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LETTERS TO THE EDITORS

The Role of CO Adsorbed on the Support in the Determination of Super Small Metal Surface Area

The work by Komai *et al.* (*1*) is an interesting attempt to characterize very high metallic fraction exposed but it calls for questions concerning the interaction of CO with alumina support and metal surfaces.

The assumption that CO is not adsorbed on support surfaces is often not founded. The amount adsorbed on basic, e.g., MgO or CeO_2—and amphoteric oxides, e.g., Al_2O_3—is far from negligible and may introduce important errors either in pulse or in static adsorption methods.

On alumina, which is the support used by Komai *et al.* (*1*) the amount adsorbed increases with the dehydration temperature and depends upon the nature of alumina. According to Della Gatta *et al.* (*2*), η-alumina and γ-alumina dehydrated at 1013 K are able to adsorb 84 and 24 μmol per gram of solid, respectively, under 10 Torr of CO. No adsorption was detected on samples dehydrated below 673 K. We have determined the amounts of CO adsorbed on alumina and performed infrared studies with pretreatment temperatures in the 373–773 K range.

Two types of alumina were used: a porous η-alumina (kindly supplied by Rhone-Poulenc) and a nonporous microspherical γ-alumina (kindly supplied by Degussa). The samples were first calcined in flowing oxygen (18 liters h^{-1}) at 673 K overnight, then heated in flowing hydrogen (18 liters h^{-1}) at a fixed temperature Tr (373 to 773 K) and finally outgassed at Tr. The adsorbed quantities were determined by volumetric measurements at room temperature under 100 Torr using a pressure sensor (Type 590 Barocel from Datametrics). Infrared spectra were recorded on a Perkin–Elmer 1750 Fourier transform spectrometer, the samples being pressed into self-supporting discs weighing about 30 mg/cm^2. The vacuum system was able to maintain the pressure below 10^{-5} Torr.

TABLE 1

CO Uptake by Alumina

Alumina	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	CO adsorbed under 100 Torr (μmol g^{-1}) after reduction and outgassing at Tr (K)				
			373	573	673	773	(K)
η	250	0.67	3.37	9.16	16.8	24.4	
γ	100	—	1.85	4.87	9.37	13.9	

Table 1 shows that significant amounts of CO are detected even after a rather low pretreatment temperature Tr.

These studies were preliminary to an in-

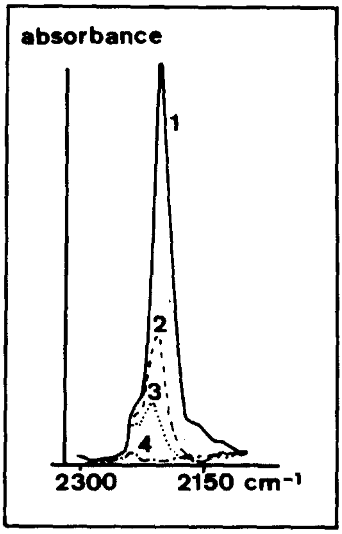

FIG. 1. IR spectrum of CO adsorbed on alumina (1) under 100 Torr, (2) under 7 Torr, (3) under 1 Torr, (4) after outgassing (15 min) at room temperature.

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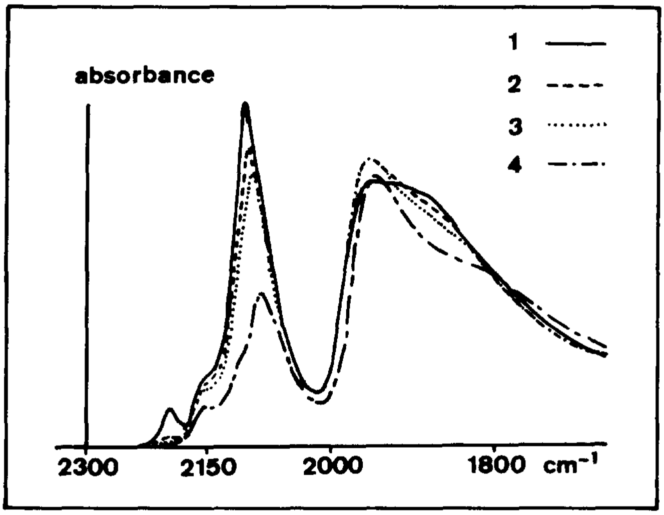

FIG. 2. IR spectrum of CO adsorbed on Pd/Al_2O_3 reduced at 573 K, (1) under 100 Torr, (2) under 7 Torr, (3) under 1 Torr, (4) after outgassing (15 min) at room temperature.

vestigation concerning palladium–alumina catalysts prepared according to various methods (capillary impregnation, ion exchange, anchoring of palladium acetylacetonate) and presenting dispersions in the 0.10–0.95 range (*3*).

When using a 1% palladium on alumina catalyst with a "super dispersion" of 90%, the amount of CO adsorbed on the metal is about 85 μmol per gram of *catalyst* if the CO/Pd ratio is taken as 1 (*4*). Results in the table clearly show that the CO uptake by alumina may represent up to 30% of this value for a pretreatment temperature of 773 K.

Evaluation of metal fraction exposed must therefore take into account the amount of CO adsorbed on the carrier through either the pulse or the static method. However, the strength of CO adsorption on alumina is rather low and the adsorbate is almost completely removed by outgassing at r.t. for 15 min as illustrated by the IR spectrum (Fig. 1).

Then the purge by H_2 performed in Komai *et al.*'s experiments should also desorb all CO adsorbed on alumina. However, on Pd–alumina catalysts, a part of linear CO adsorbed on palladium is also removed (Fig. 2) and it may give rise to an underestimation of the metal fraction exposed. Hence the interest of the method proposed by Komai could be reinforced by an infrared examination of the adsorbed species.

In the case of basic supports, additional difficulties arise from the large CO uptake by these solids with the genesis of polymer species presenting a ring structure $(CO)_n^{2-}$ and/or carbonate or carboxylate entities. Investigated in detail on MgO (*5*), these species appear also on ThO_2 (*6*) and CeO_2 (*7*, *8*). These surface compounds are not removed by outgassing or purged at room temperature and their reactivity toward hydrogen must be checked before using the sensitive titration method proposed by Komai *et al.* Investigations concerning the behavior of carriers toward molecular probes are particularly important for the evaluation of metal fraction exposed and elucidation of metal–support interactions (*9*).

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3. (a) Rakai, A., Thèse, Université Pierre et Marie Curie, Paris, 1989; (b) Bozon-Verduraz, F., Rakai, A., and Tessier, D., to appear.
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