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NOTES

Reducibility and Hydrogen Chemisorption Properties of Alumina

Alumina has long been widely used for supported catalysts in industry, but some problems remain to be further studied, e.g., its reducibility and hydrogen chemisorption properties after high-temperature treatments, which are of particular interest in the study of metal–support interaction in alumina-supported catalysts. Information is available in the literature concerning the formation of nonstoichiometric, oxygen-deficient alumina and alterations of its chemical and electric properties after high-temperature treatments in hydrogen or *in vacuo* (*1–5*). Based on the amount of hydrogen taken up at high temperatures, Weller and Montagna (*6*) have suggested a possible reduction of alumina to surface suboxides. In the case of alumina-supported platinum catalysts, den Otter and Dautzenberg (*7*) and Kunimori *et al.* (*8*) have proposed the formation of metallic aluminum and a Pt–Al alloy. However, further work with different techniques is desirable in this respect before a definite conclusion can be drawn.

The states of adsorbed hydrogen on alumina have been studied by means of temperature-programmed desorption (TPD) by Amenomiya (*9*). He found that there were five different states of chemisorbed hydrogen, referred to as H(I) to H(V), respectively, and he suggested that at least four of them, namely H(I), H(III), H(IV), and H(V), shared all or part of the surface defect sites of alumina. The samples used in his work, however, were only pretreated by evacuation, and the temperatures of chemisorption did not exceed 450°C.

In this Note new evidence for the reducibility of alumina, together with an inhibition effect on the hydrogen chemisorption of alumina after reduction at high temperatures, are reported. Temperature-programmed reduction (TPR) and desorption (TPD) have been used as the main techniques, and the feature of the present work is that high temperatures are used for the measurements of TPR and TPD (both to 1000°C) as well as hydrogen chemisorption (to 800°C), which will be shown to be necessary for the study of problems related to the reduction of alumina.

γ-Aluminas (0.9–2.0 mm in diameter) were used throughout this work and Table 1 lists their pretreatment conditions, surface areas, and impurity contents. Hydrogen chemisorption, TPR and TPD were carried out with a multifunctional temperature-programming apparatus which has been described elsewhere (*10*). The sample holder was made of quartz, and 0.3 g of sample was charged for TPR and 0.5 g for TPD. All gases were carefully purified to remove water and traces of O_2 or H_2 prior to use. The flow rate of Ar–H_2 (95 : 5) or Ar was 30 ml/min, and that of H_2 was 40 ml/min. Both TPR and TPD measurements were started from room temperature, with a constant heating rate of 16°C/min throughout. Hydrogen chemisorption was carried out directly in the course of hydrogen treatment in a H_2 stream at a given temperature followed by cooling in the same atmosphere and purging with Ar at room temperature, after which TPD was initiated. The quantities of hydrogen consumed or desorbed were determined by comparison of the peak areas obtained with that of a given pulse of hydrogen in Ar–H_2 or pure Ar. XPS was performed with a PHI 550 ESCA/SAM electron spectrometer (Mg*K*α radiation, pass energy 25 eV). Samples were treated in Ar or H_2 using the same apparatus as TPR and TPD; during transfer for XPS

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TABLE 1

Alumina Samples

Sample	Pretreatment[a]	S.A. (m^2/g)	Impurity[b] (ppm)
S-2	Calc. 600°C, 8 h; 700°C, 4 h	188	Mg 200, Fe 50, Cu < 10, Mn 10, Pb 10
C-19	S-2 + 1 wt% HCl, then calc. 500°C, 3 h	188	As for S-2
S-6	Steam-treatm. 700°C, 12 h, and then calc. 700°C, 6 h	130	Mg 30, Fe 10, Cu < 10, Mn 10, Pb 10
S-7	Calc. 550°C, 3 h	242	As for S-2
S-9	Addtl. calc. 700°C, 5 h	197	As for S-2

[a] Calcinations were conducted in air.

[b] Determined by atomic emission spectroscopy. S-2, C-19, S-7, and S-9 were from the same origin.

measurements they were exposed to air for a short time.

Figure 1 shows the TPR profiles of some alumina samples pretreated under different conditions. Two main peaks can be roughly resolved, one at around 800°C and the other at lower temperatures. It is noted that with increasing severity of precalcination the low temperature peak tends to disappear, while the peak around 800°C becomes considerably larger (Figs. 1A–C).

Chlorination causes the low-temperature peak of C-19 to be almost eliminated, but the major peak of this sample is quite similar to that of S-9, both in position and area (compare Figs. 1D with B). These effects can be rationalized assuming that the major peak around 800°C is due to reduction of some coordinatively unsaturated Al cations on the alumina surface, the number increasing with the severity of calcination; the low-temperature peak is due to reaction of hydrogen with the surface OH groups, which can be eliminated either by calcination or chlorination.

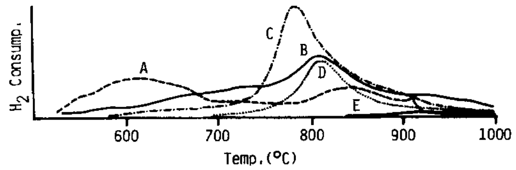

FIG. 1. TPR of alumina samples. (A) S-7; (B) S-9; (C) S-6; (D) C-19. See Table 1 for pretreatments. (E) is for comparison and was obtained from S-2 after a prereduction in H_2 at 750°C for 0.5 h followed by outgassing in Ar to 980°C.

In order to rule out the possibilities of hydrogen chemisorption and/or absorption, sample S-2 was prereduced in hydrogen at 750°C for 0.5 h, followed by outgassing in Ar to 980°C; subsequent TPR (Fig. 1E) showed that no more hydrogen consumption was detected in the original positions except an extremely small signal above 840°C, which may correspond to some Al species not reduced during the prereduction at 750°C. The interference of chloride can be readily excluded as a result of experience gained from the TPR of the chloride-containing sample, C-19. On the other hand, the hydrogen consumption around 800°C should not be due to reaction of impurities, since all of the aluminas used were very pure and, especially, the largest peak was derived from the purest sample, S-6. We therefore conclude that this peak is due to the reduction of alumina.

Some preliminary XPS work was also carried out to measure the Al 2*p* peaks over

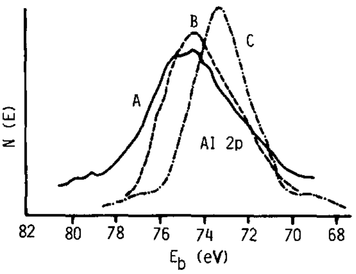

FIG. 2. XPS of alumina samples. Pretreatments: (A) Ar, 750°C, 1 h; (B) H_2, 750°C, 1 h; (C) H_2, 800°C, 1 h.

three S-2 samples: one was treated in Ar at 750°C for 1 h (A), the second in H_2 at 750°C for 1 h (B), and the third in H_2 at 800°C for 1 h (C). Figure 2 shows that the binding energies of the hydrogen-treated samples are lower than that of the argon-treated sample, and the binding energy of the sample reduced at a higher temperature is even lower. This at least indicates an alteration of the surface chemical state of the alumina, brought about by hydrogen treatment at high temperatures, and thus to some extent supports the conclusion of reduction of alumina.

Assuming that the surface layers of alumina are constructed from the (100) plane and that each Al cation is contained in an octahedral interstice and links to a surface OH group (for which the density is $1.25 \times 10^{15}/\mathrm{cm}^2$) (*11*), the concentration of surface Al cations on sample S-6 is estimated to be 1.6×10^{21}/g. If all the Al cations were reduced to the zero-valent state, 91.0 ml(STP) H_2/g would be required. Only 0.53 ml(STP)/g, i.e., about 0.6% of the stoichiometric amount according to the ideal model, was actually consumed by this sample. However, this does not necessarily mean a negligible reduction of alumina, but may suggest that the surface Al cations are far from homogeneous in their reducibilities, and that some "active Al cations" may exist on the alumina surface. In fact, the real surface of an alumina can differ greatly from that described by the ideal model due to pretreatment at high temperatures, and a substantial number of active structures such as steps and kinks made up by various coordinatively unsaturated Al cations may well be produced in our case. This is demonstrated by the increase of the area of the major peak in the TPR profiles of the alumina samples with increasing severity of pretreatment (Figs. 1A–C). The tendency of the Al 2*p* XPS peak to grow narrower with increasing reduction temperature (Fig. 2) probably indicates that as reduction proceeds the surface of alumina is becoming more and more uniform in coordination as well as in valence state. However, since different valence states of aluminum may be present before reduction, it is impossible merely from the amount of hydrogen consumed to estimate the extent of reduction of an alumina. Nevertheless, it cannot be excluded that a fraction of zero-valent aluminum could be formed on account of the surface heterogeneity as pointed out above.

TPD measurements were carried out with

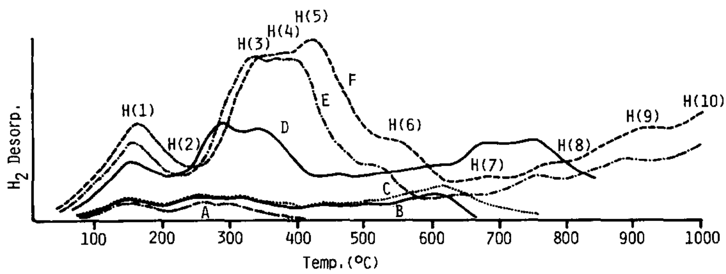

FIG. 3. TPD of alumina samples (S-2) treated in H_2 at different temperatures. Treatment conditions and amounts of H_2 desorbed (ml(STP)/g): (A) 300°C, 1 h, 0.03; (B) 400°C, 1 h, 0.08; (C) 500°C, 1 h, 0.09; (D) 600°C, 1 h, more than 0.39; (E) 750°C, 0.5 h, more than 0.56; (F) 800°C, 0.5 h, more than 0.76.

S-2 alumina samples treated in H_2 over the range from 300 to 800°C, and very complicated profiles, comprising at least 10 peaks, were obtained (Fig. 3). These peaks have been proved to result from desorption of hydrogen, and are referred to, respectively, as H(1) to H(10) in the order of increasing desorption temperatures; among them the H(1), H(2), and H(3) peaks are in good accordance with the H(III), H(IV), and H(V) peaks reported by Amenomiya (*9*). Figure 3 shows that as the hydrogen-treatment temperature increases, all of the peaks except H(1) shift toward higher temperatures, which is similar to what has been observed for alumina-supported platinum catalysts and will be discussed elsewhere (*12*). It is especially worth noting that a sharp increase in the amount of hydrogen desorbed occurred when the hydrogen-treatment temperature was raised to 600°C and above. According to the data reviewed by Knözinger and Ratnasamy (*11*), the surface OH density of alumina pretreated at 500°C is $4.2 \times 10^{14}/\text{cm}^2$; it would only decrease to about $2.4 \times 10^{14}/\text{cm}^2$ by extrapolating the pretreatment temperature to 600°C, although the real difference must be even smaller on account of the precalcination at 700°C for all S-2 samples (Table 1). Apparently the decrease of OH groups can by no means account for the sharp increase of the hydrogen uptake, nor can the diffusion of H_2 into the alumina matrix, since most of the H_2 increased was adsorbed at the same original sites as shown by Fig. 3. However, this may be explained in terms of reduction of alumina, which creates some new sites to facilitate the dissociation of H_2, for it has been established by preliminary experiments that hydrogen treatment at 600°C for 1 h reduces a catalyst to the same extent as does TPR to 710°C, and at this temperature reduction of alumina has practically occurred (see Fig. 1).

An interesting phenomenon, namely the inhibition effect on hydrogen chemisorption, has also been observed from alumina reduced at high temperatures in our TPD measurements. This is illustrated by Fig. 4 and Table 2. It can be seen from Fig. 4A that substantial amounts of hydrogen were taken up at 400°C by the alumina which was pretreated in H_2 at high temperatures. The same sample, however, lost most of its hydrogen chemisorption capacity, simply owing to an incomplete preceding outgassing (to 550°C), which allowed the retention of some strongly adsorbed hydrogen (Fig. 4B). Removal of the strongly adsorbed hy-

TABLE 2

Procedures for TPD Measurements

Procedure[a]	H_2 desorbed (ml(STP)/g)
(A) H_2 treatment (650°C, 0.5 h; 800°C, 10 min)–outgassing (to 1000°C)–exposure to H_2 (400°C, 10 min)–TPD (to 550°C)	0.35 below 550°C
(B) Exposure to H_2 (650°C, 10 min)–TPD (to 1010°C)	0.07 below 550°C 0.09 below 700°C 0.15 below 1010°C
(C) Exposure to H_2 (650°C, 10 min)–TPD (to 700°C)	0.40 below 700°C
(D) Reoxidation in O_2 (500°C, 10 min)–H_2 treatment (400°C, 0.5 h)–TPD (to 550°C)	0.23 below 550°C
(E) Ar treatment (650°C, 0.5 h; 800°C, 10 min)–exposure to H_2 (400°C, 10 min)–TPD (to 550°C)–exposure to H_2 (550°C, 10 min)–TPD	0.36 below 550°C 0.43 below 700°C 0.55 below 800°C

[a] A to D were sequential experiments over one and the same alumina sample (S-2), and E was a parallel measurement using another S-2 sample.

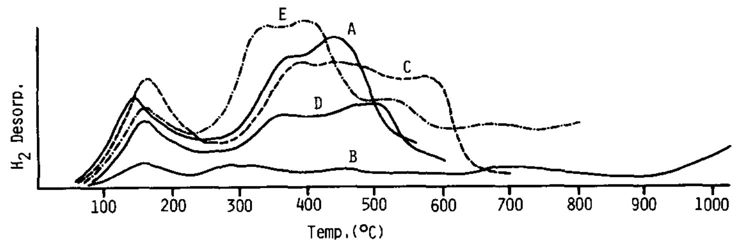

FIG. 4. TPD of alumina samples (S-2). See Table 2 for details.

drogen by outgassing to 1010°C led to a complete restoration of hydrogen uptake, and reoxidation was found to be also effective, as shown by Figs. 4C and D, respectively. On the other hand, when the pretreatments were conducted in Ar, instead of H_2, no decrease of hydrogen uptake was observed, although other conditions were similar to that of the hydrogen-treated sample (compare Figs. 4E with B). It was also found in our experiments, that the hydrogen chemisorption capacity of alumina did not change if the sample was pretreated in H_2 at a low temperature such as 300°C.

Apparently, the inhibition effect on hydrogen chemisorption by alumina is the same as that reported by Menon and Froment (*13*), and it was also observed in our work on alumina-supported platinum catalysts (*12*). However, this effect was much stronger with the alumina than observed on the Pt/Al_2O_3 catalysts and was not found to occur for pure platinum (made from $(NH_4)_2PtCl_6$). This implies that the inhibition effect for alumina-supported platinum catalysts may in fact result from the alumina support, and may be related to the reduction of alumina. Owing to the fact that desorption of only 0.08 ml(STP)/g of the strongly adsorbed hydrogen led to more than a threefold increase of hydrogen uptake (Fig. 4C), an electronic factor, rather than the strongly adsorbed hydrogen itself, must be involved in it.

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