Infrared Studies of the Isocyanate Species Formed in the Reaction of NO with CO over Pt and Rh

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The behavior of isocyanates formed on the surface of Rh and Pt in the reaction of nitrogen oxide with carbon monoxide was studied by means of IR spectroscopy using a flow reactor. The isocyanate species readily reacted with N_2O or H_2O, however, it did not decompose when dosed with NO or CO. The catalytic activity of Pt-Al_2O_3 in the reaction of NO+CO declined quickly with an increase in the amount of the surface isocyanate (-NCO). Accordingly, it is concluded that -NCO is not a reaction intermediate but an inhibitor of the reaction.

Recently, Unland¹⁾ has observed the formation of isocyanate (-NCO) on the surface of Pt-Al_2O_3 in the reaction of NO with CO. He has stated that it is a reaction intermediate on the basis of the following findings. Firstly, Pt-NCO is produced when a mixture of NO and CO is dosed over Pt-Al_2O_3 at temperatures higher than 300 °C, where the reaction of NO with CO proceeds at an appreciable rate. Secondly, the amount of Pt-NCO changes with the gas phase composition and it disappears when an NO-rich mixture is dosed.

These findings are, however, not conclusive evidence that the species is a "true" intermediate in the reaction. Bell and London²⁾ have also observed the formation of -NCO on CuO catalyst, however, they considered that it was not a reaction intermediate but some by-product.

This paper reports the dynamic behavior of -NCO on the surface of Rh and Pt, which was especially studied confirm whether or not it is a reaction intermediate.

Experimental

Catalyst. Pt(1 wt %)-Al_2O_3 and Rh(1 wt %)-Al_2O_3 were prepared by impregnating γ-Al_2O_3 with an aqueous solution of either H_2PtCl_6 or $RhCl_3$. They were then dried at 100 °C for 24 h and calcined at 650 °C for 3 h. Prereduction was performed at 500 °C for 1 h in flowing H_2. Disks for IR studies were prepared after the prereduction. They were reduced again in an IR cell (at 300 °C for 1 h at 300 Torr or H_2) or in a flow reactor (at 500 °C for 1 h in flowing H_2) just before use.

The aluminas used as supports were obtained from two sources. Al_2O_3-I was prepared from Alumina Sol 200 (supplied by Nissan Chem. Co.) by drying at 100 °C for 24 h followed by calcination at 650 °C for 3 h. Al_2O_3-II was the commercially available alumina, Alon C.

IR Studies in a Vacuum. A conventional IR cell which was attachable to an appropriate vacuum and gas handling system was employed. The reactant mixture was in contact with the catalyst at 300 °C for 5 min and then was pumped off for 1 min at the same temperature. The isocyanate was produced on the surface of the catalyst by this procedure and was subjected to various treatments as described in the legends of the figures. IR measurements were made after the system had cooled to room temperature. The reactant, NO, CO or a mixture of the two, was introduced through a KOH-packed column into a gas handling system. They were stored in gas containers and were further purified by several freeze-thaw cycles before use.

NO+CO Reaction in a Flow System. Catalytic activity tests were made using a conventional flow system. A flow diagram is shown in Fig. 1. The reaction was occasionally interrupted by replacing the reactants in the system with pure helium (He). The reactor was then immersed in a fluidized thermal bath maintained at 500 °C in order to decompose or desorb surface residues. This procedure is tentatively termed "flash desorption", although not only desorption but also decomposition of the surface residue occurred simultaneously. Several bursts of O_2 were then introduced to establish complete combustion of the surface residues. This procedure is termed "combustion". Liberated gases were analyzed by gas chromatography. An IR cell, similar to that used in the vacuum studies but with slight modification for adaptation to the flow apparatus, was also employed as a reactor in order to observe the development of surface species for changes in catalytic activity.

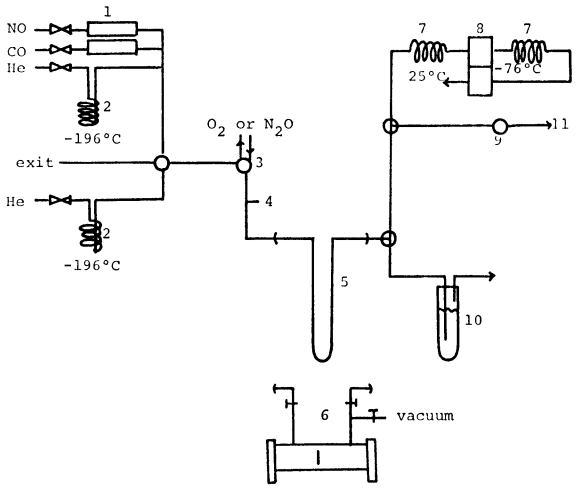


Fig. 1. Flow diagram.
1. KOH column. 2. MS-13X column. 3. O_2 or N_2O doser. 4. Liquid sample inlet. 5. Reactor. 6. IR cell. 7. Porapak Q. 8. T. C. Detecter. 9. Sampling cock. 10. Nessler's reagent. 11. Gas chromatography.

Results

Rh catalyst. The IR spectra of a mixture of NO and CO (NO=26 Torr, CO=59 Torr) which was dosed over Rh-Al_2O_3-II at 300 °C are given in Fig. 2. The spectra is quite similar, in general, to that reported by Unland,¹,³⁾ as can be seen in Table 1. The small differences in the position of the peak maxima may be explained on the basis of the different histories of the catalysts. As has been pointed out by Primet *et al.*, the peak maximum changes, though slightly, depending

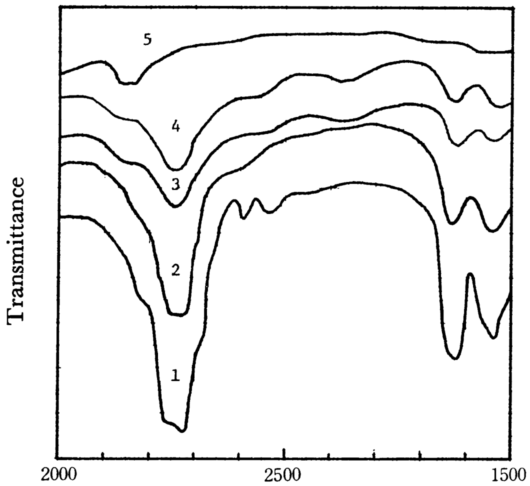


Fig. 2. Infrared spectra before and after the exposure of NO+CO mixture at 300 °C over Rh-Al_2O_3-II.
1. After the mixture (NO 26 Torr, CO 59 Torr) was exposed with following mild pumping. 2. After the subsequent pumping for 10 min. 3. After new mixture (NO 29 Torr, CO 8 Torr) was exposed over the -NCO formed catalyst. 4. After the new mixture was exposed over the fresh catalyst. 5. Back ground spectrum.

Table 1. Observed IR bands and their assignments

Present result	Unland (Rh)$^{3)}$	Unland (Pt)$^{1)}$	Assignment$^{1,3)}$
2250 vs$^{a)}$	2269	2261	-NCO
—	2175	2130	NCO^- or CN^-
2090 w	2106	2083	CO_{ad}
2020 w	2036	—	CO_{ad}
1900 w	—	—	CO_{ad} ?
1630 s	1635	1633	C=N ?
1560 s	1568	1564	CO_3^{2-} or NO_3^{2-}
1470 w	1475	1472	CO_3^{2-}

a) vs: very strong, s: strong, w: weak.

on the particle size of the metals dispersed on the supports. The band at 2250 cm^{-1} is due to -NCO$^{1,3)}$ as is noted in Table 1. The results stated hereafter are mainly restricted to its behavior.

The band did not change after pumping for 10 min at 300 °C, indicating the high stability of the -NCO, however, it did drastically decrease when a new mixture with a higher NO/CO ratio was dosed. A new equilibrium was established within 5 min. The newly obtained spectrum is quite similar to that obtained when the new mixture was dosed over a fresh catalyst (Fig. 2, sp. 4). Quite interestingly, no such species was found when the same mixture (NO=26 Torr, CO=59 Torr) was introduced into the cell at room temperature and was then heated up to 300 °C. The quantitative reproducibility for bands other than -NCO was poor in this experiment mainly because of the difficulty in controlling the rate of temperature raise. However, in general, large amounts of gaseous N_2O were found. This was confirmed by both the IR spectrum in the gas phase and gas chromatographic analysis. This experiment suggests that N_2O might react with -NCO. More reproducible experiments which show the effect of N_2O on the surface -NCO are given below.

The quick response of the band intensity to changes in the gas-phase composition (Fig. 2) suggested that a reaction of -NCO with some other species readily occurred. The unimolecular decomposition or metathesis of -NCO was negligible because no significant change was observed after the -NCO had been held at the same temperature for 10 min in the absence of any gas.

The behavior of -NCO for the introduction of various gases are shown in Fig. 3. The amount of -NCO drastically decreased when N_2O was admitted, showing that the surface -NCO reacted with N_2O. Contact with CO_2 also resulted in a decrease in the -NCO although to a lesser extent in spite of the fact that larger amounts of CO_2 were admitted for longer times. In the latter case, enhancement of the band intensity at 2020 cm^{-1}, which was assigned to the absorbed CO, was also observed. No significant decrease was found when either NO or CO alone came into contact with the -NCO. The intensity of the -NCO was rather enhanced when NO was admitted.

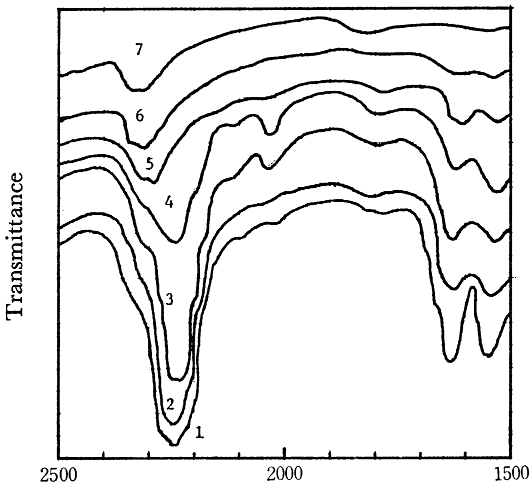


Fig. 3. Behaviors of -NCO and other species on the surface of Rh-Al_2O_3-II when various gases were admitted at 300 °C.
1. The spectrum of -NCO formed catalyst (the same as sp. 1 in Fig. 2) 2—6. After dosing, 2. NO (30 Torr for 5 min), 3. CO (50 Torr for 5 min), 4. CO_2 (50 Torr for 15 min), 5. N_2O (20 Torr for 5 min) and 6. H_2O (18 Torr for 5 min). 7. Back ground spectrum.

Pt Catalyst. The catalytic activity of Pt-Al_2O_3-I in the reaction of NO with CO declined in a rather curious fashion, as is shown in Fig. 4. The activity declined more rapidly when a reactant of lower NO/CO ratio was introduced as is indicated in Fig. 5. When the reactor containing such a deactivated catalyst in continuously flowing He was immersed in a thermal bath at 500 °C (flash desorption), CO_2 was liberated, as detected by a thermal conductivity cell located

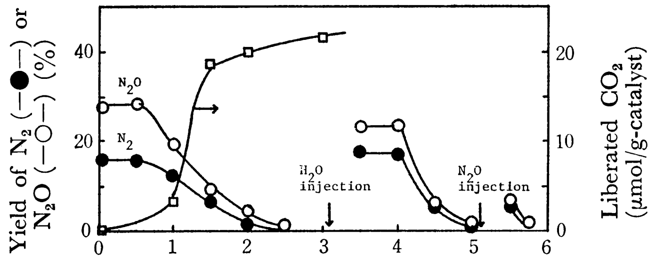


Fig. 4. The change of catalytic activity and the amount of surface residue, as expressed by liberated CO_2, with process time.
Catalyst; Pt-Al_2O_3-I, 0.3 g, reaction temperature; 300 °C, feed gas; NO: 3%, CO: 1% and He: balance, 100 cm³/min.

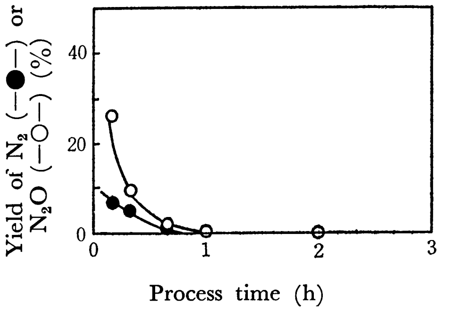
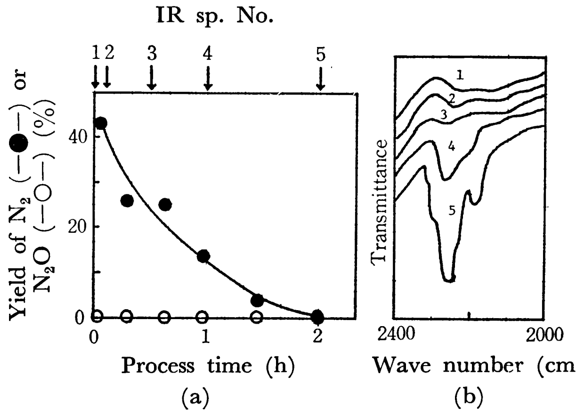


Fig. 5. The change of catalytic activity when the mixture of lower NO/CO ratio was fed.
Catalyst; Pt-Al_2O_3-I, 0.3 g, reaction temperature; 300 °C, feed gas; NO: 3%, CO: 2% and He: balance, 100 cm³/min.

downstream from the reactor. CO_2 was again found in some runs, as is noted later, when the O_2 bursts were subsequently introduced at the same temperature (combustion). The cumulative amount of CO_2 is also plotted in Fig. 4, as a function of the processing time. In the earlier stages of the processing time, all the CO_2 liberated was due to flash desorption. In the later stages, a considerable amount of CO_2 was liberated upon combustion, although, it was still to a smaller extent in comparison with that from flash desorption. It is evident from Fig. 4 that an inverse proportionality exists between the activity decline and the amount of CO_2 liberated. N_2 was also found for both the flash desorption and combustion processes, although with poor quantitative reproducibility.

The adsorption of CO_2 was independently studied by means of the burst technique. It was confirmed that no irreversible adsorption took place at 300 °C either on a fresh or on a deactivated catalyst. This indicates that the CO_2 liberated upon flash desorption was not due to simple "desorption" of adsorbed CO_2 but was due to some reaction (presumably decomposition or metathesis) of the surface complex producing CO_2. The activity was restored when either N_2O or H_2O was introduced over the deactivated catalyst, as is shown in Fig. 4. The formation of NH_3, when H_2O was introduced, was confirmed from the characteristic color change of Nessler's reagent. These findings can be summarized as follows: the species containing carbon, oxygen and nitrogen accumulates on the surface during the reaction of NO with CO and it retards the catalytic activity. If we assume that the retardation is attributed to a unique surface species, we can consider that the formation of –NCO is the primary cause for the deactivation.



(a) (b)

Fig. 6. The changes of catalytic activity (a) and the development of surface –NCO (b) with process time.
Catalyst; Pt-Al_2O_3-II, 0.025 g, reaction temperature; 350 °C, feed gas; NO: 12%, CO: 8% and He: balance, 25 cm³/min.

In order to confirm the above expectation, the development of the surface species as a function of the processing time was studied. The catalytic activity was also simultaneously measured. This was done by attaching an IR cell to the flow system instead of the reactor. The results are given in Fig. 6. The reaction conditions were not the same as those for the former experiment (Figs. 4 and 5) primarily because of the small weight of catalyst disk. In spite of this, the activity declined with a general tendency similar to that of the former experiments. The IR spectrum above 2000 cm⁻¹ was also similar to that obtained for the Rh catalyst in the vacuum experiments. It is apparent that the surface –NCO increases as the activity decreases. The IR spectrum below 2000 cm⁻¹ was complex and its reproducibility was poor. As has been pointed out by Unland,³⁾ hydrogen, which might react with NO to form NH_3 or NH_4^+ in the course of the reaction of NO with CO, is strongly adsorbed on the surface during the pretreatment. Functional groups such as NO_3^-, CO_3^{2-} and C=N, which might be produced under these conditions, also have absorption bands in this region. Since the flow system is not adequate to completely isolate the system from the atmosphere, some effect of impurities, especially of H_2O or O_2, might also be expected. What the authors would like to emphasize here is that no band other than that of –NCO corresponds to the changes of catalytic activity with the processing time.

Discussion

It is well known that Pt and Rh have similar catalytic activities in many reactions. Unland³⁾ has reported that the adsorbed species in the reaction of NO with CO on several noble metals including Pt and Rh are similar. The discussion hereafter can be applied, in many aspects, to both the Pt and Rh catalysts. This is an assumption, although it appears probable.

Unland has proposed[1] the following scheme for the formation and decomposition of –NCO.

$$\mathrm{Pt + NO + CO \rightarrow Pt\text{-}NCO + O_{ad}} \qquad (1)$$

$$\mathrm{CO + O_{ad} \rightarrow CO_2} \qquad (2)$$

$$\mathrm{Pt\text{-}NCO + NO \rightarrow Pt + N_2 + CO_2} \qquad (3)$$

The scheme explains why –NCO disappears or decreases when an NO-rich mixture is dosed. However, –NCO has been confirmed to be extremely stable when NO alone was introduced at high temperature. Accordingly, scheme of Unland, at least reaction (3), is not appropriate. All the present findings indicate that –NCO is not a typical reaction intermediate but an inhibitor which is produced under the reaction conditions. The quick response of the amount of –NCO to the change of gas-phase composition, which at first glance appears to be the characteristic behavior of a reaction intermediate, can be alternately explained as follows. Isocyanate is produced from NO and CO and reacts with N_2O. Then, the amount of –NCO reaches an equilibrium with the gas-phase components, NO, CO and N_2O. When a new mixture with a different NO–CO ratio is dosed, the gas-phase composition of NO, CO and N_2O also changes, resulting in changes of the amount of –NCO.

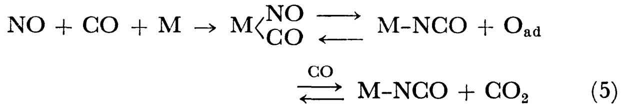
The main products in the reaction of NO with CO at lower temperatures were N_2O and CO_2.[5] A large amount of N_2O is expected to be produced upon the heating up of the reactant mixture with the catalyst from room temperature to 300 °C. This is the reason why no –NCO was observed for such a procedure.

It should be noted that –NCO may be a precursor of N_2. This is probable because N_2O is a typical oxygen atom donor. In spite of this, however, the reaction is of secondary importance because the main catalytic reaction is deactivated as the surface –NCO develops (Fig. 6). In addition, it was found in a separate experiment that a large amount of N_2 was produced when the mixture of NO and CO was passed as a burst through the bed of fresh catalyst on which no –NCO had been produced. These results indicate that path other than that through the –NCO intermediate exists for producing N_2.

To the authors' knowledge, no conclusive schemes had been proposed for the formation of –NCO. Arai *et al.* have found nitrosyl-carbonyl mixed adsorption on Rh, $\mathrm{Rh}\langle{}^{\mathrm{NO}}_{\mathrm{CO}}$, at lower temperatures. They suggested that this is the precursor of –NCO.

The overall process for the deactivation may be written as follows:

$$\mathrm{NO + CO \xrightarrow{M} N_2,\ N_2O,\ CO_2 \cdots\cdots main\ reaction} \qquad (4)$$



$$\mathrm{NO + CO + M \rightarrow M\langle{}^{NO}_{CO} \rightleftarrows M\text{-}NCO + O_{ad} \overset{CO}{\rightleftarrows} M\text{-}NCO + CO_2} \qquad (5)$$

$$\mathrm{M\text{-}NCO + N_2O \longrightarrow M + N_2 + NO + CO} \qquad (6)$$

$$\mathrm{2CO + M \longrightarrow CO_2 + M\text{-}C} \qquad (7)$$

$$\mathrm{M\text{-}NCO + H_2O \longrightarrow NH_3,\ CO_2,\ M} \qquad (8)$$

where M is a noble metal catalyst. The main catalytic reaction route, reaction (4), can be divided into several elementary steps. Since it is not the primary concern of this study to clarify them, the undefined formula (4) is tentatively written here. Reaction (5) appears to be reversible because the band of –NCO decreases upon the introduction of CO_2 (the results for the Rh catalyst, Fig. 3) and O_2 admission promotes the reaction of –NCO (the combustion procedure for the Pt catalyst). Reaction (6) is a tentative formula. What can be said with some certainty is that M–NCO reacts with N_2O to give N_2. Carbon deposition (disproportionation of CO) was also confirmed to take place at 300 °C and is therefore given in reaction (7), however, the rate is slower than that of –NCO formation.

In summary, –NCO is not considered to be an intermediate in the main catalytic reaction of NO with CO. However, the important roles of –NCO in the practical catalytic process of NO with CO, are emphasized here. Isocyanate is readily decomposed by water to form NH_3, which has already been pointed out by Unland[1,3] and also confirmed here. Most research work on the reaction were performed under water-free conditions. The catalytic activity under such conditions declines quickly because of –NCO formation. Under practical conditions, however, it will readily react with water which is always present in any combustion exhaust gases. This results in maintaining a high catalytic activity for a longer time. This is a very important point to be considered in selecting a practical catalyst for the reaction.

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