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Evidence for the Participation of Surface Nickel Aluminate Sites in the Steam Reforming of Methane over Nickel/Alumina Catalysts

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The specific activities of various Ni/Al_2O_3 catalysts for the reaction of CH_4 with H_2O have been obtained and have been shown to vary markedly with catalyst preparation and to differ considerably from the specific activities of pure nickel. This has been explained by suggesting that the unreduced catalysts contain surface *nickel aluminate* phases which, on reduction, give monodispersed nickel atoms closely associated with alumina sites in addition to metallic crystallites arising from the reduction of nickel oxide. The results of exchange experiments using deuterium and $H_2{}^{18}O$ are presented in support of the suggestion that the monodispersed nickel atoms probably participate in the $CH_4 + H_2O$ reaction.

INTRODUCTION

The reactions occurring in the steam reforming of a hydrocarbon molecule may formally be depicted by the following equations:

$$C_nH_{2n+2} + nH_2O \rightleftharpoons nCO + (2n + 1)H_2, \quad (1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \quad (2)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O. \quad (3)$$

For convenience, CO is depicted as the primary product of the breakdown of the hydrocarbon skeleton [Reaction (1)] but this is not necessarily the case; CO_2 and CH_4 are formally shown as being formed from CO by the *water–gas shift* (2) and methanation (3) reactions although they may be formed directly from monocarbon species resulting from the fragmentation of the hydrocarbon skeleton. Reactions (2) and (3) are generally considered to be at equilibrium, methane being the favored product at low temperatures and CO and CO_2 the preferred reaction products at higher temperatures. As long as (2) and (3) are at equilibrium, reaction (1) can be considered to proceed essentially to completion at all temperatures for $n \geqslant 2$ as long as this is permitted kinetically; when $n = 1$, reaction (1) becomes the reverse of reaction (3), and this is favored by high temperatures, as indicated above. A fuller discussion of the thermodynamics of the steam reforming and related reactions is given in Ref (*1*).

Nickel is generally preferred, for economic reasons, as the active component of catalysts used for steam reforming, although other metals may also be used. It exists in its reduced state under most condi-

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tions (*1–3*) and is as active as any metal other than ruthenium. Considerable effort has been put into the development of commercial catalysts. Those required for hydrogen production must be stable at the high temperatures required for the process and are generally based on inert supports such as α-Al_2O_3 or $MgAl_2O_4$ (*3, 4*). The production of Towns' gas or "synthetic natural gas" (SNG), proceeding at lower temperatures, requires a more active material but the need for structural stability is less marked and, as a consequence, coprecipitated Ni/Al_2O_3 catalyst have been developed (*5*). Both types of material often contain alkali to suppress carbon deposition (*1*).

We have previously reported studies of the steam reforming of methane [Eq. (1), $n = 1$) at temperatures around 873 K over two Ni/γ-Al_2O_3 catalysts, one being of the coprecipitated type used for the production of Towns' gas and SNG and containing 75% Ni (*2*) and the other being of the impregnated type and containing 6.3% Ni (*6*), nickel contents of both being expressed with respect to the fully reduced state. It was concluded from kinetic measurements that the rate-determining step over the former was the adsorption of methane, whereas it appears (*6, 7*) that the combination of surface CH_x species ($1 < x < 3$) with hydroxyl groups may be rate determining for the impregnated sample; these conclusions were strengthened by the fact that, when H_2O was substituted by D_2O, no exchange of methane occurred in the former case but exchange was observed with the supported sample, indicating that methane adsorption was, to some extent, reversible. Exchange of methane with D_2O was also observed under steam-reforming conditions over a number of other impregnated samples (*6*), indicating that the surface reaction was probably also rate determining over these samples. On all of these catalysts, it was found that hydrogen did not cause full reduction of the catalysts at a temperature of 873 K; exposure of an apparently fully reduced catalyst to the $CH_4 + H_2O$ reaction mixture resulted in an excess of oxygen among the products of the reaction, there being considerable proportions of CO_2 initially, but as the catalyst became fully reduced, selectivity for CO formation developed. It was suggested (*1, 2*) that the initial excess of oxygen could be due to the presence of surface nickel aluminate phases which could not be reduced by hydrogen but which could be reduced by the species participating in the reaction; this is in agreement with the work of LoJacono *et al.* (*8*) who have shown, using spectroscopic techniques, that surface nickel aluminate phases exist on *unreduced* impregnated NiO/Al_2O_3 samples.

The aim of this paper is to attempt to explain the apparently different behavior of the coprecipitated and supported catalysts outlined above. This is done by postulating that each reduced material consists, to a greater or lesser extent, of massive nickel particles and monodispersed nickel atoms, the latter resulting from the surface aluminate phase, and that each has its own type of activity. Evidence for the existence of the latter type of site is advanced, based on experiments using ^{18}O-labeled water; experiments on Ni foils and bulk $NiAl_2O_4$ samples, which are also reported, add weight to the model.

CATALYST PREPARATION AND CHARACTERIZATION

Catalyst preparation. Table 1 lists the catalysts used in this work, the nomenclature being that used in Ref. (*6*). Catalysts A and H are coprecipitated materials, prepared from $Ni(NO_3)_2$ and $Al(NO_3)_2$; the preparation of A, which uses Na_2CO_3 as precipitant, was described in Ref. (*2*), whereas H was precipitated in a similar fashion using NH_4OH. Catalysts C, E, F, and G were prepared by impregnation of the corresponding aluminas using $Ni(NO_3)_2$ solution, followed, as with A and H, by

TABLE 1

Details of the Catalysts Used in This Investigation

Catalyst	Al-hydroxide used to prepare support	Temperature of calcination of hydroxide (K)	Structure of resultant alumina	Temperature of calcination of catalyst[a] (K)	Ni content of the unreduced catalyst (%, w/w)	Total area (m^2 g^{-1})
A	—	—	γ-Al_2O_3	723	69.8	112[b]
						132[c]
C	Gibbsite	573	χ-Al_2O_3	623	7.4	206[c]
E	Bayerite	573	η-Al_2O_3	573	8.1	293[c]
F	Boehmite	623	γ-Al_2O_3	623	6.3	318[c]
				873		200[b]
				873		223[d]
G	Gibbsite	623	χ-Al_2O_3	623	23.0	172[c]
H[e]	—	—	Ni Al_2O_4	1073	33	72[b]
			+ trace NiO			67[f]

[a] Calcined in air after drying at 333 K for 16 h.

[b] Determined by Kr adsorption at 78 K.

[c] Determined by N_2 adsorption at 78 K.

[d] Using Kr, after reduction at 873 K for 2 h.

[e] Catalyst prepared by a coprecipitation technique (*5*); it also contains 1% K.

[f] Using Kr, after reaction with $CH_4 + H_2O$ at 873 K.

filtration, drying, and calcination. Table 1 shows for each sample its nickel content, together with the aluminum hydrate from which the alumina base (C, E, F, and G) was obtained, the temperature of decomposition of the base, and the structure of the resultant alumina. Nickel contents were determined by analysis of the resultant solids but, for C, E, F, and G, these contents were also determined by difference from analysis of the filtrate; the results of the two methods are in very good agreement except for sample E, for which the value obtained by the latter method was rather larger than that by the former and was used in preference. The structures of the alumina supports were determined by X-ray powder diffractometry, using a Guinier camera with Cu$K\alpha$ radiation, and the results were in good agreement with those reported by Lippens (*9*). Table 1 also gives the temperature of calcination of the precipitate H and the composition of the resultant material, again determined by X-ray powder methods. Sample A was examined using an X-ray diffractometer and the results showed that there were traces of $NiAl_2O_4$ present in the sample which could not be detected by the Guinier method. The nickel foil, better than 99% pure and 0.15-mm thick, was supplied by B.D.H., Ltd., and had a surface area of 0.024 m^2; after being degreased in CCl_4 and outgassed in the reaction system, it was given a short treatment in oxygen (873 K, 2.12 Torr of O_2) before reduction to decrease carbon contamination.

Total areas. The total and metallic areas quoted in Tables 1 and 2 were determined with conventional glass high-vacuum systems, using both N_2 and Kr adsorption at 78 K for the total area measurement and H_2 adsorption at 293 K for the active Ni areas (see Results and Discussion). The total area of sample A after outgassing at 723 K was determined using both Kr and N_2; the former value was slightly lower than the latter and this indicates that the value of the cross-sectional area of a Kr adatom (σ_{Kr}) used in the calculation (1.95×10^{-19} m^2) was somewhat too low for these materials. It is also likely that the

TABLE 2

Metallic Ni Areas Obtained from Hydrogen Chemisorption Measurements at 293 K

Catalyst	Area after reduction at 723 K (criterion *a*) (m^2 g^{-1})	Area after reduction at 873 K (m^2 g^{-1})		Rate of reaction (10^{17} mol s^{-1} g^{-1})	Specific rate [10^{16} mol s^{-1} (m^2 of Ni)$^{-1}$]	
		Criterion *a*	Criterion *b*		Criterion *a*	Criterion *b*
A	37	18.8	21.3	6.60	3.5	3.10
C	4.0	2.5	4.5	3.00	12.0	6.67
E	9.3	2.2	4.8	4.93	22.4	10.3
F	12.0	1.9	8.3	2.40	12.6	2.89
G	6.2	3.6	15.9	1.74	4.83	1.09

[a] Calculated from V_{ads} at 100 Torr.

[b] Calculated from V_m obtained from plot of Eq. (4).

total areas of all the materials were lower after outgassing at 873 K, as is shown by the results for sample G; allowing for the uncertainty in σ_{Kr} referred to above, the decrease in area is on the order of 15%. Reduction of sample G in hydrogen caused a decrease in area of ~3%. Reaction with $CH_4 + H_2O$ mixtures caused a slight decrease in the total area of sample H, this being on the same order as that caused by reduction of G. The results for G (Table 1) clearly show that the values given for A, C, E, and F are somewhat too high and they are likely to be reduced by ~25% by outgassing, reduction, and reaction at 873 K; the data are therefore only semiquantitative in relation to the results for reactions at 873 K given below, but their inclusion permits comparison between these materials and other catalyst samples described in the literature. The results of hydrogen chemisorption measurements are described under Results and Discussion.

Kinetic measurements. The kinetic measurements were carried out in a bakeable constant-volume system described previously (*2*) which is capable of background pressures of 10^{-8} Torr (1 Torr = 1.33.3 N m^{-2}) and which is maintained at a temperature of 400 K during experiments to minimize adsorption of water vapor on the walls of the reaction system. The gas phase is analyzed by a small residual-gas analyzer which is continuously pumped and which is connected to the reaction system by a capillary leak. Catalyst samples of 0.1–0.5 g were used; before each set of experiments, the sample was reduced in hydrogen at 873 K using successive doses of hydrogen until no further water was produced. Standard reaction mixtures of 2.1 Torr ($\sim 2.7 \times 10^{19}$ molecules) each of CH_4 and H_2O were admitted to the catalyst at the same temperature of 873 K. Typical results for the $CH_4 + H_2O$ reaction have been presented in previous publications (*2*, *6*). As it had also been shown that a reaction mixture was capable of reducing the catalyst more fully than was hydrogen (see Introduction), several reactions were carried out over each catalyst to ensure complete reduction; once the stoichiometry of Eq. (1) with $n = 1$ was achieved, the initial rate of reaction of the standard mixture was measured from the rate of disappearance of methane at the beginning of the experiment. More extensive results for catalysts A, G, and H (*2*, *6*, *7*) have shown that such initial rates are very reproducible, even after long series of experiments under different conditions; hence, the results reported below for the initial rates are considered to be reproducible to better than ±20%. With several samples, experiments were carried out at several temperatures in addition to 873 K in order to determine activation energies for the reaction, but the reaction conditions were otherwise the same.

RESULTS AND DISCUSSION

Determination of Nickel Area by Hydrogen Chemisorption

The work reported in this paper was carried out on two types of material, namely, coprecipitated and impregnated; strictly speaking, the coprecipitated materials cannot be referred to as being supported as they contain considerably greater quantities of nickel than alumina, but for simplicity, we will use this term for samples prepared by both methods. It is generally recognized (*10*, *11*) that supported catalysts derived from nickel oxide are more difficult to reduce than the unsupported material and that there is considerable interaction between the nickel ions and the support (*8*). Hence, there is some doubt as to the temperature at which reduction of supported materials should be carried out; for example, recent work on coprecipitated samples similar to A has shown (*12*) that reduction may not be complete until the temperature is raised to ~1000 K. However, as the kinetics of the $CH_4 + H_2O$ reaction were measured at 873 K after reduction at the same temperature, this temperature was also chosen for reduction prior to the hydrogen chemisorption measurements. Ideally, the metal areas should have been determined in the same apparatus as that in which the kinetic measurements were made, but this was not feasible. It was noted in the Introduction that reaction in $CH_4 + H_2O$ caused removal of further oxygen from the catalyst but, as this additional reduction caused only a change in the stoichiometry of the reaction without markedly affecting the rate, treatment in $CH_4 + H_2O$ was omitted prior to the chemisorption measurements.

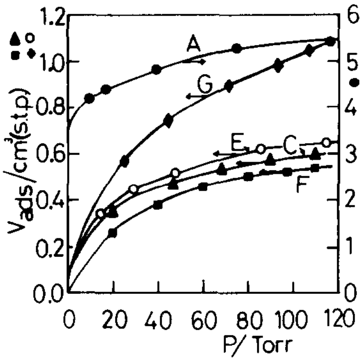


FIG. 1. Hydrogen adsorption isotherms obtained at 293 K for the various catalysts prereduced at 873 K.

Figure 1 shows the hydrogen adsorption isotherms obtained at 293 K for the supported catalysts studied here. The isotherms are relatively well defined and have reasonably sharp "knees," rising thereafter slowly with increasing pressure. These results are in sharp contrast with isotherms obtained (*13*) for the same samples reduced at 723 K; in the latter case, the plots rose slowly over the same range of pressure as shown in Fig. 1 and no well-defined knee was found. This is consistent with the fact that the reduction is far from complete at this temperature and it suggests that some adsorption may occur on the unreduced oxide.

Several criteria appear in the literature for the determination of monolayer volumes (V_m) from hydrogen chemisorption isotherms; these include determining the volume at a standard pressure under standard conditions [commonly, 100 Torr at 273 K (*14*)] or extrapolation of the straight-line portion of the isotherm backwards to zero pressure (*15*). Neither of these criteria seem to use to be entirely satisfactory because, although they allow comparison of catalysts prepared under similar conditions, they produce V_m values which are smaller than the maximum volume adsorbed by the catalyst. Logically, if hydrogen chemisorption occurs only on

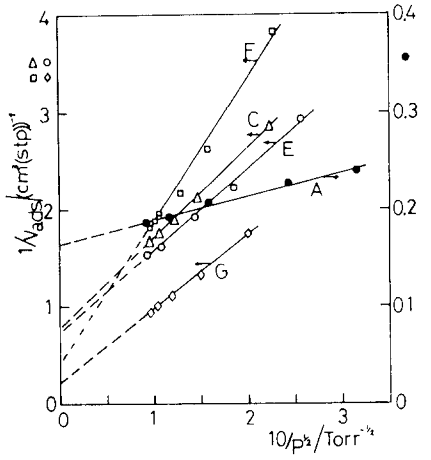


Fig. 2. Plots of Eq. (4) for the data of Fig. 1.

the metal sites, it might be expected that V_m will be approached, but never exceeded, as the pressure is increased. We have therefore attempted to fit the data of Fig. 1 to the linearized form of the Langmuir isotherm for dissociative chemisorption of a diatomic gas [see, for example, Ref. (*16*)]:

$$\frac{1}{V} = \frac{1}{V_m} + \frac{1}{CV_m P_{H_2}^{\frac{1}{2}}}, \qquad (4)$$

where V is the volume adsorbed at any pressure, P_{H_2}, and C is a constant. The results of such a treatment are given in Fig. 2 and it can be seen that satisfactory straight-line plots are obtained for all the catalysts.

Columns 3 and 4 of Table 2 give the metallic areas of the reduced catalysts calculated both using the criterion suggested by Yates *et al.* (*14*) (see above) and from the plots of Fig. 2; we refer to these as criteria *a* and *b*, respectively. [The area occupied by one hydrogen atom was assumed to be 6.5×10^{-20} m^2 (*17*)]. The results using criterion *b* are consistently greater than those using *a*; the two sets of results are quite close to one another for catalyst A but the differences are greater for the other samples, particularly F and G, and this reflects the more diffuse knee on the isotherms for these materials (see Fig. 1).

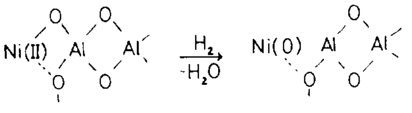
Kinetic Results for the $CH_4 + H_2O$ Reaction at 873 K on the Supported Catalysts and Ni Foil

The fifth column of Table 2 shows the initial rates of the $CH_4 + H_2O$ reaction under the standard reaction conditions described in the experimental section. From these results are calculated the specific rates of the reaction (rate per unit nickel area) using both criteria for the surface area, and these are shown in columns 6 and 7 of Table 2. The specific rates calculated using criterion *b* [i.e., from metallic areas derived from plots of Eq. (4)] are probably more reliable for comparison purposes than those obtained using criterion *a* and will be considered hereafter. The specific rates vary by a factor of ten and this indicates that the activities of the catalysts are influenced by the catalyst formulation; for example, the variation could be due to some sort of metal–support interaction. For comparison with these values, the specific rate for unsupported Ni (in the form of a foil) was obtained and the value was 61×10^{16} molecules (m^2 Ni)$^{-1}$ s^{-1}, which is much higher than the values obtained for the supported catalysts.

Possible Participation in the $CH_4 + H_2O$ Reaction of Sites Related to Nickel Aluminate

The well-recognized difficulty in reducing supported nickel catalysts as opposed to unsupported nickel has been referred to above in connection with the hydrogen chemisorption data. The interaction of nickel ions at low concentrations with various alumina supports has been investigated by Lo Jacono *et al.* (*8*) who found that nickel ions formed surface spinel structures with both γ- and η-Al_2O_3. They observed that η-Al_2O_3 favored the presence of tetrahedrally coordinated Ni^{2+} ions while γ-Al_2O_3 gave a mixture of tetrahedrally and octahedrally coordinated ions. Although Lo Jacono *et al.* did not study

χ-Al_2O_3, it would be reasonable to assume that surface aluminate species are present on this support also (*8*). It would therefore be reasonable to suppose that the *unreduced* impregnated catalysts of this study (C, E, F, G) comprise *surface nickel aluminate* species supported on particles of the base alumina, with the possibility of the coexistence of some *discrete nickel oxide crystallites*. The coprecipitated sample is likely to be somewhat different. It has recently been shown (*18*) that the precipitate formed initially has a layer structure of the approximate formula $Ni_6Al_2(OH)_{16} \cdot CO_3 \cdot 4H_2O$ in which the nickel and aluminum ions are in close proximity; it is therefore most probable that the aluminum ions of the calcined material are to be found in a geometry similar to the surface nickel aluminate species of the impregnated samples but now there will be an excess of nickel oxide crystallites due to the stoichiometry of the sample. To account for the relatively low metal surface area of sample A after reduction (H_2 chemisorption data, Table 2) compared with its total area (Table 1), it is reasonable to suggest that the nickel aluminate species are concentrated at the surface of the nickel oxide crystallites in the unreduced material and that these hinder the reduction process (compared with pure nickel oxide). For both types of catalyst, reduction of nickel oxide crystallites will give rise to nickel crystallites of similar geometry but reduction of nickel aluminate species will give rise to isolated (monodispersed) nickel atoms; the latter process might be depicted as follows.



(5)

The resultant Ni(0) atoms will remain closely associated with the alumina structure and their catalytic activity (see below) will depend on their interaction with the alumina. It is also likely that the hydrogen adsorption behavior of these sites will be considerably different from that of bulk nickel crystallites. In order to explain the variation of specific activities shown in Table 2, we suggest also that the nickel sites derived from nickel oxide and surface nickel aluminate have different intrinsic activities for the $CH_4 + H_2O$ reaction. The contribution to the activity from each type of site cannot be quantified in a satisfactory manner as we have no direct measurement of the number of each, particularly as we have no direct knowledge of the adsorption behavior toward hydrogen of the Ni(0) species derived from the surface nickel aluminate sites. The chemisorption of hydrogen on these sites is discussed more fully below in connection with the data on exchange with D_2. To explain the different kinetic behavior of the coprecipitated and impregnated samples (*2*, *6*, *7*) referred to in the Introduction, we suggest that both massive Ni crystallites and monodispersed Ni atoms [Eq. (5)] exist on each of the supported materials. The kinetic behavior of sample A is dominated by reaction on nickel sites whereas the impregnated samples have kinetics more characteristic of reaction on the sites derived from surface nickel aluminate (*7*). However, even the activity on the nickel crystallites must be modified somewhat by the presence of the alumina because the specific activity of sample A is much lower than that of the nickel foil; the activation energy results presented below also support this conclusion.

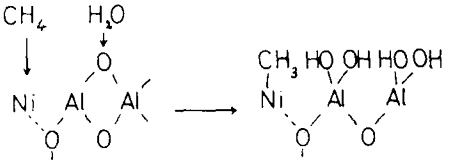
We have examined the possibility that sites derived from nickel aluminate could have some activity by examining the $CH_4 + H_2O$ reaction at 873 K on an unreduced nickel aluminate sample (sample H, Table 1) prepared by coprecipitation and subsequent calcination at 1073 K, and which was shown by X-ray measurements to contain only traces of nickel oxide. The sample was found to catalyze the

$CH_4 + H_2O$ reaction *without* prior reduction, giving an initial rate of reaction of 1.6×10^{17} molecules g^{-1} s^{-1} under the standard conditions of this work, which is comparable with the other materials studied. During the first few reactions, oxygen was produced from the catalyst, as was observed (*2*) with catalyst A (i.e., appreciable quantities of CO_2 were formed in addition to CO and little water reacted), but the rate of disappearance of CH_4 was unaffected; subsequently, CO was the predominant product and water and methane reacted at approximately the same rate. Hence, the material H has considerable catalytic activity and it is probable that this is largely associated with sites of the type depicted in Eq. (5).

Further evidence for the participation of sites akin to nickel aluminate species was obtained by measuring the activation energy for the $CH_4 + H_2O$ reaction in the temperature range from 873 to 973 K over the nickel foil and over catalysts A, F, and H. The value for the foil was found to be 78.1 kJ mol^{-1} whereas, in contrast, the values for the three catalysts were found to be 29.0, 26.2, and 27.3 kJ mol^{-1}, respectively. We therefore infer that the majority of the sites on the supported catalysts differ from those on the bulk nickel sample. It is interesting to compare these values for the activation energy with values given in the literature. Bodrov *et al.* have examined the $CH_4 + H_2O$ reaction over a supported $Ni/\alpha\text{-}Al_2O_3$ catalyst (*19*) in the temperature range 673–873 K and over Ni foils (*20*) in the temperature range 1073–1173 K and have found values of 151 and 130 kJ mol^{-1}, respectively. Rostrup-Nielsen (*21*) obtained a value of 110 kJ mol^{-1} for a Ni/MgO catalyst containing a small proportion of alumina. Interaction of nickel with either $\alpha\text{-}Al_2O_3$ or MgO would be expected to be much less extensive than with the low-temperature modifications of Al_2O_3 used in this work; in all cases, the values for activation energy are greater than our value for nickel foil but are of the same order, whereas these values are very much greater than those for the other catalysts studied here.

Evidence from Exchange Experiments for the Participation in the Reaction of Hydroxyl Groups Associated with Surface Aluminum Ions

We have concluded above from the kinetic experiments on the supported catalysts, nickel foil, and a nickel aluminate sample that sites derived according to Eq. (5) from surface nickel aluminate species or from related species are likely to be active for the $CH_4 + H_2O$ reaction. That being the case, it seems likely that the aluminium ions must participate in the reaction by adsorbing the water molecules while the methane is adsorbed on the nickel; one possible mode of reaction is shown in the following scheme.



(6)

The CH_3 and OH species subsequently react to give the product carbon monoxide (*2*). Not only will surface hydroxyl groups attached to the aluminium ions be formed by reaction (6) but some are likely to be formed on the calcined catalyst after storage in air and, by analogy with alumina, some should remain even after outgassing and reduction at 873 K and should be exchangeable with gaseous D_2 (*22*). Similarly, the hydroxyl groups should be exchangeable with labeled oxygen in the form of $H_2{}^{18}O$ if the adsorption of water is reversible (*2*). We therefore report in the following paragraphs the results of experiments on the exchange of the reduced catalysts with D_2 and with $H_2{}^{18}O$ which support the scheme suggested in Eq. (6).

Figure 3 shows the result of a D_2 exchange experiment using sample F. After reduction at 873 K in 5 Torr of H_2, the reaction vessel was evacuated and cooled to 300 K at which temperature D_2 was added. No exchange was observed, but, on raising the catalyst temperature, exchange of D_2 with surface hydrogen was detected at 578 K and more rapid exchange was observed at higher temperatures. At 773 K, a total of $\sim 5 \times 10^{20}$ hydrogen atoms per g of catalyst was exchangeable with deuterium. A similar experiment with catalyst E gave a value of 3.6×10^{20} exchangeable hydrogens per g of catalyst at 823 K. Similar results were obtained with other materials not included in this paper. The number of exchangeable hydrogens corresponds in each case to a surface concentration of $\sim 2 \times 10^{18}$ atoms m^{-2}, which is close to the value given by Hall *et al.* (*22*) for η-Al_2O_3, for a mixture of η- and γ-Al_2O_3, and also for SiO_2 and silica–alumina. The temperature at which exchange occurred was similar to that for exchange of the aluminas (*21*). If the sample was cooled to room temperature before the system was pumped and deuterium was added, there was immediate exchange at that temperature; presumably this corresponds to exchange with hydrogen adsorbed on the metallic nickel particles. The extent of exchange in a typical experiment was somewhat lower than the monolayer capacity for the sample as shown in Table 2, but was on the same order, indicating that part of the hydrogen adsorbed at 293 K is reversibly removed on pumping. These results show that two types of site, which are capable of adsorbing hydrogen, exist on the surface, although they do not argue directly in favor of surface nickel aluminate-type sites.

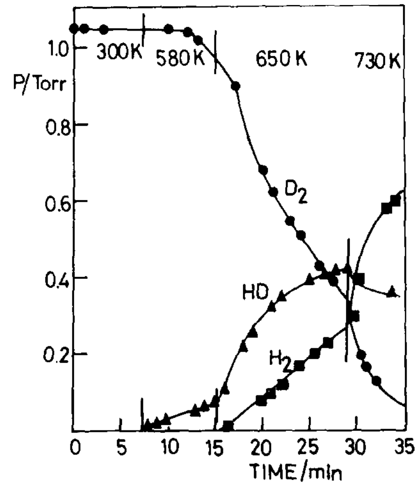


FIG. 3. Exchange of catalyst F with D_2 after reduction at 873 K and evacuation prior to commencing exchange at 300 K.

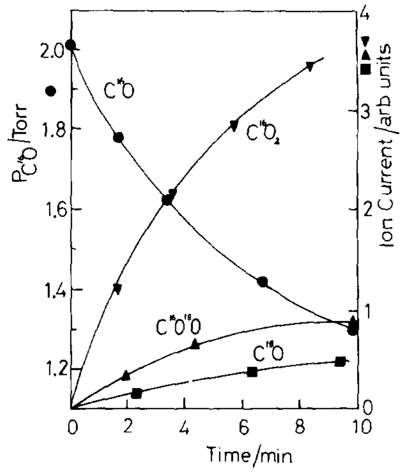


FIG. 4. The reaction of $C^{16}O$ with an ^{18}O-treated surface (see text); the partial pressure of $C^{16}O$ is given in absolute units but the other species are not, as the mass spectrometer sensitivities for these are not known. Note that, under these conditions, the ion current for $C^{18}O_2$ was negligibly small.

The ^{18}O exchange experiments were carried out with catalyst F using water enriched to 10% in $H_2{}^{18}O$. When the catalyst, after outgassing and reduction in H_2, was exposed to $H_2{}^{18}O$ at 873 K, no adsorption was observed but exchange occurred, the gas phase becoming richer in $H_2{}^{16}O$. From this and similar experiments, it was calculated that there were 5×10^{20} exchangeable oxygen atoms on the surface of 1 g of catalyst, which is somewhat greater than the number of exchangeable hydrogen atoms (see above). Taking a model of the surface of this sample in which the whole support is covered with Ni ions and assuming that each site as depicted in Eq. (5) occupies about 20 Å^2, the number of sites is approximately 15×10^{20}/g of catalyst. Hence, somewhat less than the whole surface of the support is exchangeable with ^{18}O.

A number of experiments were carried out at 873 K on the ^{18}O-treated surface. For example, a $CH_4 + H_2{}^{16}O$ reaction gave ^{18}O among the initial products (i.e., as $C^{18}O$ and $C^{16}O^{18}O$) and slight exchange of the water was also observed. As the reaction proceeded, the $C^{18}O$ and $C^{16}O^{18}O$ peaks increased steadily and this is taken as evidence for the participation in the reaction of the sites which had become exchanged with ^{18}O. Similar results were also obtained in the reaction of $C^{16}O_2$ with H_2 ($C^{18}O$ and $H_2{}^{18}O$ were observed).

In another experiment, shown schematically in Fig. 4, $C^{16}O$ was admitted alone to an ^{18}O-treated surface at 873 K when both $C^{18}O$ and CO_2 containing ^{18}O were observed among the products; however, when the surface was treated with H_2 at the same temperature, no products were observed, indicating that the oxygen species which were causing the exchange could not react with molecular hydrogen. The latter result is consistent with and helps to explain the observation that the $CH_4 + H_2O$ reaction mixture can reduce the surface more fully than can H_2 (*2*). It also suggests that the hydrogen chemisorption data refer only to adsorption on massive nickel and not on surface nickel aluminate species, although we cannot exclude the possibility that molecular adsorption occurs on the latter sites.

In conclusion, the results reported in this paper provide some evidence that two types of site exist on alumina-supported nickel catalysts, both of which can participate in the steam reforming of methane and associated reactions. We cannot quantitatively distinguish between the two types of site due to uncertainties in measurement of metallic areas, etc., but we suggest that both metallic crystallites and sites derived from surface nickel aluminate exist in the reduced catalyst. The former sites adsorb hydrogen and exchange surface hydrogen with deuterium in a fashion similar to that expected for unsupported nickel, whereas the latter only exchange hydrogen at higher temperatures. We believe that the activity of the coprecipitated catalyst catalyst (Sample A) resides largely in the metallic nickel sites whereas the supported catalysts (lower nickel content) have an activity arising more from the sites derived from nickel aluminate. This is the probable explanation of the different rate-determining steps observed (*1*, *6*) for the two types of catalyst. Further work is in progress on the related reactions of CO with H_2 which shows that sites derived from nickel aluminate probably also participate in that reaction.

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