

**OBSERVATION OF SURFACE ISOCYANATE FORMATION ON THE CeO₂
AND ON Rh SUPPORTED BY CeO₂****TÍMEA SÜLI-ZAKAR**

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ABSTRACT

Infrared spectroscopic studies showed the formation of isocyanate surface complex in the NO + CO reaction on supported noble metal catalysts. As this surface complex plays decisive role in the undesired side reaction of the catalytic transformation of the auto exhaust gases, great attention should be paid to its properties and to the mechanism of its formation. For this purpose the interaction of NO + CO gas mixture with supported gold, palladium and rhodium catalysts was investigated. When the adsorption and reaction of NO with CO two absorption bands appeared in the FTIR spectra of Rh/CeO₂ at 2180 and 2210 cm⁻¹, which were not observed following the adsorption of reactants and products. Adsorption of isocyanate acid on pure CeO₂ yielded the same spectral features suggesting that these bands belong to adsorbed isocyanate, NCO, species bonded to the CeO₂. These results suggest that spillover process of NCO from the Rh onto support proceeds even in the case of CeO₂ used as a solid oxidizer in the three-way catalyst. NCO attached to ceria reacts with H₂O resulting in the release of NH₃.

Keywords: Rh/CeO₂ catalyst, support, adsorption, NO + CO reaction, isocyanate formation,

INTRODUCTION

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 catalysts.

One of the most important areas of the environmental protection is decreasing air pollution. Converting the produced materials in catalyst way has great part in removing the toxic materials emitted by chemical factories and cars. A possible way of removing NO of the exhaust is a catalytic reaction with reduced gases, especially CO.

Infrared spectroscopic studies showed the formation of isocyanate surface complex in the NO + CO reaction on supported noble metal catalysts. As this surface complex plays decisive role in the undesired side reaction of the catalytic transformation of the auto exhaust gases, great attention should be paid to its properties and to the mechanism of its formation. This features seems to confirm the original assumption of Unland namely that NCO is responsible for the undesired formation of NH₃ in automobile exhaust catalysis (UNLAND, 1973). Recent studies performed on supported Rh confirmed both the formation of NCO, in the catalytic reduction of NO with CO and hydrocarbons and its migration from the Rh onto the support (KONDARIDES ET AL., 2000).

MATERIAL AND METHOD

Rh/CeO₂ catalyst was made impregnation of CeO₂ (ALFA AESAR, surface area: 50 m²/g) in the solution of RhCl₃·3H₂O. The dried suspension was pressed into self-supporting wafers using a Ta mesh oxidized in the IR cell at 573 K for 30 min and reduced at 673 K in

the presence of 100 Torr H₂ for 60 min. The gases used were of commercial purity (Linde), CO (99.97%), NO (99%). The isocyanic acid was prepared by the reaction of H₃PO₄ and KOCN (SOLYMOSI ET AL., 1979). NO and HNCO was purified by fractional distillation.

Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wave number accuracy of $\pm 4\text{ cm}^{-1}$ (Fig. 1). Typically 128 scans were collected. All of the spectra were taken without the use of a scaling factor ($f = 1.0$). Catalytic studies have been performed in a closed circulation system. In this case the reaction was followed by analyzing the composition of the gas phase with a Quadrupole mass spectrometer.

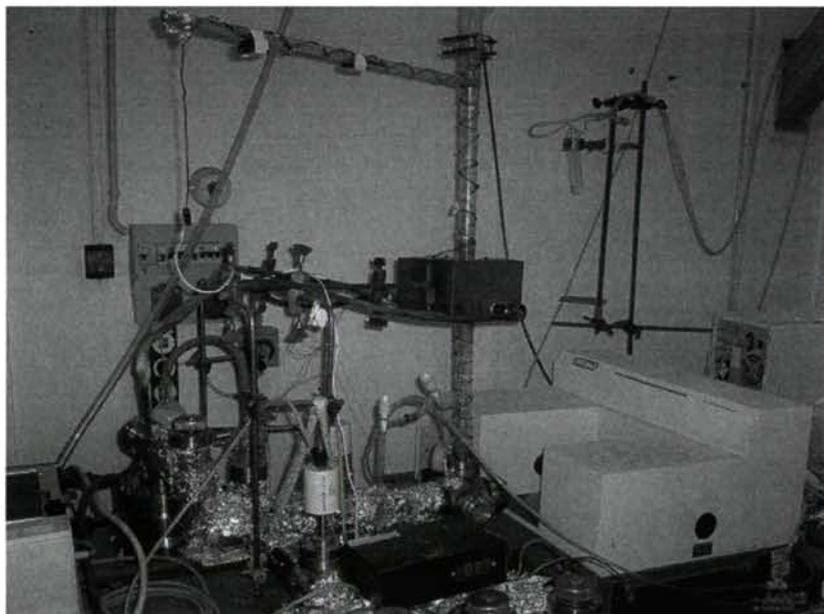


Figure 1. FTIR 155 set

RESULTS AND DISCUSSION

Co-adsorption of NO + CO (1:2) gas mixture on 5% Rh/CeO₂ at 300 K produced intensive absorption bands at 1750 and 1922 cm⁻¹ due NO, and pair of band at 2105 and 2037 cm⁻¹ corresponding to Rh⁺(CO)₂. Heating the sample to 373 K, caused only a slight shift of the position of NO and CO bands. New spectral feature peaking at 2180 cm⁻¹ was detected first at 473 K, which became larger and wider at 573 K, and attenuated only at 673 K (Fig. 2A). Deconvolution of the broad band showed that it consists of two components absorbing at 2210 and 2171 cm⁻¹. Note that these spectral features were not detected on FTIR (Fig. 1.) spectra of pure CeO₂ (T_R = 673 K) exposed to NO + CO gas mixture at 373-573 K.

Mass spectrometric analysis of the gas phase during gradual heating of the sample (6.5 K/min) in the presence of reacting gas mixture indicated that the reaction between NO and CO on 5% Rh/CeO₂ starts at ~423 K producing N₂, CO₂ and a small amount of N₂O.

The reaction was completed at 573-583 K. In the following experiments I examined the stability of the new bands produced at 573 K under continuous evacuation. I found that both bands remained practically intact up to 473 K. At higher temperature first the feature at 2210 cm⁻¹ disappeared followed by the band at 2171 cm⁻¹. As neither the adsorption of the reacting gases (NO, CO), nor that of the products (N₂O, N₂, CO₂) gave such bands, I tentatively attribute them to the vibration of isocyanate species formed in the reaction.

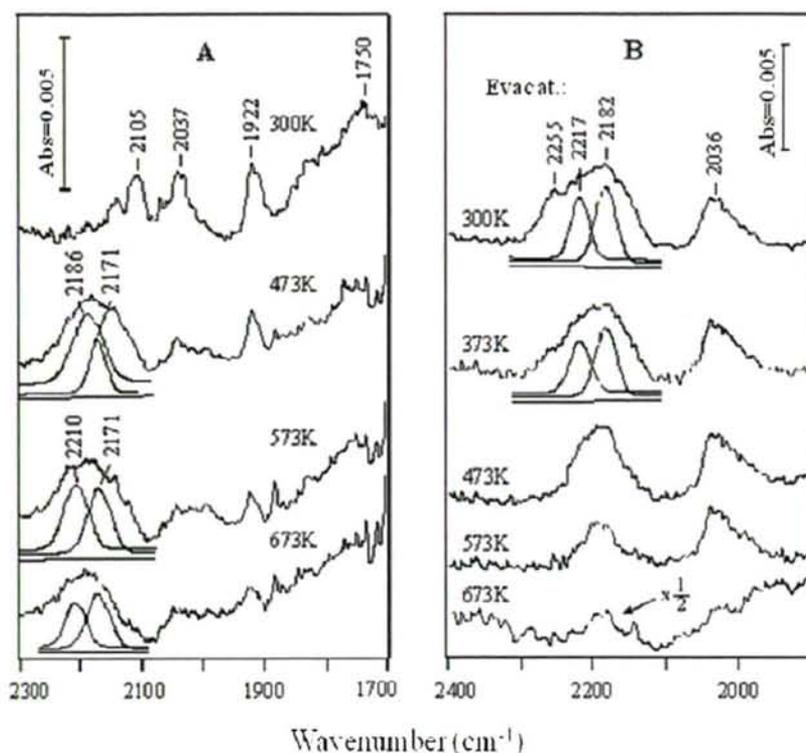


Figure 2. (A) Effect of temperature on the FTIR spectra of 5% Rh/CeO₂ in the presence of 20 Torr NO + 40 Torr CO. Sample was degassed at 300 K before registering of any spectra. (B) Effects of temperature on the FTIR spectra of adsorbed NCO produced by HNCO adsorption on 5% Rh/CeO₂. The sample was kept for 15 min at the given temperature.

In order to ascertain further the nature of absorption bands formed in the NO + CO reaction, I undertook the study of the adsorption of HNCO on samples used, which provides the easiest way to determine the position of NCO on the support and on the metals. First of the results was obtained on pure, metal-free CeO₂ ($T_R = 673$ K). Exposure of this sample to a very low pressure of HNCO at 300 K produced a weak band at 2180 cm⁻¹, the intensity of which increased with the rise of HNCO pressure and slightly shifted to higher wavenumbers (Fig. 3A). At higher HNCO pressure the band became wider clearly composed of two features at 2207-2210 and 2180-2184 cm⁻¹. Further increase of the pressure led to the appearance of absorption bands at 2254 cm⁻¹ (not shown), which belong to the molecularly isocyanic acid (HERZBERG AND REID, 1950).

Degassing the sample at 300 K eliminated these spectral features and attenuated the band at 2210 and 2184 cm⁻¹. Gradual heating of the sample under continuous degassing caused further weakening of these bands. The 2210 cm⁻¹ bands disappeared first above 473 K and then the 2184 cm⁻¹ band moving to 2176 cm⁻¹ did it at 673 K after several hours (Fig. 3B). During the heating the appearance of new bands were not experienced. Taking into account the previous results obtained on different oxides both bands at 2210 and 2180-2184 cm⁻¹ are attributed to the asymmetric stretch of NCO species attached to CeO₂. The appearance of two bands suggests the presence of two adsorption sites, perhaps Ce⁴⁺ and Ce³⁺. The stability of NCO on ceria is similar to that observed on titania and alumina (SOLYMOSI AND BÁNSÁGI, 1979).

Similar experiments were performed with 1% Rh/CeO₂ (T_R = 673 K). At very low HNCO pressure we obtained a weak band at 2182 cm⁻¹ and three others at 2103, 2053 and 2036 cm⁻¹. These latter ones clearly belong to the adsorbed CO formed in the decomposition of NCO. On 5% Rh/CeO₂ only one CO band appeared at 2036 cm⁻¹. On the increase of the HNCO pressure the 2182 cm⁻¹ band broadened and a high frequency band at ~2217 cm⁻¹ clearly developed. A spectral feature at 2255 cm⁻¹ due to molecularly bonded HNCO also appeared. This is shown in Fig. 2B. Annealing the adsorbed layer during continuous degassing caused an attenuation of the band above 373 K. The disappearance of the 2217 cm⁻¹ band occurred above ~473 K and that of the 2182 cm⁻¹ band at 673 K.

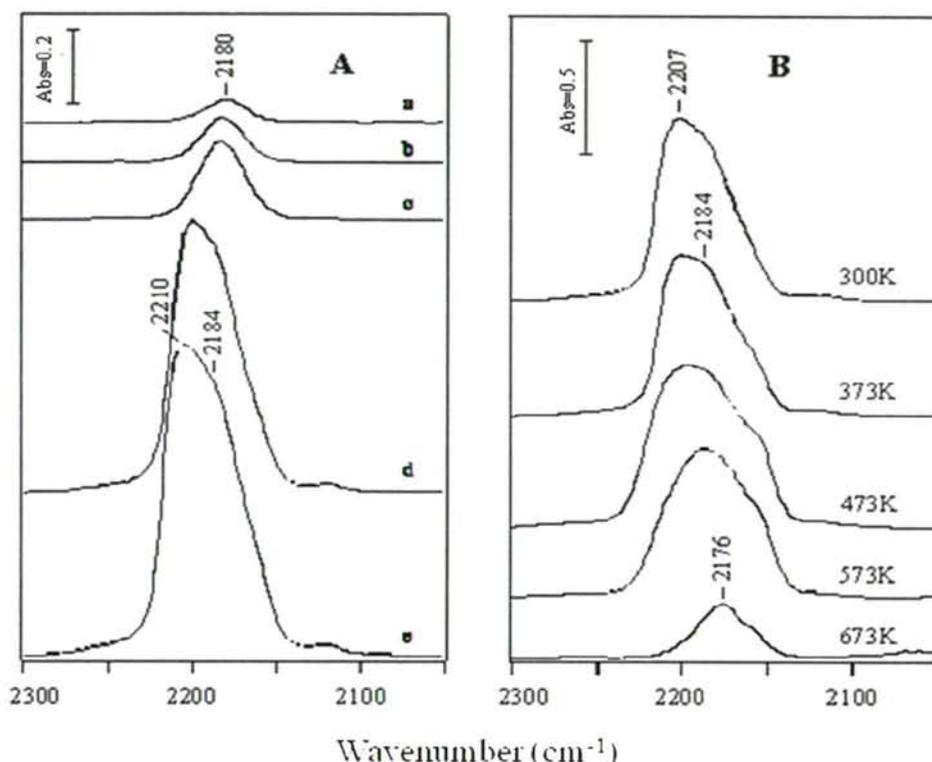


Figure 3. (A) FTIR spectra of CeO₂ (T_R = 673 K) as a function of isocyanic acid exposure at 300 K. The pressure of HNCO was (in Torr) (a) 2.8×10^{-3} , (b) 8.2×10^{-3} , (c) 1.1×10^{-2} , (d) 3.0×10^{-2} , (e) 6.0×10^{-2} . (B) Effect of degassing temperature on the stability of adsorbed NCO produced by HNCO adsorption on CeO₂. The sample was kept for 15 min at the given temperature.

Some measurements have been carried out concerning the reaction of NCO produced by HNCO adsorption over CeO₂ and Rh/CeO₂ at 300 K. Isocyanate species on ceria decomposed to N₂ and CO above 473 K. A small amount of CO₂ also evolved indicating the oxidation of NCO or CO by the reactive oxygen of CeO₂. Same products were found when Rh was deposited on CeO₂, but the evolution of gases started at somewhat lower temperature. The product distribution basically changed when H₂O was admitted in the IR cell. In this case NH₃ became the major product indicating that a fraction of NCO reacted with H₂O. The presence of Rh was advantageous for the NH₃ formation. Mass spectrometric data are presented in Figure 4.

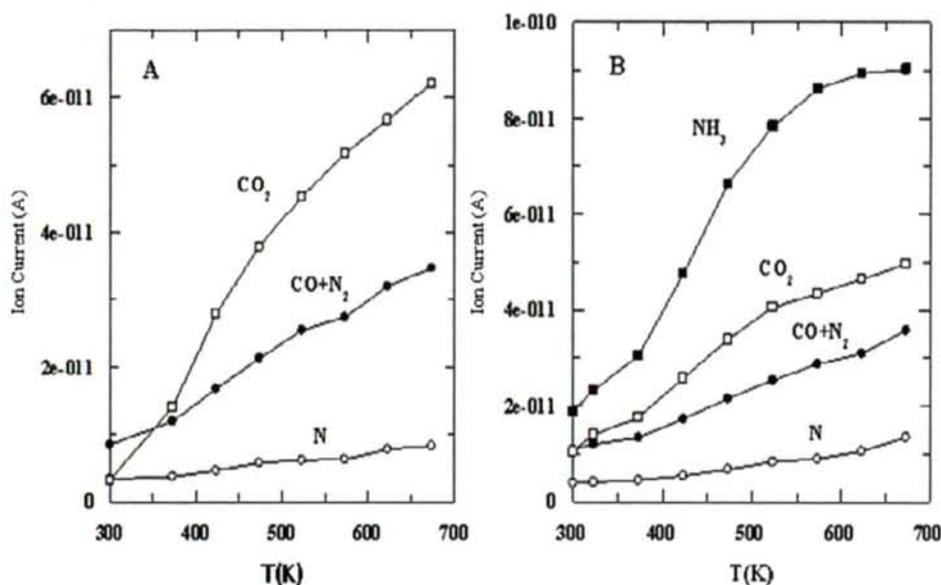


Figure 4. Effects of temperature on the reaction products of adsorbed NCO on CeO₂ in the absence of H₂O (A) and in the presence of 2.0 Torr of H₂O (B). Surface NCO was produced by HNCO adsorption at 300 K.

CONCLUSIONS

The formation of isocyanate in the NO + CO reaction and in the HNCO adsorption has been established on Rh supported by CeO₂ used as an oxidizer in the three-way catalyst. As in other cases NCO formed on the Rh spill over onto the CeO₂, where it is accumulated and stabilized.

Although NCO is residing on the CeO₂, it reacts with H₂O above 473 K yielding NH₃.

ACKNOWLEDGEMENT

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