

NOTES

Adsorption Studies on a Nickel/Alumina Methanation Catalyst

The frequent use of chemisorption techniques to monitor the area of supported metal and metal oxide catalysts is evident from recent reviews (1,2). To the skeptical mind, the critical question that must always be asked is: How well does this measurement correlate with actual performance? That is, does the amount of chemisorption correspond to the number of active sites, particularly for those situations where the adsorptions are measured under conditions considerably different from those of the actual catalytic process? Agreement for one process does not assure agreement in another, even though the catalyst is the same.

The work reported represents an important step in that hydrogen chemisorption on supported nickel catalysts at room temperature can be compared with the quantity of adsorption that occurs during an actual catalytic process. The process is the hydrogenation of carbon monoxide or methanation. Thermal gravimetric studies were performed on a Ni/Al₂O₃ catalyst in a mixture of CO and H₂. The adsorption studies were performed *in situ* at 1 atm pressure under temperature conditions of the methanation reaction. The plausibility of a relationship between the amount of CO-H₂ adsorbed, referred to as a "complex," and active sites will be developed. Furthermore, insight into the nature of the complex will be presented.

Methanation (3) is commercially carried out at pressures exceeding 20 atm. Furthermore, the precise nature of the adsorbed

complex is still questionable (4). In spite of these limitations, the data presented may be interpreted in a practical way and can lead to a useful screening tool. In addition, the effects on metal area variations due to various processing conditions which influence catalytic performance can be studied in the same reactor in which the measurements are made. Finally, this work gives insight into the nature of the adsorbed species and, hence, the rate-determining step.

A γ -alumina, fired in air at 700°C for 4 hr, was sized between 6 and 8 mesh. The BET nitrogen area was 170 m²/g. An aqueous solution of Ni(NO₃)₂·6H₂O was used to impregnate the support via the incipient wetness procedure. The weight losses due to decomposition were followed on a DuPont 951 thermal gravimetric analyzer with the associated 990 control. The proximity of the thermocouple was such that appreciable heat effects due to exothermic reactions in the catalyst bed could be observed. The nitrate-containing sample was heated in pure flowing hydrogen, 50-60 cm³/min, through a liquid nitrogen cold trap at 10°C/min to 230°C, at which point it was held for about 1 hr. This hold was necessary in order to prevent the highly exothermic reaction between hydrogen and the nitrate at about 260°C, which could cause thermal sintering of the nickel and/or support. Heating was then continued up to 480°C, where it was held until constant weight was obtained, about 30 min. While cooling to the temperature desired, the pure flowing hydrogen was re-

placed by a purified gas mixture of 8% H₂ and 92% N₂. When constant weight was obtained, a 10% mixture of research grade CO in N₂ was introduced such that the final ratio of H₂ to CO was 5 to 1. The total flow was about 100 cm³/min, and the level of CO was 1.38 mol%. Adsorption isotherms, similar to that shown in Fig. 1, were obtained at temperatures between 100 and 400°C in intervals of 50°C. The weight adsorbed at steady state was found by the intersection of extensions of the rising and level positions of the curve.

Metal areas, via H₂ chemisorption, were obtained at room temperature in a glass vacuum system. The system was equipped with a U-tube which would allow pretreatment gases to pass. The same reduction procedures mentioned above were used. After complete reduction, the sample was evacuated at 480°C for about 30 min and cooled under vacuum to room temperature. Hydrogen doses yielding pressures up to 10 cm Hg were found to be sufficient to generate the typical isotherm. The volume adsorbed at monolayer coverage was obtained by extrapolation to zero pressure. The slope of this line was close to zero, indicating little adsorption on the Al₂O₃ support. An assumption of one H atom adsorbed per exposed Ni atom was made (1).

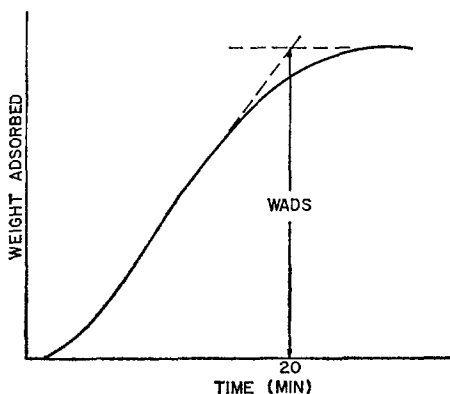


FIG. 1. Typical weight of "complex" vs time curve. H₂ to CO ratio of 5, 1.38 mol% CO; catalyst, Ni/Al₂O₃.

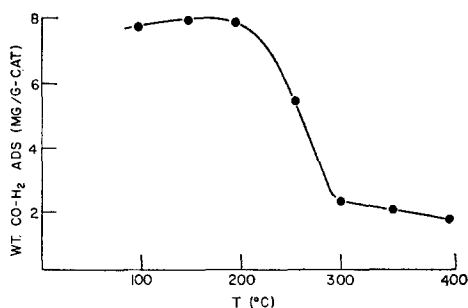


FIG. 2. Weight of "complex" at adsorption maximum vs temperature. H₂ to CO ratio is 5, 1.38 mol% CO; catalyst, Ni/Al₂O₃.

Figure 2 was generated by plotting the weight adsorbed on the catalyst surface at steady state for temperatures between 100 and 400°C. A gradual weight gain, i.e., activated adsorption, occurs up to 200°C. A rapid weight loss follows between 200 and 300°C. The amount of adsorption above 300°C appears more or less insensitive to temperature. Under a similar set of conditions, the amounts of CO consumed and hydrocarbon produced were monitored on a Beckman infrared detector and flame ionization detector, respectively. Appreciable reaction begins at about 200°C while almost complete conversion of CO is observed at 300°C. Therefore, a striking parallel is observed between the weight adsorbed between 200 and 300°C and the extent of CO consumption via hydrogenation. It is plausible to suggest the following surface conditions between these two temperatures: At 200°C, the surface reaction leading to products is slow enough that the surface is covered with the active methanation complex; as the temperature is increased, the reaction on the surface becomes competitive with the adsorption rate, and steady state coverage begins to decrease; at 300°C, the surface kinetics are so rapid that the lifetime of the active species adsorbed on the surface is quite low. In other words, the reaction is now adsorption-rate controlled with some possible diffusional influence. Maximum coverage

TABLE 1
Possible "Complex" Structure

Nickel (%)	Hydrogen adsorbed (mmol/g)	"Complex" weight ^a (mg/g)	Ratio (mmol "complex"/mmol H)		
			CO, H ₂	CH ₂	C
15.05	0.351	(7.72) 7.92	(0.73) 0.75	(1.57) 1.60	(1.83) 1.9
13.54	0.282	(5.98) 6.18	(0.71) 0.73	(1.51) 1.56	(1.77) 1.8
11.56	0.205	(4.74) 4.94	(0.77) 0.81	(1.65) 1.71	(1.93) 2.0
6.2	0.119	(2.77) 2.97	(0.78) 0.83	(1.66) 1.78	(1.94) 2.1
3.16	0.076	(1.85) 2.05	(0.81) 0.89	(1.74) 2.05	(2.03) 2.2

^a Values in parentheses are corrected for zero nickel; cf. extrapolation shown in Fig. 3.

occurs, therefore, at about 200°C, and the weight of "complex" adsorbed should be a good relative measure of active sites for methanation. The term "relative" must be used since, conceivably, not all adsorption has occurred on active sites and, furthermore, 100% selectivity to methane cannot be guaranteed.

To test the relationship between surface coverage and exposed nickel area, comparative experiments using adsorption of active "complex" and hydrogen chemisorption were made. Catalysts with nickel

loadings varying between 3 and 15% were used for the measurements. Table 1 summarizes the resulting data. Column 2, the hydrogen adsorption, is expressed as millimoles of hydrogen atoms per gram of catalyst. These data are to be compared with those shown in column 3, the weight of adsorbed "complex" expressed as milligrams per gram of catalyst. The relationship between these two quantities for the five levels of nickel is shown in Fig. 3. The linearity strongly suggests the existence of a CO-containing surface complex of definite stoichiometry. Since, because of their low atomic weight, hydrogen atoms are not recorded on this microbalance, one cannot exclude the possibility of some H adsorption alone on some sites. Table 1, in the last three columns, presents the ratios of millimoles of complex to millimoles of hydrogen atoms. The former is based on the assumption of a particular structure for the complex. The first of these three columns shows the ratio assuming a complex compound of a molecule of CO and two H atoms, i.e., H-C-OH. Values varying between 0.73 and 0.89 are indicated. If about 15–20% of the sites were occupied by only H atoms and the balance the complex, the ratios obtained are reasonable. If, however, one assumes either a CH₂ or C species as the active complex in the rate-determining step, the ratios are much greater than 1 and even exceed 2. Two CH₂ groups per Ni

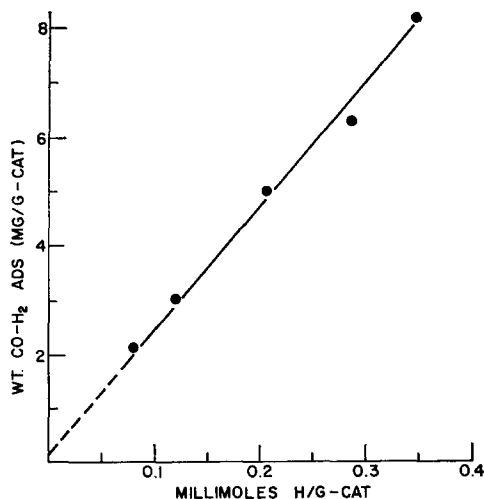


FIG. 3. Weight of "complex" at maximum vs hydrogen consumption. Complex weight measured at 200°C, H₂ to CO ratio is 5, 1.33 mol% CO; catalyst, 15% Ni/Al₂O₃; hydrogen adsorption at room temperature.

atom would be unlikely since hydrocarbons with carbon numbers greater than one are infrequently found (3). For the same reason, one would hesitate to predict that C is the active species. Furthermore, the ratio of two C per Ni atom is contrary to the assumption made by Gaidai and Kiperman (5) of one C/one Ni in their studies of the catalytic hydrogenation of carbon on nickel. The possibility of carbide formation being important in the methanation reaction is unlikely, since the rate of methane formation exceeds that of carbide formation (4).

A number of authors has studied the nature of the "complex" (6-11), but universal agreement still does not exist. The situation for Fischer-Tropsch catalysts is better understood (12-14). Based on the ratios reported in Table 1 for millimoles of complex to millimoles of H atoms and the likelihood that dehydration is probably slower than hydrogenation, this author suggests the major adsorbed species is of an enolic nature, i.e., H-C-OH.

The results presented in this note suggest a mechanism and a structure for the adsorbed species for methanation on supported nickel. Additional value should be found in using the techniques described to monitor surface behavior either during or after process parameter variations, i.e., thermal sintering, poisoning, or accessibility of the reactants to the catalyst surface.

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