LETTER TO THE EDITOR

Reply to Solymosi and Bánsági, "On the Participation of NCO Surface Species in the NO + CO Reaction"

In our recent work (1–3), a detailed investigation of the NO + CO reaction over Rh catalysts supported on TiO_2 and $TiO_2(W^{6+})$ carriers, employing transient-MS and FTIR techniques, was reported. The aim of this work was to examine *in situ* the number, nature, thermal stability, and reactivity of the surface species formed on the catalyst surface under reaction conditions and to correlate their behavior with the concentration of reactants and products in the gas phase. Depending on the experimental conditions employed, more than 20 surface species have been observed on the catalyst surface, adsorbed on the metal or on the support (1–3). It was concluded that the formation of N_2 is related to the dissociation of negatively charged $[Rh-NO^-]$ species while the formation of N_2O is related to the presence of a dinitrosyl $[Rh(NO)_2]$ complex on the catalytic surface (1, 2). The presence of reduced Rh^0 sites was found to be necessary for the production of both reduction products.

Of special interest was the observation of an IR peak located at 2000–2010 cm^{-1} (2, 3), which, based on bibliorgaphic data ((4) and references therein), was attributed to isocyanate species adsorbed on the metal [Rh-NCO]. The nature and reactivity of this species was investigated in more detail using Rh catalysts supported on W^{6+}-doped TiO_2, where isocyanates were found to be more stable compared to the undoped samples (3). It was found that surface isocyanates may react with NO to yield N_2O in the gas-phase, thus providing an alternative route for the production of nitrous oxide.

Solymosi and Bánsági (5) criticized the interpretation of the 2000–2010-cm^{-1} band observed in our work, suggesting that it is due to isocyanate species adsorbed on the support and not on the Rh metal. It should be noted that the authors performed experiments using catalysts prepared exactly in the same manner as in our case and the results obtained following adsorption and thermal decomposition of HNCO (5) are in harmony with our findings that the stability of NCO produced under NO + CO reaction conditions is increased over $Rh/TiO_2(W^{6+})$ catalyst, compared with the undoped catalyst (2, 3). However, Solymosi and Bánsági (5) suggested that our data refer to the reaction of NCO residing on the support and have nothing to do with Rh-NCO species, since, according to their findings, the low concentration and short lifetime of NCO on Rh and other

Pt-group metals prevent the establishment of their participation in this process.

In order to resolve this issue, a set of FTIR experiments has been conducted, in which the formation of isocyanate species has been examined *in situ* under NO + CO reaction conditions over a $0.5\%Rh/TiO_2(W^{6+})$ catalyst. The equipment and methodology used have been described in detail elsewhere (1–3). Typical results obtained at 300°C are presented in Fig. 1, where the development of FTIR bands following exposure of the reduced catalyst to a 0.25% NO–0.50% CO (in He) mixture are shown as a function of time-on-stream (traces a–h). It is observed that immediately upon exposure of the catalyst surface to the reaction mixture, a band located at 2165 cm^{-1} appears in the spectrum (trace b). In accordance with previous results obtained from Rh/Al_2O_3 (6) and Rh/SiO_2 (4) catalysts (NO + CO reaction) and from Rh(111) single crystals (HNCO adsorption and thermal decomposition) (7), this band is attributed to the asymmetric stretch of isocyanate species adsorbed on the metal (Rh-NCO). After one minute-on-stream, the Rh-NCO band increases in intensity and shifts to 2178 cm^{-1} (trace c). This is accompanied by the appearance of an additional band, located at ca. 2215–2235 cm^{-1}, which appears as a high temperature shoulder of the Rh-NCO band (2178 cm^{-1}). The location and order of appearance of this band indicate that it is due to NCO species which, after formation on the metal, spill-over onto the TiO_2 support (5, 8). Increasing time of exposure results in an increase of the intensity of both bands, accompanied by a progressive shift of the Rh-NCO band maximum toward higher frequencies (traces d–h). After ca. 20 minutes-on-stream both bands reach a steady-state and do not further change with time. It should be pointed out that under these conditions the above bands merge to a broad feature with its maximum located at ca. 2200–2210 cm^{-1} (traces g–h), in accordance with results reported in our previous work (2, 3).

Isothermal switching of the feed to He resulted in a rapid decrease of the intensities of the bands at 2215 and 2190 cm^{-1}, which disappeared from the spectrum in less than 5 minutes-on-stream (traces i–l). This is accompanied by the appearance of a band at 2035–2020 cm^{-1} (Rh^0-CO) which indicates that NCO species decompose toward adsorbed nitride and carbon monoxide species, in accordance

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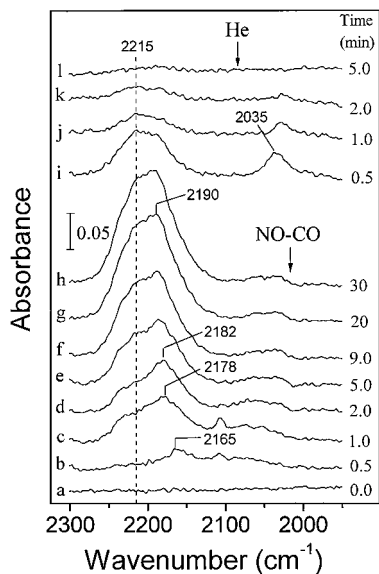**FIG. 1.** *In situ* FTIR spectra obtained as a function of time-on-stream following interaction of 0.25%NO-0.5%CO (balance He) with reduced Rh/TiO$_2$(W^{6+}) (traces a–h) and subsequent isothermal treatment with He flow (traces i–l). $T = 300°C$; total flow: 35 cc/min.

with our previous study (2). It is interesting to note that the NCO species adsorbed on the metal (2190 cm^{-1}) decompose faster than those on the support (2215 cm^{-1}).

In order to further investigate the formation of Rh-NCO and (TiO$_2$)-NCO species, similar experiments have been conducted using different NO/CO ratios in the feed. In particular, the NO concentration in the feed was kept constant at 0.25%, while that of CO varied in the range of 0.12–2.00%. Results are summarized in Fig. 2, in which the FTIR spectra obtained following exposure of the catalyst to the reaction mixture at 300°C for 20 minutes are shown for seven different feed compositions. It is clearly observed that bands due to NCO species adsorbed on the metal (Rh-NCO) at ca. 2190 cm^{-1} and on the support (TiO$_2$-NCO) at 2215–2235 cm^{-1} can be clearly distinguished, under steady state conditions, for relatively low CO concentrations in the feed (traces a and b), while at higher CO contents the Rh-NCO and (TiO$_2$)-NCO bands merge into a broad band located at ca. 2210 cm^{-1}. Clearly, the relative population of these species strongly depends on the NO/CO ratio, i.e., the population of NCO associated with the support is increased in the presence of excess CO in the feed.

Similar experiments were also conducted at the reaction temperature of 250°C (not shown). Results obtained were qualitatively similar to those obtained at 300°C (Figs. 1 and 2). Again, two bands could be clearly distinguished under certain experimental conditions, attributable to isocyanates adsorbed on the metal and the support. The only difference was that, in general, formation of NCO species

at 250°C was much slower, compared to that at 300°C, in accordance with our previous work (2, 3).

Summarizing, results of the present study show that (a) relatively stable Rh-NCO species are formed over Rh/TiO$_2$(W^{6+}) catalysts under NO + CO reaction conditions. These species produce an FTIR band in the spectral range of 2165–2190 cm^{-1}, which may be clearly observed *in situ*, under selected experimental conditions; (b) isocyanate species associated with the support, responsible for the appearance of an IR band at ca. 2215–2235 cm^{-1}, are formed following the development of Rh-NCO, most probably by a spillover process. This is evidenced by the order of formation of the Rh-NCO and (TiO$_2$)-NCO bands following exposure to the reaction mixture and by the (opposite) order of their disappearance in the subsequent isothermal switch to He; (c) the relative population of NCO species adsorbed on Rh and the support strongly depends on the feed composition: increasing the CO : NO ratio results in an increase of the amount of isocyanates located on the support.

In conclusion, it was shown that the broad band observed in our previous studies at 2003–2010 cm^{-1} (2, 3) is to a large extent due to Rh-NCO, although a contribution of NCO associated with the support is also present. Therefore, the present results support our previous finding related to the reactivity of Rh-NCO with NO, which provides an alternative route for the formation of N$_2$O in the gas phase. In reply to Solymosi and Bánsági (5), we agree that NCO species are formed on the metal and spill over onto the carrier. However, our results clearly show that, at least under certain conditions, the population and lifetime of Rh-NCO species
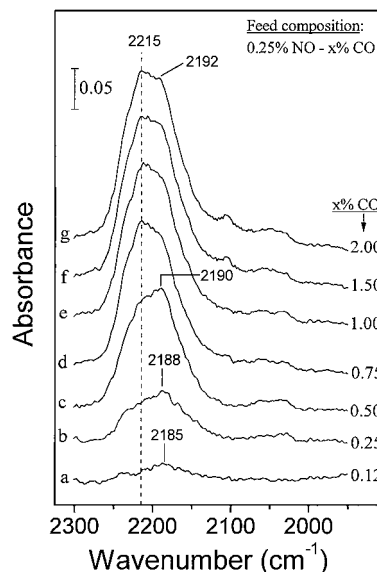

FIG. 2. *In situ* FTIR spectra obtained following interaction of 0.25%NO-x%CO (x = 0.12–2.00%) with the reduced catalyst for 20 min. T = 300°C; total flow: 35 cc/min.

become such that permits their *in situ* observation by FTIR techniques and enables the investigation of their reactivity under reaction conditions, as reported in our previous communications (2, 3).

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Dimitris I. Kondarides
Xenophon E. Verykios

Department of Chemical Engineering
University of Patras
GR-26500 Patras
Greece