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n Infrared Spectroscopic Study of the Promotion of the Metal-Catalyzed Exchange of Silica OH Groups with Gaseous Deuterium

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A study has been made of the metal-catalyzed exchange of silica OH groups of an iridium–silica catalyst with deuterium gas at 25°C. This catalytic reaction proceeds more slowly on 'hydrogen-covered' than on 'bare' iridium, and does not proceed measurably on silica alone at this temperature. However, a considerable number of preadsorbed molecules have been found to promote this catalytic reaction; acetaldehyde, chloral (1,1,1-trichloroacetaldehyde), and acetonitrile lead to an OH → OD reaction with a half life of less than 5 min.

A few experiments indicate that chloral-promoted platinum–silica also leads to very rapid exchange.

Oxide-supported metal catalysts find wide industrial use and their reactivities are of considerable interest. Hall and Lutinski (*1*) have made a number of studies of the reaction involving the exchange of deuterium gas with surface hydrogen. Infrared spectroscopy is particularly useful in detecting OH groups on oxides or on oxide-supported metal catalysts, and has been used by Eischens and Pliskin (*2*), Peri and Hannon (*3*), Carter, Lucchesi, Corneil, Yates, and Sinfelt (*4*), and Eley, Moran, and Rochester (*5*) to study the deuterium exchange reaction with OH groups of silica (*2*) and of alumina (*3–5*).

Eischens and Pliskin (*2*) first showed by ir means that a platinum–silica catalyst exchanged OH groups with deuterium considerably more rapidly than silica alone; however in their work they state that adsorbed water may have played some part in the catalytic reaction.

Peri and Hannon (*3*) showed that OH groups on alumina would exchange with gaseous deuterium above 250°C. Hall and Lutinski (*1*) showed by nonspectroscopic methods that an oxidized platinum–alumina catalyst gave the exchange reaction at lower temperature than alumina itself, but that reduced catalysts of this type prepared from H_2PtCl_6 raised the temperature for exchange. Carter *et al.* (*4*) showed that some platinum–alumina catalysts exchanged OH to OD considerably faster than alumina itself. On the other hand, the relationship of the rate to the metal concentration was complex, the reaction was slow (time for 20% exchange about 2 hr at 75°C) and the rate was at the best doubled by the presence of the metal. Eley, Moran, and Rochester (*5*) have described similar results with platinum–alumina that had been pretreated with oxygen.

We report here some ir experiments in which it is found that at room temperature the OH groups on a silica–iridium catalyst exchange with deuterium in a period of hours, but that the presence of a variety of preadsorbed promoters, such as acetaldehyde, can reduce the time for 50% ex-

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change to a few minutes only. A few experiments with silica-platinum catalysts show analogous results.

Experimental

Apparatus

A conventional vacuum system giving pressures of *ca.* 10^{-6} Torr was employed. The cell used here permitted *in situ* studies and was made from Pyrex glass except for a stainless-steel sample holder. It was of the type described by Morrow (*6*) and by Young and Sheppard (*7*).

Materials

Cab-O-Sil (grade H5) was obtained from Godfrey Cabot Inc. of U.S.A. as a gift. Prior to use it was heated in air at 600°C to remove any possible contamination.

Deuterium was supplied by the National Physical Laboratories, England and was stated to be greater than 99.9% pure.

Iridium chloride (H_2IrCl_6) was a product of Hopkin & Williams Ltd. Chloroplatinic acid (H_2PtCl_6) and nickel nitrate were obtained from British Drug Houses Ltd. The adsorbates studied here were of commercial origin and were purified by standard methods.

Sample Preparation

Silica-supported samples containing about 10% of metal were prepared by mixing the appropriate weights of the metal salt and silica; Cab-O-Sil was added slowly with stirring to an aqueous solution of the metal salt to form a paste. This was dried overnight at 120° and ground to a fine powder. Samples were in the form of circular discs of 25 mm diameter and were made by pressing the powder in a press at 2–3 tons/in.^{2}.

The discs were reduced to the metal in the following way. Prior to reduction, the samples were cleaned by evacuating for 30–60 min at 150°C. Then a small flow of hydrogen (10 Torr) was started, and the temperature of the cell was raised slowly to 350°C in about an hour. The slow temperature rise prevents the deposition of reduction products on the cell windows. The sample was maintained at 350°C in the flow of hydrogen for 3 hr, and reduction was completed at this temperature with several static doses (400 Torr) of hydrogen. Finally the cell was filled with fresh amounts of hydrogen, heating was stopped, and the sample allowed to cool to room temperature. Hydrogen was then evacuated for 1 hr at 10^{-6} Torr. This sample is conventionally termed "hydrogen-covered."

Two "bare" iridium samples were obtained by evacuating hydrogen at higher temperature after reduction, one at 350°C for 2 hr and another at 275°C for 4 hr.

The spectra of the samples were taken on Grubb Parsons GS2 and Perkin-Elmer 125 double-beam grating spectrometers.

Results

The first observations in this study were made by chance in the course of a study of the ir absorption bands from acetaldehyde adsorbed on hydrogen-covered silica-supported iridium catalysts. Acetaldehyde of pressure 10 Torr was allowed to stand overnight in contact with the catalyst sample and then evacuated for 1 hr. Ten Torr of deuterium was then added at room temperature. Within a few minutes of the addition of deuterium, the silica OH to OD exchange had occurred virtually completely.

Figure 1 shows that the sharp ν OH ir absorption band of silica near 3750 cm^{-1} and the broad companion band in the 3700–3400 cm^{-1} region, which are associated with "free" and hydrogen-bonded OH groups respectively, had been virtually completely replaced by the analogous ν OD absorption bands at 2760 cm^{-1} and below. The residual broad ν OH band near 3650 cm^{-1} is probably caused by "internal" OH groups that are not accessible to deuterium (*8*). The weak bands in the 3000–2800 cm^{-1} region are caused by CH bonds resulting from the preadsorption of acetaldehyde (*9*). Spectra were run at intervals for a further 12 hr, but no further change occurred. After evacuation of gaseous deuterium, very little change in the OH or OD bands occurred on standing, although after continuous pumping for 4 hr, free ν OH bands began to appear at the expense of ν OD. It seems

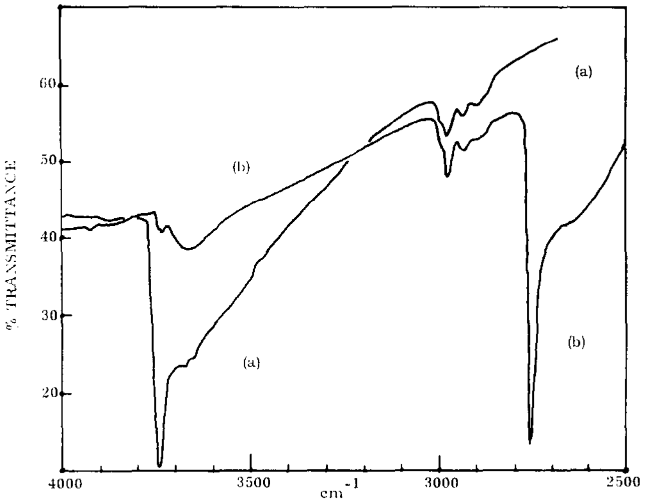

FIG. 1. (a) Infrared spectrum of a silica-supported iridium catalyst disc after adsorption of 10^{-5} Torr of acetaldehyde. (b) The spectrum obtained immediately (within a few minutes) after addition of deuterium gas to the ir cell.

probable that traces of water desorbing from the cell walls interact sufficiently with the catalyst surface to bring about this change.

In a second experiment, an exploratory study was made of the reverse reaction ($OD + H_2 \rightarrow OH + HD$) to see whether this also would be fast. After allowing the OH to OD change to go to effective completion, the gas-phase deuterium was evacuated for 30 sec, and then 10 Torr of hydrogen was added. A rapid reconversion of about 60% of OD to OH occurred within a few minutes, although for some reason, not yet further investigated, the reaction did not go to completion.

Having made this observation of rapid OH to OD exchange, another experiment was carried out with a freshly prepared hydrogen-covered iridium–silica sample that had not been pretreated with acetaldehyde. However, in this case only a very weak ν OD band appeared after deuterium had stood over the catalyst for 24 hr. It was also shown that Cab-O-Sil discs (in the absence of metal) that had been pretreated with acetaldehyde showed no exchange at room temperature; even the presence of a gaseous mixture of acetaldehyde and deuterium over silica had no effect.

Subsequently similar experiments were carried out with deuterium gas over bare iridium–silica samples, from which the hydrogen used for reduction of the chloride to the metal had been evacuated at higher temperature (see the Experimental section). In this case considerable OH → OD conversion occurred, although it was a slow process extending over many hours (Table 1) i.e., orders of magnitudes slower than over the acetaldehyde-promoted catalyst.

Acetaldehyde adsorbs on iridium and platinum with extensive decarbonylation, and chemisorbed CO is produced. This reaction occurs to only a limited extent on nickel, and it was found that preadsorption of acetaldehyde on nickel had little effect on the OH to OD exchange reaction. Experiments were, therefore, carried out with preadsorbed carbon monoxide on the first two metals, but again with little effect (Table 1). Ethanol is also probably a transient product from the adsorption of acetaldehyde on certain metals. As the active OH group of the molecule could promote H to D exchange an experiment was carried out with ethanol itself preadsorbed on iridium, the ethanol, as usual, being pumped out before the addition of deuterium. This did promote the exchange reaction (Table 1), but again the reaction

TABLE 1

THE PERCENTAGE OF INTENSITY OF THE SHARP νOH IR BAND NEAR 3750 cm^{-1} REMOVED THROUGH EXCHANGE TO νOD AT STATED TIME INTERVALS AFTER ADDITION OF GAS-PHASE DEUTERIUM OVER METAL/SILICA CATALYSTS PRETREATED WITH DIFFERENT ADSORBATES

		Time		
Metal	Adsorbate	Immediately (~5 min)[a]	30 min	1200 min
Ir	Nil[b]	3	—	52
Ir	H_2			Few %
Ir	CO			Few %
Ir	Methanol	—	—	46
Ir	Ethanol	~1	—	90
Ir	Acetone	~4	8	36
Ir	Formaldehyde	9	—	53
Ir	Isopropanol	12	38	74
Ir	Chloroform	34	70	70
Ir	Acetonitrile	73	89	89
Ir	Acetaldehyde	82	89	89
Ir	Chloral	82	95	95
Pt	CO			
Pt	Chloral	94	94	94
Ni	Acetaldehyde	—	—	Few %

[a] These intervals represent the time needed to measure the ir spectrum and are somewhat variable.

[b] With bare sample.

was very slow in comparison with the effect of acetaldehyde itself.

Experiments with chloral ($CCl_3 \cdot CHO$) promotion of iridium–silica and platinum–silica however showed very rapid exchange once again. A wider range of adsorbates was then tried with iridium catalysts and gave the results recorded in Table 1. Acetonitrile has comparable promotion efficiency with the aldehydes; chloroform, isopropanol, and formaldehyde then follow in order of descending promotion. Formaldehyde is rather readily polymerized on adsorption, and this may be the reason why it is less promotionally active than the other aldehydes.

CONCLUSIONS

These experiments have shown that certain promoters can increase the rate of OH to OD exchange by deuterium gas over an iridium–silica catalyst by several orders of magnitude. The three most effective promoters are acetaldehyde, chloral, and acetonitrile. However, as these do not have any common structural feature, it is difficult at this stage to formulate a likely type of mechanism for the promotion reaction. The above three promoters do all contain multiple bonds to carbon, but acetone, which also has this feature, has no more marked an effect than bare iridium itself.

The higher (but still very slow) exchange rate on bare iridium compared with hydrogen-covered iridium, may reflect a greater degree of mobility of deuterium on the former surface. Alternatively the 'bare' iridium would be more susceptible to contamination with traces of oxygen; this might react with deuterium to form deuterium oxide which could have sufficient mobility over the surface to effect silica OH to OD exchange. Indeed in Eischens & Pliskin's early observation of an increased rate of exchange of deuterium with platinum–silica (*2*), it was suggested that the presence of traces of water (exchanged to the deutero form) might have acted as intermediary in the reaction.

The few exploratory experiments that we have carried out indicate that platinum acts in a similar manner to iridium after preadsorption of aldehyde but that nickel does not do so, i.e., is much less active. It is of interest that in a gas-phase study of the rates of H_2 to D_2 exchange over metal catalysts, Schuit and van Reijen (*10*) concluded that platinum gives about three orders of magnitude greater reaction rates than nickel; they did not carry out any experiments with iridium.

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