JOURNAL OF CATALYSIS 83, 253–255 (1983)

Ligand Effects in Catalysis by Alloys. Reply to Toolenaar and Ponec

In their letter Toolenaar and Ponec (*1*) argue against our conclusions about Pt–Pb catalysts reported in a recent paper (*2*).

We feel that the main point which has been criticized by Toolenaar and Ponec is the interpretation of the infrared spectra from CO adsorbed on supported Pt and Pt–Pb catalysts (*2*). There is a discrepancy with their infrared study of CO coadsorption with ethylene or oxygen (*3*). Applying the isotopic dilution method, proposed by Hammaker *et al.* (*4*), they claim that the decrease in ν(CO/Pt) is due almost exclusively to dilution of the interacting CO dipoles on platinum by the ethylene molecules.

Experiments performed in our laboratory (*5*) with a series of hydrocarbons, however, cannot be explained by this model.

Two experimental findings (*5*) strongly support the importance of the electronic effect: (i) a linear plot of the CO band shift versus the ionization potentials of coadsorbed hydrocarbons, and (ii) both the frequency and intensity of the C–O stretching band are restored after hydrogen treatment of a sample with coadsorbed CO and hydrocarbon. In the presence of gas phase hydrogen σ-bonds are believed to be predominantly formed on the metal surface. It has further been suggested that only coadsorbed hydrocarbon species, if π-bonded to the surface, may shift the CO band to lower frequencies. Coadsorption of CO and methane, which is a precursor of σ-bonded species only, did not result in a detectable change of the CO band position (*5*). It is worth noting that the CO coverage used in these experiments was very low, only 0.17, and dipole interaction effects below $\Theta_{CO} \approx 0.25$ are considered negligible (*4*).

Carbon monoxide and ethylene coverages were not determined in the work of Stoop *et al.* (*3*). It is important to note that the ν(CO/Pt) shift in coadsorption experiments is dependent upon the magnitude of the coverage of both coadsorbates. By the coadsorption technique (*5*), we recently performed a few experiments with CO and butene-2 and the dependence of the red shift on Θ_{CO} is illustrated in Table 1. For these experiments the 5 wt% Pt/Al_2O_3 catalyst was applied which is denoted as sample B in Ref. (*2*).

It is clearly seen (Table 1) that $\Delta\nu$ cannot be explained by an effect of dilution of the interacting CO dipoles on platinum by the hydrocarbon species since the largest red shift is observed with the lowest coverage, i.e., when dipole–dipole interaction is expected to be negligible (*4*). Obviously an interaction via the metal is more significant and, we believe, is operating in this case.

Coadsorption of CO and ethylene on the bimetallic 5 wt% Pt–5 wt% Pb/Al_2O_3 sample did not result in any change of the CO band frequency (*2*). The electronic character of platinum (9 5*d*-electrons) suggests that addition of lead above a certain concentration may strongly suppress the ability of Pt to accept more electron density from a coadsorbed hydrocarbon.

Considering the nature of the interaction between platinum and lead, Toolenaar and Ponec proposed a model which is mostly consistent with the geometric effect (*1, 3*). Their suggestion is supported by the experimentally observed red shift as $\Theta_{^{12}CO}$ is decreased when different ^{12}CO–^{13}CO mixtures were adsorbed on alumina-supported platinum (*3, 4*). According to the geometric model dipole–dipole coupling is reduced

0021-9517/83 $3.00

TABLE 1

Variation of ν(CO/Pt) with CO Coverage after Coadsorption of CO and Butene-2 on 5 wt% Pt/Al_2O_3

Θ_{CO}	cm^{-1}		
	$\nu_1{}^a$	$\nu_2{}^b$	$\Delta\nu$
0.17	2058	2008	50
0.52	2078	2050	28
0.79	2080	2065	15

[a] ν_1-CO band frequency before addition of butene-2.

[b] ν_2-CO band frequency after addition of butene-2.

due to dilution of the platinum surface by lead atoms. Electronic interaction between platinum and lead does occur; however, it is of secondary importance (*1*, *3*).

Recent studies from various laboratories concerning CO adsorption on platinum have clearly shown that the nature of Pt–Pb interaction in bimetallic catalysts cannot only be explained on the basis of the geometric effect. On the contrary, the electronic ligand effect seems to be much more pronounced. Thus Russell *et al.* (*6*) measured the infrared spectrum of CO on a platinum electrode in acidic solutions. They applied the technique of polarization-modulated infrared reflection absorption spectroscopy and definitely established a dependence of the CO band frequency on electrode potential. A theoretical study of CO chemisorption on a platinum electrode (*7*) suggests that the increase in the C–O force constant with increasing anodic potential is connected with weakening the back-donation to the π^* level of CO. These authors also predicted an increase of the C–O stretching frequency on going from low to high CO coverage. On the basis of these results one may confidently suggest that the role of dipole–dipole coupling should be considerably limited and cannot be regarded as a main reason for the observed frequency shift. Hence, the large frequency shift of the C–O stretching vibration from CO adsorbed on Pt after Pb addition is hardly to be explained by simple dilution of platinum atoms with lead.

A very good example concerning the nature of interaction between CO molecules and platinum atoms is given in the review of Basset and Ugo (*8*). Calabrese *et al.* (*9*) prepared a family of anionic clusters with the general formula: $[Pt_3(\mu_2-CO)_3(CO)_3]_n^{2-}$, where n is equal to 2, 3, 4, 5. The frequencies of the linear and bridged CO were found to increase with n (from about 2000 to about 2060 cm^{-1} for the linear form). This was explained by a change of the donor properties of the platinum cage due to delocalization of the negative charge over the entire platinum cluster system (*8*). Dipole–dipole interaction is not operating in this case.

The geometric factor is not neglected in our study. The absence of the low frequency band from CO adsorbed on Pt–Pb catalysts is regarded as evidence for the operation of both the ensemble and ligand effects (Ref. (*2*), p. 7). The effect of Pt dispersion on the position of the CO band has been established by Solomennikov *et al.* (Ref. (*6*) in our paper (*2*)). A similar dependence has also been observed in our study. Platinum dispersion of the 0.5 wt% Pt/Al_2O_3 sample, according to hydrogen adsorption, is about 5 times higher than that of the 5 wt% Pt/Al_2O_3 sample (Ref. (*2*), Table 1). The CO band maxima of the two samples differ by only 12 cm^{-1}. Addition of lead to the 5 wt% Pt/Al_2O_3 sample results in a large 50–60 cm^{-1} red shift (Ref. (*2*), Table 2). This shift can reasonably be explained by an electronic interaction between platinum and lead.

Infrared data from various laboratories on Ni–Cu, Pd–Ag, Pd–Au, and Pt–Pb systems have been interpreted by means of a dilution model (*1*). The strong suppression of the destructive reactions with all these systems is also ascribed to the dilution effect, i.e., destructive reactions require big ensembles which are eliminated due to dilution. However, conclusions about the bimetallic systems mentioned above are not unequivocal, i.e., electronic effects are not excluded (Ref. (*1*) and references cited therein). An alternative model favoring electronic ligand effects has also been proposed (*10*). According to this model the surface active metal is sensitive to the chemical nature of its near neighbors. This is especially important for destructive reactions since large differences in the electronic character of the active metal and its near neighbors would lead to substantial changes in catalytic activity.

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Received March 15, 1983