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Catalytic Reduction of NO by CO over Rhodium Catalysts

3. The Role of Surface Isocyanate Species

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The formation, stability and reactivity of surface isocyanate species with CO, NO, and O_2 has been examined over $Rh/TiO_2(W^{6+})$ catalysts, under conditions of NO reduction by CO, using FTIR and transient MS techniques. It has been found that W^{6+} doping of TiO_2 results in stabilization of the Rh–NCO species and in expansion of the temperature window of N_2O formation toward lower temperatures by ca. 50°C. Surface isocyanates react with NO to yield gas-phase N_2O, thus providing an alternative route for the production of nitrous oxide. © 2000 Academic Press

Key Words: **reduction of NO; rhodium catalyst; surface isocyantes;** ***in situ*** **FTIR; transient reactivity.**

1. INTRODUCTION

Catalytic reduction of NO by CO or hydrocarbons has been the subject of intense investigation in recent years due to the importance of these reactions for automotive emission control [(1) and reference therein]. The reaction mechanism has been investigated in many laboratories, over different catalysts. However, open questions still exist regarding the nature and role of surface intermediates and, especially, of adsorbed isocyanates. The latter species have been observed in several FTIR studies dealing with reduction of NO by CO (2–7) and have been mostly regarded as spectator species, not directly involved in the formation of the reaction products. On the other hand, studies on the reduction of NO_x by hydrocarbons and ethanol showed that there is a correlation between the formation of $NCO_{(a)}$ and catalytic activity (8–10).

In our recent studies (11, 12), the adsorption and displacement characteristics of NO and CO have been examined over Rh catalysts supported on undoped and W^{6+}-doped TiO_2. It has been found that four kinds of nitrogen oxide species may coexist in the adsorbed mode, namely Rh–NO^-(high), Rh–NO^-(low), $Rh(NO)_2$, and Rh–NO^+. It was proposed that production of N_2 and N_2O in the gas phase involves the negatively charged and dinitrosyl species, respectively, while the positively charged species are inactive. The formation and reactivity of surface species present under NO–CO reaction conditions as well as the effect of oxygen on their nature and population was also examined over Rh/TiO_2 catalysts. It was found that formation of isocyanate species is favored on the catalyst surface under conditions where NO conversion to reduction products is observed. However, no straightforward evidence on the exact role of isocyanates was obtained due to their low thermal stability, which did not enable detailed examination.

In the present study, the formation, stability, and reactivity of isocyanates are examined over an Rh catalyst dispersed on W^{6+}-doped TiO_2, employing transient MS and FTIR techniques. The present catalyst seems to stabilize surface isocyanates, thus enabling the examination and elucidation of their role in the chemistry of NO reduction by CO.

2. EXPERIMENTAL

The W^{6+}-doped TiO_2 carrier, containing 0.45 at.% of the dopant cation, was prepared with the solid-state diffusion technique. The 0.5 wt% $Rh/TiO_2(W^{6+})$ catalyst was prepared by the incipient wetness impregnation method using $RhCl_3 \cdot 3H_2O$ (Alfa) as metal precursor. The catalytic performance of the NO–CO reaction was examined in the temperature range of 100 to 500°C. Experiments were performed using 50 mg of catalyst and a feed composition of 0.25% NO and 0.50% CO (balance He). The total feed flow was 150 cm^3/min (W/F = 0.02 g s/cm^3).

FTIR spectra were obtained using a Nicolet 740 FTIR spectrometer equipped with a TGS detector and a KBr beam splitter. The catalyst, in finely powdered form, was placed into a holder, which enables gas flow through the sample, and its surface was carefully flattened to increase the intensity of the reflected IR beam. The transient MS

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experiments were carried out in an independent reactor by switching the feed composition to the reactor with the use of chromatographic valves equipped with electronic actuators. The concentrations of the gases used in the transient MS experiments were the same as those used in the corresponding FTIR experiments, but were diluted with He instead of Ar. In all experiments presented here, an amount of Ar was added to the feed. This was done because the Ar response curve represents the flow pattern and the residence time distribution of gaseous reactants flowing through the reactor and the transportation lines, since Ar does not interact with the catalyst. Since the principal peaks of CO and N_2 ($m/z = 28$) and CO_2 and N_2O ($m/z = 44$) cannot be separated, isotopic ^{15}NO was used in the transient MS experiments reported here.

The flow rate in all experiments reported here was 35 ml/min (ambient). It should be mentioned that all experimental conditions (gas concentrations flow rate, mass of catalyst, pretreatment conditions, etc.) were kept the same as those in the corresponding FTIR experiments and, therefore, a direct comparison between the transient FTIR and MS results can be made. Further details on the procedures and techniques employed are discussed elsewhere (11, 12).

3. RESULTS AND DISCUSSION

The catalytic performance of 0.5% Rh/TiO_2 (W^{6+}), expressed in terms of steady-state conversion of NO to reduction products and in terms of yield of N_2O, as functions of the reaction temperature, is presented in Fig. 1. For comparison, the corresponding results obtained over the undoped catalyst [from Ref. (12)] are also shown. Regarding the doped catalyst, it is observed that the conversion of NO abruptly increases with increasing reaction temperature above 200°C and reaches 100% at 270–280°C. In the temperature range of ca. 200–300°C the catalyst is highly selective toward N_2O formation; the yield of N_2O goes through a maximum in the temperature range of 250–270°C and drops to zero at temperatures above 350°C. Comparison with the results obtained from the undoped 0.5% Rh/TiO_2 catalyst shows that W^{6+} doping of TiO_2 results in lowering of the temperature at which 100% conversion of NO is observed by 40–50°C, mainly by widening the temperature window for N_2O formation toward lower temperatures.

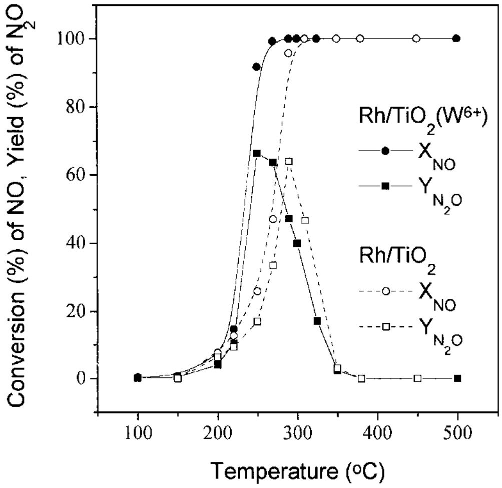

FIG. 1. Conversion (%) of NO and yield (%) of N_2O obtained over Rh catalysts supported on undoped and W^{6+}-doped TiO_2 as functions of reaction temperature. Feed composition: 0.25% NO, 0.5% CO (balance He), $W/F = 0.02$ g s/cm^3.

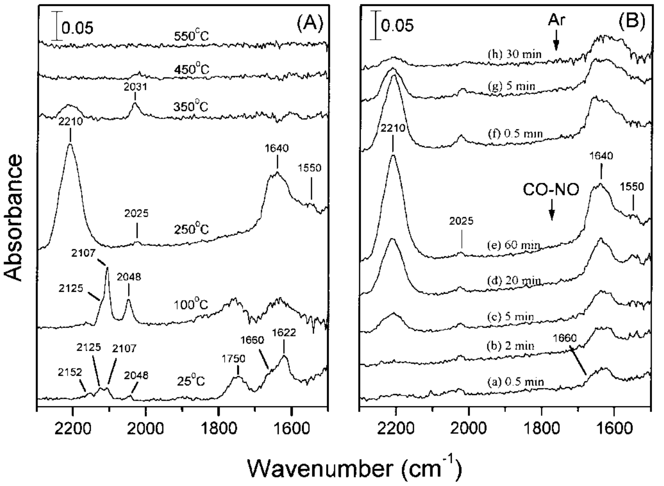

FIG. 2. (A) FTIR spectra recorded following interaction of 0.25% NO–0.5% CO (balance Ar) with reduced $Rh/TiO_2(W^{6+})$ in the temperature range of 25–550°C. (B) FTIR spectra obtained as a function of time-on-stream following interaction of the reduced catalyst with 0.25% NO–0.5% CO (in Ar) at 250°C (a–e) and subsequent isothermal treatment with Ar flow (f–h).

FTIR spectra obtained following interaction of the catalyst with the NO/CO mixture in the temperature range of 25 to 550°C are presented in Fig. 2A. It should be noted that prior to each experiment the catalyst was reduced in an H_2 flow at 300°C. Spectra were obtained after steady state was reached. It is observed that interaction of the reaction mixture with the catalyst leads to the formation of several surface species, the nature and population of which depend on the reaction temperature. The assignment of the FTIR bands has been discussed in detail elsewhere (11, 12). Briefly, these bands are attributed to isocyanates (2210 cm^{-1}), carbonyls (2150–2020 cm^{-1}), and nitrosyls (1920–1660 cm^{-1}) bonded to rhodium, and to C- and N-containing species associated with the support (bands below 1660 cm^{-1}).

As observed in Fig. 2A, at 250°C, i.e., just above the light-off temperature (compare with Fig. 1), the spectrum is dominated by an intense band at 2210 cm^{-1}, attributed to Rh–NCO, and is accompanied by a weak band, due to Rh^0–CO, located at 2025 cm^{-1}. Increasing the reaction temperature to 350°C results in a decrease of the intensity of the Rh–NCO band and in an increase of the intensity of the Rh^0–CO band. Further increase of the reaction temperature to 450 and 550°C leads to the progressive disappearance of all bands from the spectra (Fig. 2A).

Comparison of the results presented in Figs. 1 and 2A shows that there is a correlation between the population of the surface isocyanate species and the yield of N_2O in the gas phase. In particular, it is observed that both the yield of N_2O and the intensity of the Rh–NCO band at 2210 cm^{-1} increase with increasing reaction temperature, go through a maximum above the light-off temperature (ca. 250°C), and then diminish at temperatures above 350°C.

In order to elucidate the role of the isocyanate species, their formation, stability, and reactivity have been further examined at the reaction temperature of 250°C, at which the population of this species is maximized. The IR spectra obtained as a function of time-on-stream following exposure of the reduced catalyst to the NO/CO mixture at 250°C are shown in Fig. 2B. It is observed that immediately after exposure to the reaction mixture, weak bands at 1660 (sh) and 2025 cm^{-1} appear in the spectral region of interest, attributed to $Rh–NO^-$ and Rh^0–CO species, respectively (11, 12). Increasing time of exposure results in the development of additional bands in the frequency region below 1650 cm^{-1}, attributed to N- and C-containing species associated with the support. The weak band at 1660 cm^{-1} disappears in less than 2 min on stream. It is only then that the Rh–NCO band at 2210 cm^{-1} starts to develop. This behavior is in accordance with the results of Hecker and Bell (3) who found that the intensities of the bands for $Rh–NO^-$ and Rh–NCO varied inversely in response to changes of the NO and CO partial pressures and suggested that the surface coverages of these species are closely related.

The intensity of the Rh–NCO band continuously increases with time and reaches a plateau after ca. 60 min on stream. During this period, the intensity of the Rh^0–CO band at 2025 cm^{-1} does not significantly change. Isothermal switch of the flow from CO/NO to Ar (Fig. 2B, f–h) results in a slow decrease of the intensity of the Rh–NCO band, which is initially accompanied by an increase of the Rh^0–CO band, giving additional evidence that there is an interconversion between these species, as reported previously (12). The isocyanate species are very stable and cannot be removed from the catalyst surface even after 30 min on stream. This is also the case for the various species associated with the support. Comparison with the corresponding experiments obtained over the undoped catalyst (12), where isocyanates were removed from the surface after ca. 5 min on stream, shows that W^{6+} doping of TiO_2 stabilizes Rh–NCO species. It should be noted that the thermal stability of isocyanate species was also examined with the transient MS technique by isothermal switching of the feed composition from CO/NO/He to He at 250°C, under conditions identical to those reported in Fig. 2A. However, under the experimental conditions employed, the possible formation of reduction products, originating from the slow decomposition of isocyanates, was not possible.

The interaction of the reduced catalyst with the NO/CO mixture, at 250°C, was also examined with the transient MS technique, in order to investigate the transient behavior of reactants and products in the gas phase. As observed in Fig. 3A, purging with He and switching to NO/CO results in the immediate appearance of CO_2, CO, and N_2 at

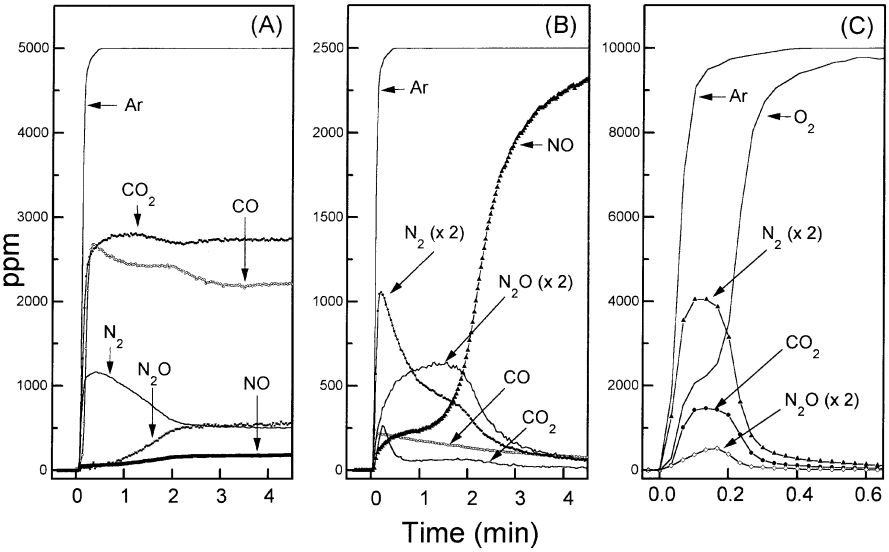

FIG. 3. Transient MS responses of reactants and products obtained at 250°C after the switch (A) He → 0.25% NO–0.5% CO (in He) over the reduced catalyst and after the switches (B) He → 0.25% NO/He and (C) He → 1% O_2/He over catalysts previously treated with 0.5% CO–0.25% NO mixtures at 250°C.

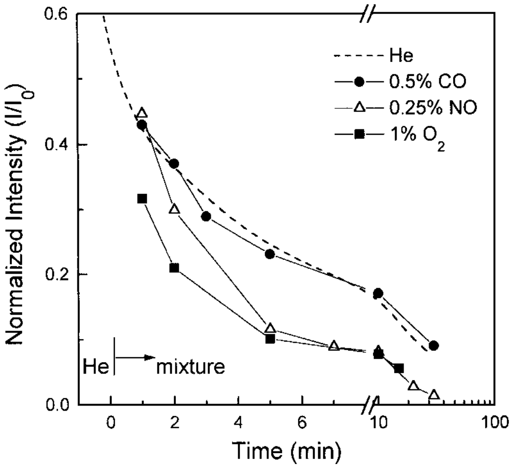

FIG. 4. Variation of the normalized intensity of the 2210 cm^{-1} band, formed under 0.5% CO–0.25% NO reaction conditions at 250°C, as a function of time on stream under isothermal flow of He and following interaction with 0.5% CO, 0.25% NO, and 1% O_2.

the exit of the reactor. The response of N_2 progressively decreases with time of exposure and reaches a plateau after ca. 2.0 min on stream. The response of N_2O follows the opposite trend, i.e., it gradually increases with time on stream and reaches a plateau, also after ca. 2.0 min. Comparison with the corresponding FTIR experiments of Fig. 2B shows that the plateau is reached when the Rh–NO^- band at 1660 cm^{-1} disappears from the spectra and the isocyanate species start to populate the catalyst surface.

The reactivity of the adsorbed species, formed under CO–NO reaction conditions at 250°C, was investigated by monitoring the change of the IR bands after purging with Ar for 1 min and switching to 0.5% CO, or 0.25% NO, or 1% O_2 (in Ar) flow. Results are summarized in Fig. 4 where the normalized intensity of the Rh–NCO band at 2210 cm^{-1} (I/I_0) is plotted as a function of time-on-stream. For comparison, the corresponding curve obtained upon isothermal switch to He (results obtained from Fig. 2B, f–h) is also plotted. It is observed that the isocyanates do not interact with the incoming CO, as indicated by the rate of disappearance of the 2210 cm^{-1} band, which is similar with that observed under He flow. However, in our previous study it was shown that there is an interconversion between the Rh–NCO and Rh^0–CO species accompanied by the formation of nitride (12).

On the other hand, interaction of isocyanates with O_2 or NO results in faster disappearance of the 2210 cm^{-1} band (Fig. 4). In order to further examine this behavior, similar experiments have been conducted employing the transient MS technique. Results are presented in Figs. 3B and 3C, where the transient responses of reactants and products are plotted as functions of time-on-stream under 0.25% NO (B) and 1% O_2 (C) flow. It is observed that a small concentration of NO appears at the exit of the reactor immediately after the He → 0.25% NO/He switch, due to adsorption on the catalyst surface and to formation of reduction products in the gas phase, and it rapidly increases after ca. 2.0 min on stream. The responses of CO_2 and N_2 follow the same trend exhibiting two maxima, one immediately after the switch and a second after ca. 2 min on stream. The responses of both species then decrease and drop to zero when the concentration of NO in the gas phase reaches that of the feed. N_2O formation also takes place immediately after the switch, reaches a plateau, and drops following the responses of N_2 and CO_2. The amounts of N_2, N_2O, CO, and CO_2 formed during the first 10 min on stream were 12.4, 12.9, 14.9, and 4.3 μmol/g-cat., respectively.

It is of interest to note that in the case of the undoped Rh/TiO_2 catalyst (12), where isocyanates are not stable and are almost completely removed from the catalyst surface upon purging with He, significantly different results were observed in a similar experiment. Switching the flow to NO initially resulted in the observation of only N_2 and CO_2 in the gas phase. It was only when the response of N_2 started to decrease that N_2O and NO were observed at the exit of the reactor. In that case, formation of N_2O was attributed solely to interaction of surface dinitrosyl species with NO and adjacent reduced Rh sites (12). In the present case, N_2O, CO, and NO appear at the exit of the reactor immediately upon switching to NO (Fig. 3B). The appearance of NO indicates that there are fewer vacant Rh^0 sites, compared with the undoped catalyst, for the dissociative adsorption of NO. This is probably because these sites are in the present case occupied by Rh–NCO species, which are relatively more stable on the doped catalyst. It is then reasonable to suggest that isocyanates are responsible for the production of N_2O and CO, thus providing an additional route for the production of nitrous oxide:

$$\text{Rh–NCO} + \text{NO} \rightarrow \text{Rh} + N_2O + \text{CO}. \qquad [1]$$

This is further supported by the ratio of N_2O and CO produced, which is close to unity (see above), as predicted by Eq. 1. This reaction could explain the expanded temperature window for N_2O formation observed under steady-state conditions over $Rh/TiO_2(W^{6+})$ (Fig. 1) compared with the undoped catalyst. This behavior may be related to the higher ability of the present catalyst to stabilize isocyanates under given reaction conditions.

Regarding the reactivity of isocyanates with oxygen, the transient MS results obtained following the switch He → 1% O_2 over a catalyst previously exposed to the CO–NO mixture for 10 min are shown in Fig. 3C. Immediately after the exposure to oxygen, CO_2 is produced accompanied by evolution of N_2 and small amounts of N_2O. Formation of all products stops after less than ca. 0.3 min. The amounts of N_2, N_2O, and CO_2 formed were 6.9, 0.8, and 5.2 μmol/g-cat., respectively. Comparison with the corresponding FTIR results of Fig. 4 clearly shows that isocyanates are not responsible for the formation of these products since the intensity of the Rh–NCO band varies much more slowly. Similar results were reported by Hadjiivanov *et al.* (13) who studied by FTIR the formation and reactivity of isocyanate species on Fe–ZSM-5 and found that they are inert toward oxygen. However, the authors observed that isocyanates disappeared in an $NO + O_2$ atmosphere (i.e., in the presence of NO_2) even at ambient temperature.

4. CONCLUSIONS

(1) Isocyanate species adsorbed on Rh are significantly stabilized over the W^{6+}-doped Rh/TiO_2 catalyst and are present on the catalyst surface under all experimental conditions which lead to formation of N_2O in the gas phase. As a result, reduction of NO by CO over doped catalysts occurs at lower temperatures (ca. 50°C) compared to the undoped catalyst mainly due to expansion of the temperature window of N_2O formation.

(2) Rh–NCO species do not interact directly with CO and O_2. In contrast, isocyanates react with NO to yield N_2O, thus providing an alternative route for the production of nitrous oxide.

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