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Relation between Catalytic Properties and Structure of Metal Films

I. Deuterium Exchange of Methane, Ethane, and Propane over Nickel

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To assess the influence of surface structure on the mode of adsorption of saturated hydrocarbons, deuterium exchange reactions with propane, ethane, and methane were studied over various ultra-high-vacuum-deposited nickel films. Reactions were studied over {111} and {100} surfaces, prepared by nickel evaporation onto mica and sodium chloride, respectively, at elevated substrate temperatures, as well as over sintered and unsintered random polycrystal films. Reactions with propane and ethane gave initial product distributions from which the following conclusions are drawn: (i) at exchange temperatures, it is very unlikely that a monoadsorbed hydrocarbon residue will be retained on {111} or {100} surfaces because of the ready formation of a double bond between the carbon and the metal; (ii) surface sites for the retention of a monoadsorbed hydrocarbon residue are present on low-temperature random polycrystal films, but they are thermally unstable in that they are much reduced by sintering, and are completely absent in {111} or {100} surfaces; (iii) exchange by a process of rapid interconversion between monoadsorbed and α,β-diadsorbed surface species does *not* occur on {111} or {100} surfaces and, *ipso facto,* is unlikely on sintered surfaces; (iv) multiple exchange occurs mainly by desorption from extensively dehydrogenated surface residues.

It is suggested that the thermally unstable sites suitable for monoadsorption are associated with atomically rough areas of surface, either as high index planes or facets, or at quasi-macroscopic features such as steps and terrace edges. Although the product distributions were sensitive to surface structure, activation energies and frequency factors were not. Methane exchange did not show discrimination with respect to surface structure, and reasons for this are discussed. The possible unreliability of exchange data obtained under conditions of poor surface cleanliness is emphasized.

INTRODUCTION

A central problem of continuing interest in heterogeneous catalysis is the influence of surface geometry on the mechanism of the reaction. This question may be considered in various ways, and the approach adopted will largely determine the design of the experiment. In any case, it should be clear that surface structure in a crystallographic sense and the detailed electronic and valence properties of the surface are intimately related. The main reason for focusing attention on surface geometry is that this is an external manifestation which is, to some extent at least, directly observable.

One may, for instance, attempt to inquire how a reaction depends on the crystal plane exposed at the catalyst surface. In such work use may be made of various surfaces, each of as high a degree of crystallographic perfection as possible. Examples of such an approach are to be found in the work of Cunningham and Gwathmey (*1*) and Leidheiser and Gwathmey (*2*). On the other hand, one may seek to understand the influence on a reaction resulting from the departure of a given crystal plane from the crystallographically perfect state. Into this category of surface imperfection we would class surface rearrangements such as are known for covalent semiconductors (*3*), but which appear to be absent for most metals (*4*), as well as surface imperfections such as those arising from emergent screw dislocations, stacking faults, twin boundaries, surface vacancies, self-adsorbed metal atoms, and quasi-macroscopic features such as steps and terrace edges. As methods of studying surface structural details have improved, it has become aparent that the problems of isolating structurally homogeneous surfaces are severe. Furthermore, it is not uncommon, particularly in reactions where a reactant is itself able readily to react with the metal surface, for the catalytic reaction to result in gross surface rearrangement of the metal: typical examples are to be found in the reaction of hydrogen and oxygen catalyzed by copper (*2*), and in the reaction of xenon and fluorine catalyzed by nickel (*5*).

Attempts to correlate catalytic activity with dislocation density have on the whole been inconclusive or else have demonstrated the absence of such a correlation. Thus it was shown that no correlation exists between dislocation density and the activity of silver for the decomposition of formic acid (*6*). Although annealing of cold-worked metal specimens has been shown by Uhara (*7*) to decrease their catalytic activity in a number of reactions, the dislocation density was not directly measured, and the behavior was not phenomenalogically disentangled from the influence of point defects, quasi-macroscopic features, or even surface cleanliness More recently, Willhoft (*8*) has shown that the catalytic activity of clean nickel for formic acid decomposition is independent of the degree of cold-work over a large range, and presumably therefore independent of dislocation density. We believe that with the techniques at present available, the influence of dislocations on catalytic activity is likely to be swamped by the effect of the other types of surface imperfections which are present in considerably greater effective surface concentration.

With these ideas in mind, we decided to compare some relatively simple reactions over randomly oriented polycrystalline nickel films and over epitaxially grown or oriented nickel films, these two classes of catalyst being chosen to represent extremes of surface imperfection and perfection, within the limitations imposed by available experimental methods. The experimental method was designed to eliminate surface contamination (in the sense of adventitious impurity) as an experimental variable.

The reactions chosen for study were deuterium exchange with the lower aliphatic hydrocarbons, since there exists a good deal of mechanistic data from previous work (*9*); moreover, methane, ethane, and propane are a series within which there exists a range of different possible adsorption modes which may be sensitive to surface structure.

We would point out that in selecting a catalytic reaction as a diagnostic tool in relation to surface structure, there are some criteria to be followed. A reaction which occurs very readily may well occur easily over all of the available surface irrespective of the details of surface structure, and this will be particularly so if the reacting molecules are so simple that they make only trivial stereochemical demands on the surface. A typical case would be H_2–D_2 exchange, which would be a poor diagnostic choice. This criterion has recently been emphasized by Boudart (*10*). A corollary to this idea is that a diagnostic reaction may well be unsatisfactory if the stereochemically significant reactant is very strongly adsorbed. For instance, formic acid decomposition over most metals is zero order in formic acid pressure, and the reaction proceeds by decomposition from an adsorbed formate layer covering most of the surface (*11*). In this circumstance, formic acid decomposition may well not be a good diagnostic reaction for metal catalysts in relation to their surface structure. In the present exchange reactions, the satu-

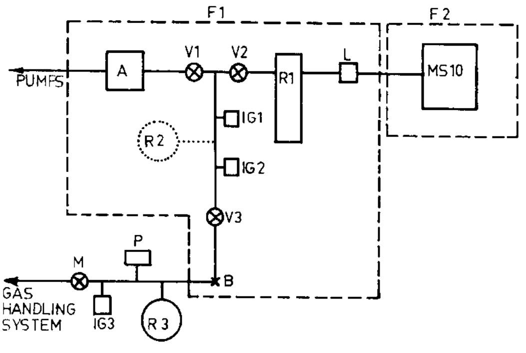

Fig. 1. Schematic diagram of experimental apparatus.

rated hydrocarbons are weakly adsorbed compared to the deuterium.

Experimental

The reaction system is illustrated schematically in Fig. 1. In a functional sense this system resembles that used previously (*9*), but with modifications necessary for ultra-high-vacuum operation. The valves V1, V2, and V3 were Granville-Phillips Type C. During bake-out and film preparation the system was isolated from the gas-handling system by the break-seal B. System pressures were monitored by the ionization gauges IG1 and IG2. The composition of the reaction mixture in the reaction vessel R1 was monitored via the leak L with the MS10 mass spectrometer. A glass capillary leak was found to be unstable to bake-out, and therefore L was constructed from a silicon carbide Metrosil pellet (*12*). The portions of the system enclosed by the dashed lines F1 and F2 were separately bakeable.

The reservoir R2 was added when needed expressly for the measurement of deuterium adsorptions.

The reaction vessel R1 was cylindrical in shape, of diameter 46 mm and the total volume of the reaction volume was 380 ml. The nickel film was deposited by evaporation from a filament of previously thoroughly outgassed 0.5-mm diameter pure nickel wire, situated near the axis of R1.

Three substrates were used for the nickel deposition; these were the glass wall of R1, fresh air-cleaved mica placed as a cylinder against the inside wall of R1, and a sodium chloride layer deposited on to the inside glass wall of R1 by evaporation. The bottom of R1 was flattened so that when a mica substrate was used, a mica disc could be used to cover the bottom of the vessel. When required, the evaporated sodium chloride was deposited from a sodium chloride-coated tantalum filament also situated near the axis of R1. The details of this procedure have been previously described (*13*). The nickel was either Johnson Matthey spectrographically standardized grade, or Materials Research Corporation electron beam zone-refined grade; the two samples behaved essentially identically.

Pure deuterium gas was obtained from Bio-Rad Corporation, and was further purified by diffusion through a heated thimble of 75% palladium/25% silver. Deuteroethanes used for calibration purposes were obtained from Bio-Rad Corporation. The other hydrocarbons were Phillips Petroleum Research Grade, and they were further purified by fractional distillation on the vacuum line. As used, they were mass spectrometrically pure. The pressure of the gas mixture in the reservoir R3 from which it was expanded into the reaction system, was measured with a bellows manometer P, and to avoid contamination of the gas mixture, particularly cross-contamination between hydrocarbons, the valves such as M were grease-free metal valves. By modest thermal outgassing the gas-handling line could be evacuated to better than 10^{-6} torr, so that relative to the sample pressures, the adventitious contamination level should not have exceeded about 1 part in 10^7–10^8.

The procedure of film preparation was as follows: By the usual baking procedure a vacuum of about 1×10^{-9} torr or somewhat better was obtained in the whole ultra-high-vacuum system. The reaction vessel was then heated separately at about 400°C and the nickel filament degassed with a heating current of 4 A. The temperature of the reaction vessel was then adjusted in the range 300–350°C and pumping continued until the pressure was about 10^{-9} torr. For deposition of nickel on mica or glass, the reaction vessel temperature was then adjusted as desired, and the nickel evaporation effected at 6 A for 30 min. In all experiments when an epitaxed or oriented film on mica was required, the temperature of the substrate was 300°C. Nonepitaxed randomly oriented films were deposited with the substrate at 0°C. The pressure at the end of the deposition was about 10^{-8} torr. For films deposited on evaporated sodium chloride, after achieving about 10^{-9} torr, the reaction vessel was adjusted to 350°C with no heating current through the nickel filament and the sodium chloride was evaporated as previously described (*13*). During this process the pressure rose to about 10^{-6} torr. Therefore, after this was complete, the reaction vessel was rebaked until the presure recovered to $<10^{-8}$ torr, when the filament was again outgassed, and the nickel evaporated.

After deposition of the film, the reaction vessel was valved off, cooled to ice temperature, and the reaction mixture then admitted.

The standard reaction mixture contained a deuterium/hydrocarbon molecular ratio of 4/1, and at 0°C the total pressure in the reaction vessel was 20 torr. Under these circumstances, the reaction volume was estimated to contain 2.15×10^{20} D_2 molecules and 5.37×10^{19} hydrocarbon molecules.

The recorded mass spectra were corrected by linear time interpolation so that all time-corrected peaks in a given set corresponded to a single time. Corrections were applied for naturally occurring deuterium and ^{13}C. Mass spectra were measured at reduced electron energy to minimize fragmentation corrections: about 15-eV (nominal) electrons were used. For the methanes, fragmentation corrections were calculated from data obtained on CH_4, with isotopic corrections applied from the results of Schissler *et al.* (14). Fragmentation corrections for the ethanes were obtained from calibration experiments on C_2H_6, C_2D_6, 1,1,2,2 - $C_2H_2D_4$, and 1,2 - $C_2H_4D_2$. For the propanes, fragmentation corrections were obtained from data obtained on C_3H_8 and C_3D_8, modified for the increased probability of the loss of an H atom relative to a D atom by using the corresponding data obtained from the deuteroethanes. A final correction was applied to the results for fractionation across the leak. The entire processing of the raw data was programmed for an IBM 1130.

Fragmentation corrections were carried out using mixtures of compositions that were in the range actually encountered during catalytic reactions; thus calibration mixtures were

$$D_2/[xC_2H_yD_{6-y} + (1-x)C_2H_6] = 4$$
$$\text{with } x \not> 0.1 \quad \text{and} \quad y = 0, 2, 4$$

The results of these calibrations was to provide empirical factors over and above the appropriate statistical factors, for the dependence on y of the chance of loss of H in $C_2H_yD_{6-y}$. The success of the fragmentation corrections was judged in practice by the accuracy with which the pure fragment peaks (e.g., masses 27, 28, 29 from ethane; 41, 42, 43 from propane) were corrected to zero. It is considered that the individual deutero components are known with an accuracy such that if $x\%$ is the proportion of a given component present, the likely error range on x is about $(x \pm 3)\%$.

All electron diffraction and electron microscopic results were obtained using a Phillips EM200 operating at 100 kV. The general techniques have been described previously (*15*).

RESULTS

Film Catalysts

It is convenient to consider the film catalysts under the following classifications: (a) low-temperature films of random polycrystal orientation; these were deposited onto either glass or mica with the substrate at 0°C; (b) sintered films of random polycrystal orientation; these were deposited as for (a), but were sintered by heating in vacuum to about 350°C before reaction; (c) {111} films; these were deposited on mica with the substrate at 300°C, and for which the orientation is known by electron diffraction examination; (d) {100} films; these were deposited on to evaporated sodium chloride with the substrate at

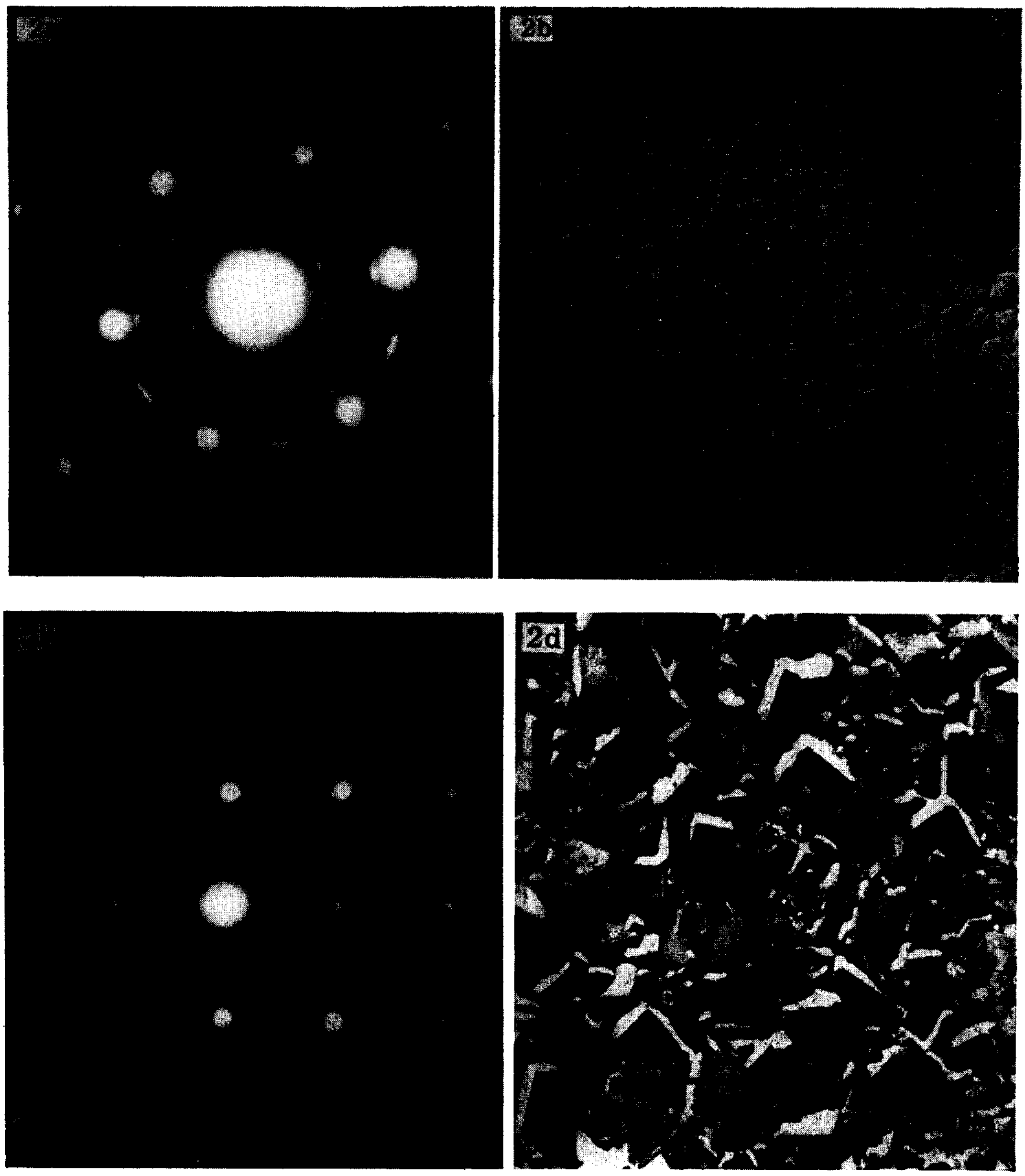

FIG. 2. (a) transmission diffraction of epitaxed {111} nickel film deposited on mica at 300°C; (b) surface replica from random polycrystalline nickel film deposited at 0°C and not heated above room temperature; (c) transmission diffraction of epitaxed {100} nickel film deposited on evaporated sodium chloride at 250°C; (d) transmission micrograph corresponding to 2(c).

250°C, and for which the orientation is known by electron diffraction examination.

In the majority of cases of {111} nickel films, transmission electron diffraction showed a prominent 220 ring and an extremely low intensity for the innermost 111 and 200 rings, indicating that the crystals in the film were, to a very high degree, oriented with the <111> axes at right angle to the substrate. The surface replicas were flat and almost featureless. This type of film is not a true single crystal although the {111} plane is predominately exposed to the gas, as judged in relation to the surface replica. The behavior is thus very similar to that reported previously with platinum (*13*). On some occasions, a high degree of epitaxy was observed, and a typical micrograph is shown in Fig. 2(a). No difference in catalytic behavior was, however, found between such films.

Figure 2(b) shows a typical surface replica from a random polycrystal film which had been deposited at 0°C and not heated above room temperature. By comparison, a film deposited at 0°C and subsequently heated to 300°C for 30 min showed in replication an almost flat surface with only the faintest outline of the crystal boundaries visible. Figures 2(c) and 2(d) show data for a typical film deposited on evaporated sodium chloride at 250°C. The transmission diffraction result in Fig. 2(c) clearly shows {100} orientation. The nickel forms a single crystal over the face of the sodium chloride crystal, and dislocations are clearly seen in the nickel. Although the sodium chloride crystals are randomly arranged, it is clear that the {100} nickel surface is the one predominately exposed to the gas (*18*).

In no case was any evidence found from surface replicas for gross surface rearrangement due to the catalytic reaction.

Catalytic Reactions

Reactions were generally studied at various increasing temperatures, and at each temperature the reaction rate and the exchange product distribution were evaluated, the latter from the rate of increase in the individual exchange products. The total extent of reaction in a whole experiment never exceeded 10%, and all of the product distributions can be regarded as initial distributions. The initial reaction rates R_{HC} and R_ϕ were evaluated using the rate equations previously described (*9*a). In order to calculate R_ϕ an assumption is required about the total number of exchangeable hydrogens in the molecule. The assumption was made that all of the hydrogens were equally available for exchange, the justification for this assumption being that exchange extended to all of the hydrogen atoms in the molecule in those cases where R_ϕ was evaluated. The rate R_{HC} is for the rate of disappearance of parent hydrocarbon, and R_ϕ is the rate for the number of deuterium atoms entering 100 hydrocarbon molecules per unit time. Thus R_{HC} and R_ϕ are expressed as percent per unit time for a given film area. The mean number of deuterium atoms entering a hydrocarbon molecule in the exchange act (M) was obtained both as the ratio R_ϕ/R_{HC}, and also from the product distributions; in general these methods gave reasonable agreement, but the latter was considered to be rather more accurate and was given rather greater weight.

Reactions with propane. There was a very large difference between the catalytic behavior of low-temperature nickel films on the one hand, and {111} and {100} films on the other. With low-temperature films, a rapid exchange reaction occurred at 0°C yielding propane-d_1 as the exclusive initial exchange product. However, over {111} and {100} films no reaction was detectable at 0°C. Reaction first became detectable on {111} at about 120°C and on {100} at about 160°C: in both cases propane-d_2 and propane-d_8 were the products, with the latter predominating, and in both cases at higher temperatures propane-d_8 became the only major product, being then accompanied by minor amounts of other deutero isomers. On a sintered low-temperature film no reaction was detectable until about 120°C; however, in this case both propane-d_1 and propane-d_8 were the main initial products and were of comparable importance, but propane-d_1 became of lesser importance relative to propane-d_8 at higher temperatures. Table 1 summarizes the product distribution data, while Fig. 3 shows the temperature dependence of the overall rate constants R_ϕ. The corresponding activation energies and frequency factors are collected into Table 2. The reaction rate over {100} surfaces was not of sufficient reproducibility to evaluate an activation energy. The reaction rate depended on the thermal history of the period during which thermal equilibrium was being established at the beginning of the reaction, and at the upper end of the reaction temperature range there was a tendency for

TABLE 1
INITIAL PRODUCT DISTRIBUTIONS

Hydrocarbon	Surface	Exchange temperature (°C)	Distribution[a] (%)								
			d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	M
C_3H_8	Low-temp. random polycrystal; deposited at 0°C	0	100	—	—	—	—	—	—	—	1.00
	Sintered random polycrystal; deposited at 0°C, sintered at 350°C	127	40	6	2	9	—	5	5	33	4.23
		152	13	5	2	5	—	5	13	57	6.26
		162	10	4	3	4	—	6	17	56	6.46
	{111}	120	—	19	—	—	—	—	—	81	6.86
		139	—	4	3	—	—	4	—	89	7.53
		150	—	4	—	7	—	4	5	80	7.35
		170	—	—	—	—	—	5	8	87	7.82
	{100}	160	—	37	—	—	—	10	—	53	5.58
		212	—	—	6	—	—	—	12	82	7.58
C_2H_6	Low-temp. random polycrystal; deposited at 0°C	0	98	—	2	—	—	—	—	—	1.04
		152	25	33	5	6	3	28	—	—	3.13
		189	5	8	2	4	11	70	—	—	5.18
		215	8	8	1	4	24	55	—	—	4.93
	Sintered random polycrystal; deposited at 0°C, sintered 340°C	168	45	10	—	—	—	45	—	—	3.34
		206	22	12	—	2	11	53	—	—	4.29
	High temp. random polycrystal; deposited 300°C	164	60	—	—	—	8	32	—	—	2.92
		174	30	11	—	2	6	51	—	—	3.96
		195	7	10	2	2	20	59	—	—	4.94
	High-temp. random polycrystal; deposited at 400°C	166	—	72	—	19	—	9	—	—	2.74
		199	—	—	3	1	11	85	—	—	5.78
	{111}	170	—	48	—	11	5	36	—	—	3.81
		205	2	3	4	1	13	77	—	—	5.48
	{100}	189	—	53	—	6	—	41	—	—	3.76
		202	—	13	—	6	11	70	—	—	5.25
		213	—	12	—	3	6	79	—	—	5.40
CH_4	Low-temp. random polycrystal; deposited at 0°C	242	37	—	1	62	—	—	—	—	2.88
		251	27	3	8	62	—	—	—	—	3.05
	{111}	247	41	—	—	59	—	—	—	—	2.77
		271	29	—	6	65	—	—	—	—	3.07
	{100}	268	31	—	—	69	—	—	—	—	3.07
		279	17	2	7	74	—	—	—	—	3.38

[a] All figures less than 5% are subject to substantial uncertainty, and the figures then quoted are only approximate.

the rate to fall with increasing temperature. Thus, the irreproducibility is ascribed to a self-poisoning reaction by strongly adsorbed residues.

Reactions with ethane. As with propane, there was a large difference in initial product distribution depending on the nature of the film catalyst. Over low-temperature films exchange occurred at 0°C to give ethane-d_1 as the almost exclusive product. However, on increasing the temperature this reaction ceased and exchange did not

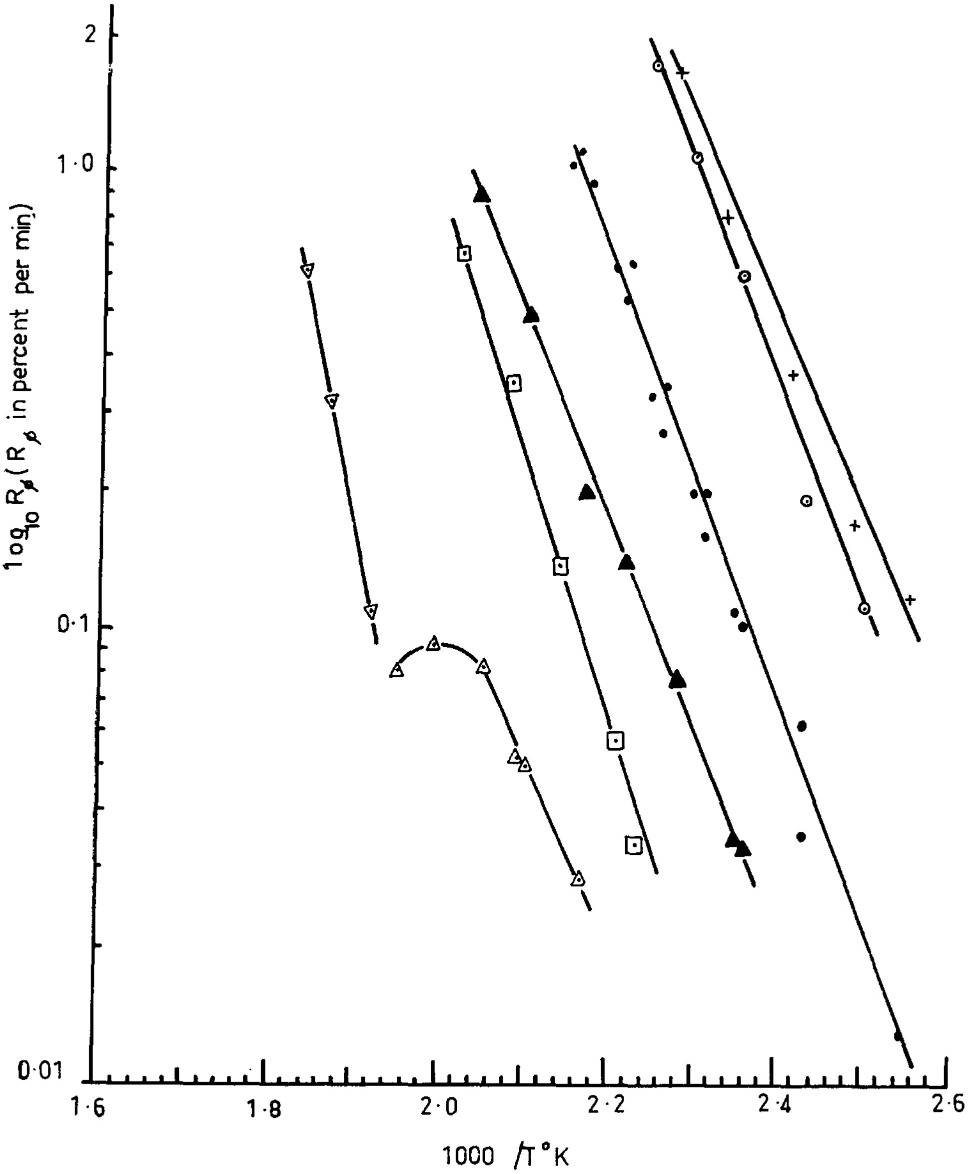

FIG. 3. Dependence of rate R_ϕ on temperature: ●, C_3H_8 on {111} nickel films; ○, C_3H_8 on nickel films deposited on glass at 0°C and sintered before reaction at 340°C for 30 min (sintered random polycrystal films); +, C_3H_8 on nickel films deposited on glass at 0°C (low-temperature random polycrystal films); □, C_2H_6 on {111} nickel films; ▲, C_2H_6 on nickel films deposited on glass at 0°C (low-temperature random polycrystal films); △, C_2H_6 on {100} nickel films; ▽, CH_4 on {111} nickel films. In all cases R_ϕ is in percent per minute for actual film areas.

recommence until about 150°C: it then did so to give ethane-d_1, -d_2, and -d_6 as the main products, and at temperatures above 150°C ethane-d_6 became the dominant product. Over {111} and {100} films, however, no exchange occurred at 0°C, and exchange was first detected at about 160–170°C. Over {111} films at 170° ethane-d_2, -d_4, and -d_6 were the products, with ethane-d_2 predominating; however, at higher temperatures ethane-d_6 became the dominant product. Very similar behavior was found for exchange on a film which was deposited on mica at 400°C but which failed to epitax

TABLE 2
Activation Energies and Frequency Factors

	E (kcal mole^{-1})	$\log_{10} A$ (A in D atoms cm^{-2} sec^{-1})[a]
CH_4, {111} surface	43 ± 2	29.5 ± 0.5
C_2H_6, {111} surface	26 ± 3	23.6
C_2H_6, {100} surface	21 ± 4	20.4
C_2H_6, low-temperature random polycrystal film	21 ± 1	20.4
C_3H_8, {111} surface	22 ± 1	23.0
C_3H_8, sintered random polycrystal film	22 ± 2	22.6
C_3H_8, low-temperature random polycrystal film	19 ± 1	21.0

[a] The frequency factors, A, were expressed per unit surface area by assuming that for {111} and sintered polycrystalline films the ratio of actual film surface area/geometric film area was 1.3 and that for {100} films this ratio was 1.6 (an approximate estimate from the electron microscopic evidence); for low-temperature random polycrystal films the film areas were taken from previous data (*15*, *20*, *22*).

or to orient and grew with a largely random polycrystal orientation. However, film deposition at 300°C, or sintering a film to 340°C which had been deposited at 0°C both resulted in product distributions mainly resembling those from the low-temperature films rather than high-temperature films. The distribution data are recorded in Table 1. Figure 3 records the dependence of R_ϕ on temperature, and the corresponding activation energies and frequency factors are recorded in Table 2. The reaction over {100} surfaces showed a falling rate with increasing temperature at the top end of the temperature range, due presumably to self-poisoning by strongly adsorbed residues; for this reason the kinetic parameters on this surface could only be obtained with poor accuracy.

Reactions with methane. Over low-temperature films, as well as over {111} and {100} films, methane exchange commenced at a measurable rate at about 240–250°C. The distribution of reaction products did not depend significantly on film structure: in all cases methane-d_1 and methane -d_4 were the main initial products. The product distributions are recorded in Table 1. Figure 3 records the dependence of R_ϕ on temperature, and the corresponding activation energies and frequency factors are contained in Table 2. The reaction rate over {100} surfaces was not of sufficient reproducibility to evaluate an activation energy and the circumstances were similar to the situation with propane; the reasons are probably similar.

Discussion

We first comment on whether films prepared at high temperatures (i.e., epitaxed or sintered) suffered from appreciable surface contamination compared to low-temperature films. It should be noted that all of the present films were prepared under vacuum conditions that were very much better than those previously employed in studying these reactions (*9*); we estimate that in the previous experiments the pressures during film preparation were worse by a factor of at least 10^2. Yet the general behavior of the films used previously was very similar to that of the low-temperature films used in the present work. We consider, therefore, that the differences found in the present work between reactions over low-temperature films and high-temperature films (epitaxed, oriented, or sintered) reflect real differences in the surface structures. Evidence for the absence of significant contamination is also provided by the following observation. On a typical {111} film, deuterium adsorption was measured at 90°K, and the uptake was $1.58 \times 10^{17} D_2$ when the equilibrium deuterium pressure was in the range 10^{-3}–10^{-2} torr and the isotherm was virtually parallel to the pressure axis. If one assumes that this corresponds to a monolayer coverage of deuterium with a surface stoichiometry for the ratio adsorbed D/surface Ni of 1/1, one may compare this deuterium uptake with that expected for the estimated film area. For random polycrystal nickel films deposited on glass at 300°C under very similar geometric conditions to those used in the present work, McConkey (*16*) used a BET measurement with xenon at 90°K to estimate that the ratio of actual surface area to geometric area was about 1.3. Since the appearance of the surface replicas of those films was generally similar to the present {111} films, it is not unreasonable to assume the above roughness factor for the present {111} films; in this case, the latter have a true surface area of about 160 cm^2, and this corresponds to 3.01×10^{17} surface nickel atoms. It is clear from the data of Quinn and Roberts (*17*) that, particularly if attention is restricted to rapid deuterium adsorption at low temperatures, the deuterium uptake will be depressed by surface contamination by preadsorbed CO_2 and O_2, these (with CO) being likely important components of the residual gas in an ultrahigh-vacuum system. Although this comparison is only quite approximate, a comparison of the deuterium uptake with the estimated number of surface nickel atoms makes it seem likely that surface contamination of the {111} films could not have been appreciable. A similar comparison with {100} films cannot be made because there are no data from which to estimate an actual film area. The electron micrographs make it clear that the effective roughness factor must be appreciably greater than unity, but it is now apparent (*18*) that on {100} nickel the surface area cannot be easily estimated by the BET method using xenon adsorption at 90°K (or below). However, since {100} nickel films were deposited under vacuum conditions that were similar to those used for {111} films, we believe it is reasonable to conclude that {100} films were, like {111} films, free from serious surface contamination.

The exchange reactions at 0°C observed in the present work with propane and ethane on low-temperature random polycrystal films closely resemble the corresponding reactions studied previously; (*9*b, c) in all cases the d_1 compound was the almost exclusive product. However, this low-temperature reaction is apparently confined to specific sites on the nickel surface which are removed by high-temperature treatment of the film. Thus, on sintered random polycrystal films, as well as on {111} and {100} surfaces, no reaction could be detected at 0°C, but reaction could be studied in the general range 120–200°C, and it then occurred to yield a different product distribution to the exchange at 0°C.

On {111} and {100} surfaces, the following features may be noted about the product distributions from propane and ethane: (i) the d_1 compound is, within experimental error, completely absent; (ii) at the lower end of the reaction temperature range, the d_2 and the perdeutero compounds are the dominant products, but the distributions vary strongly with temperature and towards the upper end of the temperature range the perdeutero compound is the overwhelmingly dominant product. It is important to recognize that these product distributions (particularly those at the lower end of the temperature range) are incapable of explanation in terms of the basic multiple exchange model previously proposed (*9*b) which assumes rapid interconversion between an adsorbed alkyl and an adsorbed alkene group,* since this theory requires that in a one-parameter (P) distribution the proportions of deutero compounds shall either increase or decrease monotonically from d_1 to perdeutero, depending on the value of P. Superposition of

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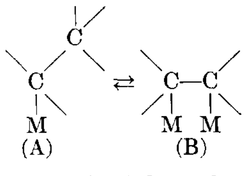
* This interconversion is $(\text{alkyl})_s \rightleftarrows (\text{alkene})_s$,



and the parameter P defines the ratio of the chance of the process $(A) \rightarrow (B) \rightarrow (A)$, relative to the chance of desorption of (A). For future use, it will be convenient to use a terminology by which is specified both the particular carbon atom which is attached to the surface, as well as the nature of the bonding. The numbers 1, 2, 3 will be used to designate single, double, and triple bonds respectively, and these will appear as subscripts on the appropriate carbon number. Thus, the general species (A) above is designated $(1_1)_s$ and (B), $(1_1 2_1)_s$, while for specific hydrocarbons, CH_3, CH_2–M for instance, designated ethane- $(1_1)_s$, and $CH({=}M)CH({-}M)CH_2({-}M)$ as propane – $(1_2 2_1 3_1)_s$, etc. This type of terminology is used irrespective of whether the double bond, for instance, is to a single metal atom, i.e., as C=M, or the carbon is bonded to two surface atoms as M–C–M.

two or more one-parameter distributions can generate distributions with a minimum lying between d_1 and perdeutero, but no reasonable combination can reproduce, for instance, a distribution consisting of d_2 and perdeutero only, nor can such a distribution be accounted for by assuming that (with propane) the interconversion is extended to include a triadsorbed residue such as $(1_1\ 2_1\ 3_1)$s (*19*). It must be emphasized that the central feature of this mechanism is the rapid interconversion among these adsorbed species by a specified path.

With propane, reaction on a sintered random polycrystal film (deposited at 0°C, sintered at 350°C) gave a product distribution intermediate in character between that for a low-temperature reaction (i.e., all d_1 at 0°C) and for reaction over {111} or {100} surfaces. It appears, therefore, that this sintering treatment diminished but did not totally eliminate the number of sites responsible for d_1 formation. Reaction of ethane on a random polycrystal film which had been deposited with the substrate at 400°C gave a product distribution similar in its main features to that obtained over {111} of {100} surfaces. In this case, the more severe thermal treatment had apparently removed the d_1 sites completely, whereas the milder treatment of deposition of 300°C still gave an appreciable amount of ethane-d_1 product. In this connection, it is of interest to note that Anderson and McConkey (*20*) found that if a nickel film was deposited on a glass substrate at 0°C and subsequently sintered at 300°C to constant area, the area was about 20% greater than that for a film deposited at 300°C.

The absence of d_1 from the exchange products formed from ethane and propane on {111} and {100} surfaces clearly shows that $(1_1)_s$ or $(2_1)_s$* species do not exist in an appreciable steady state concentration. The products from reactions of ethane and propane over {111} and {100} surfaces showed a tendency for deuterium atoms to enter in pairs, so that the products with even numbers of deuterium atoms are the most important. This is most evident at the lower end of the reaction temperature range. The question immediately arises as to whether the important d_2 product is formed from $(1_2)_s$ or $(2_2)_s$ or from $(1_1 2_1)_s$. The following arguments suggest the former. If the reaction involved $(1_1 2_1)_s$, one would expect some degree of interconversion with $(1_1)_s$ or $(2_1)_s$ and the d_2 product should then be accompanied by at least some d_1, but the latter was not detected. Furthermore, *pairwise* deuterium introduction involving $(1_1 2_1)_s$ would have to proceed, for instance, via interconversion between $(1_1 2_1)_s$ and $(1_2 2_2)_s$. It is not easy to reconcile the degree of synchronization required for this to occur without proceeding via species such as $(1_1 2_2)_s$, and if this occurred products with odd numbers of deuterium atoms could be easily produced. The present product distributions are thus most reasonably accounted for in terms of species in which carbon atoms are doubly bonded to the surface. The simplest of these are $(1_2)_s$ and $(2_2)_s$, desorption of which yields the d_2 product. In addition there are species bonded at more than one carbon atom: these are ethane-$(1_2 2_2)_s$, propane-$(1_2 2_2)_s$, and propane-$(1_2 2_2 3_2)_s$, and desorption of these yields ethane-d_4, propane-d_4, and propane-d_6, respectively. With regard to the likelihood of extensively dehydrogenated surface species such as these, we may note that Galwey and Kemball (*21*) found an H/C ratio of about 1.4 in the surface residue produced by the adsorption of *n*-pentane on nickel at 60–200°C. Similarly, Anderson and Baker (*22*) found an H/C ratio of about 1 from the adsorption of propane on nickel at about 210°C. For the adsorption of ethane on nickel at about 200°C, the data of Anderson and Baker (*22*), and of Wright, Ashmore, and Kemball (*23*) suggest that the H/C ratio of the adsorbed residue is certainly not greater than 2, and may well be less, since Wright, Ashmore, and Kemball's (*23*) data give, by a short extrapolation, an H/C value of about 1.2 at 120°C.

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* Kinetic evidence obtained by Kemball (*9c*) suggests that in low-temperature propane exchange on nickel with propane-d_1 as the dominant product, the initial product is mainly propane-2-d_1.

In short, it may be concluded that there is every likelihood of the formation of extensively dehydrogenated residues during ethane and propane exchange reactions on nickel at temperatures in the range 120–200°C and the present work strongly suggests that these are involved in the exchange reactions.

We must next comment on the mode of formation of perdeutero products from ethane and propane. Firstly, it should be noted that if there were an interconversion process such as ethane-$(1_2)_s \rightleftarrows$ ethane-$(1_22_2)_2$ with free rotation about the carbon–carbon bond in ethane-$(1_2)_s$, this would readily give ethane-d_5 as a product, and analogous interconversions in adsorbed propane would give propane-d_7 and propane-d_5. Indeed the quite significant amounts of ethane-d_5 and propane-d_7 formed at the upper region of the reaction temperature range may well be formed in this way. However, at the lower region of temperature, the absence of these deutero products makes it unlikely that these interconversions occur, and it is therefore equally unlikely that the perdeutero products can be formed in this way either. There are two distinct but related paths by which the perdeutero product could be formed. The first, and most likely path, is the exchange of the remaining hydrogens in the residues ethane-$(1_22_2)_s$ and propane-$(1_22_23_2)_s$. This would be entirely analogous to the mode of formation of CD_4 suggested by Kemball (*9*a) and presumably proceeds, as in the methane case, by further dissociation and reconversion to the original residue; that is, there is an interconversion ethane-$(1_22_2)_s \rightleftarrows$ ethane-$(1_32_2)_s$, etc. If the lifetime of the ethane-$(1_22_2)_s$ and propane-$(1_22_23_2)_s$ residues is substantial, there would be little chance of the formation ethane-d_5 or propane-d_7, but if this is so one would expect the perdeutero product substantially to exceed the amount of deutero isomer with two less than the maximum number of deuterium atoms. This is, in fact, the case. The alternative path for perdeutero product is via a completely dehydrogenated surface residue. It should be remembered that H/C values for surface residues are average figures and, for instance, if the value for propane on nickel is 1, that is, the average residue is $(C_3H_3)_s$, the presence of some $(C_3H_6)_s$ implies also the presence of some C_3H_n with $n < 3$. However, although some completely dehydrogenated residues are to be expected, they may be expected on energetic grounds to be less abundant than partially dehydrogenated residues, and it then becomes difficult to account for the importance of perdeutero product.

The exchange reactions of methane differ from those of ethane and propane in a number of important respects. The methane reaction shows no dependence on surface structure, since similar product distributions were obtained on low-temperature random polycrystal films as on {111} and {100} surfaces. The d_1 and d_4 compounds were the dominant products, the d_2 and d_3 compounds being formed only in trivial amounts. Methane exchange occurred in a temperature range some 50–100°C above that required even for the high-temperature reactions of ethane and propane, and it occurred with markedly higher activation energy.

The difficulty of exchanging methane compared to the other saturated hydrocarbons has been noted previously (*24*), and may arise from the fact that the C–H bond strengths in methane are higher than in ethane (*25*). However, methane-$(1_1)_s$ residues are clearly formed with comparable ease on all surfaces. We suggest that this marked difference in behavior compared to ethane and propane may lie in differences in relative C–H bond strengths for successive dissociations, so that there is a substantial energy barrier for further dehydrogenation of methane-$(1_1)_s$ to methane-$(1_2)_s$. The result is that methane-$(1_1)_s$ is retained as an important surface species on {111} and {100} under conditions where ethane and propane readily give $(1_2)_s$ and $(2_2)_s$. However, the importance of methane-d_4 product and the trivial amounts of d_2 and d_3 products shows that when the necessary activation energy is available to dehydrogenate beyond methane-$(1_1)_s$, the formation of methane-d_4 is facile and, following the previously suggested mechanisms, (*9*a) this is because it is then either easy to produce methane-$(1_4)_s$, or (more likely), there is an easy interconversion between methane-$(1_2)_s$ and methane-$(1_3)_s$.

At least on nickel, it is clear that, unlike ethane and propane, the exchange of methane is a poor diagnostic reaction with which to study the effects of surface structure. The primary reason for this lies in the type of carbon-to-metal bonding accessible to the carbon atom.

The sites responsible for the formation of singly adsorbed residues from ethane and propane are associated with surface features that are thermally unstable. For this reason one may speculate that these sites are metal atoms with a low coordination number—possibly metal atoms self-adsorbed on a low index plane, or atoms at the edge of a terrace or at a kink in a terrace. The ability to form carbon–metal double bonds is apparently a characteristic of atoms in a {111} or {100} surface. The general behavior of {111} and {100} surfaces is quite similar and the data in Table 2 show that, within experimental error, there is no significant dependence of the activation energy on the nature of the surface. Certainly we have no evidence to support a belief that a perfect {111} surface has qualitatively different catalytic properties to {100}. Low coordination metal atoms at terrace edges or kinks can arise both in high index surfaces as well as associated with macroscopic crystal features, such as crystal corners and edges, and we have no evidence to distinguish these possibilities.

So far, this discussion has been constructed entirely within the framework of σ-bonded surface species. Proposals for the exchange of saturated hydrocarbons which invoke π-bonded surface intermediates (*26*) assume that the π-orbitals involve at least three carbon atoms, so that π-allylic species are the smallest envisaged. On the other hand, in the present work the exchange behavior of ethane and propane is quite similar, and any π-bonded surface intermediate from ethane would of necessity be limited to π-bonded ethylene or acetylene. We shall therefore limit our discussion to the possibility of surface species of the π-bonded olefinic and acetylenic types. Both π-olefinic and π-acetylenic nickel complexes are known (*27*, *28*). However, although this circumstantial evidence would support the proposition that adsorption into this mode may occur, at least to some extent, it remains a matter of some speculation whether such species necessarily play an essential role in the exchange mechanism. It is known (*27*), for instance, that in a π-olefin complex such as π-cyclododeca-1,5,9-triene nickel, the π-bonds are quite weak and this substance decomposes readily at 140–150°C to give nickel and the olefin. It also reacts easily with hydrogen to give cyclododecane and nickel. It seems therefore that under exchange conditions the surface concentration of π-olefinic residue must be small. If it be admitted that two hydrogen atoms are extracted in a concerted fashion from ethane to yield $[\pi\text{-ethylene}]_s$ and two more in a similar fashion to yield $[\pi\text{-acetylene}]_s$, a reaction scheme providing for the formation of deuteroethanes with even deuterium numbers can obviously be constructed. However, if the hydrogens are removed singularly then a reaction sequence such as the following is likely,

$$C_2H_6(g) \rightarrow [\sigma - C_2H_5]_s + (H)_s \rightarrow [\sigma - C_2H_4]_s + 2(H)_s \rightarrow [\pi - C_2H_4]_s + 2(H)_s \text{ etc.}$$

with the reverse of this sequence leading to desorption. Here the exchange is dominated by the behavior of the σ-bonded species and the discussion would reduce in its essentials to that already given, irrespective of the formation of the π-bonded species.

It is clear from this work that on all these nickel surfaces there is likely to be an appreciable concentration of very strongly bound hydrocarbon residues. In this connection, it is of interest to note that an attempt to carry out an exchange reaction between ethane and deuterium over an ultra-high-vacuum chromium film deposited at 350°C, failed completely. In the reaction temperature range 0–300°C no deuteroethanes were formed, but at the upper end of this temperature range some hydrocracking occurred with the formation of deuteromethanes. This behavior is in marked contrast to that reported previously (*9*b) for exchange over a chromium film prepared under ordinary high-vacuum conditions and where ready exchange was found. We attribute the lack of reactivity of the ultra-high-vacuum film to complete self-poisoning by strongly adsorbed residues, and it is likely that the reactivity of the earlier film was due to the presence of adventitious oxide; that is, exchange occurred on a chromium oxide surface upon which self-poisoning did not occur. Thus, a clean chromium surface behaves with respect to the saturated hydrocarbons in much the same way as iron, and a detailed interpretation of this behavior has previously been presented (*2*c). This behavior of chromium is an illustration that a clean metal surface is not necessarily a better catalyst for hydrocarbon exchange than a contaminated one. The following conclusion seems inescapable. Since most of the existing data for hydrocarbon exchange have been obtained over evaporated metal films prepared under conditions where appreciable, and possibly substantial, contamination may have occurred, the results must be assumed to be suspect insofar as they relate to the behavior of the clean metal. Furthermore, the results of the present work clearly show the need to study hydrocarbon reactions over metal surfaces which are as structurally homogeneous as possible, since with molecules of any degree of complexity different types of surface sites can lead to substantially different catalytic behavior. For diagnostic purposes in relation to surface structure, a reaction having multiple reaction paths is likely to be more satisfactory than one which depends only upon studying variations in kinetic parameters such as activation energy and frequency factor. It is often difficult to measure these kinetic parameters with sufficient accuracy, but also their variation with surface structure may well only be relatively small. It is likely that in general it will be easier and more instructive to attempt to correlate product distribution and molecular geometry with surface structure.

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