*).

In the previous work (*2*) we determined the heat evolved during the adsorption of propylene for one dose of 8–9 μmol/g_{cat}. To obtain good reproducible values it was not possible to divide this dose into more than two smaller doses. The decrease of the pressure of propylene during the adsorption at 170°C for the individual doses was approximately the same as in Fig. 3 of Ref. (*2*). The heat evolved during the adsorption of propylene for the first dose is 28 kcal/mol and for the second dose is 13 kcal/mol (Fig. 1a). The mean (integral) value of the heat for both doses, i.e., for the adsorption of 9 μmol/g_{cat}, is 19 kcal/mol. This value comes close to the 22.3 kcal/mol determined previously for the dose of 8–9 μmol/g_{cat} (*2*).

After the adsorption of propylene was terminated the catalyst was evacuated for 30 min at the same temperature and the adsorption of oxygen was estimated in three doses. The heat of adsorption of oxygen decreases with the coverage (reoxidation) of the surface of the catalyst from 93 to 36 kcal/mol (Fig. 1b). It is very interesting that the value of the heat of adsorption of 93 kcal/mol for the first dose, is according to the tables (*4*), nearly the same as the values of the heat of reaction for $MoO_2 + \frac{1}{2}\ O_2 = MoO_3$ (100.8 kcal/mol O_2) and for $2\ Bi + 3/2\ O_2 = Bi_2O_3$ (92 kcal/mol O_2).

The heats given in Fig. 1a and 1b were determined with an accuracy of 10%. The adsorption of propylene on the carrier component of the catalyst is assumed to be negligible.

The estimated values of the heat of adsorption refer to a very low degree of the surface coverage. When we use the idea (*5*) that 1 m^2 of the active constituent (Bi–Mo oxide) on the surface contains 6×10^{18} atoms (i.e., 5×10^{-6}mol O_2), then our doses of propylene and oxygen are adsorbed only on a very small part of the active surface. If we suppose that the participation of the active substituent in the surface is the same as in the bulk, then the coverage of the surface is about 6%. Because the heat of adsorption decreases for this coverage very strongly, it is very important for the reproducibility of the measurement to activate the catalyst in exactly the same conditions.

Our results can be considered as a supplement to the results described in the previous work (*2*). They throw further light on the fact that the selectivity of the catalyst is changed during the oxidation of propylene in the absence of gas-phase oxygen (*6*). From the point of view of the adsorption of propylene and oxygen, the

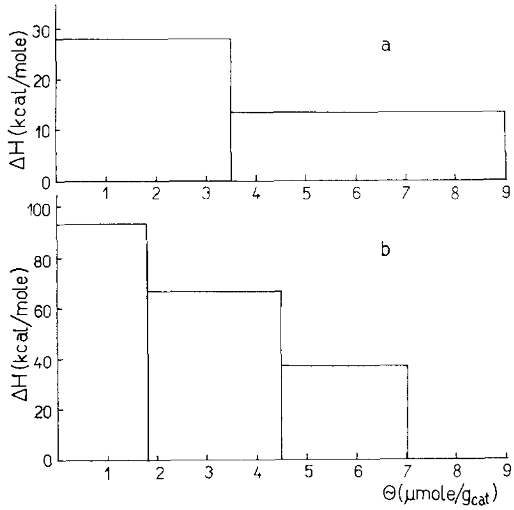

FIG. 1. Dependence of heat of adsorption of propylene (a) and oxygen; (b) on the occupation of the surface of Bi-Mo/SiO_2 oxide catalyst at 170°C.

surface of the catalyst is heterogeneous. The oxidation of propylene starts on the most active part of the surface and reduces it. In the presence of the gas-phase oxygen, this part of the surface is regenerated, but in the absence of the gas-phase oxygen the oxidation of propylene continues on parts of the surface, with more and more of a decrease in activity.

The heterogeneity of the surface was found also for the catalyst without a carrier [Fig. 5 of Ref. (*2*)]. In the range of 8% coverage of the surface the heat of adsorption of propylene at 35°C decreases from 12 to 7 kcal/mol.

From this point of view, the equations of the isotherm for a homogeneous surface cannot be used for the description of the adsorption of propylene on Bi–Mo/SiO_2 oxide catalysts.

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M. KŘIVÁNEK
P. JÍRŮ

Institute of Physical Chemistry
Czechoslovak Academy of Sciences,
Prague, Czechoslovakia
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Relative Importance of Intraparticle and Interphase Heat Transport in Gas–Solid Catalysis

Two criteria have been developed to indicate the relative importance of intraparticle and interphase temperature gradients in catalytic reactors. We undertake in this note to evaluate these criteria, compare typical values for different types of catalytic reactors, and compare this result with actual experiments in which temperature differences associated with catalyst pellets have been measured.

Carberry (*1*) showed that in order for interphase heat transfer effects to predominate over intraparticle effects,

$$hd_p/\lambda < 1, \qquad (1)$$

where h is the gas–solid heat-transfer coefficient, d_p the particle diameter, and λ the effective thermal conductivity of the particle. For the same situation, Mears (*8*) developed the criterion,

$$hd_p/\lambda < 10. \qquad (2)$$