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An FTIR Study of the Species Adsorbed on a Rh/Al_2O_3 Catalyst in the Selective Reduction of NO by Propylene

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An *in situ* FTIR study of the reduction of NO by propylene in O_2 has shown that the reaction on the Rh/Al_2O_3 surface at 623 K leads to the formation of IR bands assigned to adsorbed hydrocarbons, -NCO, -CN, -NO^+, -CO_3^{2-} and CO_2 species. The intensity of the bands depends on the reaction time and the presence or absence of the individual reactants.

The catalytic reduction of NO_x with hydrocarbons in the presence of oxygen is widely studied because of the possible application of this process in the NO_x removal from automobile emissions. Until recently, most studies have focused on the development of catalysts in order to improve the activity for NO_x conversion and selectivity to di-nitrogen molecule.1) The objective of this study was to obtain information concerning the species adsorbed on Rh/Al_2O_3 during the reduction of nitric oxide by propylene, in the presence of oxygen, in order to identify chemisorbed species which could act as catalytic intermediates.

A 1 wt% Rh/Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 (Sumitomo Chemical, KHS-24) with an aqueous solution of $RhCl_3 \cdot 3H_2O$, followed by evaporation to dryness in a rotary evaporator at 323 K. The resulting paste was dried at 373 K for 10 h, calcined in air overnight at 773 K and finally reduced in flowing 50% H_2 in He at 673 K for 2 h. The dispersion of rhodium on alumina was ~ 52% as determined by CO adsorption.

Diffuse reflectance IR spectra were recorded at 623 K on a JASCO FTIR-7300 spectrometer equipped with an MCT (HgCdTe) detector and an IR stainless-steel cell (JASCO DR-800/H) designed to treat the samples *in situ*. The cell was fitted with a furnace, cooling water jacket, gas inlet and outlet, and with a KBr window at the top. Prior to experimentation, the catalyst (20 mg, 75-90 μm) was pretreated in 20% O_2 in He at 873 K for 1 h. The feed was prepared by mixing all reactants before dosing to the catalyst and consisted of 1000 ppm NO, 1000 ppm C_3H_6, and 5% O_2 with He as the balance gas, at a total flow rate of 200 cm^3 min^{-1}. With this setup the time needed to exchange the reactant composition was about 30s. Absorbance spectra from 50-100 scans, at a 4 cm^{-1} resolution, taken over 1-2 min were averaged for one spectrum. The reported absorbances were obtained from spectra referenced to the background spectra which were taken under helium flow prior to the introduction of the reactants to the catalyst.

After the introduction of oxygen and propylene to the catalyst, intense bands at 1465 and 1583 cm^{-1} ascribed to carbonate species on the catalyst were detected, as shown in Fig. 1b. Also weak bands at 2010 and 2083 cm^{-1} were observed and were assigned to the stretching vibrations of adsorbed carbon monoxide on Rh, $Rh(CO)_2$ and Rh(CO), respectively.2) The weak band at 2347 cm^{-1} is attributed to adsorbed carbon dioxide. The bands at 2939 and 2986 cm^{-1} may be assigned to asymmetric C-H stretching vibrations in CH_2 and CH_3 groups of hydrocarbon fragments adsorbed on the catalyst.2,3) The nature of the shoulder at ~1725 cm^{-1} is still unclear.

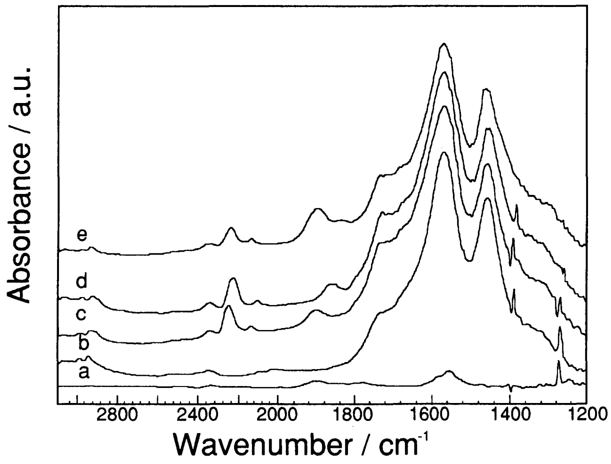

Fig.1. FTIR spectra of the surface Rh/Al_2O_3 species arising from NO reduction by C_3H_6 in O_2 at 623 K: (a) NO, 30 min; (b) O_2+C_3H_6, 60 min; (c) O_2+C_3H_6+^{14}NO, 100 min; (d) O_2+C_3H_6+^{15}NO, 100 min; (e) O_2+C_3H_6 cut, 100 min.

After the addition of NO to the feed stream the bands at 2010 and 2083 cm^{-1} due to adsorbed CO disappeared completely, probably as a result of competitive NO adsorption on the same sites and/or its oxidation to CO_2. In addition, new bands at 1894, 2123 and 2230 cm^{-1} were observed (see Fig.1c). The bands at 1894 cm^{-1} and 2123 cm^{-1} are attributed to positively charged nitrosyl species, Rh(NO$^+$), and cyanide species, Rh(CN), respectively.[2,4] The band at 2230 cm^{-1} is assigned to an asymetric stretching vibration of a surface isocynate which is probably bound to alumina.[5-7] Also, the bands at 2347 and 2358 cm^{-1} due to CO_2 became somewhat intense. Only slight changes were noted in the intensities of the bands in the low-frequency region below 1800 cm^{-1}.

To verify the assignments of nitrogen containing species, the flow of ^{14}NO was replaced by ^{15}NO. Figure 1d shows the spectrum obtained when ^{14}NO was replaced by ^{15}NO. For the band observed at 1894cm^{-1} with ^{14}NO, a frequency shift of 37 cm^{-1} to 1857 cm^{-1} was observed with ^{15}NO, whereas for bands at 2123 and 2230 cm^{-1} frequency shifts of 31 and 13 cm^{-1} to 2092 and 2217 cm^{-1} were noted, respectively. This observation confirms that these three surface species contain a nitrogen atom. No shift was observed with other bands in the spectra shown in Fig. 1. Figure 1a shows the spectrum obtained, in a separate study, by flowing only NO in helium on a fresh catalyst. Strong bands at 1556, 1900 cm^{-1} and a weak band at 1778 cm^{-1} were observed and were assigned to adsorbed NO_2, Rh(NO$^+$) and to neutral Rh(NO), respectively. Unfortunately, the bands at 1556 and 1778 cm^{-1} could not be followed in normal experiments because they appear in the region where the spectrum is crowded with strong, broad bands from the carbonate species (1200-1800 cm^{-1}).

Figure 2 illustrates the variations of the IR band intensities of nitrogen containing species adsorbed on Rh/Al_2O_3 as a function of reaction time. In addition to hydrocarbons, CO_2 and -CO_3^{2-}, only -NCO was detected as a nitrogen containing compound on pure γ-Al_2O_3. The intensity of the -NCO band on γ-Al_2O_3 was about one tenth of that noted over Rh/Al_2O_3. As shown in Fig. 2a, after the introduction of NO to the feed stream, the intensity of nitrogen containing species increased steeply with time, and leveled off after ~50 min in the case of nitrosyl and cyanide species while the isocynate band continued to grow slowly. Cutting NO from the feed stream (only $O_2+C_3H_6/He$ flow) resulted in a sharp decline in the intensity for the -NCO and -NO^+ bands, a slow decrease for the -CN band and the appearance and progressive growth of the CO bands at 2010 and 2083 cm^{-1}. After the reintroduction of NO to the feed, the intensities of -NCO, -CN, and -NO^+ bands immediately returned nearly to their previous values with a corresponding fast disappearance of the CO bands. Removing all the reactants from the feed (He flow alone) led to a less rapid decrease in the -NCO and -NO^+ bands than when NO was cut off, and to a slow decrease of the -CN band.

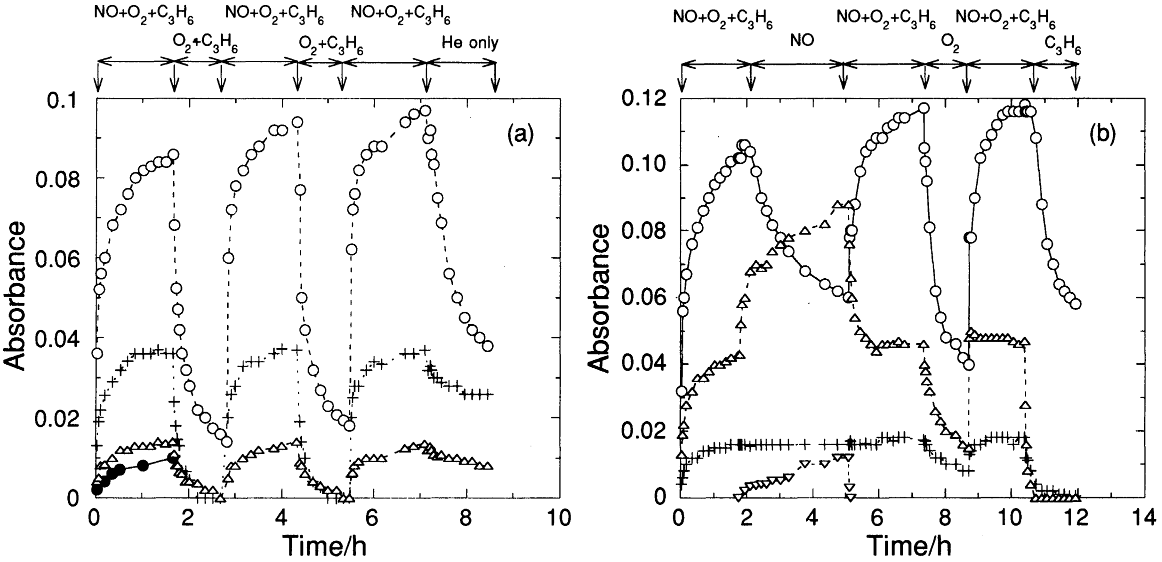

Fig. 2. Variation of IR band intensities of species adsorbed on Rh/Al_2O_3 at 623 K as a function of reaction time: (○) Rh/Al_2O_3-NCO (2230 cm^{-1}); (●) pure Al_2O_3-NCO (2233 cm^{-1}); (△) -NO^+ (1894 cm^{-1}); (+) -CN (2123 cm^{-1}); (▽) -NO (1829 cm^{-1}).

The effects of removing other reactants from the reaction stream on the intensities of bands are shown in Fig. 2b. Cutting off $O_2+C_3H_6$ (NO/He flow) resulted in a sharp increase in the intensity of the -NO^+ band, a progressive decline of the -NCO band and the appearance of a new band at 1829 cm^{-1} attributed possibly to neutral Rh(NO) (see Fig. 1e). The intensity of the -CN band remained constant. Readmission of $O_2+C_3H_6$ led to the drastic decline of the intensity of -NO^+ and eventually reached the level of that prior to removing $O_2+C_3H_6$. Also, the -NCO band increased rapidly, whereas the Rh(NO) band at 1829 cm^{-1} vanished. On the other hand, removing $NO+C_3H_6$ (O_2/He flow) led to a drastic decline of the -NCO band and a slow decrease of the -NO^+ and -CN bands. Turning off $NO+O_2$ (C_3H_6/He) led to a sharp decline of the -NCO, -NO^+, and -CN bands and the simultaneous appearance of bands due to CO at ~2010 and 2083 cm^{-1}. From the comparison of the intensities under O_2 and C_3H_6 in He (Fig. 2b), it is also noticeable that the decline of -NO^+ and -CN is more drastic in a C_3H_6 than in an O_2 atmosphere, while the opposite is true in the case of -NCO species. It is also worth noting that the intensity of the $-NO^+$ band decreases sharply in the presence of C_3H_6 indicating the existence of an interaction between these two species.

Results in Fig. 2 clearly indicate that isocyanate species are one of the intermediates in the selective reduction of NO. It is tentatively suggested that the observed consumption of -NCO in the NO and O_2 atmospheres proceeds through the interactions between adsorbed -NCO with gaseous and/or surface oxygen and NO as follows:

$$\text{-NCO} + O_2 \rightarrow NO + CO_2 \quad (1)$$
$$\rightarrow NO_2 + CO \quad (2)$$

$$2\text{-NCO} + O_2 \rightarrow N_2 + 2CO_2 \quad (3)$$

$$\text{-NCO} + [O] \rightarrow NO + CO \quad (4)$$

$$\text{-NCO} + NO \rightarrow N_2 + CO_2 \quad (5)$$
$$\rightarrow N_2O + CO \quad (6)$$
$$\rightarrow N_2 + CO + [O] \quad (7)$$

$$2\text{-NCO} \rightarrow N_2 + 2CO \quad (8)$$

There may be several probable paths for the consumption of -NCO and CN under the C_3H_6 atmosphere. Much additional knowledge of these species on the catalyst surface is required before a reliable prediction of the reaction scheme can be made.

This series of experiments has shown that flowing oxygen, nitric oxide and propylene on a Rh/Al_2O_3 surface, at 623 K, gives adsorbed hydrocarbons, $-NO^+$, -NCO, -CN, $-CO_3^{2-}$, CO_2 and possibly NO_2 species. The observed rapid responses in the intensities of $-NO^+$ and -NCO species with changing reactant composition indicate that these species are directly involved in the NO reduction scheme as precursors and reaction intermediates, respectively. The comparison of the time-dependence of the intensity of -NCO species in different gas compositions shows that further reactions of -NCO are more pronounced in the oxygen atmosphere.

References

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