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Catalytic Demonstration of Hydrogen Spillover from Nickel–Alumina Catalyst to Alumina

The adsorption and the dissociation into atoms of molecular hydrogen by a metal is a well recognized experimental phenomenon (*1*). When the metal is supported on a carrier the possibility of the migration of hydrogen species (atoms or ions) onto the nonmetal part of the catalyst ("spillover") may be envisaged. This has been verified for platinum supported on silica (*2*), platinum on carbon (*3*) and platinum on zeolite (*4*). This migration of the hydrogen species on the carrier seems now to be widely accepted (*5*) but its mechanism (in the adsorbed phase or in the gas phase) is so far unknown. Some authors (*6*) claim that organic residues coming from the preparation of the catalyst and carrier and from the greased stopcocks may play an important and decisive part as bridges in the migration of the hydrogen species, and it has been reported that an apparent absence of the spillover effect is pertinent to relatively clean systems (*7, 8*).

Experimental evidence for hydrogen spillover has been produced from chemisorption measurements (*3*), by ESR (*4*) and also by the reduction at room temperature of some oxides or sulfides which normally are not reduced at this low temperature (*9*). Measurements of hydrogen spillover by a catalytic method were attempted in an indirect way (*2*) by the hydrogenation of ethylene in the presence of a mechanical mixture of alumina and platinum-on-silica catalyst. The influence of various thermal treatments on the catalytic activity of platinum supported on delta alumina for the hydrogenation of ethylene was also explained by hydrogen spillover (*10*). The present work attempts to give direct evidence of the presence of hydrogen (active in the hydrogenation of ethylene at room temperature) on alumina which had been previously in contact with a nickel–alumina catalyst under an atmosphere of hydrogen at 300°C.

Because the catalyst involved in these experiments is of an entirely new type, a short description of its preparation and some of its properties is provided. The carrier is alumina aerogel on which nickel is dispersed by a method involving the preparation of the aerogel itself (*11*). A solution (20 g) of aluminum *sec*-butylate (2.5 g) in *sec*-butanol (17.5 g) is added to a solution (5 g) of hydrated nickel acetate (1 g) in methanol (4 g) containing a total amount of water representing a ratio $[H_2O]/[(BuO)_3Al]$ equal to 3. A precipitate of alumina is immediately formed in the mixture of solvents. This heterogeneous system (without any separation) is placed in an autoclave (1 liter) together with a quantity of methanol (350 cm^3) so that hypercritical conditions for this solvent are obtained in the autoclave. Before heating, the autoclave is flushed by hydrogen. The hypercritical conditions (270°C) are then realized and maintained for 30 min. The autoclave valve is then opened and the system is flushed with pure nitrogen to remove the last traces of organic solvents. After cooling to room temperature the autoclave is opened. The aerogel of alumina with nickel dispersed on it does not exhibit any pyrophoric properties and can be safely handled in the air. The ratio Ni/Al is equal to 2:5 and the amount of metallic nickel, determined by magnetic measurements, is 4.7% by weight. This amount of metallic nickel represents roughly 25% of the total nickel present. A further reduction of the catalyst by hydrogen at 300°C does not increase the initial amount of metallic nickel (4.7%). The mean diameter of nickel particles, also determined from magnetic measurements (*12*), is of the

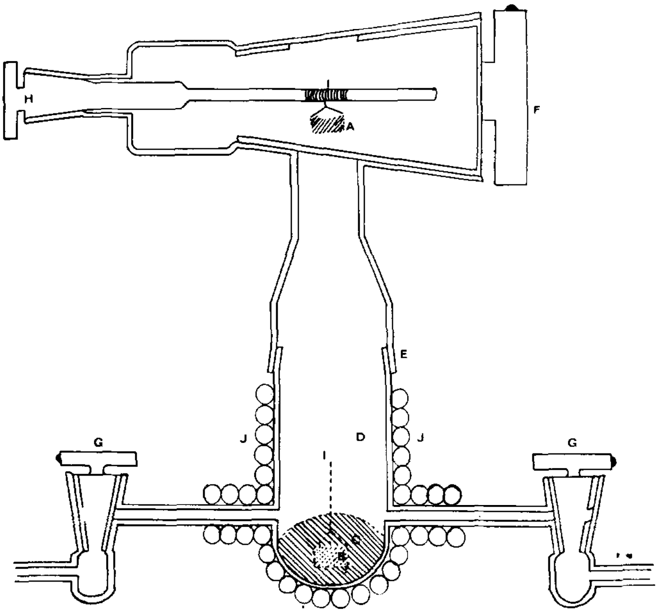

FIG. 1. Catalytic reactor allowing the removal of the catalyst before the reaction. (A) Porous quartz pan containing the catalyst removed from the reactor; (B) the same pan initially introduced into the reactor and covered by pure alumina; (C) pure alumina aerogel; (D) reactor; (E) conical ground joint; (F) stopcock which permits isolation of the catalyst; (G) stopcock for gaseous reagents and vacuum; (H) lifting device of the pan; (I) wire; (J) heating mantle.

order of 70 Å. The surface area of the catalyst is 660 m^2/g and its pore volume (determined with a mercury porosimeter) (*11*) is 9.7 cm^3/g. The alumina aerogel without nickel, was prepared in the same conditions. Its surface area is 470 m^2/g and its pore volume, 7.2 cm^3/g.

Hydrogenation of ethylene was carried out in the Pyrex reactor shown in Fig. 1. The catalyst placed on the bottom of a porous quartz pan (B) was covered by pure alumina aerogel (C). The lifting device (H) removed the catalyst (and some alumina), which could then be isolated from the reactor by the stopcock (F). About 3 g of pure alumina aerogel (C) and 0.060 g of nickel alumina aerogel were used. The volume in which the reaction took place was of the order of 0.6 liter. Silicone grease was used in the stopcocks.

The catalyst in the pan, at position (B) and covered by alumina aerogel, was evacuated at 350°C (10^{-6} Torr) for 24 hr. It was then exposed to a hydrogen confined atmosphere (700 Torr) at 300°C during 14 hr (with a recirculation pump and liquid nitrogen trap). After cooling to 200°C or to room temperature the pan containing the catalyst was removed (position A) and the stopcock (F) closed. During this manipulation it was impossible to lose any catalyst particles since they were covering only the bottom of the pan. The reactor which then contained only aerogel (designated by alumina C) was filled with ethylene (50 Torr) which raised the total pressure to 750 Torr. Gas chromatographic analysis was then performed on gas samples through stopcock (G). A second reactor, connected in parallel with the first contained only alumina aerogel (designated by alumina K) and was submitted to the same treatments as the first reactor.

After 4 hr of exposure of aluminas C and K to hydrogen and ethylene at room temperature the gas chromatographic analysis shows that the ratio of ethane to ethylene is 4:1 for alumina C. It is equal to 5:1 if the reaction is carried out in a second experiment at 200°C during 4 hr.

For alumina K this ratio is equal to 1:5000 for the reaction at room temperature during 4 hr. The same ratio is still registered if the contact time is extended to 12 hr. Finally the same ratio is still observed if alumina K is in contact at room temperature during 12 hr with a mixture of ethylene (50 Torr) and of nitrogen (700 Torr) instead of hydrogen. The small proportion of ethane present for alumina K is therefore not connected with hydrogen which would be eventually adsorbed during the contact of alumina with hydrogen but may be due to a small self-hydrogenation of ethylene (only minute traces of ethane are present in ethylene supply).

These results clearly show that hydrogenation of ethylene occurred on alumina C which was previously in contact with the catalyst (nickel on alumina) under an atmosphere of hydrogen at 300°C. Almost no hydrogenation of ethylene is observed on alumina K, also heated at 300°C in hydrogen but in the absence of the catalyst. Obviously molecular hydrogen was activated by the catalyst and transferred onto alumina C, where hydrogen species, after the catalyst was removed, were able to hydrogenate ethylene, even at room temperature. The ratio of catalytic activities in the formation of ethane for aluminas C and K after 4 hr of contact with the mixture of hydrogen (700 Torr) and ethylene (50 Torr) at room temperature is therefore in the order of 20,000:1.

After the experiment both samples of alumina were analyzed by atomic absorption for the nickel content which was found to be equal to 175 ppm for alumina C and 73 ppm for alumina K (*13*). This amount is equal to the amount of Ni impurity in the *sec*-aluminum butylate. Therefore, even if a migration of nickel from the catalyst occurred during its contact with alumina C under hydrogen (*14*) this will not explain the catalytic activity of alumina C if the hydrogen spillover is denied.

In conclusion, it is considered that atomic hydrogen, formed on nickel, can then migrate onto alumina where it reacts with ethylene. The problems which are now under investigation concern the state in which hydrogen can migrate (gaseous or adsorbed) and the mechanism of hydrogenation of ethylene on alumina C (Langmuir–Hinshelwood, Rideal with ethylene coming from the gas phase or chain reaction mechanism). Also quantitative measurements of the hydrogenation of ethylene are in progress in order to check if the amount of ethane formed on alumina C is correlated with the amount of hydrogen adsorbed by the alumina after its contact with the catalyst. Moreover, ir experiments (including D_2–H_2 exchange) are under way in order to investigate whether carbonaceous residues interfere in the hydrogen transport. All these problems will be discussed in detail in a full paper to be published later.

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