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A Comparison of Activated Hydrogen Chemisorption on Some Supported Metal Catalysts

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Hydrogen chemisorption on 10% Fe/Al_2O_3, 10% Fe/SiO_2, 10% Ni/Al_2O_3, and 5% Rh/TiO_2 reduced at 473 and 773 K was compared using temperature-programmed desorption and, for two of these, using chemisorption isobars. Adsorption into the strongest states was slow at 300 K for each catalyst previously reduced at 723 or 773 K. The similarity of the effect for each catalyst suggets that they share a common cause. Decoration by reduced titania species is known to influence chemisorption; however, reduced alumina and silica species are not expected after reduction at 723 K. Estimation of the surface charge density due to charge transfer with the support suggests that this will never be of importance, except near the metal–support interface. It is suggested that decoration may have resulted after small amounts of SiO_x and AlO_x originally dissolved in the impregnating solution accumulated at the metal surface. © 1988 Academic Press, Inc.

INTRODUCTION

In the study of hydrogen and adsorption on Group VIII and other metal single-crystal surfaces, it has been found that saturation can usually be approached after a few hundred Langmuirs (1 L = 10^{-6} Torr s) or less of H_2 at temperatures around 100 K (*1–9*). Chemisorption on these surfaces is therefore substantially nonactivated. In a few cases, ordering has been observed in the adsorbed phase (*2–4, 10–15*) at low temperatures, indicating the existence of weak adsorbate–adsorbate repulsive forces and the absence of significant surface diffusion barriers. Adsorption geometries have also been proposed (*11, 13, 15*). In a number of cases, it was concluded that saturation corresponds to more than one monolayer of H atoms (*2–4, 14, 16*); however, many of these determinations are difficult to make and some controversy exists (*17, 18*).

It is well known (*19–25*) that hydrogen chemisorption on certain supported metal catalysts is activated, apparently due to a change in the electronic structure of the metal component. Electronic effects have been discussed with regard to alloys (*26, 27*), poisons (*28*), promoters (*29*), decoration (*30*), and supports (*31, 32*), but only the latter four are important for the present purpose. In each case, the experimental evidence (*28–32*) suggests that at least a portion of the changes in catalytic activity are due to some kind of electron transfer or localized electrical modification of the metal. With respect to charge transfer, it is not always clear where the changes have been supposed to occur. Most investigators emphasize changes that take place in the vicinity of the additive or the metal–support interface (*28–32*). Others have also considered the apparent lack of influence of charge transfer on the bulk properties of supported metals (*30, 33, 34*). In considering this question we recall that when a

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charge is placed on an electrical conductor, the charge resides solely on the surface (*35*). Electrostatic principles then allow an estimate to be made of the surface charge density. The significance of this contribution and that of two decoration mechanisms will be compared.

METHODS

Catalysts. Four catalysts were examined in this study. A 10 wt% Fe/Al_2O_3 catalyst was prepared (*36*) by precipitation onto Alon-C (Degussa). CO chemisorption at 199 K suggested a fraction exposed of about 0.08 (*36*). Iron particles with diameters between 1.6 and 2.0 nm were detected by electron microscopy (*36*). Reduction by H_2 at 723 K for 16 h gave 76% Fe^0 (*36*). Similar results were obtained for 10% Fe/SiO_2 prepared by impregnation of Cab-O-Sil with aqueous $Fe(NO_3)_3$ (*37*). Ni/Al_2O_3 (10%) was prepared by impregnation of Alon-C with $Ni(NO_3)_2$ (*38*). Reduction by H_2 for 16 h at 723 K is expected to give about 95% Ni^0 (*39*). Line broadening and H_2 chemisorption (*38*) suggested a Ni particle size of 4.5 nm and a fraction exposed of 0.2. The 5% Rh/TiO_2 catalyst was prepared by D. Resasco at Yale University by impregnation of Degussa P-25 TiO_2 with $Rh(NO_3)_3$. Our H_2 chemisorption results on the low-temperature reduced (LTR) catalyst obtained at 300 K suggest a dispersion of about 23%.

Temperature-programmed desorption. TPD measurements were made using a stainless-steel microreactor with an internal volume of 0.5 cc. Calculations (*40*) and mixing curve measurements (*41*) suggest that the chamber is gradientless under the conditions used here, at least above 300 K. The catalysts were screened to give 0.6- to 1.2-mm particles, in order to reduce diffusion limitations (*42, 43*). Heating was accomplished by suddenly applying power to the heater; no rate controller was used. Cooling was obtained by passing air through cooling tubes or immersing the reactor in liquid nitrogen. The reactor could be isolated by switching a chromatographic valve to prevent the accumulation of impurities.

The He carrier gas was purified by passage over a reduced copper catalyst at 650 K, followed by molecular sieve at 300 K. H_2 was purified by using a manganese oxide catalyst followed by molecular sieve, both at 300 K. The concentration of H_2 in the carrier was followed with a mass spectrometer (Nuclide 12-90-G), using high resolution to eliminate background due to He^{2+}. The instrument was calibrated against a known mixture of H_2 in He. All adsorptions were done using 1 atm of H_2.

Isobars. Hydrogen isobars were deter-

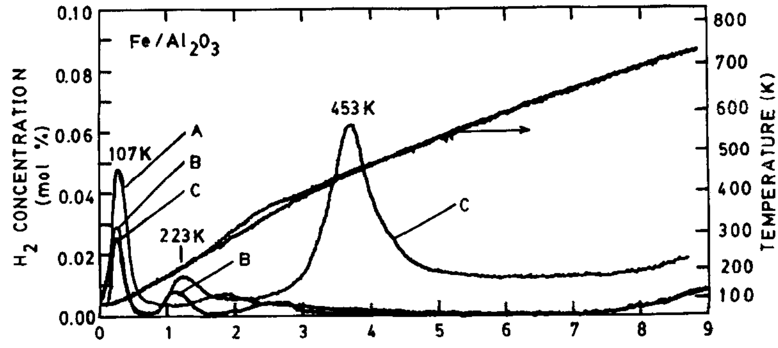

FIG. 1. TPD of H_2 from Fe/Al_2O_3 after adsorption (A) for 10 min at 300 K and then cooling in H_2 to 77 K; (B) for 20 h at 300 K and then cooling to 77 K; (C) at 423 K with slow cooling over 3 h to 300 K, and then to 77 K.

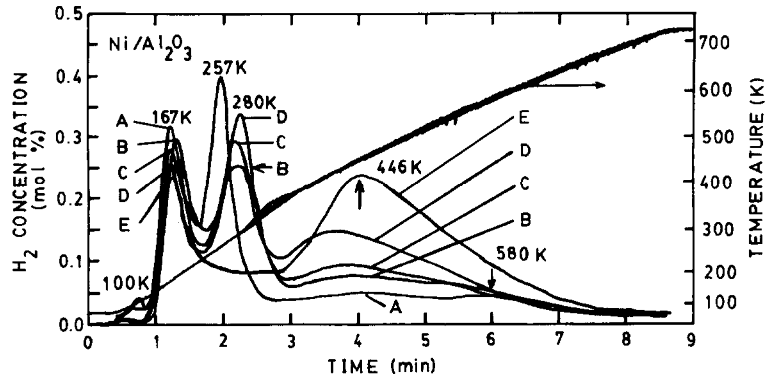

FIG. 2. TPD of H_2 from Ni/Al_2O_3 after adsorption at 300 K (A–D) for (A) 15 s, (B) 10 min, (C) 1 h, (D) 20 h, or (E) at 423 K with cooling to 300 K. Each of these treatments was followed by cooling under H_2 to 77 K.

mined using the apparatus and procedure described elsewhere (*44*).

RESULTS

Fe/Al_2O_3. Figure 1 shows the TPD of hydrogen obtained with a 50-mg sample by various adsorption procedures. If the adsorption was carried out at 300 K for either 10 min (A) or 20 h (B), essentially no hydrogen desorbed above 300 K. By adsorbing initially at 423 K (C) and then cooling slowly to 300 K and then to 77 K under H_2, a substantial TPD peak was detected at about 453 K.

Blank runs were made with just the support and with an empty reactor. These showed that the support alone did not yield any significant desorption peaks for the above adsorption procedures. The tail on curve C above about 600 K is attributed to hydrogen which dissolved in the steel of the reactor during exposure to H_2 at 423 K. Much larger amounts were dissolved at higher temperatures, so that extended outgassing was required after catalyst reduction. The hydrogen dissolved in the iron is negligible. The peak at about 107 K must be due at least partly to chemisorption on the iron. This peak was observed even for 10 min adsorption at 77 K. It is important to note that, since the critical temperature of H_2 is 33.3 K, physical adsorption of H_2 will never be observed above 77 K.

Fe/SiO_2. Elevated temperatures were also required to obtain adsorption in the important states on Fe/SiO_2. Chemisorption on the support was very significant at low temperatures, however. An adsorption isobar was determined at 0.2 atm for 10 min adsorption between 300 and 723 K. The shape was similar to the isobar of Emmett and Harkness (*20*), with an adsorption maximum at about 420 K.

Ni/Al_2O_3. Figure 2 shows the TPD spectra obtained by various adsorption procedures on a 50.8-mg sample of the nickel catalyst. After adsorption at or above 300 K, the sample was cooled under 1 atm H_2 to 77 K, as in Fig. 1.

As with the iron catalysts, adsorption of hydrogen into the states which desorbed above 300 K is a slow process. Adsorption at 423 K with subsequent cooling gave the largest uptake (curve E). A number of desorption peaks appear which were not observed on the iron catalyst (note the scale change), and these are similar to those reported by Scholten *et al.* (*45*) for unsupported Pt and Ir. One of these peaks has been linked to the hydrogenation activity of the catalyst (*45*). Iron is a poor hydrogenation catalyst. When the adsorption on Ni/Al_2O_3 was carried out for 10 min at 77 K, only the first TPD peak appeared.

Figure 3 shows the isobars determined using a 10-min exposure to H_2 at the given

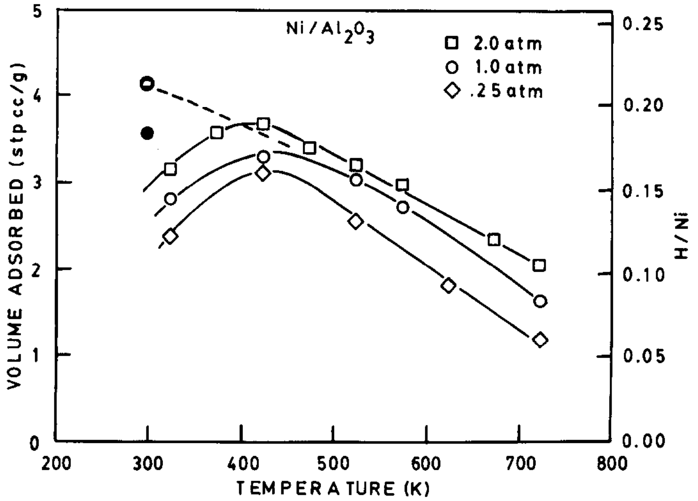

FIG. 3. Isobars for Ni/Al_2O_3 after 10 min adsorption at the indicated temperature and pressure. Other points indicate the results found after more severe adsorption procedures.

pressure and temperature. We used a flow system and a steel reactor (*44*) so that these parameters could be controlled precisely. The quantity adsorbed increased between 300 and about 423 K, again indicating activated adsorption (*19*). Larger quantities adsorbed could be obtained at 300 K by adsorbing for 20 h (solid circle) or by cooling very slowly under 1 atm H_2 (half-filled circle) from 423 K. The points obtained at high temperatures include some contribution from hydrogen dissolved in the steel, however, so that they are only semiquantitative.

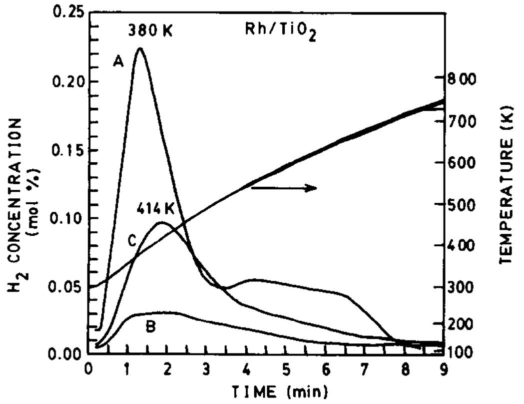

FIG. 4. TPD of H_2 from Rh/TiO_2 after (A) LTR and 10 min adsorption at 300 K; (B) HTR and 10 min adsorption at 300 K; (C) HTR and adsorption at 423 K, with cooling to 300 K.

Rh/TiO$_2$. The catalyst received by us had been reduced and oxidized at 773 K. An 84.6-mg sample was reduced at 473 K for 1 h in flowing H_2 and then degassed for 30 min using flowing He at 3 ml/min at 473 K. After cooling to 300 K under He, hydrogen was adsorbed for 10 min at 1 atm and 300 K. We obtained TPD curve A in Fig. 4 by this pretreatment/adsorption procedure. The results are similar to those of Rieck and Bell (*46*) for low-temperature reduced Pd/TiO_2. Huizinga and Prins (*47*) and Apple *et al.* (*48*) have presented ESR and ^{1}H NMR evidence which leaves little doubt that the second peak, observed here above 550 K, is due to spilled over hydrogen on the partially reduced support. In determining the fraction of Rh atoms exposed on this sample, we therefore neglected the hydrogen desorbed during the second peak.

The catalyst was next reduced 16 h at 773 K in flowing H_2, degassed, and cooled to 300 K in He. H_2 at 1 atm was then adsorbed for 10 min at 300 K. TPD gave curve B in Fig. 4 and chemisorption was typically suppressed. Curve C was obtained by adsorbing H_2 at 1 atm initially at 473 K with subsequent cooling under H_2 to 300 K. Repeated high-temperature reduction (HTR) and adsorption reproduced this result.

The second peak due to spillover on the LTR sample was absent in the HTR case, in accord with the model of Huizinga and Prins (*47*). Since the support was reduced and dehydroxylated, no spillover occurred.

Hydrogen chemisorption was not always activated. For adsorption on the LTR catalyst, adsorption was rapid at 300 K. The same preparation methods, apparatus, and procedures were used on samples of Rh/SiO_2 and Ru/SiO_2, and it was found that adsorption into the strongest states on these catalysts was rapid even at 77 K.

DISCUSSION

The results indicate that strong chemisorptions are activated processes on these catalysts. Dumesic and co-workers (*49–51*) and van't Blik and Prins (*52*) have emphasized the slow uptake of H_2 by HTR metal-on-titania catalysts and suggested that this hydrogen is actually adsorbed on the TiO_x (*49–51*) or the support (*49, 52*). As mentioned above, since the support is reduced after HTR, the mechanism for spillover (*47*) should be removed. The appearance of our TPD peak after adsorption at 473 K on HTR Rh/TiO_2 (Fig. 4) is similar to the peak at about 380 K on the LTR catalyst. The 34 K shift in the desorption maximum may have been due to differences in the initial coverage and the higher activation barrier. The shapes of the HTR desorption curves also compare favorably with those of the nickel and iron catalysts and those of the unsupported Pt and Ir powders used in the experiments reported by Scholten *et al.* (*45*). The success of this comparison suggests to us that the hydrogen is adsorbed on the metallic portion of our catalysts, and therefore that the Rh surface on the HTR Rh/TiO_2 catalyst is not completely blocked. Since the unobstructed but electronically modified segment of the HTR Rh/TiO_2 makes up a significant proportion of the metal surface, while another significant proportion is apparently blocked by dispersed TiO_x, it is easy to see why various reactions (*53*) are found to be suppressed, largely unaffected, or actually promoted by SMSI.

SIMS and AES depth profiles obtained (*54–57*) using model film catalysts have established that diffusion of TiO_x through Rh, Pt, and Ni and decoration of the surface does occur during high-temperature reduction or annealing. Similar Rutheford backscattering experiments (*58*) showed that this can also occur with Al_2O_3 after reduction and oxidation at 1273 K, but we do not expect this to occur at 723 K. However, when Raupp and Dumesic (*51*) decorated a Ni polycrystalline foil with Al_2O_3, the effects on H_2 and CO chemisorption were found to be qualitatively similar to the results for decoration by titania, although less severe. The questions whether a 16-h reduction at 723 K is capable of introducing a substantial coverage of AlO_x on Fe and Ni and SiO_x on Fe and whether the influence of such species is sufficient to explain the experimental results naturally arise then.

The more conventional explanation, an electronic effect through charge transfer from the support (*31, 32*), appears no less controversial owing to the insulating properties of SiO_2 and Al_2O_3. The influences of these types of effects have been discounted in the case of TiO_2 because charge transfer has failed to cause an observable change in the electronic structure of the bulk of metals supported on TiO_2 (*34, 58, 59*) or because of a lack of a suitable mechanism for such influence to be exerted on large particles (*34, 55*). Although these ideas have led to the discovery of decoration by TiO_x, some of the arguments presented need to be examined carefully, as becomes apparent below. Also, evidence in support of the electron transfer model continues to appear (*60, 61*).

Gauss' law of electrostatics (*35*) requires that any surplus charge placed on a conductor be located on the surface. Therefore, no modification of the bulk properties of supported metals is expected as a result of electron transfer. Thus, in deciding whether charge transfer can be significant catalytically, it is better to compare the quantity of charge transferred to the number of surface metal atoms than to the total number of electrons in the crystallite. For a highly conducting support, an analogy to thermocouples is useful. The electric potential difference between the two conductors depends on the absolute thermoelectric power of each phase and the temperature. The quantity of charge transferred depends on the number of charge carriers and the electrical capacitance of each phase, as does each absolute electric potential. The surface charge density at a given point on the surface depends on the potential difference and the local geometry; the charge density is greatest where attractive coulombic forces operate at short distances. In general, charge is spread over the entire surface.

It is possible to estimate the order of magnitude of the surface charge density based on these principles (*35*). One can then use this charge density to decide whether electron transfer can contribute significantly to metal–support effects. For our model system, we choose a parallel plate capacitor where the distance separating the plates is characteristic of a catalyst pore diameter, and the potential difference is characteristic of a thermoelectric potential easily detectable by XPS. Taking as a basis for calculation then a potential of 1 V (*59, 62*) on a parallel plate capacitor separated by 1 nm gives a charge density of about 5×10^{-4} electrons/Å^2, which is equivalent to about one electron for a 20-Å crystallite. Since the charge density varies as the reciprocal of the distance, higher densities are to be expected at the metal–support interface. Vanselow and Mundschau (*63*) point out that this can lead to very steep potential gradients, but the charge densities are still expected to be modest. At short distances then, this amounts to a physical description of the ligand effect. The results suggest that the charge densities for insulating and conducting supports may be more similar than previously thought, and of course that the effects are most severe for small metal particles. In both cases, however, it appears to be too small to have any observable effect over most of the surface. The validity of this conclusion should be tested by measuring the influence of the electric potential and surface charge density on the kinetics of reactions on clean metal wires or crystals.

It is possible that neither of the above models is responsible for the slow adsorption on these Al_2O_3- and SiO_2-supported catalysts. Thermally induced decoration is not expected after reduction at such low temperatures. However, small amounts of silica and alumina species may have dissolved during the impregnation procedure and eventually decorated the metal surfaces. Ponec and co-workers (*64*) have discussed this type of mechanism in detail as it pertains to Rh on vanadium oxides and concluded that the high selectivity of some of these catalysts toward C_2 oxygenates during the CO/H_2 reaction is due to promotion by vanadium species which decorate the metal surface. Although this mechanism for decoration is expected to be less important in the case of silica and alumina supports, they may be dissolved to an extent in certain acidic and basic solutions (*64*). Wet impregnation may also provide the opportunity for various impurities to dissolve and ultimately accumulate on the metal surface. Again, however, it is important to recall that the effects of such species are only apparent using certain metal–support combinations, with the noble metals on silica and alumina supports being notable exceptions.

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