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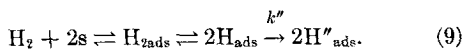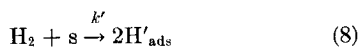*Dalhousie University*
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Methanation of CO on a Ni Catalyst

In a recent article (*1*) the methanation of CO on some Ni catalysts was studied. A mechanism was proposed, the rate of hydrogen adsorption being the rate determining step. The adsorption could take place in two ways in parallel:

$$H_2 + s \xrightarrow{k'} 2H'_{ads} \tag{8}$$

$$H_2 + 2s \rightleftharpoons H_{2ads} \rightleftharpoons 2H_{ads} \xrightarrow{k''} 2H''_{ads}. \tag{9}$$

The equation numbers refer to the numbers in the above article.

The methanation rate was determined by the rate with which hydrogen in the "active" states H'_{ads} and H''_{ads}, could be supplied to reaction with CO adsorbed on dual sites. With nearly all sites covered by CO and H_2 adsorbed on dual sites and Eq. (8) determining the rate, the rate equation became:

$$r_1 = k' p_{H_2}^{0.5} \Big/ \left(1 + A\, \frac{p_{CO}}{p_{H_2}}\right)^{0.5}, \tag{13}$$

and in the case of Eq. (9) determining the rate:

$$r_2 = k'' \Big/ \left(1 + A\, \frac{p_{CO}}{p_{H_2}}\right)^{0.5}. \tag{14}$$

In the previous article, the pressure dependence was tested in the range 1–15 atm absolute where, however, a single rate equation with $p_{H_2}^{0.15}$ in the numerator fitted as well with the experiments (within the experimental errors) as did the rate expressed by the sum of Eqs. (13) and (14) with the ratio $k':k'' = 1:4$.

New experiments with catalyst No. 1 in a pressure range extended to 110 atm have shown that the pressure dependence at high pressures actually approaches proportionality to the square root of the total pressure (at constant CO concentrations). Typical experiments with catalyst No. 1 are presented in Fig. 1; these experiments fit well with either of the rate equations:

$$r = 0.048(1 + 0.2\, p_{H_2}^{0.5}) \quad \text{i.e., } k':k'' = 1:4,$$

or

$$r = 0.041(1 + 0.25\, p_{H_2}^{0.5}) \quad \text{i.e., } k':k'' = 1:5.$$

Besides, the numerator activation energies at 1 atm and 90 atm were found to be nearly equal (24–26 kcal/mole) in the temperature range 220–270°C with catalyst No. 1 and 1% CO in H_2. This means that the ratio $k':k''$ is practically independent of the temperature.

The two hypothetical forms of active hydrogen, H'_{ads} and H''_{ads}, are possibly formed with different preference on different crystallographic planes and are dis-
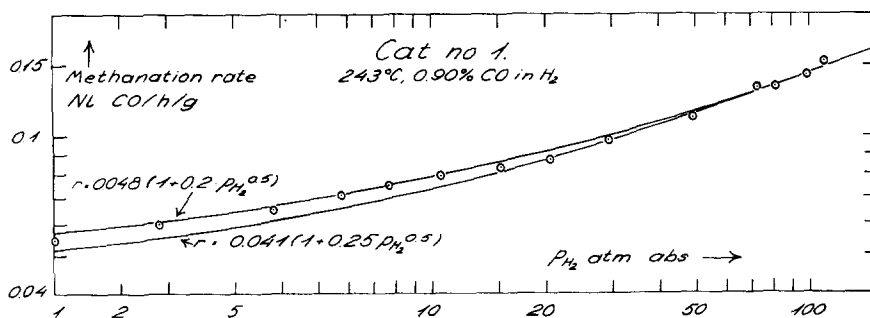
FIG. 1. Methanation rate on catalyst No. 1, reduced at 450°C. Temperature and gas composition kept constant at 243°C and 0.90% CO in H_2, respectively.

tinguished physically from one another. For this among other reasons, different values of the ratio $k':k''$ can be expected with different Ni catalysts.

We have also found that the rate of hydrogenation of ethylene on catalyst No. 1 is already large at about 60°C, which indicates that the adsorbed states H'_{ads} and H''_{ads} are not involved in this reaction.

It should be mentioned that Rideal, in a recently published book (2), described the finding by adsorption studies of three states of chemisorbed hydrogen on nickel similar to those proposed in reaction (9).

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Dissociation of *trans*-Dichlorobis(benzonitrile)palladium(II)

In a sequel to studies of intensities of IR C–N absorption bands and dipole moments of complexes of metals (1) extensive dissociation of *trans*-dichlorobis(benzonitrile)palladium(II) (1) in benzene solution was observed. While it was initially expected that dissociation of 1 should lead to benzonitrile and the Cl-bridged dimer, $[PdCl_2 \cdot C_6H_5CN]_2$, investigations of the system revealed other features of interest relevant to the use of 1 in the synthesis of organometallic complexes and as a homogeneous catalyst. Complex 1 is a homogeneous catalyst for reactions such as isomerization of olefins (2), olefin–acetylene addition-rearrangement (3) and cyclotrimerization of acetylenes (4).

EXPERIMENTAL METHODS

Reagent grade methylene chloride and benzene were refluxed over P_2O_5 and fractionated. Eastman white label benzonitrile and nitrobenzene were used without further treatment. *trans*-Dichlorobis(benzonitrile)palladium(II), (1) was prepared by the usual method (5). Anal. Calc. for $C_{14}H_{10}N_2Cl_2Pd$: C, 43.80; H, 2.63; N, 7.29; Cl, 18.5; Pd, 27.8. Found: C, 44.60; H, 2.70; N, 7.31, Cl, 18.5; Pd, 27.3. Mp. 110° dec.

Isolation of $PdCl_2$. A mixture of 155 mg of 1 and 10 ml of benzene was vigorously shaken for a few minutes and then filtered. The filtrate was allowed to stand overnight. A red-brown precipitate which formed was