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Hydrogen Spillover in the System Pt/Al_2O_3

I. Fundamental Observations

Hydrogen spillover was followed by FTIR spectroscopy in the system Pt/γ-Al_2O_3. The reactions may be resolved into a fast and a slow part, both being reversible. The amount of OD groups exchanged in the fast partial reaction is decreasing with pretreatment temperature. H–D exchange in physisorbed water is nearly in equilibrium with that of surface hydroxyl (deuteroxyl) groups. © 1985 Academic Press, Inc.

1. INTRODUCTION

Hydrogen spillover, the transfer of hydrogen (or deuterium) from metal (Ni, Pt metals) to an oxide carrier (Al_2O_3, SiO_2, etc.) was observed by different authors (*1–8*). The results seem to be contradictory to a certain degree: Carter *et al.* (*1*) found an acceleration of the exchange reaction only with samples of small Pt content (about 10^{-3}% Pt), while other authors described positive experiments with greater Pt concentrations. This article shall describe some more fundamental investigations with respect to the H–D exchange in the system Pt/Al_2O_3. This system was chosen because of its great technical importance.

2. EXPERIMENTAL

The exchange reactions were followed, using a Fourier–Infrared spectrometer (Digilab FTS-14) with a measuring cell described earlier (*9*), which allowed to investigate wafers of the catalyst sample (up to 10% Pt on γ-Al_2O_3) at temperatures to about 600 K. The carrier gas (He) and the reaction gases (H_2, D_2) were passed over Oxisorb (Messer Griesheim) and dried with molecular sieve 3A at 96 K. After mixing the reaction gas streams (H_2 in He or D_2 in He), these were passed over a catalyst Pt/Al_2O_3 to get rid of last oxygen traces, and were dried again as described.

The preparation of the samples took place in several steps:

1. Alumina powder (γ-Al_2O_3, Degussa type C, specific surface: 100 m^2/g) was mixed with a solution of $[Pt(NO_2)_2(NH_3)_2]$ in diluted ammonia. The mixture was dried at 120°C. This complex was preferred to the hexachlorocomplex because of the absence of chlorine.
2. Wafers (ϕ 22 mm, 10–30 mg/cm^2) were pressed (100 bar) from this material.
3. The samples were reduced in the measuring cell with hydrogen at about 500 K.
4. Now the samples were treated with water vapor at about 500 K to hydrolyze traces of chlorine present on the alumina surface.
5. A temperature treatment (2 h at 800 K) in helium was carried out every day to obtain a constant starting state, as it had turned out that the activity of alumina is not uniquely defined by the degree of OH or OD coverage.
6. The remaining OH groups were exchanged by a treatment with deuterium at the same temperature.
7. The OD coverage may be adjusted by either injection of D_2O or $O_2 + D_2$ at a suitable temperature (above the final measuring temperature).

The reaction was started after reaching the measuring temperature by changing from helium to hydrogen (10 kPa in He, 50

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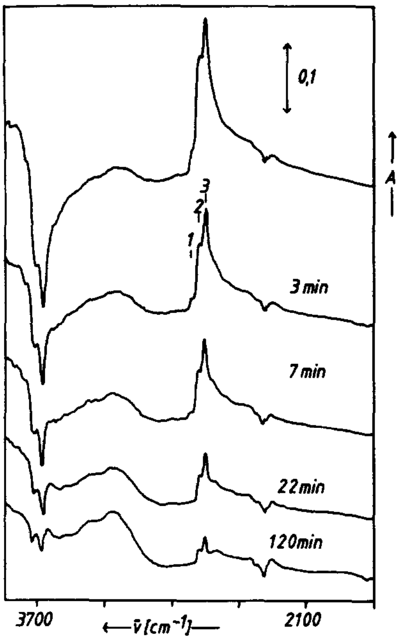

FIG. 1. Time dependence of the ir spectra of a wafer with 10% Pt on γ-Al_2O_3 pretreated (and rehydrated) at 803 K ("dry" conditions) obtained at a measuring temperature of 478 K. (Difference spectra with completely hydrogen exchanged sample as reference to compensate undesired background.) OD bands: 1, 2770 cm^{-1}; 2, 2745 cm^{-1}; 3, 2715 cm^{-1}.

ml/min). The maximal absorbances of the OD bands were used as a measure of the degree of deuteration. OD bands were preferred to OH bands because of the better signal to noise ratio.

3. RESULTS AND DISCUSSION

3.1. *Typical Reaction*

Taking the deuterated form of the wafer one gets typical spectra as shown in Fig. 1 for the reaction of the wafer with H_2 at 478 K on a dry sample with 10% Pt (pretreated at 803 K). A similar sequence of spectra, obtained under "wet" conditions with 0.17% Pt (rehydration temperature 365 K) is shown in Fig. 2, with the forward reaction on the left and the reverse reaction on the right side (here only the OD region of the spectrum is shown).

The following qualitative statements may be made:

1. Reaction takes place with high and low Pt content.
2. Different OD bands react but with slightly different velocities.
3. The reactions are widely reversible.
4. In contrast to pure oxide the reaction on "wet" samples is faster than on "dry" ones.

3.2. *Time Dependence*

The time dependence of absorbances are shown in Figs. 3 and 4 for "wet" and "dry" conditions. Under "wet" conditions the reaction of the pure oxide is extremely slow (c, Fig. 3). Platinum (10%) is increasing the reaction velocity drastically (a, Fig. 3). A third sample, consisting of an oxide wafer with an outer zone of Pt containing oxide, was investigated under the same conditions. From this measurement it follows that either an activated H species may

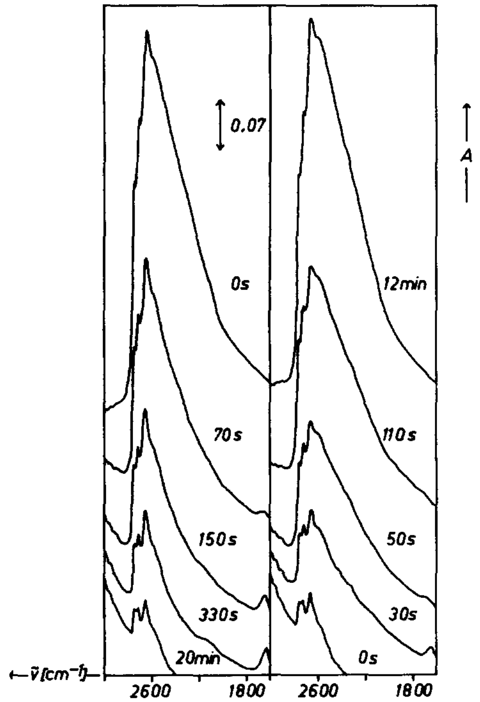

FIG. 2. Time dependece of hydration (left side) and redeuteration (right side) of a "wet" sample with 0.17% Pt. (Only OD region of difference spectra with completely hydrated sample as reference. Rehydration and measuring temperatures: 365 K.)

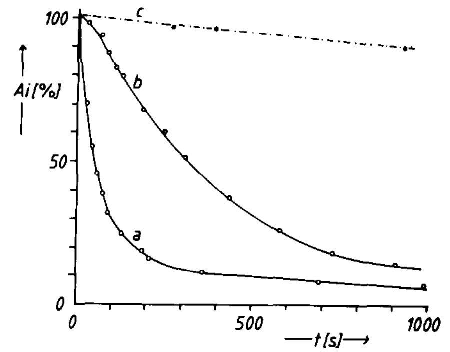

FIG. 3. H–D exchange on "wet" wafer. Rehydration and measuring temperature: 365 K. (Integral absorbance of OD bands vs time.) (a) Sample with 10% Pt. (b) Oxide wafer (22-mm diameter with 3.5-mm outer ring with 1% Pt; spectra from inner zone of wafer by applying suitable aperture). (c) Pure oxide.

migrate over a considerable distance, or the exchange of this species takes place in a very fast reaction close by the platinum crystallite, followed by a fast exchange diffusion on the oxide surface. This method resembles somewhat a method used for the investigation of spillover on silica (*7*, *8*), where a central spot of metal containing substance was used.

On the dry samples the difference of the reactivities of pure oxide and oxide with platinum is smaller. The initial velocity is clearly greater with Pt but the reaction is slowing down after a while. Generally it may be said, that on platinum containing samples, at least two partial reactions must be distinguished: a fast initial reaction followed by a much slower one. The amount of deuteroxyl groups reacting during the fast step is greater in wet than in dry samples. From the reversibility of the reactions it could be seen that the retardation was not caused by poisoning. Under these conditions it should be possible to restore the initial concentration of OD groups (or the corresponding absorbance) in a fast back-reaction by reversing the reaction just after completion of the fast part of the forward reaction. Figure 5 shows that this assumptions is really fulfilled. The initial values of absorbances are reached in both experiments, a proof for the purity of the gas streams. This experiment further shows that there is a certain number of OD groups, which do exchange fast, while the rest can be exchanged but slowly.

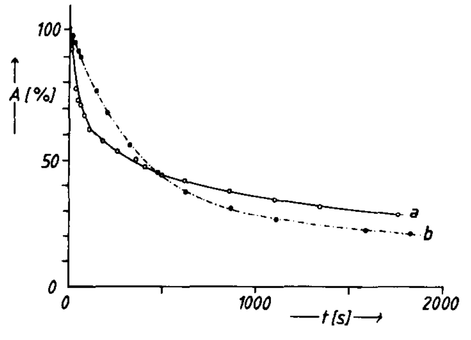

FIG. 4. H–D exchange on a "dry" wafer. (a) γ-Alumina with 10% Pt, (b) pure oxide. Pretreatment and rehydration temperature: 803 K; measuring temperature: 673 K. Maximal absorbance of OD bands vs time.

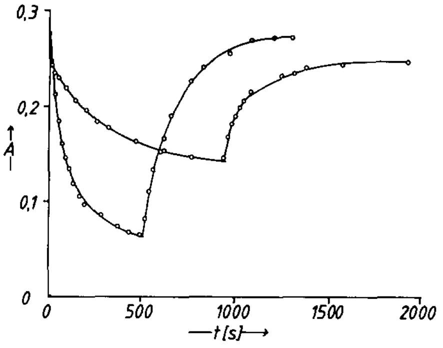

FIG. 5. Hydration and following redeuteration at the end of the fast reaction part as a proof for reversibility and constance of OD coverage (absorbance of OD band vs time).

3.3. H–D Exchange in Physisorbed Water

"Wet" samples contain physisorbed water, which causes typical bending vibrations in the 1200- to 1700-cm^{-1} region (H_2O, 1640 cm^{-1}; HDO, 1445 cm^{-1}; and D_2O, 1218 cm^{-1}) in addition to an increase in the band intensities of associated OH or OD groups. The bending vibrations may be evaluated with respect to H–D exchange too, and the results may be compared with those obtained for the valence vibrations.

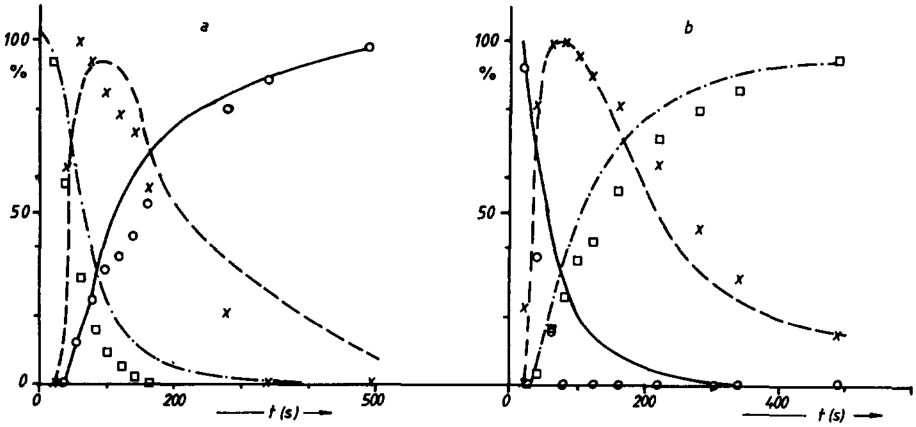

FIG. 6. H–D exchange of physisorbed water during hydration (a) and deuteration (b) reactions (percentage of maximal values of absorbances vs time). Measuring points obtained from integral absorbances of bending bands of water species (O: H_2O, 1640 cm^{-1}; ×: HDO, 1445 cm^{-1}; □: D_2O, 1218 cm^{-1}). Lines (—— H_2O, — — — HDO, —·— D_2O) calculated from degree of deuteration, assuming equilibrium between water species and surface OH and OD groups. Degree of deuteration obtained from absorbances of OD valence bands at 2090 and 2070 cm^{-1}.

Figure 6 shows the results of a hydration (a) and a deuteration (b) reaction. The measuring points from direct measurements of the relative amount of water species may be compared with theoretical curves, which should be expected for equilibrium between surface OH and OD groups on one side and the different water species on the other. The theoretical curves were calculated from the relative concentrations of OH and OD groups according to the intensities of the valence bands. Though the precision of the measuring points is limited because of the small intensity of the bending vibrations, one may see that equilibrium is almost reached at any time.

Small deviations in the beginning show a certain excess of HDO compared with equilibrium values. This effect may be interpreted either by the assumption of HDO as a carrier for spilt over hydrogen, reacting with OD groups with a certain retardation, or by assuming that some OD groups don't take part in the normal exchange process (occluded groups).

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