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NOTE

Ruthenium as a Dispersing Agent in Carbon-Supported Palladium

Among the various metals able to catalyze hydrogenation reactions, palladium is probably the most interesting one, due to its special feature of interacting with hydrogen in two different ways, surface adsorption and bulk absorption, both of them having relevance to the catalytic phenomenon (1). Various Pd-based bimetallic systems have been investigated with very interesting results, for instance Pd–Ni (2), Pd–Co (3), Pd–Fe (4), and Pd–Mo (5).

As very few data are available on the Pd–Ru system (6–8), the latter was chosen as the subject of our investigation, in particular to look for the presence of metal–metal interaction. An active carbon was used as support in order to minimize metal–support interactions. Temperature-programmed reduction (TPR) and wide-angle X-ray scattering (WAXS) were chosen as experimental techniques.

Catalysts were prepared by impregnation of a commercial active carbon (apparent surface area 1100 m^2/g, pore volume 0.90 ml/g) with $PdCl_2$ and $RuCl_3$ solutions in order to obtain the following nominal contents expressed as wt%: Pd(0.5); Pd(0.4)–Ru(0.1); Pd(0.25)–Ru(0.25); Ru(0.5). The two precursors were dissolved in HCl (1 *M*) and were slowly added to a slurry of the support in H_2O. The samples were stirred until the solution was colorless, then filtered and washed with H_2O until disappearance of the chloride ions ($AgNO_3$ test). Drying was performed at 110°C for 4 h.

TPR measurements were performed in a previously described standard apparatus (9). The dried samples were heated at a linear rate of 15°C/min from 25 to 900°C in 5% H_2 in Ar flowing at 40 ml_{stp}/min). In a low-temperature TPR experiment the sample was cooled to −78°C before the reduction mixture was fed and then left to warm to room temperature at a rate of 8°C/min.

X-ray diffraction patterns were collected using a Philips vertical goniometer connected to a highly stabilized generator and equipped with a graphite focusing monochromator. CuK_α radiation and a proportional counter with a pulse-height discriminator were used. A step-by-step technique was employed: steps were 0.05° with an accumulation counting time of 100 s per angular abscissa. The transformation between the metallic and hydride phase was followed *in situ* by using a special brass holder (10) with a Kapton window where hydrogen or air could flow. The same weight was used for samples reduced at 250°C.

A standard best-fitting procedure (11), using pseudo-Voigt functions superimposed on the background due to the halo of carbon, was performed in order to determine the peak position of the crystalline metal phase and, after Fourier analysis, the corresponding XRD detectable average volume-weighted crystallite size $\langle D \rangle$.

The TPR profiles of catalysts Pd(0.5)/C, Pd(0.4)–Ru(0.1)/C, Pd(0.25)–Ru(0.25)/C, and Ru(0.5)/C are reported in Fig. 1. TPR peaks appear in the following temperature ranges:

- 70–80°C, a negative peak due to the decomposition of Pd hydride (12), which disappears after the addition of Ru.
- 180–220°C, a first peak due to the reduction of Ru species, always present in Ru-containing samples.
- 280–320°C, a second peak due to the reduction of Ru species, which apparently disappears after the addition of Pd.
- 500–750°C, a broad band which is always present and which is probably related to the support.

In order to identify the species involved, further TPR experiments were carried out on the active carbon and on some Ru compounds. The results of the TPR experiments performed on the active carbon are shown in Fig. 2. It was confirmed that the broad band centered at about 700°C is related to the support and in particular to the reduction of oxygenated species present at the carbon surface. In fact, it is known that various oxygen-containing functional groups are usually present on the surface of active carbons, mainly carboxyls, phenols, and quinones (13). It is also known that upon heating in an inert atmosphere they can decompose to give CO and CO_2. However, in our case this possibility can be excluded, because neither CO nor CO_2 were ever detected when the gas leaving the sample was analyzed by a quadrupole mass spectrometer. Moreover, the thermal conductivity of CO_2 is very similar to that of Ar, while that of CO is higher, thereby producing either no peaks or a negative peak, respectively, under TPR conditions. The presence of oxygenated species is

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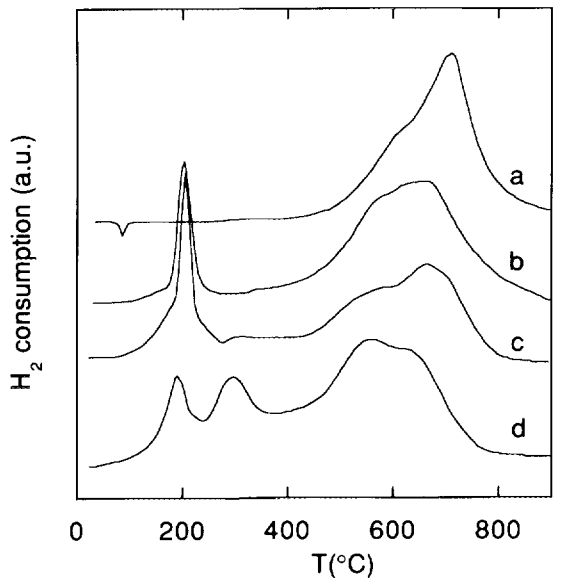

FIG. 1. TPR profiles of the samples: (a) Pd(0.5)/(C; (b) Pd(0.4)–Ru(0.1)/C; (c) Pd(0.25)–Ru(0.25)/C; (d) Ru(0.5)/C.

also demonstrated by the subsequent TPR experiments shown in Fig. 2. In fact, the peak centered at about 700°C disappears in a second run carried out after cooling the sample and reappears only after reoxidation in air at 250°C. From these observations, it might be inferred that an unusual hydrogen activation occurs at a carbon surface, but it should be taken into account that carbons from natural sources contain large amounts (up to 5–6%) of oxidic impurities, some of which, upon reduction, can give metallic species able to activate hydrogen (for instance, Fe and Ni).

As the preparation of our Ru-containing samples involves the impregnation of a basic carbon with a $RuCl_3$ solution, the possible Ru species involved in the TPR profiles of Fig. 1 were considered to be a hydrous oxide like RuO(OH) and $RuCl_3$.

The TPR profiles of these two compounds, compared with that of Ru(0.5)/C, are reported in Fig. 3. As can be seen, in the Ru(0.5)/C sample the peak at 200°C can be reasonably assigned to the Ru oxide species while that at 290°C can be assigned to Ru chloride or oxychloride species. Such assignments are in agreement with previous studies (14).

The disappearance in Fig. 1 of the 290–300°C peak in the Pd-containing samples does not seem to depend on the presence of Pd, but is more likely to depend on the Ru content of the samples. In fact, a Ru(0.25)/C sample, prepared by the same procedure as Ru(0.5)/C, shows only the TPR peak around 200°c. We can infer that during the preparation procedure $RuCl_3$ interacts at first with the basic centers of the carbon surface (Na, Mg, Ca carbonates) giving Ru oxides, while, when these centers have been consumed, it is adsorbed by the carbon as chloride species, which are reduced by H_2 at a higher temperature.

It was previously observed (Fig. 1) that the negative peak due to Pd hydride decomposition disappears after the addition of Ru. This could be ascribed to the fact that Pd oxide is not reduced by hydrogen below room temperature as usual, but is reduced around 200°C together with the coimpregnated Ru oxide, due to some

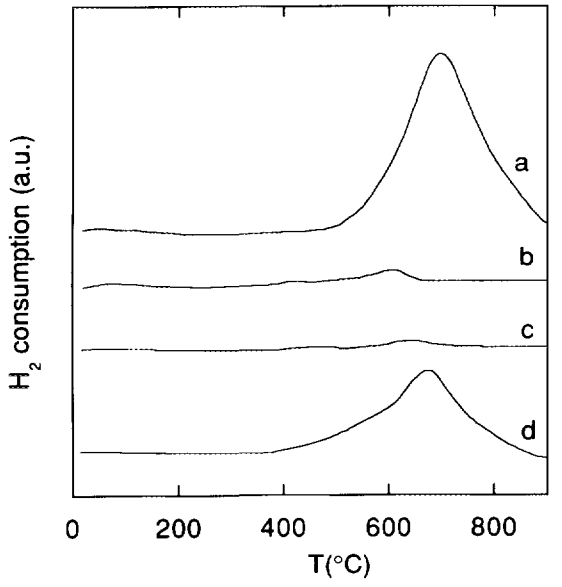

FIG. 2. TPR profiles of active carbon: (a) first run; (b) second run after cooling at room temperature; (c) third run after reoxidation in air for 1 h at 25°C; (d) fourth run after reoxidation in air for 1 h at 250°C.

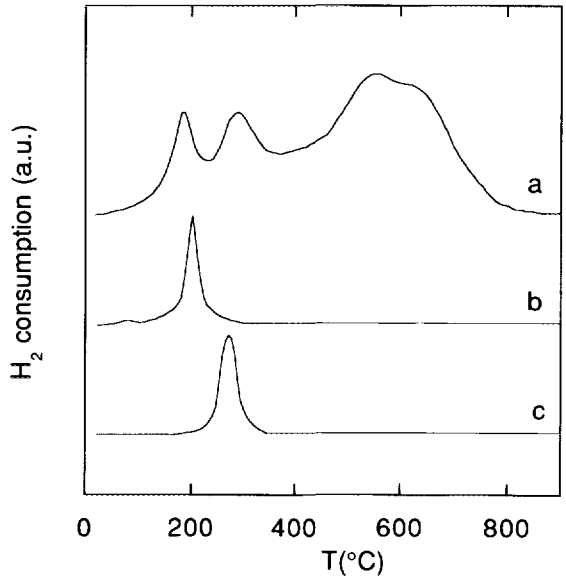

FIG. 3. TPR profiles of Ru species: (a) Ru(0.5)/C; (b) hydrous Ru oxide; (c) $RuCl_3$.

kind of interaction with the latter. However, this possibly was ruled out by the results of a low-temperature TPR experiment on the Pd(0.4)–Ru(0.1)/C sample, showing that the reduction of Pd oxide starts at −20°C. Therefore, other reasons should be considered to explain the disappearance of the Pd hydride decomposition peak in the TPR profiles of the bimetallic samples of Fig. 1. For this purpose, a WAXS study was made on the Pd–Ru/C system.

The WAXS profiles of Pd(0.5)/C ($\langle D \rangle$ = 60 Å) and Pd(0.4)–Ru(0.1)/C samples reduced with H_2 at 25°C are reported in Fig. 4: pattern a shows (i) the Pd111 peak at $2\theta \cong 40°$, (ii) the broad 10 peak of the active carbon used as support at $2\theta \cong 43°$, (iii) a shoulder corresponding to the Pd(200) peak at $2\theta \cong 46.5°$. It can be seen that the Pd dispersion is much higher in the Ru-containing sample. In fact, the complete disappearance of the Pd111 peak points to a Pd crystallite size lower than 15 Å (15). The absence of Pd hydride in the Ru-containing samples can thus be easily explained, as it is well known that for such small-size Pd crystallites the formation of Pd hydride is strongly hindered (16, 17). The above-mentioned samples were also reduced with H_2 at 250°C and the WAXS profiles recorded (Fig. 5). Comparing the heights of the Pd111 peaks, it can be seen that at this temperature a pronounced sintering occurs for the monometallic Pd sample (Fig. 5a), while the Ru-containing one still retains a very high Pd dispersion (Fig. 5b). In fact, even on the prudent assumption that the whole of the Pd in the 250°C reduced Pd(0.5)/C ($\langle D \rangle$ = 90 Å) is XRD-detectable, from the areas of the Pd111 peaks it can be estimated that 85%

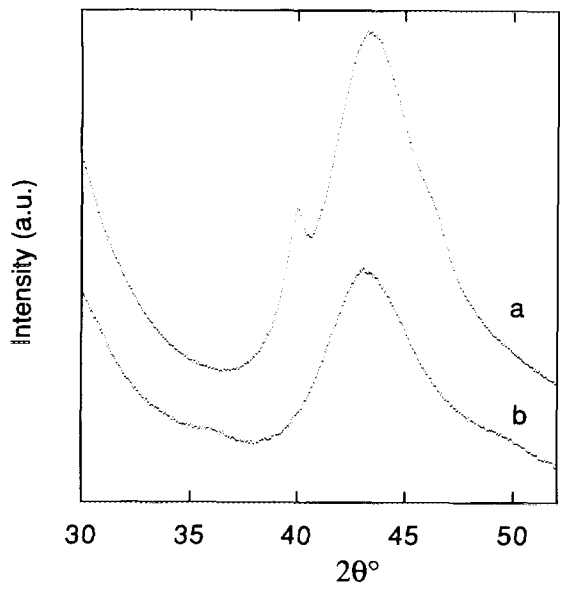

FIG. 4. XRD patterns of samples reduced at 25°C and passivated under 5% O_2 in Ar at room temperature: (a) Pd(0.5)/C; (b) Pd(0.4)–Ru(0.1)/C.

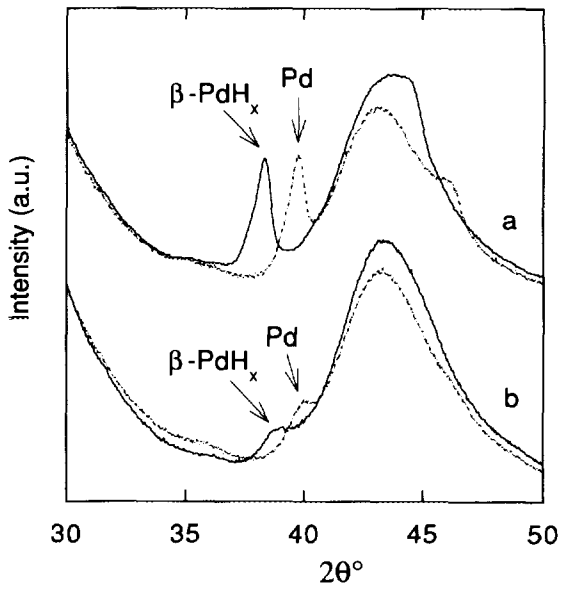

FIG. 5. XRD patterns (a) Pd(0.5)/C reduced at 250°C and passivated (dotted line) under 5% O_2 in Ar at room temperature; (solid line) under H_2 flow; (b) Pd(0.4)–Ru(0.1)/C reduced at 250°C and passivated (dotted line) under 5% O_2 in Ar at room temperature: (solid line) under H_2 flow.

of Pd crystallites in Pd(0.4)–Ru(0.1)/C reduced at 250°C ($\langle D \rangle$ = 70 Å) are still smaller than 15 Å. As expected, when at least a fraction of large-size Pd crystallites is present, the formation of Pd hydride takes place upon H_2 treatment (see Fig. 5). It is noteworthy that in the bimetallic sample, alloy formation seems to be excluded, since no shift to higher angle of the Pd111 peak position has been observed (18, 19).

A confirmation of the WAXS results was obtained through additional TPR experiments. A TPR run up to 300°C of the Pd(0.4)–Ru(0.1)/C sample was repeated after cooling under H_2. No peak due to Pd hydride decomposition was detected, thus confirming that after a treatment at 300°C, Pd is still highly dispersed in this sample. Conversely, when the TPR run is driven up to 800°C, thus giving rise to a sintering of the Pd crystallites, the subsequent TPR profile shows the Pd hydride decomposition peak around 80°C.

The factors giving rise to a very high Pd dispersion in our catalysts when Ru is present probably reside in the coimpregnation step, when the hydrous Pd and Ru oxides and/or oxychlorides are formed. It can be suggested that the interactions with the basic centers of the carbon surface will initially occur with the Ru ions. Indeed, we have verified that hydrous Ru oxide precipitates at lower pH with respect to the Pd one, thus exhausting the more basic centers of the carbon surface. As a consequence, Pd ions will be forced to absorb mainly through an exchange with the oxygen-containing surface groups present on the carbon surface, thereby producing more dispersed species.

This, in turn, will lead to a more dispersed metal after reduction.

It can be concluded that, although TPR and WAXS did not reveal the presence of metal–metal interaction in the Pd–Ru/C system, Ru addition, even in very low percentages, can be used as a means to increase Pd dispersion in Pd/C catalysts, unless some other type of negative effect on the catalytic activity is expected.

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