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Effects of Potassium on the Formation of Isocyanate Species in the NO + CO Reaction on Rhodium Catalyst

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The effect of potassium on the formation of isocyanate species in the NO + CO reaction on supported Rh catalysts was investigated by means of infrared spectroscopy. Addition of potassium to 5% Rh/Al_2O_3 significantly decreased the uptake of H_2, CO, and NO at 300 K, as indicated by adsorption and infrared spectroscopic measurements. All absorption bands of adsorbed CO and NO registered for K-free Rh/Al_2O_3 have been identified for K-containing samples. However, the relative intensity of bands of Rh_x–CO and $Rh(CO)_2$ species decreased with the increase in potassium content. At the same time, the band at 1650 cm^{-1}, attributed to negatively charged NO^-, intensified. Preadsorbed potassium exerted a significant increase on the formation of the NCO complex, characterized by a broad absorption band at 2240–2265 cm^{-1} (Al–NCO): the maximum intensity was obtained for a sample containing 2.5% K. The same effect was observed on Rh/SiO_2, where two NCO species were identified (2180 cm^{-1} for Rh–NCO and 2310 cm^{-1} for Si–NCO). The effect of potassium is attributed to the promotion of the dissociation of NO and to the stabilization of adsorbed nitrogen atoms. It is concluded that both the migration of NCO from Rh onto the supports and the stability of NCO located on the support are influenced only slightly by potassium.

INTRODUCTION

The study of the formation and reactivity of surface intermediates is an important subject of heterogeneous catalysis. The best tool for this kind of investigation is no doubt infrared spectroscopy (IR), which is capable of detecting surface compounds in a very low concentration under reaction conditions.

One of the most widely studied systems from this point of view is the reduction of NO by CO on supported metals. The high-temperature NO + CO reaction produces NCO surface species which give intense absorption bands in the IR spectra of the catalysts (*1–9*).

As regards the role and location of NCO in the NO + CO reaction, it was initially thought that NCO is bonded to the metals and participates in the reaction, particularly in the undesired formation of ammonia in automobile exhaust catalysis (*1–8*). However, a great number of observations suggested that the NCO, yielding intense absorption bands at 2210–2310 cm^{-1}, actually resides not on the metal, but rather on the support (*9–14*). Accordingly, the NCO species forms on the metal, but it migrates onto the support, where it is accumulated and stabilized. Decisive evidence for this view was presented by Solymosi *et al.* (*11–14*), who demonstrated that (i) the number of NCO groups greatly exceeds that of the surface metal atoms (*11*) and (ii) the location of the asymmetric stretch of the NCO band is independent of the metals, but primarily determined by the nature of the support. The highest position of the NCO band (2310 cm^{-1}) was found for M/SiO_2 (M = metal), and the lowest (2210 cm^{-1}) was registered for M/TiO_2 (*12, 13*). The absorption band of NCO attached to the metal was detected at 2170–2190 cm^{-1} and was found to be unsta-

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ble at 300–350 K (*9, 14*). Although this view on NCO chemistry was initially questioned (*15*), it was accepted and confirmed later by Bell *et al.* (*16, 17*) in the case of a supported Rh catalyst. The migration of NCO from Rh onto the support was clearly established by following the simultaneous decay in the intensity of the Rh–NCO band at 2180 cm^{-1} and the increase in the intensity of the Si–NCO band at 2310 cm^{-1} (*16–18*).

Further progress in this field was provided by the study of the chemistry of NCO complexes on unsupported Rh films (*19, 20*) and on Rh single-crystal surfaces (*21, 22*). The instability of the NCO complex on the clean surface has been confirmed, and a stabilizing effect of coadsorbed oxygen has been demonstrated.

Although it is clear now that the NCO species located on the support material does not play an important role in the NO + CO reaction (*23, 24*), we cannot automatically rule out that the NCO bonded to the Rh (and stabilized by coadsorbed oxygen) cannot function as a reaction intermediate in the main and side reactions (NH_3 and HCN formation) during automobile exhaust catalysis (*23*). Recent investigation disclosed several details concerning the reactivity of NCO on different supported metals (*24–31*) which might help to establish the role of the NCO complex in the NO + CO reaction.

In the present work we examine the effect of adsorbed potassium on the formation of the NCO complex on a Rh/Al_2O_3 catalyst. Recently it was found that the potassium adatom strongly influences the bonding and the reactivity of NO on the Rh(111) surface (*32, 33*). Its effect was also manifested in the NO + CO reaction on supported Rh catalyst (*34*).

EXPERIMENTAL

Rh/Al_2O_3 samples were prepared by coimpregnation of Al_2O_3 (Degussa, BET area 100 m^2/g) with an aqueous solution of $RhCl_3 \cdot 3H_2O$ and KNO_3. After impregnation, the samples were dried in air at 373 K.

For IR studies, the dried Rh/Al_2O_3 powder was pressed into self-supporting wafers (30 × 10 mm, 20 mg/cm^2). The pretreatments of samples were performed in a vacuum IR cell: the samples were (a) heated (20 K/min) to 573 K under continuous evacuation; (b) oxidized with 100 Torr of O_2 (1 Torr = 133.3 Pa) for 60 min at 573 K; (c) evacuated for 30 min; and (d) reduced in 100 Torr of H_2 for 60 min at 673 K. This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment. The gases were circulated during the oxidation–reduction and NO + CO adsorption by a small magnetic pump.

The gases used were of commercial purity. CO (99.9%) was purified by bubbling through a $Mn(OH)_2$ suspension. Water vapor was frozen out by a trap cooled with a dry ice–acetone mixture. A gas mixture containing 5% NO, 10% CO, and 85% N_2 (in volume) was made and used in the experiments.

IR spectra were recorded with a Specord 75 IR double-beam spectrometer (Zeiss, Jena) with a wavenumber accuracy of ±5 cm^{-1}. The experiments were performed in a Kiselev-type, greaseless IR cell, which was connected to a closed circulation system. All spectra were recorded at the temperature of the IR beam, ca. 313 K.

The dispersion of reduced rhodium was determined via hydrogen adsorption at 298 K. Characteristic data are shown in Table 1, which also contains adsorption data for NO.

TABLE 1

Adsorption of H_2 and NO on 5% Rh/Al_2O_3 Samples at 300 K

Potassium content (%)	H/Rh	Amount of NO (mg) adsorbed on 1 g catalyst
0	0.43	5.68
1	0.20	4.08
2.5	0.15	1.77
5.0	0.14	—

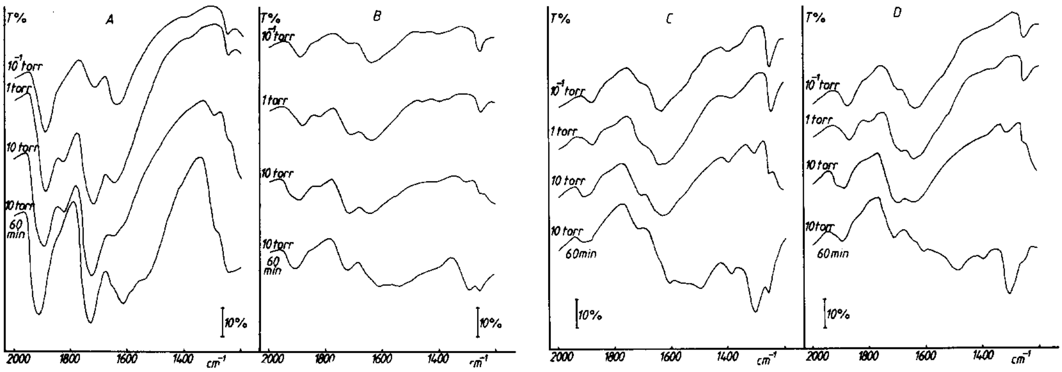

FIG. 1. Infrared spectra of adsorbed NO on 5% Rh/Al_2O_3 at different potassium contents at 300 K. (A) 0% K; (B) 1% K, (C) 2.5% K; (D) 5% K. Adsorption time, 10 min.

1. NO Adsorption

Before studying the formation of NCO species on K-promoted surfaces, we examined how the potassium influences the adsorption of NO on Rh/Al_2O_3. Measurements were performed at 300 K. Figure 1 displays some characteristic IR spectra.

Following the NO adsorption on a K-free surface, strong absorption bands developed at 1910 and 1730 cm^{-1}, and a weaker one at 1825 cm^{-1} (*8, 9*). A band also appeared at 1640 cm^{-1}, which became broad after longer contact time with NO. This was accompanied by the intensification of strong bands at 1290 and 1250 cm^{-1}. After evacuation at 300 K, the bands were somewhat attenuated, but no other spectral changes occurred.

A drastic reduction in the intensities of the absorption bands at 1910, 1825, and 1730 cm^{-1} was observed in the presence of potassium even at 1% content; however, the position of the bands remained unaltered. Further increase in the K-content prevented the development of a 1825-cm^{-1} band. The dominant feature was the rather broad band at 1650 cm^{-1}, which was seen even at 10^{-1} Torr of NO pressure. The band at 1300 cm^{-1} was more intense than in the previous case.

2. CO Adsorption

Similar measurements have been performed with CO (Fig. 2). Adsorption of CO on K-free Rh/Al_2O_3 produced intense absorption bands at 2100 and 2030 cm^{-1}, which are due to the $Rh^1(CO)_2$ species (*8, 9*). A broad weak band at 1890–1900 cm^{-1} due to bridge-bonded CO also appeared, but there was only a slight indication of the presence of linearly bonded CO at 2070 cm^{-1}. No significant changes were observed in the presence of 1% potassium; the linerly bonded CO at 2060–2070 cm^{-1} and that of the bridge-bonded CO at 1880–1890 cm^{-1} became somewhat more pronounced. At 2.5% K content, the intensity of the twin band greatly decreased and, at 5% content, the initial intensity of the 2065-cm^{-1} band exceeded that of the twin CO band. In Fig.

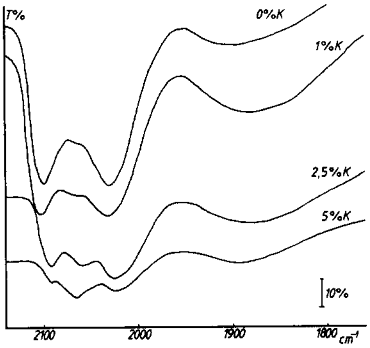

FIG. 2. Infrared spectra of adsorbed CO on 5% Rh/Al_2O_3 at different potassium contents at 300 K. CO pressure, 5 Torr; adsorption time, 5 min.

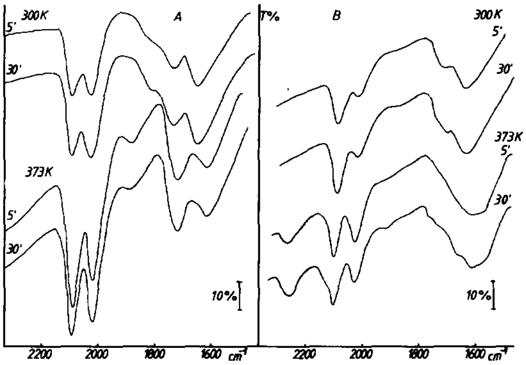

FIG. 3. Infrared spectra following NO + CO coadsorption (mole ratio 1 : 2) on K-free (A) and 2.5% K-containing (B) 5% Rh/Al_2O_3 at 300 and 373 K.

2 we show the spectra obtained after 5 min adsorption time. We note here that, in agreement with our previous findings (*35–37*), after an extended adsorption time observable spectral changes occurred in these cases, too. The main feature of this change is an increase in the intensity of gem-dicarbonyl at the expense of linearly and bridge-bonded CO. This process occurs appreciably more slowly in the presence of K additive (*37*).

3. Formation of Isocyanate Surface Complex

Following the adsorption of 50 Torr of gas mixture (5% NO, 10% CO, 85% N_2) on the Rh/Al_2O_3 at 300 K, the dominant bands were at 2100 and 2030 cm^{-1} due to gem-dicarbonyl. In addition, NO bands appeared at 1890, 1830, 1720–1730, and 1620–1650 cm^{-1}. On the K-dosed surface the basic difference was that the intensities of all these bands were much weaker (Fig. 3). The picture was practically the same at 373 K, where after a longer reaction time a weak band at 2260 cm^{-1}, associated with the asymmetric stretch of NCO species (*1, 2, 8, 9*), was also identified in the spectrum of K-dosed sample (Fig. 3).

At 423–448 K, where the NCO band was produced with an increasing intensity, the twin CO band was still a dominant spectral feature for the K-free sample. The intensity of the gem-dicarbonyl band remained unaltered, even when the NCO band attained its highest intensity. It is important to mention that at 423 K we also found a weak absorption at 2180 cm^{-1}, which could not be identified following the NO + CO reaction at higher temperatures. At the beginning of the reaction, weak bands due to adsorbed NO at 1910, 1830, and 1740 cm^{-1} were also seen.

The same features were observed in the presence of K (1–2, 5%) with the difference that the NCO band at 2260 cm^{-1} developed significantly faster, and the intensity of the twin CO-species bands was less during the reaction. Further increase in the potassium content (5%) led to a decrease in the NCO formation. At the beginning of the reaction, a weak band at 2170–2180 cm^{-1} was also observed for K-dosed samples. Some selected spectra obtained at 448 K are shown in Figs. 4A and 4B.

When the reaction temperature was raised to 473 K, in the early stage of the NO + CO reaction the situation was qualitatively the same as that at 448 K. However, when the majority (~90%) of NO has been reacted, a new band appeared at 2065 cm^{-1} between the 2030- and 2100-cm^{-1} bands; then the 2030- and 2100-cm^{-1} bands strongly attenuated, and a band at 2065 cm^{-1} remained dominant. This is valid for clean, 1, and 2.5% K-containing samples. At higher K content (5%) only very weak bands were seen at 2095 and 2020 cm^{-1} even after 2 h, when the NO bands were still detectable. Characteristic spectra for this phenomenon are displayed in Figs. 4C and 4D. At higher temperature, 523 K, the changes observed at 473 K occurred at shorter reaction times.

In Fig. 5 is plotted the intensity of the NCO band at 2240–2265 cm^{-1} as a function of time at different temperatures. The NCO band grows in intensity in the IR spectra of every sample with increase in reaction time at 423–473 K. The data presented clearly show that the *formation of isocyanate is promoted by potassium, and the extent of promotion increases up to 2.5% K content.*

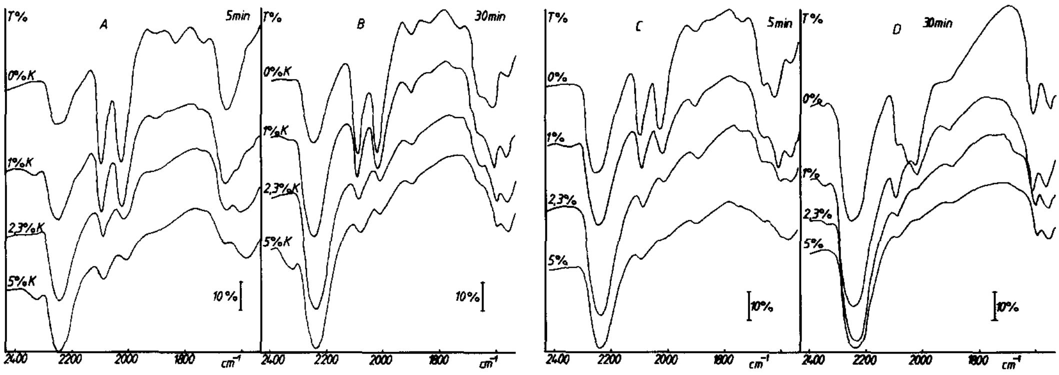

FIG. 4. Effects of potassium content on the infrared spectra of 5% Rh/Al_2O_3 produced by NO + CO reaction (1 : 2 mole ratio) at 448 K (A and B) and 473 K (C and D).

The characteristics of the intensity–time curves are altered at 473 K, where a maximum is exhibited in the early stage of the reaction. The obvious reason is that the NO + CO reaction is fast in this temperature range, and after the consumption of reacting gases, the decomposition of NCO comes into prominence.

The effect of potassium on NCO formation was also examined for Rh/SiO_2. In the case of a K-free sample a stable band produced by the NO + CO reaction which is associated with NCO bonded to the silica support appeared at 2315 cm^{-1} (*9, 12–14, 26*). At the beginning of the reaction another band was identified at 2180 cm^{-1} (attributed to Rh–NCO; see Discussion), which disappeared at the latter stage of the reaction, when the band at 2315 cm^{-1} became stronger (Fig. 6A). In the presence of potassium, an absorption band much more intense than in the previous case was produced at 2180 cm^{-1}; its intensity increased up to 30 min. The band at 2315 cm^{-1} was detected only in a later stage, when the 2180-cm^{-1} band attenuated (Fig. 6B). The trans-

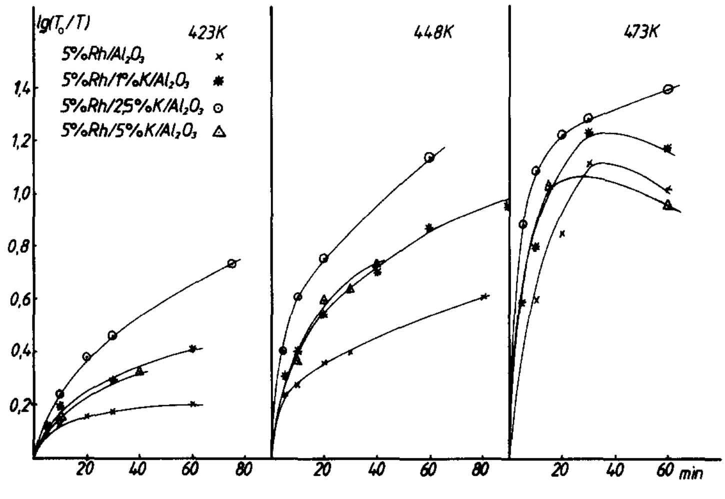

FIG. 5. Intensity of NCO band at 2260 cm^{-1} as a function of reaction time at different potassium contents.

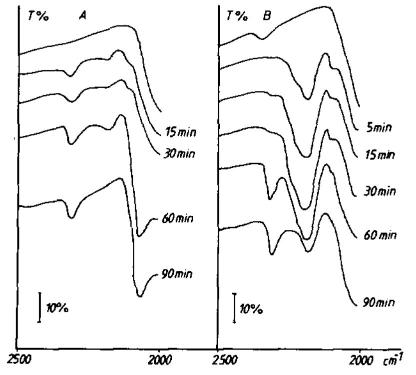

FIG. 6. Infrared spectra obtained in the NO + CO reaction (mole ratio 1 : 2) on K-free (A) and 2.5% K-containing (B) 5% Rh/SiO_2 at 448 K.

formation of the 2180-cm^{-1} band into the 2310-cm^{-1} band occurred more rapidly at 473 K.

4. *Stability of Isocyanate*

In the subsequent measurements we examined the effect of potassium on the stability of NCO species. In this case the NCO band was produced at approximately the same intensity by the NO + CO reaction at 473 K, then the sample was cooled to 300 K, and the cell was evacuated for 10 min. In addition to the NCO band at 2240 to 2265-cm^{-1}, the spectra showed only intense CO bands at 2035–2055 cm^{-1} and 1910 cm^{-1}, respectively. Afterward the sample was moved into the zone of the reactor preheated to 473 K, and at certain times the IR spectrum was registered at 300 K.

A continuous decay in the intensity of the NCO band, which slowed down after ~60 min, was observed for every sample. In this case, the intensity of the NCO band was less than 50% of the initial value. There was no spectral indication of a development of any new bands. In Fig. 7 the intensity–time curves for the four samples are displayed. It appears that the potassium exerts a practically negligible influence on the decay of the NCO band at 473 K. Although the decomposition of the NCO species was accompanied with an attenuation of CO bands, the latter remained quite strong even after complete decomposition of the NCO complex at 473 K. It is important to point out that there was no or only very slight indication of the presence of bands due to the gem-dicarbonyl species. Introduction of 5 Torr CO led to a shift of the Rh_x–CO band to higher frequency and to the very slow development of a band at 2100 cm^{-1}, indicative of the formation of Rh^1 $(CO)_2$ species. The latter spectral change occurred markedly lower in the presence of potassium additive (Fig. 8). The original spectrum obtained following CO or NO + CO adsorption on fresh samples could not be restored even after 24 h.

DISCUSSION

Before discussing the results obtained concerning the formation and decomposition of isocyanate species in the presence of potassium additive, we will deal briefly with the effects of potassium on the adsorption of NO and CO on Rh/Al_2O_3.

Adsorption of NO

In the case of K-free sample the adsorption of NO produced four absorption bands

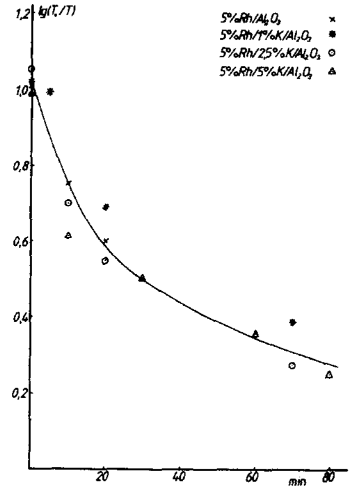

FIG. 7. Stability of NCO band at 2260 cm^{-1} on 5% Rh/Al_2O_3 at different potassium contents at 473 K. Isocyanate was produced by NO + CO reaction at 473 K; then the samples were kept at 473 K under continuous evacuation and the intensity changes were registered at certain times at 300 K.

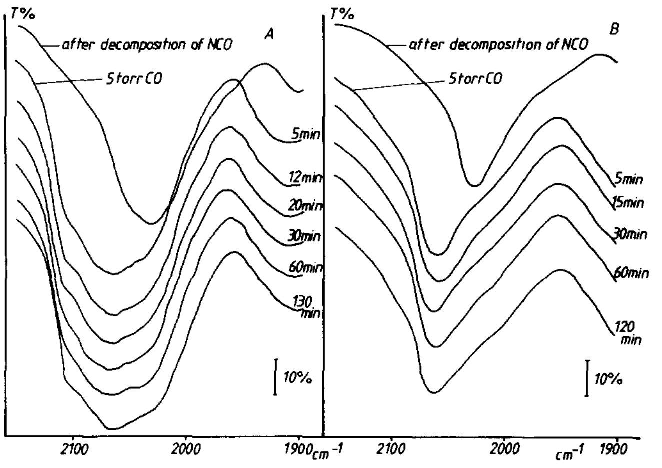

FIG. 8. Spectral changes of Rh/Al_2O_3 samples in the presence of 5 Torr CO at 300 K after complete decomposition of NCO species at 473 K. (A) 5% Rh/Al_2O_3, (B) 5% Rh +2.5% K/Al_2O_3.

at 300 K: these were assigned to Rh–NO^+ (1905 cm^{-1}), Rh–NO (1830 cm^{-1}) and Rh–NO^- (1740 and 1640 cm^{-1}) (*8, 9, 15, 38, 39*). Alternatively, the 1830- and 1740-cm^{-1} bands were attributed to the symmetric and asymmetric stretch of the dinitrosyl species, $Rh(NO)_2$ (*38–40*). A more detailed description of the formation of NO bands on supported and unsupported Rh was given in our previous paper (*36*).

Adsorption studies indicated that the NO uptake of Rh/Al_2O_3 at 300 K is significantly decreased with the increase in potassium content. At the same time all absorption bands are drastically attenuated with the exception of the 1630–1640-cm^{-1} band (Fig. 1). Its intensity relative to those of the other three bands is greatly increased in the presence of potassium additive. If we accept the above assignment for NO bands, this result means that the surface concentration of partially negatively charged NO species is increased in the presence of potassium relative to those of other NO species.

This feature is in agreement with expectations based on the results obtained on single-crystal surfaces (*32, 33*). The adsorption of NO on the K-dosed Rh(111) surface led to a much larger work function increase compared to that of the clean surface (*32*). This suggests that in the presence of K we can reckon with a more significant charge transfer to the adsorbed NO, i.e., to a more extended formation of partially negatively charged NO species. However, the present system differs from K + Rh(111) surfaces prepared under UHV conditions where the potassium deposited on Rh single crystals is in metallic form. In the present case, there is no doubt that, in spite of the high reduction temperature, potassium remained in the oxidized form, so a much more limited charge transfer, if any, can occur. In this respect we refer to the work of Praliaud *et al.* (*41*), who studied the properties of K (K_2O)-modified Ni/SiO_2 systems with XPS and magnetic measurements. They found a shift both in the binding energy for Ni ($2p_{3/2}$) and in the Curie point of Ni in the presence of K_2O. Both phenomena were thought to be the result of an electron transfer from K_2O additive to Ni metal. The electron-donating character of K oxide has been considered in other works as well (*42–45*).

Recently, in the study of adsorption of CO_2 on potassium-doped Rh/SiO_2, a similar electron transfer was assumed: the formation of new absorption bands induced by potassium was assigned to the production of CO_2^- anions bonded to K^+ ions (*46*).

Adsorption of CO

Potassium exerted a similar influence on the adsorption of CO on metal single crystals (*47, 48*). A significant increase in the binding energy and a shift in the position of CO peaks in vibration EELS has been observed, suggesting the formation of more negatively charged CO species. The effect of potassium on the adsorption of CO on supported metals has been the subject of several papers, where less effect was observed than on single crystals under UHV conditions (*49–51*). In the present case the main effects of potassium additive were a decrease in the adsorption of CO and the inhibition of the development of gem-dicarbonyl absorbing at 2100 and 2030 cm^{-1} (Fig. 2). This effect was more pronounced at higher potassium contents. This supports the idea that potassium prevents or slows down the oxidative disruption of Rh_x crystallite and the formation of Rh^1 centers (*37*). This feature may also be associated with partial electron transfer from K_2O to the Rh, which hinders its oxidation to Rh^1.

Spectral Features during NO–CO Adsorption and Reaction

In recent studies on the interaction of CO with supported Rh it appeared that the adsorption of CO causes a dramatic change in the morphology of rhodium (*35, 52–59*). At 150–373 K it leads to the oxidative disruption of Rh_x crystallites, i.e., to the formation of Rh^1 centers, while above 448 K it promotes the reductive agglomeration of Rh^1, i.e., the reformation of Rh_x crystallites. The addition of a very small amount of NO to CO efficiently promoted the oxidative disruption process of Rh_x (*36*).

Analysis of IR spectra taken during the NCO formation at 373–573 K suggests that the presence of NO prevented the completeness of the reductive agglomeration of Rh^1 by CO as indicated by the intense absorption bands due to gem-dicarbonyl, $Rh^1(CO)_2$ (Fig. 4). This is valid for K-free and K-containing samples. In the latter case, the intensity of the gem-dicarbonyl is significantly less. The presence of Rh_x crystallite—which is considered an active site for the dissociation of NO—is indicated by absorption bands of NO at 1830, 1730, and 1640 cm^{-1}. As NO adsorbs more strongly on Rh_x metal than CO does, the absorption bands due to Rh_x–CO appeared only at the end of the reaction, when the NO had been consumed. In this case the reductive agglomeration of Rh^1 was also completed, as indicated by the disappearance of bands due to $Rh^1(CO)_2$ species. When NO was used in excess, the reaction was much slower, but the gem-dicarbonyl was eliminated even in this case.

Formation of NCO Complex

Potassium exerted a measurable influence on the formation of NCO species. In order to interpret this finding, we must take into account the possible mechanism of the NO–CO reaction and that of NCO formation (*8, 9, 15–17, 23*). Apart from the adsorption and desorption processes we can propose the following steps

$$\begin{aligned} NO_{(a)} &= N_{(a)} + O_{(a)} \\ O_{(a)} + CO_{(a)} &= CO_{2(g)} \\ N_{(a)} + N_{(a)} &= N_{2(g)} \\ N_{(a)} + CO_{(a)} &= NCO_{(a)}. \end{aligned}$$

The key reaction in the NCO formation is no doubt the dissociation of NO. It is very likely that the effect of potassium can be accounted for by the promotion of this process. From the analysis of IR spectra of adsorbed NO on different samples (Fig. 1), it was suggested that the formation of partially negatively charged NO species is more abundant on K-dosed Rh/Al_2O_3 samples. Taking into account the chemistry of nitrosyl complexes, the formation of an anionic NO^- leads to the strengthening of the Rh–N bond and to the weakening of the N–O bond in the Rh–N–O species, so a more extended dissociation of NO is expected on K-dosed samples. This was clearly established in the case of the Rh(111) surface (*32, 33*).

However, kinetic measurements on the NO + CO reaction on the same catalysts showed that the rate of reaction is decreased in the presence of potassium additive, for example, at 2.5% K content by a factor of 2.5 (*34*). As potassium strongly stabilized the adsorbed N atoms on the Rh(111) surface (*60*), the peak temperature of the associative desorption of nitrogen was shifted by about 100 K to higher temperature; we may speculate that the reduced rate of the NO + CO reaction can be accounted for by the stabilization of adsorbed nitrogen by potassium. This process, i.e., an increase in the lifetime of adsorbed nitrogen atom, is favorable for step 4, i.e., for the formation of NCO complex on Rh.

As was mentioned in the Introduction the NCO band detected at 2240–2265 cm^{-1} on Rh/Al_2O_3, is associated with an NCO group formed on the Rh, migrates by means of a fast process onto the acceptor sites of alumina. Accordingly, the development of the NCO band can be influenced by the migration of NCO from the Rh onto alumina, which could be different in the presence of a potassium additive. Unfortunately, there was only an extremely slight indication of the presence of Rh–NCO species, which has a characteristic vibration at 2170–2180 cm^{-1} (*13–19, 25–28*), for either samples. This means that the spillover of NCO from the Rh to the alumina support is an unmeasurably fast process in the temperature range studied on all Rh/Al_2O_3 samples.

However, this diffusion process is much slower on Rh/SiO_2, where the Rh–NCO band at 2180 cm^{-1} was easily detected (*9, 12, 14, 15, 18, 26*). We observed that the development of this band did occur more rapidly in the presence of potassium (Fig. 6), which confirms that potassium additive promotes the NCO formation on Rh and supports the idea that the main role of potassium in the NCO formation is to promote the dissociation of NO on Rh metal.

Stability of NCO Species

The effect of potassium on the stability of the NCO group has been investigated in the case of CH_3NCO adsorbed on a Cu(HO) surface (*61*). Whereas CH_3NCO adsorbs molecularly on a clean surface and desorbs without any dissociation (*62*), the presence of potassium adatoms induced the cleavage of the N–CO bond (*61*). The effect was attributed to the significant increase in the binding energy of CO on the potassium-dosed Cu(110) surface.

The NCO species formed on Rh/Al_2O_3 decomposed under vacuum around 473 K. It appeared that the attenuation of the band at 2240–2265 cm^{-1} was not, or only insignificantly, influenced by the presence of potassium. This is partly due to the fact that NCO is located on the support of a large surface area and partly due to the lesser influence of K_2O compared to that of potassium metal on single-crystal surfaces. Attempts to determine the effect of potassium on the stability of Rh–NCO on silica are complicated by its weak band at 2180 cm^{-1} and by the occurrence of two simultaneous processes: the migration of NCO from Rh onto the support and the decomposition of NCO; both lead to the attenuation of the NCO band at 2180 cm^{-1}.

CONCLUSIONS

1. Preadsorbed potassium strongly influenced the IR spectra of adsorbed CO and NO: the formation of gem-dicarbonyl $Rh^1(CO)_2$ was suppressed, while that of Rh–NO was favored.

2. The reductive agglomeration of Rh^1 induced by CO adsorption above 423 K was greatly retarded by the presence of NO for both K-free and K-containing samples.

3. Preadsorbed potassium greatly promoted the formation of NCO complex in the NO + CO reaction at 373–473 K. This conclusion is valid for the development of NCO species on Rh (as indicated by the formation of an absorption band at 2180 cm^{-1} for Rh/SiO_2), as well as for the production of NCO complex on alumina (as indicated by the formation of a broad absorption band at 2240–2265 cm^{-1}).

4. It appeared that the stability of NCO located on the support is insignificantly influenced by the potassium additive.

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