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LETTER TO THE EDITOR

On the Participation of NCO Surface Species in the NO + CO Reaction

In the elucidation of the reaction mechanism of a catalytic process it is important to establish the reaction intermediates and their possible role in the reaction. In most cases, however, this is not an easy task, as a real reaction intermediate exists only transitorily and in a very low concentration on the catalyst.

Recently Verykios *et al.* (1, 2) carried out detailed kinetic measurements on the NO + CO reaction over Rh catalysts. They paid great attention to the role of NCO (2), the formation and reactivity of which was followed by transient MS and FTIR techniques. In the FTIR spectra the most intensive absorption band was registered at 2210 cm^{-1} and was attributed to the vibration of Rh-NCO. They assumed that this surface species reacted with NO to yield N_2O, thus providing an alternative route for the production of N_2O. The stability of the NCO species giving the 2210 cm^{-1} band was greatly enhanced when TiO_2 has been doped with W^{6+}: and it cannot be removed from the catalyst surface even after 30 min on stream at 523°C (2). As the stability of Rh-NCO was much less using pure TiO_2, it was concluded that W^{6+} doping of TiO_2 stabilizes Rh-NCO complex (2).

Unfortunately, the authors neglect several important findings on the NCO chemistry which led them to the wrong conclusions.

Unland (3, 4) was the first to discover the formation of isocyanate (NCO) surface complex in the NO + CO reaction on supported Pt metals by means of infrared spectroscopy. He assumed that NCO is a real intermediate of the reaction, and the undesired formation of NH_3 may also occur through the formation and reaction of this isocyanate species. In subsequent work many details have been disclosed on the chemistry of this surface compound (5–15). An important finding was that the NCO giving intensive absorption bands is bonded not to the metal but rather to the support. The quantitative determination of the surface concentration of NCO complex formed after 2–3 h of reaction showed that the number of NCO is more than an order of magnitude higher than that of the surface Pt atoms (6). As the NCO species is not produced by NO + CO reaction on the metal free-support, it was suggested that it forms on the metal, but after its formation it spills over onto the support, when it is stabilized and accumulated. This spillover process was fairly demonstrated by a model experiment performed at low temperature (13).

Furthermore, it was found that the position of the asymmetric stretch of the NCO species produced by the NO + CO reaction sensitively depends on the nature of the support, and not at all on the metals (7–10). This is illustrated by the selected data of previous works presented in Table 1, which shows that the NCO band for titania-supported metals is located at 2210 cm^{-1}. The differences in the location of the NCO band were explained by the assumption that the NCO is bonded to the support. This conclusion was further strengthened by the adsorption of HNCO on the oxides, which resulted in identical absorption bands, as observed following the NO + CO reaction on supported metals (Table 1) (8). Another important finding was that the stability of the NCO complex is primarily determined by the support: it was very stable on silica-, and much less stable on titania-containing catalyst (10).

Further studies performed at low temperature and/or on Rh(111) single crystal surfaces revealed that the position of the asymmetric stretch of NCO bonded to the Rh and to other Pt metals is at 2170–2190 cm^{-1} (11, 16–19). The lifetime of NCO on Rh is very limited: in the absence of a support it decomposes completely to N_2 and CO around room temperature (11, 16–20). Coadsorbed O atoms, however, extend the stability region of Rh-NCO, maximum by 60–70 K (19, 21).

All these findings suggest that Verykios *et al.* (2) studied the reaction of NCO located on the titania support, and not that bonded to the Rh.

As the pretreatment of the titania was different in the work of Verykios *et al.* (1, 2), compared to the cited papers (8, 10), and because they used TiO_2 doped with W^{6+}, for the sake of certainty we prepared catalysts exactly in the same manner and followed the FTIR spectra of the sample after adsorption of HNCO starting at 200 K. Adsorption of HNCO on pure TiO_2 at 200 K produced absorption bands at 2274 and 2215 cm^{-1}. Evacuation of the cell removed the intense band at 2274 cm^{-1}, but altered only slightly the intensity of the 2215 cm^{-1} feature. Allowing the sample to warm up, a decay in its intensity started only above 300 K, and the band disappeared around 573 K. When similar experiments were carried out with Rh/TiO_2, a new spectral feature was identified at 2180 cm^{-1}, which was detectable up to 373–423 K. Qualitatively similar results were obtained when the titania sample was previously doped with W^{6+} ion.

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TABLE 1

The Position of the Asymmetric Stretching Frequency of the NCO Band Formed in the NO + CO Reaction and after HNCO Adsorption on Oxides (10)

	Pt (1 wt%)	Pd (1 wt%)	Rh (1 wt%)	Ru (1 wt%)	Ir (1 wt%)	HNCO adsorption
TiO_2 (Degussa P25)	2210	2215	2210	2210	2210	2212
TiO_2[a] (sintered at 900°C)	—	—	—	—	—	2215
$TiO_2 + 0.5\%\ WO_3$[a] (sintered at 900°C)	—	—	—	—	—	2218
MgO (DAB 6)	2228–2241	2235	2235	2230	2230	2223
Al_2O_3 (Degussa P110 Cl)	2272	2264	2272	2265	2270	2272
SiO_2 (Cab-O-Sil)	2318	2317	2315	2315	2310	2313

[a] These data were obtained in the present study.

In harmony with the observations of Verykios *et al.* (2), the stability of NCO on TiO_2 doped with W^{6+} exceeded that of NCO on undoped titania, but the doping of titania hardly influenced the stability of Rh-NCO species characterized by absorption band at 2170–2180 cm^{-1}.

These results confirm the above conclusions that the data obtained by Verykios *et al.* refer to the reaction of NCO residing on the titania support and have nothing to do with Rh-NCO species. All these considerations, however, do not exclude the possibility that the NCO species transitorily formed on Rh (which is somewhat stabilized by coadsorbed oxygen (19, 21)) is involved in the NO–CO catalytic reaction. The low concentration and short lifetime of NCO on Rh and on the other Pt metals have prevented so far the establishment of its participation in this process.

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