lished later, we report now some new interesting data on this catalytic system. Kinetic data were obtained by the differential reactor technique.

During this research we have found a marked inhibiting effect of H_2O on the reaction rate, especially at lower H_2O partial pressures. In Fig. 1 the reaction rate is plotted versus the partial pressure of H_2O for fixed values of the reactants partial pressure and catalyst temperature. The partial pressure values are the mean ones between the inlet and the exit of the differential reactor. The catalyst temperature in the bed was constant within ±0.5°C. We have obtained also similar behavior for other values of these parameters.

These experimental results may be explained in terms of competitive adsorption of H_2O with CH_3OH on free active catalyst surface. Surface acidity seems to be necessary for the reaction to go on (*7*); therefore we may explain competitive adsorption in terms of higher basicity of H_2O than CH_3OH.

Indeed the retention time of CH_3OH in a chromatographic catalyst column is lowered by the presence of H_2O (*8*).

It is possible to explain why the influence of H_2O on the reaction rate was not found by previous workers. Jiru *et al.* obtained their data by means of recycle reactors, therefore at rather high H_2O concentrations. As may be seen from Fig. 1, at high partial pressures the relative effect of water is rather small and probably of the order of magnitude of experimental errors.

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N. PERNICONE
F. LAZZERIN
G. LANZAVECCHIA

G. Donegani Research Institute
Montecatini Edison S.p.A.
Novara, Italy

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Application of the Power Rate Law to the Compensation Effect Observed in Propylene Oxidation over Metal Oxides

The compensation between the activation energy E and the pre-exponential factor A for a given reaction over a series of related catalysts, has been reported with many systems (*1*). It is usually of the form

$$\log A = mE + C \qquad (1)$$

and is referred to as the compensation effect. Some interpretations for this effect have been offered (*2*), whereas none of them can be a sole interpretation. We wish to report here briefly an instance in which the Power Rate Law (*3*) is successfully applied to the compensation effect observed in the oxidation of propylene over a series of metal oxides.

In a previous study of the catalytic oxidation of propylene (*4*), the authors determined the activation energies, pre-exponential factors, and reaction orders over a series of metal oxides. As already reported (*4*), the variations of the activation energy and pre-exponential factor are accompanied by variations in the reaction orders. Mostly the order in propylene varies between zero and unity and that in oxygen between zero and 0.5, which suggests the slow step of the reaction between adsorbed propylene and adsorbed oxygen atoms. The relationship between the activation energy and pre-exponential factor is shown in Fig. 1, where those cases of oxygen orders higher than 0.6 are omitted. This omission may be reasonable because the slow step of the reaction might be different in these cases, while the compensation effect should be discussed with those reactions with the same slow step. The higher oxygen order might have resulted from the slow step of oxygen adsorption.

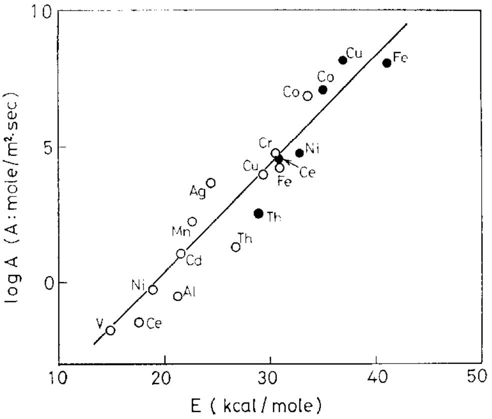

FIG. 1. Compensation effect in the oxidation of propylene: ○, low concentration of propylene; ●, high concentration of propylene.

On the other hand, according to Van Reijen and Schuit (*3*), a pre-exponential factor and an activation energy for the bimolecular reaction between A and B on a catalyst surface are expressed as follows:

$$A = \frac{kT}{h}\left[P_A \exp\left(\frac{\varphi_A^\circ}{R}\right)\right]^m \left[P_B \exp\left(\frac{\varphi_B^\circ}{R}\right)\right]^n \qquad (2)$$

$$E = \epsilon' + m\Delta h_A^\circ + n\Delta h_B^\circ$$

$$\epsilon' = h_X - a h^\circ_{A,\mathrm{ads}} - b h^\circ_{B,\mathrm{ads}} \qquad (3)$$

where P denotes the partial pressure, φ the free energy function in gaseous state; m and n, the reaction orders; Δh°, the standard heat of adsorption; h°, the standard enthalpy of adsorbed species; a and b, the stoichiometric numbers. The suffixes A and B denote the reactants A and B, and X, the activated complex. While the derivation of Eq. (2) and (3) by Van Reijen and Schuit is fairly complicated, these equations are easily obtained by differentiating the Langmuir type of rate equation by $(-1/RT)$, which is the conventional process of determination of activation energy. In this treatment the free energy function of adsorbed species is neglected as compared with that of gaseous species.

The calculated pre-exponential factors A_{cal} are obtained from the observed reaction orders and the free energy functions of propylene and oxygen according to Eq. (2) and are plotted against the observed pre-exponential factors A_{obs} in Fig. 2. It can be seen that a linear relationship exists between two pre-exponential factors, though the values for A_{obs} are expressed by mole per unit area of catalyst surface per second and A_{cal} by molecules per site per second. This linearity suggests that the Power Rate Law is applicable to the compensation

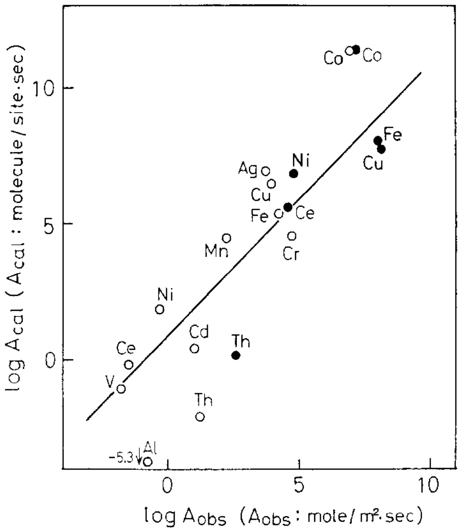

FIG. 2. Correlation between the calculated pre-exponential factor A_{cal} and the observed pre-exponential factor A_{obs}.

effect accompanied by the variation in reaction orders.

If this is the case, observed variation of activation energy must be explained by Eq. (3), whereas the verification of Eq. (3) encounters a difficulty in estimation of the heats of adsorption $\Delta h_A°$ and $\Delta h_B°$ under the reaction condition. In this respect the determination of heat of adsorption during the reaction will be helpful for the elucidation of the compensation effect.

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YOSHIHIKO MORO-OKA
ATSUMU OZAKI

Tokyo Institute of Technology
Ohokayama, Meguro-ku
Tokyo, Japan

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The Role of a Metal–Oxygen Double Bond in the Activity of Molybdates in Oxidation Reactions[*]

We have studied the catalytic behavior of several molybdates in the oxidation of NH_3 and of propene. The kinetic measurements were made by a pulse microreactor with a chromatograph in series, in the range of temperature between 300° and 500°C. The data of activity are reported in Table 1. The same table reports the IR bands of the molybdates in the 900–1000 cm^{-1} region.

The table suggests that the molybdates studied may be classified depending on the nature of IR spectra:

(a) molybdates presenting bands between 940–970 cm^{-1}; these are molybdates of transition metals;

(b) molybdates presenting bands between 900–930 cm^{-1}; Al and Bi molybdates belong to this class;

(c) molybdates that do not present characteristic bands in the region between 900 and 1000 cm^{-1}; calcium, lead, and thallium molybdates belong to this class.

The characteristic spectra of the three classes are reported in Fig. 1.

The catalysts of the first and second class are active in the oxidation of propylene and ammonia, while those of the third class are practically inactive. Besides, the same catalysts that are active for the oxidation of ammonia and propylene are also active for the oxidation of methanol (*1, 2*).

It is known that in metal oxides and in mixed oxides, the presence of a band between 900 and 1000 cm^{-1} may be attributed to the presence of a metal–oxygen bond having properties of a double bond (*3, 4*).

From Table 1 it is seen that all the active molybdates have a metal–oxygen bond with double-bond character and the inactive ones have not this kind of metal-oxygen bond.

The greater activity of the molybdates with respect to the MoO_3 is accompanied by a shifting of Me═O to lower frequency.

Mars (*5*) had previously suggested that in the catalyst based on vanadium anhydride the most reactive oxygen is that bound to vanadium by a double bond. Subsequently (*6*) the promoting effect of

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