INFRARED STUDY OF GASEOUS POLLUTANTS (NO +CO) OVER CATALYST

STUDIU CU INFRAROSII PE EFECTELE POLUANTILOR GAZOSI (NO+CO) ASUPRA CATALIZATORILOR

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Abstract: *The adsorption and reaction of NO with CO has been investigated on supported Au Catalysts. The main method was FT IR spectroscopy. Although very limited dissociation of NO was noticed on reduced Au catalyst, catalytic tests showed that all the samples used effectively catalyse the NO+CO reaction above 573 K. By means of FTIR spectroscopy several new absorption bands have been detected on the Au samples, the position of which depended on the nature of the support: it was 2305 cm^{-1} for Au/SiO_2, 2256 cm^{-1} for Au/Al_2O_3, 2212 cm^{-1} for Au/TiO_2 and 2220-2230 cm^{-1} for Au/MgO. These bands were attributed to the asymmetric stretch of NCO attached to the oxides.*

Keywords*: catalyst, support, adsorption, NO + CO reaction on Au*

INTRODUCTION

Data on the properties of the adsorbed species and/or surface intermediates playing decisive role in the catalytic reactions have been previously obtained only indirectly through the study of the kinetics of the whole reaction, or through isotope exchange investigations. Vibration spectroscopic studies in the infrared range, however, give direct proofs on the structure of adsorbed forms. The infrared spectroscopy became one of the most effective surface science methods due to its easy handling and cheapness.

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 exhausted 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. For this purpose the interaction of NO + CO gas mixture with supported gold catalysts was investigated.

MATERIAL AND METHOD

Supported Au catalysts with a gold loading of 1 and 5 wt% were prepared by a deposition-precipitation method from$HAuCl_4$·aq p.a. 49% Au, Fluka AG with NaOH. Following supports were used: SiO_2 (CAB-O-SiL, and MS Scintran BDH); Al_2O_3 (Degussa); TiO_2 (Degussa P25) and MgO (DAB). The fine powder of oxidic support was suspended and kept at 343 K for 1 hour with continuous stirring. The suspension was aged for 24h at room temperature and repeatedly washed then dried at 353 K and then calcined in air at 573 K for 4 h. The dried samples were reduced at 673 K for 60 min.

The gases used were of commercial purity (Linde), CO (99,97%), NO (99%). HNCO was prepared by the reaction of H_3PO_4 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) with a wave number accuracy ±4 cm^{-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 gas phase with a Quadrupole mass spectrometer.

RESULTS AND DISCUSSION

Before infrared spectroscopic measurements we examined the reactivity of our Au samples towards the decomposition of NO on 5% Au/oxides. We

found an easily measurable reaction above 573 K, producing mainly N_2O with a small amount of N_2.

The aim of the catalytic study is to confirm that the Au samples used in this work can catalyze the reduction of NO with CO and to establish the temperature range of the process. Reaction started above 473-523 K, as indicated by the consumption of reacting gases and the evolution of CO_2 and N_2. At 623 K the reaction occurred rapidly and was almost complete in 15 min. The most effective sample was Au/TiO_2 and the least active was Au/MgO.

Before the examination of isocyanate complex we registered the spectrums of gases separately and NO + CO together. Adsorption of NO no bands were detected above1800 cm^{-1}. The adsorption of CO on 1 % Au/TiO_2 produced one band at 2185 cm^{-1}, which was eliminated by degassing. On 5% Au/SiO_2 sample in the gas mixture a new band at 2190 cm^{-1} developed at 573 K. The band at 2303 cm^{-1} appeared with a less intensity, which slowly grew with the progress of adsorption. After evacuation at 300 K both bands remained unchanged (Fig.1.)

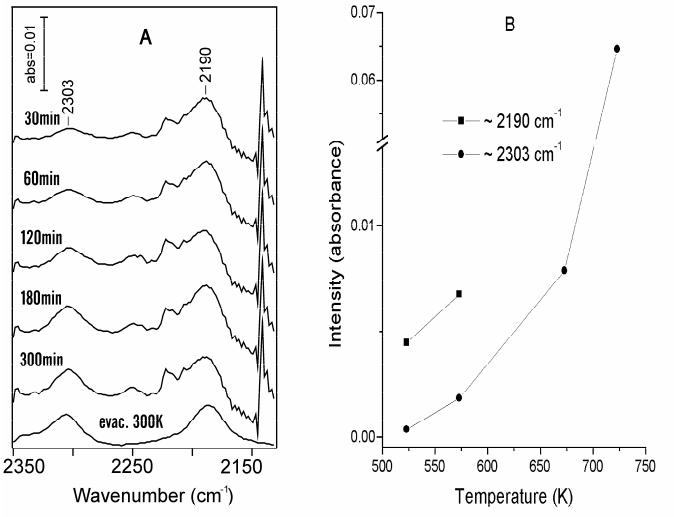


Figure 1: (A) Infrared spectra of 5% Au/SiO_2 following NO + CO adsorption at 573 K. (B) Intensities of the bands at 2190 and 2300 cm^{-1} formed following the adsorption of NO + CO on 5% Au/SiO_2 at different temperatures. The values were taken at 60 min.

Performing similar measurements on reduced 5wt% Au/Al_2O_3, we detected new absorption bands at 2234 and 2254 cm^{-1} After evacuation at 300 K both bands remained unchanged (Fig. 2A).

The time dependence of the 2254 cm^{-1} band at different temperatures is shown in Fig. 2B.

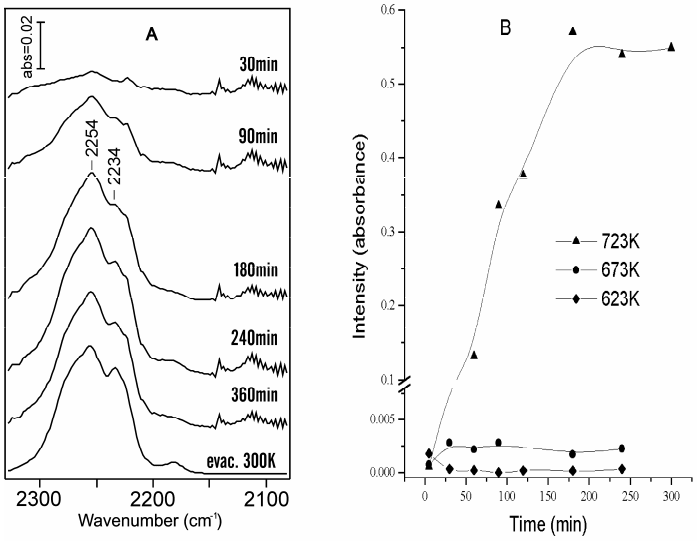


Figure 2: (A) Infrared spectra of 5% Au/Al_2O_3 following NO + CO adsorption at 673 K. (B) Intensities of the bands at 2254 cm^{-1} formed following the adsorption of NO + CO on 5% Au/Al_2O_3 at different temperatures.

On Au/TiO_2 sample two absorption bands indicating of the formation of surface complexes appeared at 2187 and 2210 cm^{-1}. The result of evacuation at 300 K their intensity decreased slightly (Fig. 3A). Two absorption bands were detected at 2208 and 2190 cm^{-1} on metal-free TiO_2 but they disappeared at higher temperatures (Fig. 3B).

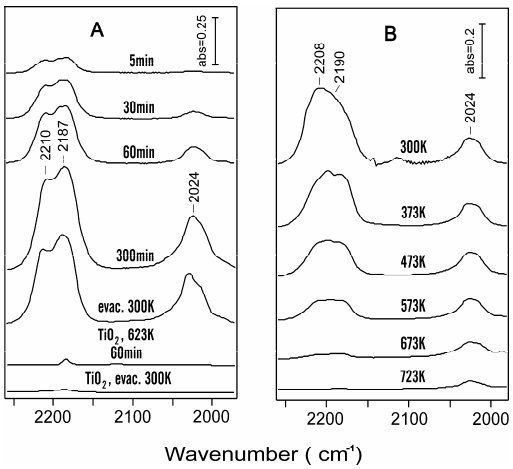


Figure 3: (A) Infrared spectra of 5% Au/TiO_2 following the NO + CO adsorption at 623 K and (B) Spectra of Au-free TiO_2, treated with NO+CO gas mixture at 623 K for 60 min and evacuated at 300 K (A).

In Figure 4 we show spectra of 5% Au/MgO following the reaction of NO+CO. Significant spectral changes were first observed at 573 K, where a new absorption band appeared at 2221 cm^{-1}.

The intensity of this band increased at higher temperatures and with the extension of the adsorption time.

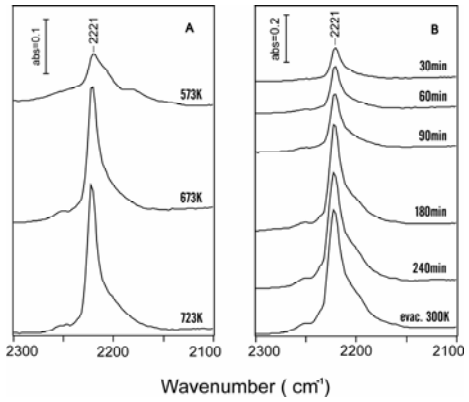


Figure 4: The effect of temperature (A) and the reaction time at 673 K (B) on infrared spectra of 5% Au/MgO following the adsorption NO + CO.

In order to help assignment of the new absorption bands observed in the NO+CO mixture the IR spectra of adsorbed HNCO have been taken on 5 % Au/SiO_2 and metal-free SiO_2 (Fig. 5.)

The adsorption of HNCO at 200 K produced a strong absorption band at 2190 cm-1. Annealing the catalyst under continuous degassing the intensity of the 2190 cm^{-1} band slightly decreased and at the same time a weak band at 2305 cm^{-1} developed. A strengthening of the 2305 cm^{-1} band occurred above 300 K with simultaneous weakening of the band at 2190 cm^{-1}. When the adsorption of HNCO was performed at 300 K the 2305 cm^{-1} band appeared with higher intensity. Heating the sample in HNCO caused a dramatic growth of the 2305 cm^{-1} band above 300 K, whereas the 2185-2190 cm^{-1} band remained practically the same in the temperature range 373-523 K. Performing similar experiments with Au-free SiO_2 we obtained an absorption band at 2305 cm^{-1}, but it was much weaker at all temperatures.

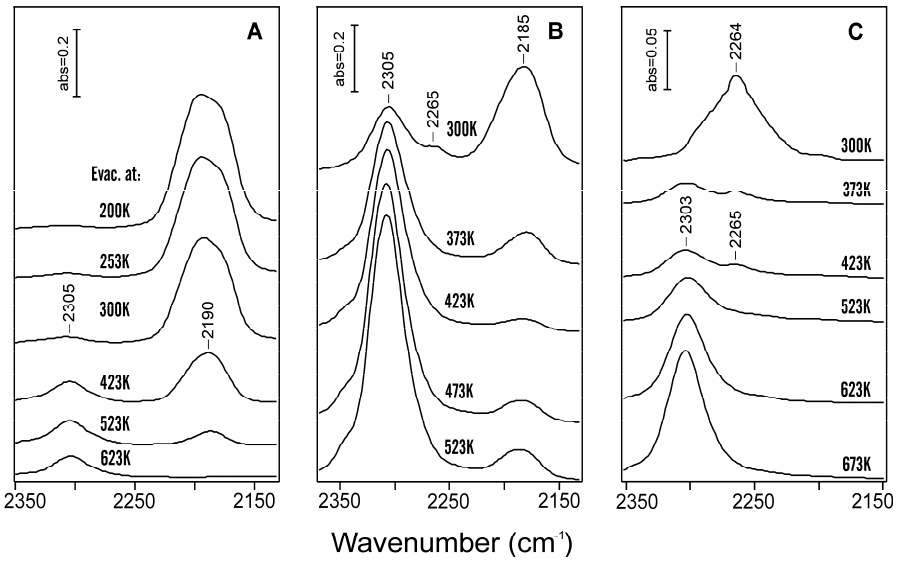


Figure 5: Infrared spectra of 5% Au/SiO_2 following the adsorption of 0.02 Torr HNCO at 200 K and after subsequent heating to higher temperatures under continuous evacuation. (A) Infrared spectra of 5% Au/SiO_2 (B) and SiO_2(C) following the adsorption of 1.0 Torr HNCO at 300 K and after subsequent heating to higher temperatures in the presence of HNCO.

CONCLUSIONS

The primary aim of this work was to examine the NO + CO interaction on supported Au catalyst and to identify the possible surface intermediates formed during the reaction. Summarizing the above results, we can conclude that the intense absorption bands appeared in the NO + CO reaction in the range of 2180-2310 cm^{-1} and remained after evacuation on the spectra. We observed this effect only in gas mixture.

The positions of new bands depended on the nature of the support. It was 2212 cm^{-1} for Au/TiO_2 2220-2230 cm^{-1} for Au/MgO 2256 cm^{-1} for Au/Al_2O_3 and 2305 cm^{-1} for Au/SiO_2. These bands were attributed to the asymmetric stretch of NCO attached to the oxides. This idea was strengthened by the results obtained following HNCO adsorption on supports alone which gave the same absorption bands.

NCO species is formed on Au crystallites, and then migrates from the Au onto the acceptor sites of support where it is accumulated and stabilized. Spectral changes following the adsorption of HNCO on Au/SiO_2 at 200-400 K provide evidences for the spillover process.

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