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Studies of Supported Metal Catalysts

II. The Effect of Dispersion on Methane–Deuterium Exchange Over Supported Nickel

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The exchange reaction between methane and deuterium has been studied over a series of nickel–silica catalysts. Meaningful reaction rates were obtained between 225 and 250°C on impregnated catalysts which varied from 2 to 50% nickel by weight. Multiple exchange was promoted by increased reaction temperature and increased nickel crystallite size. The apparent activation energy of the stepwise and multiple exchange reactions proved to be a function of nickel crystallite size: for the stepwise reaction the apparent activation energy increased from 12 to 27 kcal/mole with increasing crystallite size; the multiple exchange activation energy showed a corresponding increase from 20 to 33 kcal/mole.

INTRODUCTION

Recently there has appeared in the literature several reports which show concern with the important problem of dispersion and its effect on the catalytic properties of supported metals. The pioneering work in this area was accomplished by Yates, Taylor and Sinfelt (*1*) who studied the specific activity for the hydrogenolysis of ethane as a function of particle size. For 10% nickel on silica, these workers found that specific activity was insensitive to particle size; however, in later work (*2*) on dilute nickel catalysts they did discover such a dependence. Subsequent to this work a large number of reactions have been studied in an effort to correlate crystallite sizes to specific activities. These reactions include various catalytic oxidations (*3*, *4*), hydrogenations and dehydrogenations (*5–8*), and isomerizations (*9*). In a majority of cases it was found that specific activities were insensitive to crystallite size and to the manner in which the surface was prepared. The term *facile* (*5*) was coined to characterize these reactions while reactions whose specific activities were dependent on crystallite size and surface preparation were termed *demanding*.

In addition to changes in specific activities a relatively small number of reactions have been studied which show a selectivity dependence on crystallite size. Reactions showing such a dependence have for the most part involved rather complex molecules which possibly interact with the support in a subtle way, stereochemical considerations being of primary importance. In particular Boudart *et al.* (*9*) have shown that the ratio of the rate of neopentane isomerization to that for hydrogenolysis is sensitive to crystallite size.

In this investigation we chose to study the effect of crystallite size on the methane–deuterium exchange reaction. We felt that in addition to being fairly well characterized (*10–21*) this reaction should not be subject to stereochemical and geometric considerations to the extent of other reactions studied. Moreover, since this reaction possibly involves several different adsorbed "methane" species the likes of which may be sensitive to surface structure, it might

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prove to be a superior probe to study surface properties.

Supported nickel was chosen in view of results (*10, 18*) reported in the literature which show that nickel films catalyze multiple exchange (i.e., more than one deuterium incorporated into the methane per period of residence on the surface) rather than stepwise exchange. It has also been shown (*18*) that this reaction displays insensitivity to nickel film surface structure. We hoped that studies on very small nickel crystallites might demonstrate stepwise exchange and/or sensitivity to surface structure.

METHODS

Except for the following discussion the methods and materials used in this work have been described previously in this series (*27*). Ultrapure methane (99.97%) used in these exchange experiments was obtained from the Matheson Co.

After reduction at 400°C hydrogen was removed from the catalyst surface as before. Then the reactor was brought to the appropriate reaction temperature at which time a standard mixture of reactants consisting of a methane/deuterium molecular ratio of 2:1 was rapidly admitted and immediately circulated over the catalyst. In addition, the total pressure in the reaction loop was quickly adjusted to an initial pressure of 50 Torr.

Gas phase analysis was conducted initially at regular intervals to determine initial reaction rates, then irregularly until equilibrium was attained, usually at 24 hr, on a CEC (Du Pont) model 21-104 mass spectrometer equipped with an electron multiplier. The *m/e* peak for residual water and its mass spectrometer produced fragments were adequately resolved from the *m/e* 18, 17, and 16 peaks, respectively. After correcting for naturally occurring carbon-13, the fragmentation corrections were applied in accordance with patterns reported by Schissler, Thompson and Turkevich (*22*). All processing of raw data was accomplished by appropriately programming an IBM 360/50 computer.

No noticeable change in nickel surface area was observed between successive experiments and surface area measurements.

RESULTS AND DISCUSSION

On the assumption that each hydrogen atom of a methane molecule is equally available for exchange, the initial methane–deuterium reaction rates were evaluated using the first order rate equations previously described by Kemball (*24*). If k_ϕ is the rate constant for the appearance of deuterium in the methane, one has

$$-\log_{10}(\phi_\infty - \phi) = \frac{k\phi t}{2.303\phi_\infty} - \log_{10}\phi, \quad (1)$$

where ϕ is defined by

$$\phi = \sum_{i=1}^{4} ix_i, \quad (2)$$

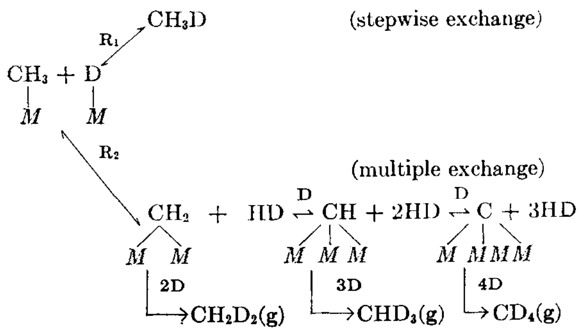
where x_i is the percentage of the species containing i deuterium atoms and ϕ is the equilibrium value of ϕ.

A second first order rate constant k may be used to define the rate of disappearance of *light* methane. One has then

$$-\log_{10}(x - x_\infty) = \frac{kt}{2.303(100 - x_\infty)} - \log_{10}(100 - x_\infty) \quad (3)$$

where x and x_∞ are percentages of CH_4 in the gas phase at time t and equilibrium, respectively.

If only one hydrogen atom is replaced during each period of residence of a methane molecule on the surface and if no isotope effect is considered, it is apparent that $k = k_\phi$ provided we consider only low total conversions. In general two different mechanisms for exchange are found for hydrocarbons on metal surfaces: stepwise for which $k = k_\phi$, and multiple exchange in which more than one deuterium is incorporated during each period of residence. In the case of multiple exchange it is evident that $k \neq k_\phi$ and it is useful to define a new parameter M, such that $k_\phi = Mk$, where M essentially represents the number of hydrogen atoms replaced during each period of residence on the surface. A reasonable mechanism (*10–12*) for stepwise and multiple exchange is shown below



Prior to conducting the exchange reaction on the nickel–Cab-O-Sil catalysts, we performed a preliminary experiment in which a methane–deuterium mixture was circulated over Cab-O-Sil. As the temperature was increased, the gas phase was monitored for possible methane–deuterium exchange, and a very slow stepwise exchange appeared at 300°C. This is somewhat below the temperature, 600°C, as reported by Larson and Hall (*25*) for a similar exchange. Our nickel catalyzed methane–deuterium exchange investigation was conducted at 250°C, or lower, thereby eliminating possible catalytic effects of the support. Typical results for exchange reactions conducted at 250°C on catalysts having different crystallite sizes are shown in Figs. 1 and 2. For a 2% nickel catalyst it is apparent that stepwise exchange is initially dominant with only trace amounts of CD_4, CHD_3, and CH_2D_2 being formed. On the 50% nickel catalyst multiple exchange is initially dominant. The corresponding M values are 1.79 ± 0.2 and 3.3 ± 0.2, respectively. We have reported uncertainties in M values of ± 0.2 as we found them to be rather sensitive to equilibrium values of ϕ.

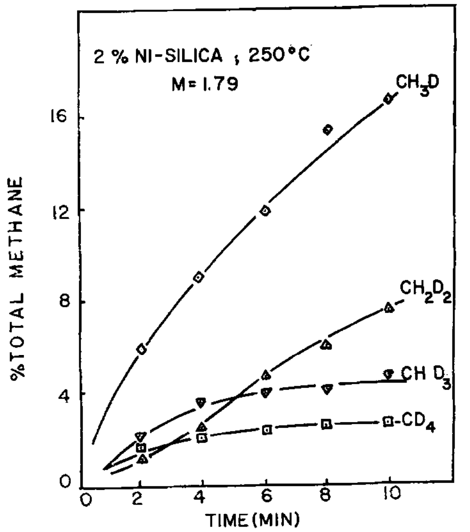


FIG. 1. Methane–deuterium exchange on 2% nickel-Cab-O-Sil. Initial rates shown.

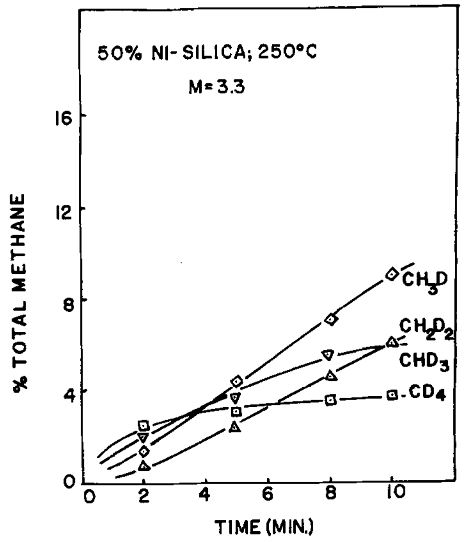


FIG. 2. Methane–deuterium exchange on 50% nickel-Cab-O-Sil. Initial rates shown.

The results obtained on the 50% nickel catalyst compare favorably with those (*10*, *13*, *18*) obtained on nickel films. It is also interesting to note that in both previous investigations CD_4 predominates as an initial product and all deuterated species are not always initially present. In our study, however, a considerably larger amount of

CHD_3 was formed and we found *all* deuterated species present initially.

Our studies on the 2% nickel catalyst are in striking variance to those obtained on nickel films. Anderson and MacDonald (*18*) have shown the substitution of deuterium in methane to be rather insensitive to surface structure with little or no difference in M values for [111], [100] or randomly deposited crystal planes. We find a definite correlation between M values and dispersion. Table 1 summarizes the effect of dispersion on M values for reactions conducted at 225 and 250°C. That the rate of exchange is a function of both temperature and dispersion is apparent.

The effect of crystallite size on apparent activation energy is also summarized in Table 1. The activation energy E_s for stepwise exchange is computed from the initial appearance rate of CH_3D. The initial rate of formation of CH_2D_2, CHD_3 and CHD_4 were considered collectively in computing the apparent activation energy E_m for multiple exchange. Justification for this is based on evidence reported in the literature (*10–13*) that there are only two operating mechanisms. Activation energies for both multiple and stepwise exchange increase with particle size; however, $E_m - E_s$ exhibits a decreasing trend from the 2% catalyst to the 50% catalyst, thereby explaining why multiple exchange occurs at lower temperatures on larger crystallites and metal films. Activation energies on the 50% nickel catalysts are in agreement with results (*10*, *13*, *18*) obtained on nickel films.

Reasons for changes in activation energies with particle sizes might be severalfold. One, for example, might expect that as crystallite size decreases the number of adjacent sites per particle necessary for multiple exchange would decrease. The smaller crystallite cubes also contain many more nickel atoms located on either edges or corners possibly invoking a stereochemical hindrance to a methane molecule exchanging with more than one adsorbed deuterium atom. It has also been suggested (*15*) that the stepwise/multiple exchange mechanisms could be a function of the metal atomic radius. A fair correlation between the rates of the two mechanisms and the lattice parameters show that Pt, Pd, and W (1.38, 1.37, 1.37 Å, respectively) promote the stepwise mechanism whereas Ni, Rh, Ru (1.24, 1.34, 1.32 Å, respectively) with smaller radii, promote multiple exchange. The smaller radii of the latter metals are thought to permit the methane to adsorb more easily as methylene, methyne, or even as a carbon atom. Since we have shown that nickel can promote both stepwise and multiple exchange (dependent upon crystallite size) we feel that the role of lattice parameters is somewhat less than previously thought.

Having considered geometrical factors, one should next review the possible contribution of the electronic properties of the

TABLE 1

Effect of Crystallite Size on Apparent Activation Energy

Wt % Ni	Av crys size (Å)	M 225/250°C (±0.2)	E_s (kcal/mole)	E_m (kcal/mole)	$E_m - E_s$ (kcal/mole)
2	19	1.66/1.79	12 ± 2	20 ± 2	8
10	30	1.83/2.65	15 ± 2	18 ± 2	3
23	44	2.06/2.97	16 ± 2	20 ± 2	4
50	140	2.30/3.10	27 ± 3	33 ± 3	6
100[a]	—	—	24	32	(8)
100[b]	—	2.88/3.05 (242/251°C)	—	43 ± 2	
100[c]	—	—	24	33	(9)

[a] Kemball, C., *Proc. Roy Soc., Ser. A* **207**, 539 (1951) (*10*).

[b] Anderson, J. R., and MacDonald, R. J., *J. Catal.* **13**, 345 (1969) (*18*).

[c] Markham, M. C., Wall, M. C., and Laidler, K. J., *J. Phys. Chem.* **57**, 321 (1953) (*13*).

metal. The ferromagnetic properties of bulk nickel are believed to be the result of parallel coupling of d-band electrons. Magnetization studies (*23*, *26*) have shown that these ferromagnetic properties disappear in smaller nickel crystallites. The gradual disappearance of ferromagnetism in the smaller crystallites is the result of the larger fraction of surface atoms present so that the parallel coupling of d-band electrons is incomplete. We have shown that the catalytic properties of small nickel crystallites are related to their size; and if the electronic properties are also a function of size, there could be a correlation with the overall catalytic properties of the metal.

There also exists the possibility that the metal crystallites contain surface defects or active sites the concentration of which may be a function of crystallite size. This effect, alone, could account for the trends we have observed.

Finally we should remember that there exists a size distribution among the crystallites of a supported metal catalyst. Certainly in this environment we would expect to find a correlating distribution of the factors we have discussed, and not until we can produce a supported catalyst with only one size crystallite will we be able to isolate these factors.

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REFERENCES

1. YATES, D. J. C., TAYLOR, W. F., AND SINFELT, J. H., *J. Amer. Chem. Soc.* **86**, 2996 (1964).
2. TAYLOR, W. F., SINFELT, J. H., AND YATES, D. J. C., *J. Phys. Chem.* **69**, 3857 (1965).
3. BORESKOV, G. K., AND CHESALOVA, V. S., *Zh. Fiz. Khim.* **30**, 2560 (1956).
4. BORESKOV, G. K., SLIN'KO, M. G., AND CHESALOVA, V. S., *Zh. Fiz. Khim.* **30**, 2787 (1956).
5. BOUDART, M., ALDAG, A., BENSON, J. E. DOUGHARTY, N. A., AND HARKINS, C. G. *J. Catal.* **6**, 92 (1966).
6. POLTORAK, O. M., AND BORONIN, V. S., *Zh. Fiz. Khim.* **40**, 2671 (1966).
7. DORLING, T. A., AND MOSS, R. L., *J. Catal.* **5**, 111 (1966).
8. POLTORAK, O. M., AND BORONIN, V. S., *Russ. J. Phys. Chem.* **39**, 1329 (1965).
9. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
10. KEMBALL, C., *Proc. Roy. Soc., Ser. A* **207**, 539 (1951).
11. KEMBALL, C., *Proc. Roy. Soc. Ser. A* **217**, 376 (1953).
12. THOMPSON, S. O., TURKEVICH, J., AND IRSA, J. P., *J. Amer. Chem. Soc.* **73**, 5213 (1951).
13. MARKHAM, M. C., WALL, M. C., AND LAIDLER, K. J., *J. Phys. Chem.* **57**, 321 (1953).
14. KLEMPERER, D. F., AND STONE, F. S., *Proc. Roy. Soc. Ser. A* **243**, 375 (1958).
15. MCKEE, D. W., AND NORTON, F. J., *J. Phys. Chem.* **68**, 481 (1964).
16. MCKEE, D. W., *Trans. Faraday Soc.* **61**, 2273 (1965).
17. MCKEE, D. W., *J. Phys. Chem.* **70**, 525 (1966).
18. ANDERSON, J. R., AND MACDONALD, R. J., *J. Catal.* **13**, 345 (1969).
19. MORIKAWA, K., BENEDICT, W. S., AND TAYLOR, H. S., *J. Amer. Chem. Soc.* **58**, 1445 (1936).
20. MCKEE, D. W., AND NORTON, F. J., *J. Catal.* **3**, 252 (1964).
21. MCKEE, D. W., AND NORTON, F. J., *J. Catal.* **4**, 510 (1965).
22. SCHISSLER, D. O., THOMPSON, S. O., AND TURKEVICH, J., *Discuss. Faraday Soc.* **10**, 46 (1951).
23. CARTER, J. L., CUSUMANO, J. A., AND SINFELT, J. H., *J. Phys. Chem.* **70**, 2257 (1966).
24. KEMBALL, C., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood and P. B. Weisz, Eds.), Vol. 11, p. 223. Academic Press, New York, 1959.
25. LARSON, J. G., AND HALL, W. K., *J. Phys. Chem.* **69**, 3080 (1965).
26. SELWOOD, P. W., STEPHEN, A., AND PHILLIPS, T. R., *J. Amer. Chem. Soc.* **77**, 1462 (1955).
27. CECE, J. M., AND GONZALEZ, R. D., *J. Catal.* **28**, 2718 (1973).