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The Adsorption of Hydrogen Atoms on Support Oxides Active in Promoting Hydrogen Atom Spillover

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The adsorption of hydrogen atoms generated in the gas phase to a variety of oxide supports, reported to be active in promoting hydrogen atom spillover, has been studied at 77 and 273°K. Hydrogen uptake was insufficient to account for catalytic enhancement due to hydrogen atom migration followed by adsorption. Supports prepared under alkali conditions in general adsorbed more active hydrogen. Hydrogen uptake by tungsten trioxide was about two orders of magnitude greater than on the other support oxides investigated.

INTRODUCTION

The catalytic process in which hydrogen atoms are generated on the metallic component of a supported metal catalyst and can then migrate across the support has been called hydrogen atom spillover (*1*). Under certain conditions, it has been suggested that hydrogen atom spillover can lead to an increase in the catalytic activity of a supported metal catalyst. This would be most obvious in such cases where the support can adsorb at least one of the reactants. Sinfelt and Lucchesi (*2*) suggested this to be the case in the hydrogenation of ethylene over supported platinum, however Schlatter and Boudart (*3*) discounted these results in the light of additional data showing that hydrocarbon contamination might account for this apparent enhancement in catalytic activity. When the catalyst was treated in air for short periods of time, these authors showed that rates of ethylene hydrogenation over supported platinum were identical to those over unsupported platinum. These initial experiments, have generated a vigorous discussion on the subject which has resulted in a rapid increase in the recent literature concerning hydrogen atom spillover (*4–10*). At present, advocates and opponents of spillover seem to be about equally divided. Undoubtedly, hydrogen atom spillover can and does occur under certain conditions. Levy and Boudart (*4*) have recently published a plausible mechanism for the platinum catalyzed reduction of tungsten trioxide at room temperature. Benson *et al.* (*5*) showed that water was required in order to obtain reduction at room temperature. They suggested that water acted as a cocatalyst by solvating a proton on the platinum surface. The solvated proton then diffuses across the support to the reduction site where it is released to form a hydrogen analogue of the tungsten bronzes. In addition to water, alcohols were also shown to act as cocatalysts in this reaction. The work of Ravi and Shepard (*6*) is in agreement with the need for a co-catalyst to promote hydrogen atom spillover. In studying deuterium–hydroxyl exchange over supported iridium, these authors found a marked increase for the exchange in the presence of certain adsorbed alcohols and aldehydes. In the more recent literature, one cannot help but reflect on the work of Gardes *et al.* (*7*), a very dramatic case of hydrogen atom spillover. In this study, a nickel–alumina catalyst was contacted with alumina and exposed to hydrogen gas at 300°C. The nickel-alumina catalyst was then removed and the alumina was contacted with ethylene at room temperature. Hydrogenation occurred, implying that hydrogen atoms formed on the surface of the nickel diffused across the support where they were adsorbed. A similar report, involving hydrogen activation at a metal surface, followed by migration and hydrogenation on the support has recently appeared (*8*). In this work, it was postulated that hydrogen atoms were generated on iron impurities (2000 ppm) and then diffused to the support (alumina treated with NaOAc) where they reacted with ethylene. In these experiments, it should be noted that a co-catalyst was not present as in the work of Levy and Boudart (*4*).

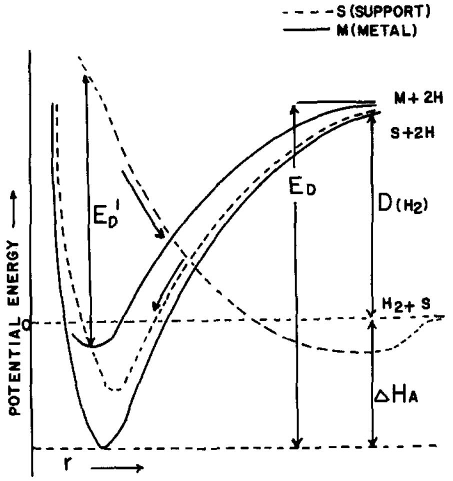

FIG. 1. Lennard Jones potential energy diagram for a plausible transfer mechanism from a metal surface to the support.

A central problem in the understanding of hydrogen atom spillover, is the mechanism by which a hydrogen atom is transferred from the chemisorbed state on the metal to the support. It has been argued (*4*) that the strength of the metal hydrogen bond, which is equal to one half the strength of the hydrogen bond plus the heat of adsorption, is much too large to account for spillover at room temperature. In fact, temperatures in excess of 800°K are necessary to break a metal hydrogen bond if the adatom is to migrate across the support in the absence of a co-catalyst. This point of view however, is perhaps an oversimplification. Conceivably, one might be able to transfer a hydrogen atom from a weakly bound chemisorbed state on the metal to a physically adsorbed state of hydrogen on the support which might then revert to a stronger chemisorbed state on the support. This point of view is expressed schematically in Fig. 1. Other suggestions as to how this transfer might occur include, the formations of bonds between the adatom and hydroxyl groups on the support (*11*), gas phase migrations (*7*), mechanisms involving hydrocarbon contaminants (*3*), and possibly some less attractive suggestions such as quantum mechanical tunneling.

If we accept for the moment, that the transfer from the metal surface to the support can occur, we must also be able to accommodate the adatom on the support. This of course presents no problem in the case of the platinum catalyzed reduction of tungsten trioxide or the hydrogenation of ethylene since an actual chemical reaction is taking place to remove hydrogen atoms from the system. It might also be possible that actual catalytic enhancement might occur due to a high degree of mobility of the reactant, i.e., an adsorbed ethylene molecule, on the support. If the area at the metal–support interface is enriched in hydrogen atoms, one might get diffusion of a reactant to the interface followed by hydrogenation. In this case, one would expect highly dispersed catalysts to be more active in hydrogenation reactions due to their larger interfacial surface area. This appears to be the case for supported nickel. For high nickel dispersions, Taylor *et al.* (*12*) found specific activities to be dependent on dispersion. No such dependence has been found for catalytic hydrogenations over supported platinum, however selectivities seem to be somewhat sensitive to particle size (*13*). What does seem a little puzzling, however, is the kind of hydrogen atom spillover suggested by Gardes *et al.* (*7*). Here the implications are that hydrogen atoms are generated at the nickel surface, and then in some manner diffuse across the support where they must be ultimately adsorbed, no co-catalyst being required for this transfer. It is to this aspect of hydrogen atom spillover that we have addressed ourselves in this report.

Rather than generate hydrogen atoms on a metal surface, we have adopted a procedure which excludes the metal surface entirely. In this work, hydrogen atoms are generated in the gas phase on a hot tungsten filament and allowed to diffuse to the surface. The adsorption can readily be followed by measuring the decrease in hydrogen pressure. In this way, we have evaluated several supports that have been reported active in promoting spillover.

EXPERIMENTAL PROCEDURES

The reaction vessel, illustrated in Fig. 2, was a 600 ml conical flask. A coiled-coil filament (area, 1.35 cm^2) from a 100 W light bulb silver-soldered to vacuum-tight leads through the top of the flask was used to generate hydrogen atoms from molecular hydrogen. The filament was electrically heated by a Variac and its temperature could be determined with a disappearing filament pyrometer. The concentration of hydrogen atoms in the reaction vessel could be readily changed by variation of the filament temperature T_W. In general, filament temperatures between 1600 and 2000°K were found to be the most satisfactory. For example, at 1950°K and a pressure of 760 μm, a simple kinetic theory calculation assuming equilibration at the filament, showed that the number of bimolecular collisions, $Z_H - H_2$ was roughly 1.67×10^{22} collisions/sec cm^3. A random walk calculation assuming a mean free path of 6.2×10^{-3} cm, showed that the average number of collisions before reaching the surface was about 2.7×10^5. This would indicate, that the hydrogen atoms were well thermalized.

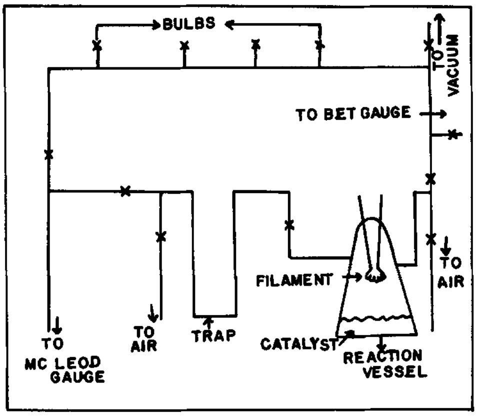

FIG. 2. Reactor and associated vacuum glassware.

The absorbent was spread over the bottom of the flask to form a layer roughly 0.2 cm thick. The reactor was isolated from all mercury containing parts of the system through liquid nitrogen traps. This was found to be important as mercury contamination either of the flask or the support could account for a significant hydrogen uptake. When care was taken to isolate the reactor, a blank run in the absence of the adsorbent, showed no hydrogen uptake. Periodic checks were made to insure a contamination free surface. The reactor was thermostated by immersing the entire flask either in liquid nitrogen or for the runs performed at 273°K, in an ice water bath. In a typical adsorption experiment, an inlet of hydrogen consisting of approximately 4 μmoles yielding a total pressure of about 90μm was taken. The pressure did not vary when the filament was turned off indicating that adsorption of molecular hydrogen on the support was not a factor under these experimental conditions. The filament was then turned on, and the pressure decrease was followed using a Mcleod gauge. Surface area measurements were made using nitrogen adsorption at 77°K via the standard BET technique. The entire reactor and associated vacuum components were attached to a conventional vacuum system backed by an oil diffusion pump capable of an ultimate pressure of about 10^{-3} μm.

METHODS

Cab-O-Sil was obtained from the Cabot Corp., Boston, Mass. It is a high-area silica material consisting of microspheres with little or no pore structure. It is widely used as a support. Alon-C, also obtained from the Cabot Corp., Boston, Mass., is the alumina analogue of Cab-O-Sil. It is reported to consist of about 90% γ-alumina, its main impurities being iron and nickel. The support referred to in this report as Teichner's alumina, was prepared according to the procedure described in Ref. (*7*). In this procedure, a relatively pure alumina (sodium free I might add) is formed through the hydrolysis of aluminum secondary butoxide. The alumina treated with NaOAc was prepared according to the procedure described in Ref. (*8*). γ-Alumina (Alon-c) (18 g) were refluxed with 200 ml of 1 *M* NaOAc for 26 hr. It was then filtered, washed with hot water and dried at 120°C for 16 hr. Tungsten trioxide was prepared according to the method described in Ref. (*4*). Tungstic acid was obtained from the Matheson, Coleman and Bell Corp. and was reagent grade. The cracking catalyst was a typical commercial Davison silica–alumina catalyst with a nominal 28% alumina and was

TABLE 1

THE ADDITIONS OF HYDROGEN ATOMS TO VARIOUS SUPPORT OXIDES AT 77°K[a]

		No. of μmoles		
Catalyst	BET surface area (m^2/g)	Adsorbed g^{-1}/m^2 of surface × 10^2	Coming off the surface g^{-1}/m^2 at room temp × 10^2	Adsorbed on the surface g^{-1}/m^2 × 10^2
Cab-O-Sil	581	0.67	0.03	0.64
Alon-c	96	0.96	0.07	0.91
Teichner's Al_2O_3	465	0.38	0.04	0.34
(After heating to 250°C and cooling to room temp)			0.14	0.20
Al_2O_3 treated with NaOAc	415	0.22	0.03	0.19
(After heating to 250°C and cooling to room temp)			0.16	0.03
SiO_2-Al_2O_3 (cracking catalyst)	424	0.49	0.04	0.45
(After heating to 250°C and cooling to room temp)			0.11	0.36
Mechanical mixture of SiO_2 and Al_2O_3	565	0.66	0.03	0.63
(After heating to 250°C and cooling to room temp)			0.37	0.26
Tungsten trioxide	30	Tr		

[a] Experimental temperature, 77°K.

TABLE 2

THE ADDITION OF HYDROGEN ATOMS TO VARIOUS SUPPORT OXIDES AT 273°K[a]

Catalyst	No. of μmoles of gas: Adsorbed at 273°K g^{-1}/m^2 of surface × 10^2	Coming off the surface (after heating to 250°C and cooling to room temp) g^{-1}/m^2 × 10^2	Adsorbed by the surface g^{-1}/m^2 × 10^2
Cab-O-Sil	1.18	0.06	1.12
Alon-c	1.97	0.29	1.68
Teichner's Al_2O_3	0.74	0.51	0.23
Al_2O_3 treated with NaOAc	0.23	0.13	0.10
SiO_2–Al_2O_3 (cracking catalyst)	0.94	0.26	0.68
Mechanical mixture of SiO_2 and Al_2O_3	0.98	0.26	0.72
Tungsten trioxide[b]	42.5		

[a] Experimental temperature, 273°K.

[b] Reaction not carried to completion.

supplied by the W. R. Grace Chemical Co. Its main impurities were reported to be iron (0.03%) and sodium oxide (0.04%). Hydrogen gas was purified by passing it through a charcoal train at 77°K to remove all traces of oxygen. Its purity was periodically checked by analyzing a gas sample in a mass spectrometer. Prior to each adsorption experiment, the support under investigation was heated in flowing hydrogen for 12 hr at 400°C.

RESULTS AND DISCUSSION

The hydrogen uptakes at 77°K for the adsorbents investigated in this study, are shown in Table 1. Column II gives the measured BET surface area. A noteworthy point to be made here is that the surface area of the alumina prepared according to the procedure described by Teichner is 465 m^2/g, compared to the reported area of 470 m^2/g. Treatment of Alon-c with NaOAc also seems to have a marked effect on the surface area. The measured BET surface for this support was 415 m^2/g as compared to only 96 m^2/g for Alon-c. Column III shows the hydrogen uptake per gram per unit surface area at 77°K. Cab-O-Sil and Alon-c both showed a relatively larger adsorption than the other adsorbents studied, however this adsorbed hydrogen did not desorb when the reactor was allowed to warm to room temperature. In fact, when the reactor was warmed up to 250°C and cooled back down to room temperature only a very small portion of this hydrogen was desorbed (i.e., less than 10%). This implies an irreversible adsorption; possibly a chemical reaction involving rehydroxylation of the surface. Even though the total hydrogen uptake was lower for the other adsorbents studied, a significant fraction of this hydrogen was desorbed when the reactor was heated to 250°C and cooled back down to room temperature. This would imply that this hydrogen might be catalytically more active in hydrogenation reactions than the irreversibly adsorbed hydrogen on Cab-O-Sil or Alon-c. Table 2 shows that at 273°K, all adsorbents showed an increase in hydrogen adsorption. Again, heating to 250°C and cooling back down to room temperature suggests that hydrogen uptake on Cab-O-Sil and Alon-c is probably due to chemical reaction rather than chemical adsorption. Tungsten trioxide did not react with hydrogen atoms at 77°K, however extensive reduction was observed at 273°K, the hydrogen uptake being about two orders of magnitude greater than on the other adsorbents. This datum is included in Table 2 even though the reduction was not carried to completion. The intense blue color usually associated with the tungsten bronze (H_xWO_3) was observed. Since no uptake was observed at 77°K, it must be concluded that the reduction of tungsten trioxide by hydrogen atoms is activated.

In two experiments (on NaOAc treated alumina), the reactor was thermostated at 373°K. The higher adsorption temperature, did not increase the total hydrogen atom uptake.

In Figs. 3 and 4, the rates of hydrogen uptake at 273°K are shown on pressure–time plots. Again, the rapid rate of reduction of tungsten trioxide is contrasted to the rather slow rate of hydrogen uptake by the other adsorbents.

The choice of 90 μm as an initial pressure was made for two reasons. First, at this pressure, virtually all of the hydrogen atoms generated at the filament reach the surface; and second, all of the adsorbents studied were exposed to similar concentrations of hydrogen atoms. At higher pressures (above 1000 μm), recombination of hydrogen atoms, occurring at the walls of the reactor, reduce the concentration at the surface. The overall hydrogen uptake, was not a significant function of pressure.

If we speculate that the hydrogen which comes off at temperatures below 250°C might be catalytically active, a glance at column III in Table 2 shows that it would seem unlikely that adsorption arising from

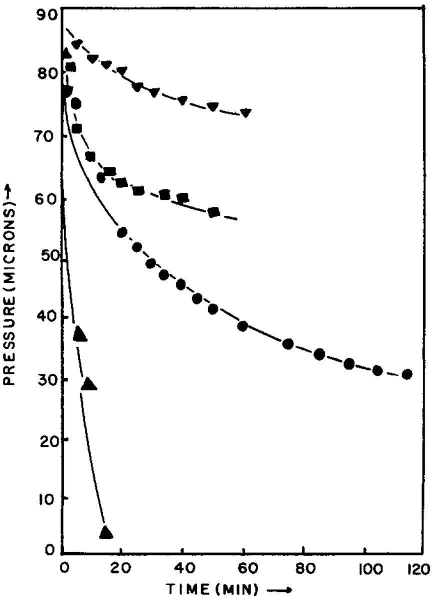

FIG. 3. Pressure vs time plot for the addition of hydrogen atoms to (●) Teichner's alumina, (▼) silica–alumina cracking catalyst, (■) mechanical mixture of silica–alumina + silica and (▲) tungsten trioxide at 273°K.

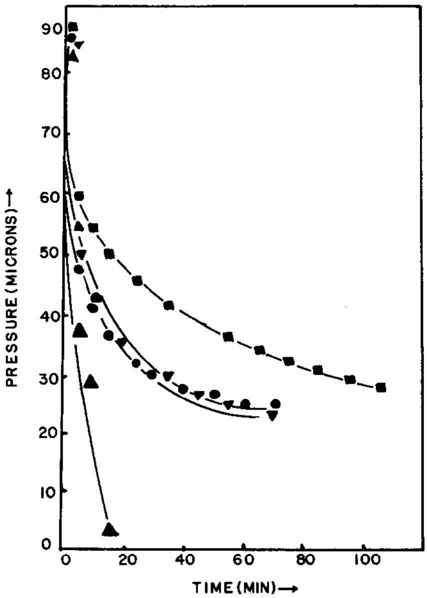

FIG. 4. Pressure vs time plot for addition of hydrogen atoms to (●) Cab-O-Sil, (▼) Alon-c, (■) alumina treated with NaOAc and (▲) tungsten trioxide at 273°K.

hydrogen atom spillover could lead to a large enhancement in the rate of a catalytic reaction such as a hydrogenation. Even in the case involving the largest removable hydrogen adsorption (Teichner's alumina), the amount of this hydrogen when translated into atoms/g cm^2 is only about 1×10^{11} atoms/g cm^2 compared for example to 2×10^{14} hydroxyl groups/g cm^2 for a typical alumina or silica support (*11*). This is not sufficient hydrogen to give the catalytic enhancement suggested by Gardes *et al.* (*7*), in the presence of supported nickel. In several experiments, an attempt was made to scavenge these adsorbed hydrogen atoms with nitric oxide as hydrogen atoms react very rapidly with nitric oxide even at 77°K (*14*). There was no evidence of any reaction occurring, which is not surprising in view of the very small amounts of hydrogen adsorbed.

It is interesting that in both preparations involving mild alkali conditions, the amount of removable hydrogen increased. This may in part be due to the neutralization of certain acid centers which might then serve as sites for hydrogen adsorption.

The fact that the reduction of tungsten trioxide by hydrogen atoms is activated, is in agreement with the mechanism proposed by Levy and Boudart (*4*), who argued that proton release at the reduction site is the rate determining step. It should be pointed out, however, that in this work the reduction was carried out with hydrogen atoms rather than protons. The concept of a solvated proton as the migrating species is an attractive one but not essential.

The results obtained in this work, do not of course negate the possible occurrence of hydrogen atom spillover, which can occur and undoubtedly does occur in the presence of a co-catalyst or possibly at a metal–oxide interface, however in the light of the relatively low levels of hydrogen adsorption, it does seem unlikely that spilled over hydrogen should diffuse to cover large areas of the support in the absence of a co-catalyst. Since most support oxides are insulators, it would seem unlikely that if hydrogen were transferred from the metal surface to the support, that it would get very far. It might very well be that hydrogen atom enrichment can occur at the metal–oxide interface through hydrocarbon contamination or for other reasons and that this additional hydrogen might then lead to an enhanced catalytic activity if the reactive surface area also includes the interfacial surface. This, suggests motivation for further study.

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