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Studies of Topochemical Heterogeneous Catalysis

3. Catalysis of the Reduction of Metal Oxides by Hydrogen

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The reactions of hydrogen gas with solid samples of the oxides Co_3O_4, Fe_2O_3, UO_3, Ni_3O_4, MnO_2 and V_2O_5 have been studied in the presence of a platinum catalyst either deposited on the oxide surface, or supported on alumina and physically mixed with the oxide. Activation energies measured for the catalyzed reactions have a common value of 23 ± 2 kcal mole^{-1} which is equal to the activation energy for the desorption of hydrogen atoms from a platinum surface. The reduction mechanism involves transfer of hydrogen atoms both by surface and gas diffusion. Gas diffusion is significant only at temperatures above 350°C.

INTRODUCTION

In previous publications (*1*, *2*) we reported details of the topochemical heterogeneous catalytic reaction of solid uranium tetrafluoride with gaseous oxygen to produce solid uranyl fluoride and gaseous UF_6. A systematic study of this reaction revealed that the activation energy for the catalyzed reaction was independent of the physical properties and chemical type of catalyst but was related to the activation energy for the production of activated oxygen species at the catalyst surface. Differences in catalytic activity were due only to differences in the entropies of adsorption of gaseous oxygen on the materials involved, this being a function of surface properties. In the same studies we observed that the reaction of hydrogen with both UO_2F_2 and UO_3 could be catalyzed by a number of metals, and again the activation energies for these catalyzed reactions were, within experimental error, the same.

Catalysis of the reduction of metal oxides by hydrogen has been the subject of a number of papers in recent years since, in 1964, Khoobier (*3*) reported the catalytic action of platinum on the reduction of WO_3 (*5*, *6*). Subsequent papers discussed the oxides V_2O_5 (*4*), MoO_3 (*6*), NiO (*7–9*), Fe_2O_3 (*10*), Fe_3O_4 (*10*) and CuO (*11*), all of which it was claimed could be catalytically reduced by hydrogen in the presence of platinum or other metal additives. A recent review by Il'chenko (*12*) emphasized the limited extent of understanding of the mechanism of such reactions and made apparent the obvious need for detailed experimental studies covering a number of metal oxides in order to gain a more comprehensive insight into the reaction mechanism. This study examined the reduction of a large number of metal oxides both in the presence and absence of catalysts in an attempt to fulfill this need.

EXPERIMENTAL METHODS

Materials

Table 1 lists the sources or methods of preparation of the oxides used in this study. Platinum or ruthenium was deposited on the oxides or on an alumina support by slurrying the appropriate weight of chloroplatinic acid or ruthenium(III) chloride with the support using a minimum volume of water, evaporating to dryness in a rotary evaporator, drying at 100°C in air for 1 hr, followed by reduction to the metal at 400°C in flowing hydrogen for 3 hr. Both

TABLE 1
METHODS OF PREPARATION OF OXIDES

Oxide	Method of preparation or source
Co_3O_4	Heating $Co(NO_3)_2 \cdot 6H_2O$ in air at 700°C
V_2O_5	Heating $(NH_4)_2VO_3$ in air at 400°C
Ni_3O_4	Heating $Ni(NO_3)_2 \cdot 6H_2O$ in air at 450°C
UO_3 (15 m^2 g^{-1})	Heating $(NH_4)_2$ U_2O_7 in air at 350°C
UO_3 (1.4 m^2g^{-1})	Heating $UO_2(NO_3)_2$ $6H_2O$ in air at 350°C
Fe_2O_3 (<0.5 m^2g^{-1})	Merck (Germany)
Fe_2O_3 (≈30 m^2g^{-1})	By method of Parks and De Bruyn (*13*)
MnO_2	Ajax Chemicals (Australia)

coated and uncoated oxides were sieved; the −300 mesh (50 μm) fraction was retained. X-Ray powder patterns confirmed the compositions of the oxides which were found to be unchanged by coating with catalyst.

Commercial purity hydrogen and oxygen free dry nitrogen were supplied by Commonwealth Industrial Gases Ltd., Australia. All gases were dried by passage through columns filled with molecular sieves.

Apparatus and Procedure

Rates of reduction were measured using the apparatus described previously (*1*). The Cahn thermobalance was operated isothermally at temperatures such that the times for complete reaction varied between 5 and 60 min, thus permitting accurate rate measurements. Fifty or 100 mg samples of oxides were used. Reductions were carried out at atmospheric pressure in flowing hydrogen (900 ml/min).

RESULTS

The reduction by gaseous hydrogen of the oxides Co_3O_4, V_2O_5, Fe_2O_3, MnO_2, UO_3 and Ni_3O_4 has been studied both in the presence and absence of a platinum catalyst.

The ability of the platinum catalyst to promote the reduction was examined in the cases: (a) with catalyst deposited on the surface of the metal oxide and (b) with catalyst, either as the metal alone or supported on an inert support, mechanically mixed with the oxide.

Data on reaction order and activation energy were obtained over the initial 25% of the reaction where interferences due to the formation of intermediate products were minimal. Activation energies were calculated from measurements of the time required for a fixed weight loss.

Table 2 summarizes the results of such measurements for the different oxide systems and these are discussed individually below.

TABLE 2
DATA FOR THE CATALYZED REDUCTION OF METAL OXIDES WITH HYDROGEN

Oxide	Uncatalyzed reduction		Catalyzed[a] reduction	
	Temp range (°C)	E_A (kcal $mole^{-1}$)	Temp range (°C)	E_A (kcal $mole^{-1}$)
Co_3O_4	150–260	6–14	70–105	22
V_2O_5	486–556	18	187–240	25
			212–280	23[b]
Fe_2O_3 (<0.5 m^2 g^{-1})	354–444	18	276–357	20
Fe_2O_3 (≈30 m^2 g^{-1})			235–307	21
UO_3 (15 m^2 g^{-1})	380–480	25	285–310	23
UO_3 (1.4 m^2 g^{-1})	380–480	24	380–460	26
Ni_3O_4	203–274	23	234–282	21
MnO_2	212–280	22	200–250	23

[a] 0.5 wt% platinum on oxide surface.
[b] 0.5 wt% ruthenium on oxide surface.

Cobalt Oxide Co_3O_4

Our observations of the Co_3O_4 reduction in the absence of catalyst confirm those of Bracconi and Dufour (*14*) who showed the reduction kinetics to be a function of reaction temperature. At a low temperature, 217°C, the rate curve was clearly sigmoidal, the apparent reaction order changing from zero to second order over the first 70% of the reaction, this being typical of an autocatalytic reaction. At a higher temperature, 256°C, the rate curve was linear for at least 50% of the reaction (Fig. 1).

The reaction kinetics are therefore temperature dependent probably as a result of differences in the rates of reaction of Co_3O_4 and the autocatalytic intermediate with increasing temperature. The activation energy was of little significance and varied between 6 and 14 kcal $mole^{-1}$. With platinum deposited on Co_3O_4, the reduction occurred at significantly lower temperatures (Table 1), with the reaction order constant over the initial 50% of the reaction and independent of temperature. The activation energy measured under these conditions was 22 kcal $mole^{-1}$. Figure 1 clearly shows a change in the kinetics of Co_3O_4 reduction in the presence of catalyst.

Vanadium Pentoxide V_2O_5

In the absence of catalyst, the rate curves for the reduction of V_2O_5 are S-shaped over the temperature range 486 to 556°C (Fig. 2). The activation energy for this reaction lies in the range 18 to 24 kcal $mole^{-1}$, being a function of the temperature range and fraction of the reaction over which the measurement is made. A surface coating of 0.5 wt% platinum on V_2O_5 significantly lowered the reduction temperature by nearly 300°C. Under these conditions, the rate curve obeyed first order kinetics over the first 25% of the reaction and the activation energy so calculated was 25 kcal $mole^{-1}$. In the presence of the same concentration of ruthenium catalyst, a value of 23 kcal $mole^{-1}$ was obtained.

The procedure adopted in the thermogravimetric studies involved heating to temperature for 10 min in flowing nitrogen before introducing hydrogen and recording the weight loss. When higher surface platinum concentrations (5%) were used, sample weight loss was almost instantaneous at temperatures as low as 100°C. No reaction occurred on exposing the sample at 30°C to hydrogen, but when the sample temperature was slowly raised to

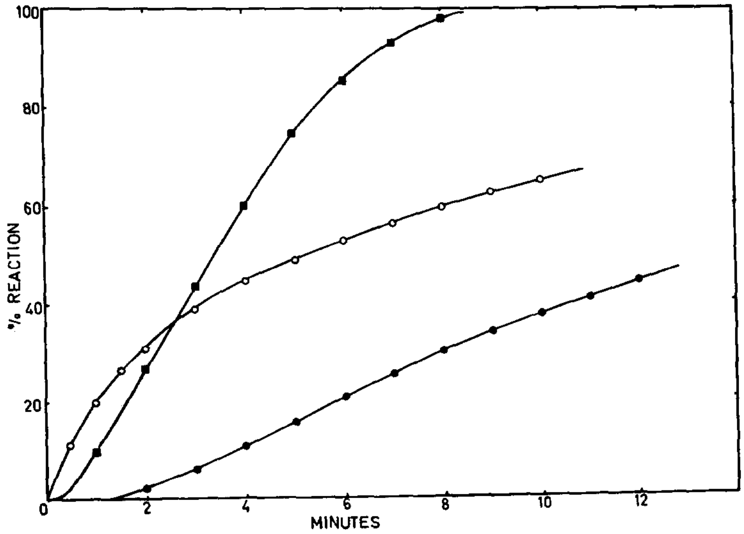

FIG. 1. Reaction of Co_3O_4 with hydrogen: (●) at 217°C, no catalyst; (■) at 256°C, no catalyst; (○) at 102°C, Co_3O_4 coated with 0.5% Pt.

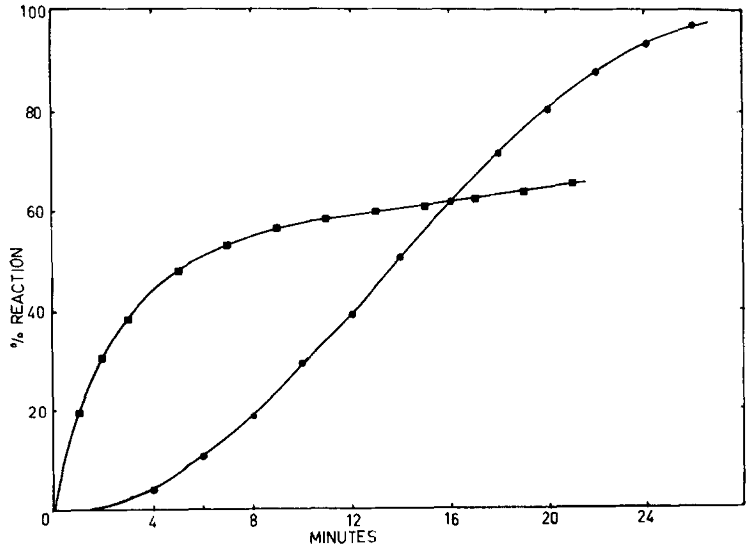

FIG. 2. Reaction of V_2O_5 with hydrogen: (●) 570°C, no catalyst; (■) 239°C, V_2O_5 coated with 0.5% Pt.

200°C in flowing nitrogen and the sample was again exposed to hydrogen, a slow weight loss was observed. This is in contrast to the instantaneous loss in weight when a sample is introduced to a furnace already at 200°C. This unusual behavior was unaltered by the presence of moisture in the gas streams.

In the presence of 10 wt% of a 5% platinum on alumina catalyst, the reduction of V_2O_5 at 350°C proceeded slowly but nevertheless significantly faster than in the absence of catalyst.

Ferric Oxide Fe_2O_3

The reduction of Fe_2O_3 by hydrogen is known to proceed through the stages $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. The first of these transformations appears as a distinct break in the kinetic curve (*15*). In keeping with the known effects of surface properties on the reactivity of metal oxides, we observed that a low surface area Fe_2O_3 (<0.5 $m^2\,g^{-1}$) gave an apparent single step reduction of variable order at temperatures between 354 and 444°C (Fig. 3). At the lower temperature of 308°C at which the reaction time was in excess of 12 hr, the transformation Fe_2O_3 to Fe_3O_4 was clearly revealed. A higher surface area sample (≈ 30 $m^2\,g^{-1}$) studied at 308°C similarly showed this transformation.

The reduction could be catalyzed by the surface deposition of 0.5 wt% platinum on Fe_2O_3 (<0.5 $m^2\,g^{-1}$), such that in the range 276 to 357°C the clearly visible steps appeared in the kinetic curves equivalent to the transformations $Fe_2O_3 \rightarrow Fe_3O_4$ and $Fe_3O_4 \rightarrow Fe$. The activation energy determined on the second of these steps was 20 kcal mole^{-1}. The higher surface area Fe_2O_3 in the presence of deposited catalyst exhibited the same behavior, now in the range 235 to 307°C with an activation energy of 21 kcal mole^{-1}.

Uranium Trioxide UO_3

We have previously reported data for the catalyzed reduction of UO_3 (*1*). We observed that by platinum coating the sample it was possible to alter the reaction curve from S-shaped to an apparent first order curve with the reaction temperatures being decreased by approximately 100°C. Activation energies measured in the presence and absence of catalyst were 23 and 25 kcal mole^{-1}, respectively. When a low surface area UO_3 sample was used, the reaction followed essentially the same rate laws irrespective of the presence of catalyst,

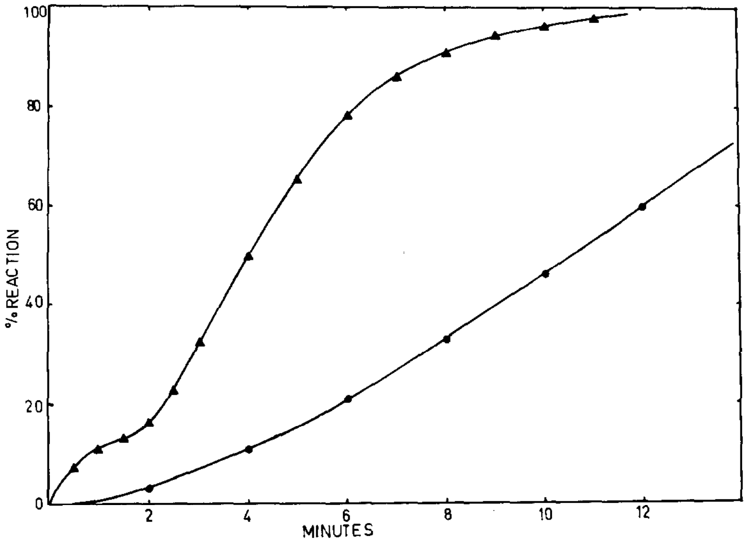

FIG. 3. Reaction of Fe_2O_3 with hydrogen: (●) 378°C, no catalyst; (▲) 378°C, Fe_2O_3 coated with 0.5% Pt.

although the catalytic effect was less marked (Table 2). The latter reaction was also catalyzed by the presence of an alumina-supported platinum catalyst.

Nickel Oxide Ni_3O_4

The addition of catalyst to the surface of Ni_3O_4 produced essentially little change in the shape of the reduction curve although the presence of catalyst appeared to lower the reaction temperature by approximately 30°C. The magnitude of the catalysis was therefore only small and may be attributable to differences in surface properties, although every attempt was made to eliminate such differences by pretreating the uncoated Ni_3O_4 sample in the same manner as that used in the deposition of catalyst.

Manganese Dioxide MnO_2

As in the case of Ni_3O_4 we observed a small but significant lowering of the temperature of the catalyzed reaction with little change in reduction kinetics.

DISCUSSION

In any investigation of solid state reactions, the surface properties of the materials being studied are of prime importance. It has been demonstrated previously (*14*) that the kinetics of the reduction of solid oxides by hydrogen gas depend greatly on the thermal history of the sample. Transitions from linear to S-shaped reaction curves are not uncommon as the sample is pretreated at higher temperatures. Such changes reflect differences in surface properties; typically increasing the temperature sinters the particles, with a reduction in surface area. Although we have taken particular care to ensure that the surface properties of the oxides on which catalysts are deposited are as similar as possible to those of the free oxide samples such differences are none the less possible. Because of this possibility, the results for the "uncatalyzed" reactions have been examined more from the point of their differences from the catalyzed reactions rather than from a consideration of their absolute significance. Our interest was primarily in the catalyzed reactions and in particular in the activation energies for these reactions.

The results for ferric oxide indeed reveal the effect of changing surface area since in the absence of catalyst the rate curves lose their sigmoidal character if the surface area of the oxide is increased or if the reaction temperature is decreased. All reactions at 308°C irrespective of surface area, reaction time and the presence of catalyst, had a similar reaction order. The unusual behavior of V_2O_5 with high surface concentration of platinum is also probably attributable to changes in surface properties.

It is important to emphasize the limited significance of the concept of reaction order in solid state reactions. Order is normally defined in terms of concentration of reactants and these may well have variable values throughout a solid. It is the growth of nuclei and the time dependence of reaction intermediates which are significant in determining reaction order. We used the measurement of reaction order as an indication of whether the reaction kinetics were changing with temperature for that portion of the reaction over which we were calculating the activation energy. Obviously the significance of the latter parameter in systems where the kinetic equations are changing is limited. This will be particularly so for V_2O_5, Fe_2O_3 and Co_3O_4 for which the reaction curves are sigmoidal, with varying induction periods. Although it is possible to fit linear equations to such curves (*16*), we found it preferable, having shown that the kinetics were unaltered by temperature in the initial stages of reaction, to calculate activation energies from the time for a fixed weight loss. Activation energies so calculated, for reactions in the absence of catalyst, were in general agreement with previously reported values.

In the presence of catalyst, a clear pattern emerges:

i. Reaction curves lose any sigmoidal shape with the reaction kinetics approaching first order behavior.

ii. Activation energies for the reaction are constant within experimental error at 22 kcal mole^{-1}.

The mechanism of the reaction is we believe very similar to that for the catalyzed UF_4–oxygen reaction (*1*) for which we postulated the formation of atomic or excited molecular oxygen on the catalyst surface which is subsequently transferred by both surface and gaseous diffusion to the UF_4 surface. The ability of noble metals to dissociate hydrogen gas into atoms is well known (*17*). Kubokawa, Takashima and Toyama (*18*) have shown that the activation energy for the desorption of hydrogen chemisorbed on a platinum catalyst varies with temperature from 10 kcal mole^{-1} at below 30°C, through 19 kcal mole^{-1} at 120°C, approaching a constant value of 23 kcal mole^{-1} above 325°C. It is however outside the order of accuracy of our measurements to seek such changes in activation energies with temperature.

The ability of hydrogen atoms to undergo activated surface diffusion away from platinum centers on platinized carbon has been demonstrated by Robel, Ballou and Boudart (*19*). Our inability to promote the reduction of Co_3O_4, Fe_2O_3, and the high surface area UO_3 by using a separated catalyst would imply that in these cases transfer of hydrogen atoms occurs principally by surface diffusion. Significantly, these reactions occur at low temperatures, below 300°C. Those oxides which could be catalytically reduced using a separated catalyst, V_2O_5 and the low surface area UO_3 samples, did so at temperatures in excess of 350°C, which is evidence of the ability of atomic hydrogen to diffuse through the gas phase under these conditions. Confirmation of this was obtained by physically separating a catalyst and UO_3 pellet by several millimeters using the apparatus described previously (*1*). Reaction of the yellow oxide occurred only on the surface immediately below the catalyst pellet (Fig. 4).

In the absence of a catalyst the reaction of hydrogen on the oxide surface is believed to proceed through the formation and growth of nuclei (*4*, *16*). The rate law followed is governed by the number of such nuclei originally present and the manner in which they grow. From a physical viewpoint the catalyst crystallites may be regarded as reaction nuclei on the oxide surface. Such centers are more plentiful and more efficient nucleation sites than those present in the oxide alone so that the nucleation rate laws are altered in the presence of catalyst. This was observed in all cases except that of Ni_3O_4 and MnO_2 where the catalytic effect was very small. Not surprisingly Ni_3O_4 and MnO_2 were

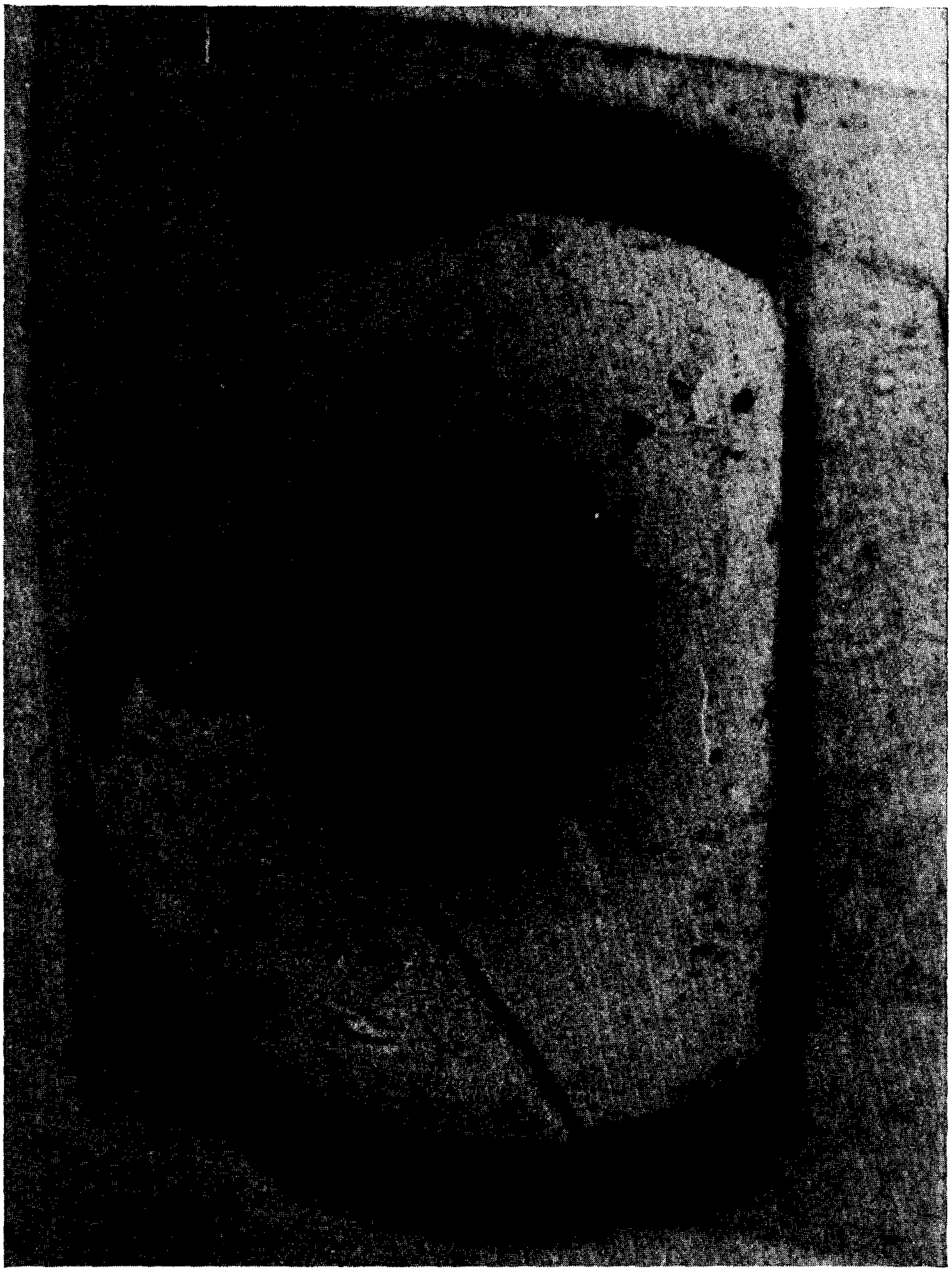

Fig. 4. Pellet of UO_3 reduced in hydrogen at 400°C, 1 mm below a ⅛ in. diameter Pt on alumina pellet.

themselves shown to be active catalysts for the reduction of UO_3 by hydrogen.

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