CHEMISTRY LETTERS, pp. 823-826, 1985.

HYDROGEN PRESSURE-INDUCED OPTICAL DENSITY CHANGES OF METAL-LOADED TITANIA OBSERVED BY HIGH-PRESSURE INFRARED SPECTROSCOPY

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A high-pressure in situ IR study revealed a reversible hydrogen pressure-induced optical density change of titania catalyzed by metals dispersed on its surface. The phenomenon may be attributed to a reversible charge transfer from the adsorbed hydrogen to the titania support.

The activation of hydrogen over supported metal catalysts has induced many interesting phenomena, including the hydrogen migration (spillover and reverse spillover) at the Pt/alumina surfaces¹⁾ and the strong metal support interaction (SMSI) in Pt/titania.²⁾ Reported here is a hydrogen activation by supported metals, which results in a pressure-dependant optical density changes of a metal-loaded titania. The process is reversible with respect to the hydrogen pressures in the range of 0 and 1.3 MPa.

A metal-loaded titania was prepared by impregnating titania powder (Degussa P-25) with an aqueous solution of an appropriate metal salt such as hexachloroplatinic acid, nickel nitrate or cupric nitrate. The resultant slurry was heated over a water bath to dryness, and dried further in an air-oven at about 400 K overnight. The metal content was 1.0 wt %. As controls, silica-supported catalysts were also prepared in the same manner. Self-supporting discs of these and blank titania samples were pre-reduced at 673 K with atmospheric hydrogen and transferred in air into the high-pressure IR cell.³⁾ After re-reduction at 523 K, the cell was cooled, and air was introduced. Then the cell was evacuated up to 10^{-2} Pa, heated to a predetermined temperature when necessary, and then pressurized and depressurized stepwise by flowing hydrogen at the temperature. For the purpose of comparison, other gases such as helium and nitrogen were also employed for the pressurization. Optical density changes of the sample discs during the pressurization-depressurization process were recorded by time-driving a home-computerized IR spectrometer (Hitachi 260-50) fixed at a wavenumber of 2300 cm^{-1}. While the optical density changes, when observed, occured in the entire range of the wavenumber covered by the spectrometer, 2300 cm^{-1} was chosen as an observation point since at around this wavenumber titania is the most transparent, and at this specific wavenumber sample absorbance is not affected by the metal-H absorption band.

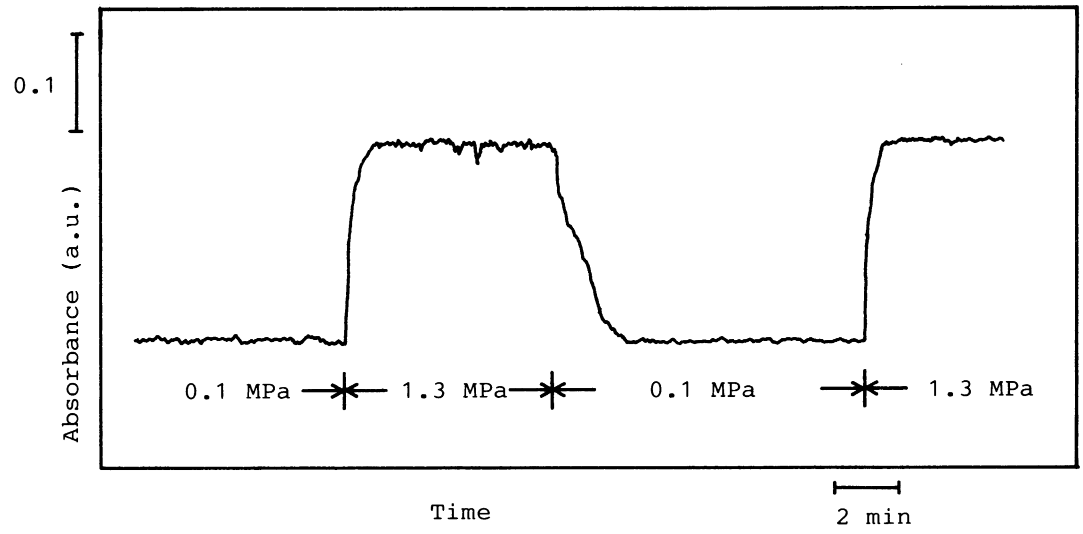

Fig. 1. Reversible optical density change of Ni/TiO_2 with gas phase hydrogen pressure. Measurement was made at 435 K and at 2300 cm^{-1}.

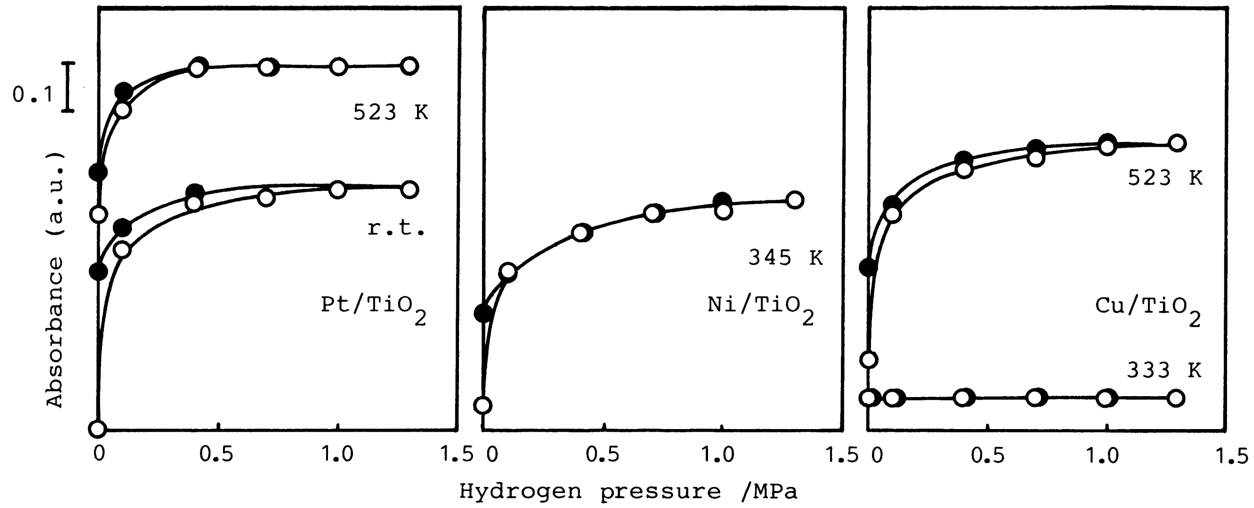

Fig. 2. Hydrogen pressure-dependent optical density changes of metal-loaded TiO_2. (○) First pressurization, (●) first depressurization.

Figure 1 shows the time-course of the optical density change of Ni/titania sample at 2300 cm^{-1} at 435 K as the hydrogen pressure is changed. The curves shown in Fig. 1 were recorded after several pressurization-depressurization cycles by hydrogen. As may be obvious from the figure, step increase of hydrogen pressure was accompanied by instantaneous increase of sample optical density. Depresurization reversed the course. While the optical density change is completely reversible with hydrogen pressure as seen in Fig. 1, it was observed that the optical density increase during the first pressurization by hydrogen was greater than the reversible optical density changes (see Fig. 2). Only after the first pressurization cycle the optical density changes become reversible.

It is noted here that under the present experimental conditions neither blank titania nor metal-loaded silica show any optical density changes. The pressurization of metal-loaded titania with other gases (helium or nitrogen) does not produce the phenomenon either. The failure to observe this phenomenon with nitrogen is interesting in the light that reduced titania adsorbs large amount of nitrogen.4) We would also like to note that the major portion of the optical density change observed here occurs between the hydrogen pressure of 0 and 0.1 MPa. This means that the same phenomenon should be observable with regular atmospheric or subatmospheric IR cells.

Figure 2 compares the optical density changes of Pt-, Ni-, and Cu-loaded titania as a function of applied hydrogen pressure. Plotted here is the first pressurization cycle (open circle) and the following depressurization cycle (closed circles). It is interesting to note that the onset temperature, at which this phenomenon is observed, depends on the kind of metals supported. While Pt/titania shows the optical density change already at room temperature, Ni/titania needs temperature above 330 K and Cu/titania above 400 K to show the phenomenon.

Our tentative explanation for this reversible optical density change involves hydrogen adsorption and activation over the supported metal surfaces and its protonic polarization. The activated hydrogen may present on the metal surface or may be spilled over to the support surface. The donated electrons by this protonic hydrogen would push up the Fermi level of the dispersed metal crystallites and drives the electronic charge through the metal-titania junctions to the titania conduction band, or when the protonic hydrogen is on the support surface the electrons would directly flow into the titania conduction band. These electrons may be delocalized in the conduction band and work as photon scatterers, or may be localized at a specific titanium site to reduce Ti(IV) to Ti(III) or to create F-centers. In either case darkening of the sample, i.e., increase of its optical density, should be observed. The number of electrons donated to the titania support in such a way would be proportional to the amount of hydrogen adsorbed, and thus the curves in Fig. 2 may be considered to parallel the adsorption isotherm of hydrogen on the catalyst system. Hydrogen desorption from the metal surface during the depressurization would reverse the above process, thus decreasing the the optical density.

According to the above tentative picture the present phenomenon depends on the ability of the catalyst metal to activate hydrogen. It is also noted that this phenomenon coincides with the reversible production of Ti(III) or delocalized electron in Rh-loaded titania by subatmospheric hydrogen observed by ESR.5,6)

References

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(Received March 25, 1985)