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Adsorption-induced structural changes of supported Pt-Rh catalysts

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Abstract

Addition of NO to CO greatly promotes the CO-induced disruption of Rh_x clusters in the Pt-Rh/Al_2O_3 catalyst and retards the CO-induced agglomeration of Rh.

Keywords: Pt-Rh bimetallic catalyst; Carbon monoxide; Nitrogen oxide

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1. Introduction

The study of the surface properties of Pt-Rh bimetallic catalyst is of interest owing to its use in controlling automobile exhaust emission. Recent EXAFS and IR spectroscopy revealed that adsorption of CO on supported Rh at 300 K leads to the disruption of Rh_x cluster to isolated Rh^0 atoms, which are readily oxidized to Rh^1, very probably via the participation of OH groups of the support [1–4]. At higher temperature, above 448 K, the effect of CO is reversed; it induces the reductive agglomeration of Rh^1 to Rh crystallites [2]. No such structural changes have been observed for supported Pt [5,6].

The influence of other reactant gases, supports and additives has been also investigated [7–10], however, the extent to which other metals may affect these structural changes has received less attention [5,6]. It was found that the influence of platinum was to decrease the rate at which the rhodium gem-dicarbonyl species was formed and to increase the rate at which metal clusters were reformed on Pt-Rh/Al_2O_3 and Pt-Rh/SiO_2 catalysts. Coupling effects between Pt–CO and Rh–CO was observed at lower temperatures [6], which indicated that crystallites exist containing well mixed surface layers of platinum and rhodium atoms.

The primary aim of the present study is to examine the influence of NO on the CO-induced structural changes of Rh_x crystallites in the Pt-Rh bimetallic catalyst. An attention is also paid to the reactivity of the Rh_x clusters in the Pt-Rh/Al_2O_3 sample produced by the CO-induced morphological changes at high temperature.

2. Experimental

Rh and Pt (1 wt.-%) and Pt-Rh (1 wt.-% each) catalysts were prepared by impregnation of Degussa alumina with aqueous solutions of $RhCl_3 \cdot 2H_2O$ and/or $H_2PtCl_6 \cdot 6H_2O$ followed by drying in air at ca. 353 K.

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Self-supporting wafers (15–20 mg cm^{-2}) of the catalyst material were subjected to heat treatment in situ in the infrared cell at 573 K for 30 min under continuous evacuation, oxidation in 100 Torr of O_2 for 30 min at 573 K, evacuation for 30 min and reduction at $T_R = 573–1273$ K (T_R is the reduction temperature) in 100 Torr of H_2 for 60 min. The gases were circulated during oxidation and reduction processes, and the water formed in the latter case was frozen in a cold trap. This procedure was followed by degassing at 573 K independent of the reduction temperature. Thereafter the samples were cooled to the adsorption temperatures.

Spectra of adsorbed CO were recorded at a resolution of 5.3 cm^{-1} with a Specord M 80 double beam spectrophotometer and with a Fourier transform IR spectrometer (Biorad, type FTS 7). The wavenumber accuracy was in both cases better than ± 2 cm^{-1}. An in situ IR cell was used which permitted IR spectra to be recorded in the temperature range 100–573 K.

X-ray photoelectron spectroscopic (XPS) measurements were performed in a Kratos XSAM800 instrument using MgKα primary radiation (14 kV, 15 mA). For XPS study the Pt-Al_2O_3 and Rh/Al_2O_3 samples were reduced at 673 K and 573 K, respectively, and 10 Torr of CO was admitted at 300 K for 30 min.

3. Results and discussion

3.1. Adsorption of CO on Rh/Al_2O_3 and Pt-Al_2O_3

Adsorption of CO on 1% Pt-Al_2O_3 ($T_R = 573–973$ K) at 300–473 K gives a single band at 2056–2076 cm^{-1} due to linearly bonded CO. We observed no spectral changes even after extended adsorption time indicative of any structural rearrangements for Pt_x cluster. In harmony with this the admission of CO caused no change in the position of the $4(d_{5/2})$ emission at 316.2 eV characteristic for metallic Pt in the XPS spectra. We note that after H_2 treatment at high temperature, the small XPS peaks due to chloride disappeared from the spectra of the samples investigated.

Spectra of 1% Rh/Al_2O_3 ($T_R = 573$ K) exposed to CO at 300 K gave immediately intense bands at 2100 and 2030 cm^{-1} due to gem-dicarbonyl $Rh^1(CO)_2$ indicating that the oxidative disruption of Rh crystallite

$$2Rh + 4CO + 2AlOH \rightarrow 2Al\text{–}O\text{–}Rh(CO)_2 + H_2$$

or

$$2Rh^0 + 2OH = 2Rh^1 + 2O^- + H_2$$

proceeded completely. In this case the binding energy at 307.5 eV in XPS for $Rh(3d_{5/2})$ measured for reduced sample moved to 308.1 eV following the CO adsorption. This shift corresponds to the formation of Rh^1 [11]. When the reduction temperature was 1073–1273 K, we obtained only one band at 2040–2050 cm^{-1} due to Rh_x–CO. The presence of $Rh^1(CO)_2$ species was even indicated by weak shoulders at 2098 and 2035 cm^{-1}. More intense bands due to $Rh^1(CO)_2$ species appeared only after extended adsorption time.

3.2. Adsorption of CO and NO on Pt-Rh/Al_2O_3

First we examined the effect of the reduction temperature on the development of the gem-dicarbonyl species for bimetallic catalyst. Following the adsorption of 10 Torr CO the absorption bands of gem-dicarbonyl are the dominant spectral features for low-temperature reduced ($T_R = 573–773$ K) samples, even at the shortest adsorption time (5 min). These bands developed somewhat slower for the samples characterized with $T_R = 773–973$ K. For catalysts with $T_R = 1073–1273$ K, these bands can be seen only after an extended adsorption time. In this case the dominant CO band appeared at 2060–2070 cm^{-1}. Fig. 1A presents the development of gem-dicarbonyl, $Rh^1(CO)_2$, for Pt-Rh/Al_2O_3 reduced at 1073 K. From the comparison of these results with those obtained on Rh/Al_2O_3 samples reduced at the same temperatures [2–10] we can state that

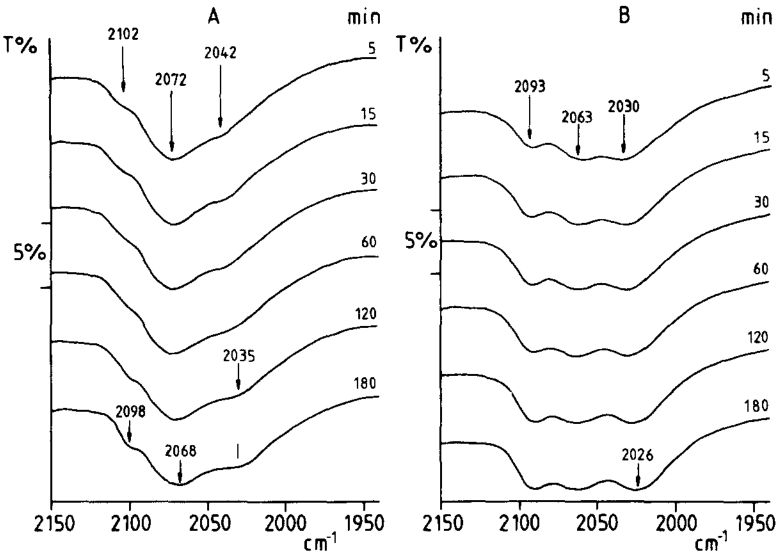

Fig. 1. Spectral changes of 1% Pt-1% Rh/Al_2O_3 ($T_R = 1073$ K). (A) in 10 Torr CO and (B) in 0.1 Torr NO + 10 Torr CO at 300 K.

the presence of platinum significantly decreases the rate of the development of $Rh^1(CO)_2$ (indicative of oxidative disruption) from Rh_x clusters.

NO (10 Torr) caused the appearance of the bands at 1783, 1709 and 1656 cm^{-1} on 1% Pt-1% Rh/Al_2O_3 ($T_R = 1073$ K) at 300 K. The intensities of these bands increased with the increase of NO pressure and new bands developed at 1904, 1450 and 1230 cm^{-1}. Keeping the sample in 10 Torr NO at 300 K, spectrum very similar to $NO/Rh/Al_2O_3$ system [12] was observed after extended time. After 5 h of adsorption, Rh–NO^+ (1939 cm^{-1}), Rh–NO (1847 cm^{-1}) and Rh–NO^- (1740 cm^{-1}) species could be clearly distinguished on the spectrum. Parallel with the development of these bands, the band at 1656 cm^{-1} (probably due to NO adsorbed on large metal crystals) decayed with the time and after 5 h it disappeared (Fig. 2).

In the subsequent measurements we examined the effect of NO on the CO-induced processes. For this experiment we choose the Pt-Rh/Al_2O_3 sample reduced at 1073 K. Whereas in the absence of NO the development of gem-dicarbonyl occurred very slowly at 300 K, the addition of only 0.1 Torr of NO to 10 Torr CO (NO:CO ratio 1:100) caused a marked spectral changes: the formation of $Rh^1(CO)_2$ band at 2100 and 2030 cm^{-1} developed at early stages and their intensities slowly increased in time. This is demonstrated in Fig. 1B. This influence was more pronounced at higher NO pressure.

The marked effect of NO on the CO-induced structural changes was also exhibited when CO

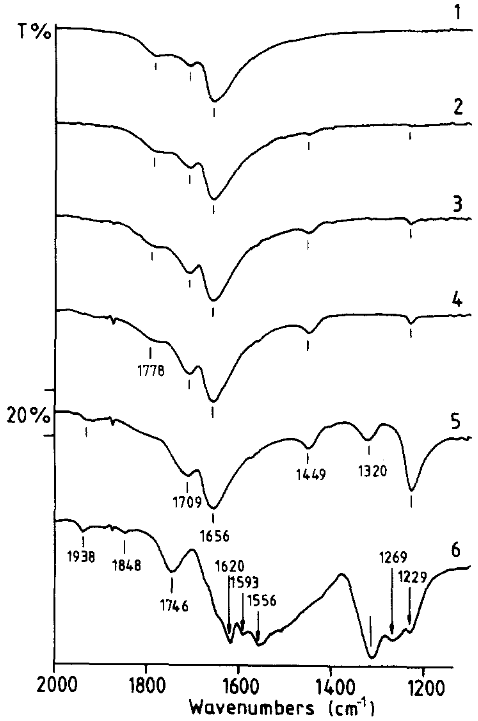

Fig. 2. Infrared spectra of NO adsorbed at 300 K on 1% Pt-1% Rh/Al_2O_3 ($T_R = 1073$ K): (1) 0.1 Torr NO, 5 min; (2) 1 Torr NO, 5 min; (3) 5 Torr NO, 5 min; (4) 10 Torr NO, for 5 min; (5) for 60 min and (6) for 300 min.

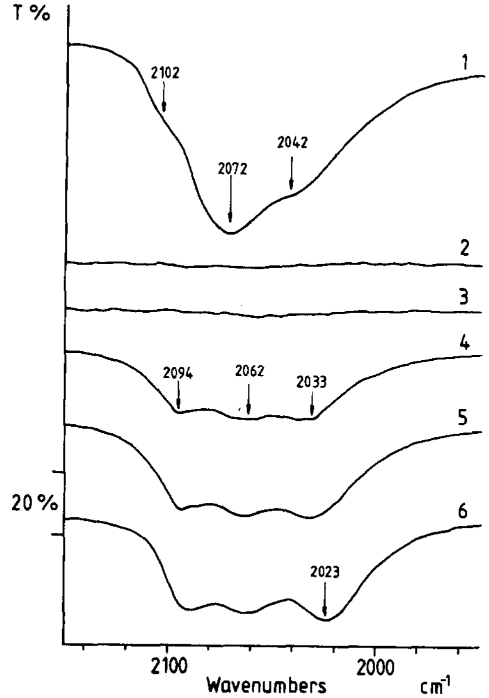

Fig. 3. Effect of preadsorbed NO on the spectra of CO adsorbed at 300 K on 1% Pt-1% Rh/Al_2O_3 (T_R = 1073 K): (1) 10 Torr CO, 300 K, 10 min; (2) 5 Torr NO, 10 min; (3) evacuation for 10 min; (4) 10 Torr CO added for 5 min; (5) for 60 min and (6) for 300 min.

was admitted on the Pt-Rh/Al_2O_3 containing preadsorbed NO. Whereas the admission of CO on reduced sample (T_R = 1073 K) produced very weak twin bands even after 180 min, after NO treatment (10 min) the twin bands due to $Rh^1(CO)_2$ appeared immediately and grew with the time at 300 K (Fig. 3). A band at 2062 cm^{-1}, very probably due to Rh_x–CO species, was also detected. Parallel with the development of the CO bands, the bands due to adsorbed NO species vanished and disappeared on CO admission (not depicted).

In the explanation of the effect of NO we can assume that NO participates directly in the CO-induced disruption of Rh_x crystallites or, independently of this process, the adsorption of NO can also disrupt the Rh–Rh bonds, leading to isolated Rh^0 atoms, or through oxidation, to Rh^1 sites on which CO binds in the twin form. This proposal seems reasonable if we accept the idea that the driving force of the CO-induced oxidative disruption of Rh_x crystallites is the high bond strength between CO and Rh [1,2]. The binding energy of NO to Rh_x cluster is higher than that for CO [12,13], thus the driving force assumed to be decisive in the disruption of the Rh–Rh bond will be also greater than that for CO adsorption. By the same argument, the products of dissociation of NO on Rh_x (adsorbed nitrogen and oxygen), which form very strong bonds with Rh_x, could also contribute to the disruption of Rh_x crystals. Although the presence of Pt decreases the rate of oxidative disruption process, this retarding influence is less pronounced in the presence of NO.

In the next experimental series, the Pt-Rh/Al_2O_3 sample (T_R = 573 K) was first treated with CO (10 Torr) at 300 K, which immediately produced intense peaks of the dicarbonyl species. The temperature was then raised to 473, 503, 543 and 573 K in the presence of CO and the spectral changes were registered in situ in several h. Some characteristic spectra registered are displayed in Fig. 4. In all cases the dicarbonyl species was transformed into linearly bonded CO absorbing at 2050–2062 cm^{-1}. The rate of transformation increased with increasing temperature. This process can be characterized by the reaction

$$2Rh^1(CO)_2 + O^{2-} = Rh_x\text{–}CO + CO_2 + 2CO$$

$$x = 2$$

From the comparison of the rate of transformation of $Rh^1(CO)_2$ to Rh_x–CO with that measured for Pt-free Rh/Al_2O_3 [2] we can conclude that platinum increases the rate of the reductive agglomeration of Rh^1, i.e., the reformation of Rh_x clusters from highly dispersed Rh^1 species.

This process, however, was significantly retarded in the presence of NO. This is illustrated by spectral changes displayed in Fig. 5. While the twin band at 2100–2030 cm^{-1} transformed rapidly in CO into a band at 2050–2062 cm^{-1} at 473 K (Fig. 5A), in the presence of NO the gem-dicarbonyl bands remained the dominant spectral feature even after extended adsorption time (Fig. 5B).

The retarding effect of NO on the reductive agglomeration of Rh^1 by CO was manifested at

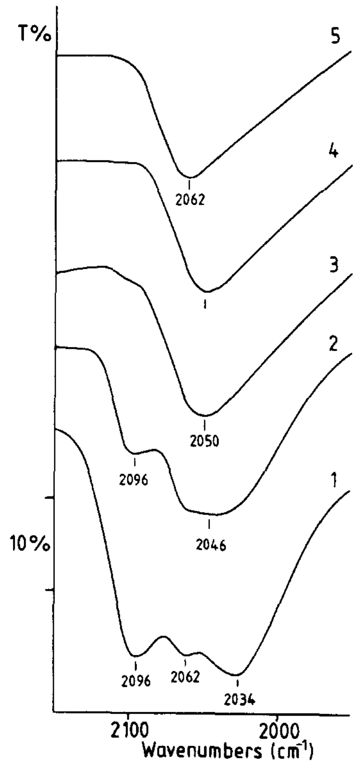

Fig. 4. Spectral changes due to CO (10 Torr) adsorption on 1% Pt-1% Rh/Al$_2$O$_3$ (T_R = 573 K) at different temperatures: (1) 300 K, 10 min; (2) 473 K, 165 min; (3) 503 K, 120 min; (4) 543 K, 1 min and (5) 573 K, 1 min.

higher temperatures too. This is demonstrated in Fig. 6, where we plotted the intensity of the band at 2096 cm^{-1} (due to the asymmetric stretching of gem-dicarbonyl) as a function of time at different temperatures. In CO the 2096 cm^{-1} band decreased in intensity relatively fast even at 473 K. At 503 K this band disappeared after 120 min and its disappearance occurred already in the first min of the treatment at 543 and 573 K, respectively (Fig. 6A). The decrease of the 2096 cm^{-1} band was accompanied by the concomitant increase of the 2062 cm^{-1} band. The presence of NO practically hindered the decay of the 2096 cm^{-1} band for extended time at 473 K. At higher temperatures (503–543 K) the rate of the disappearance of this band was much slower in the presence of NO, than in pure CO (Fig. 6B). In harmony with these findings the development of the 2062 cm^{-1} band was retarded due to NO.

The finding that NO greatly hinders the CO-induced reductive agglomeration, i.e., the reformation of Rh$_x$ cluster from highly dispersed Rh^1, is very likely associated with the oxidizing properties of NO.

3.3. Reactivity of the Rh$_x$ cluster formed in the CO-induced morphological changes

After CO treatment of the Pt-Rh/Al$_2$O$_3$(T_R = 573 K) sample at 543 K for 1 min,

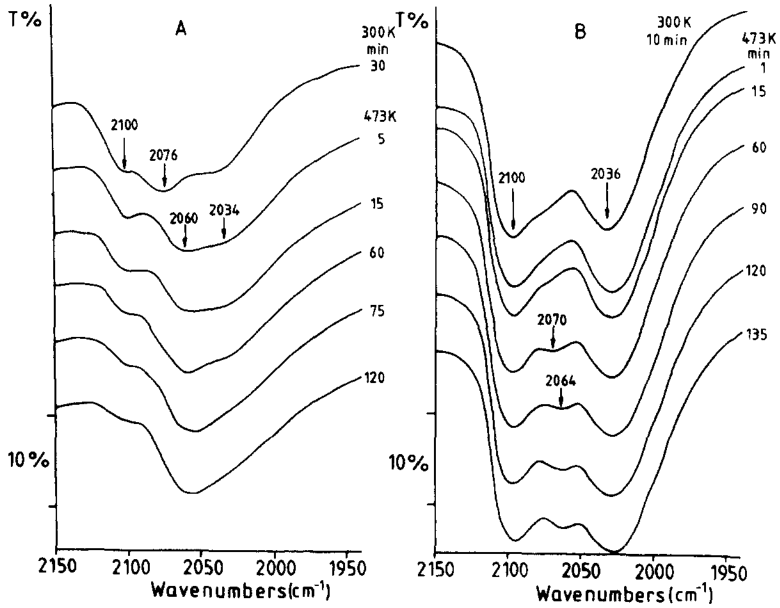

Fig. 5. Spectral changes of 1% Pt-1% Rh/Al$_2$O$_3$ (T_R = 573 K) at 473 K in 10 Torr CO (A) and in 0.1 Torr NO + 10 Torr CO (B).

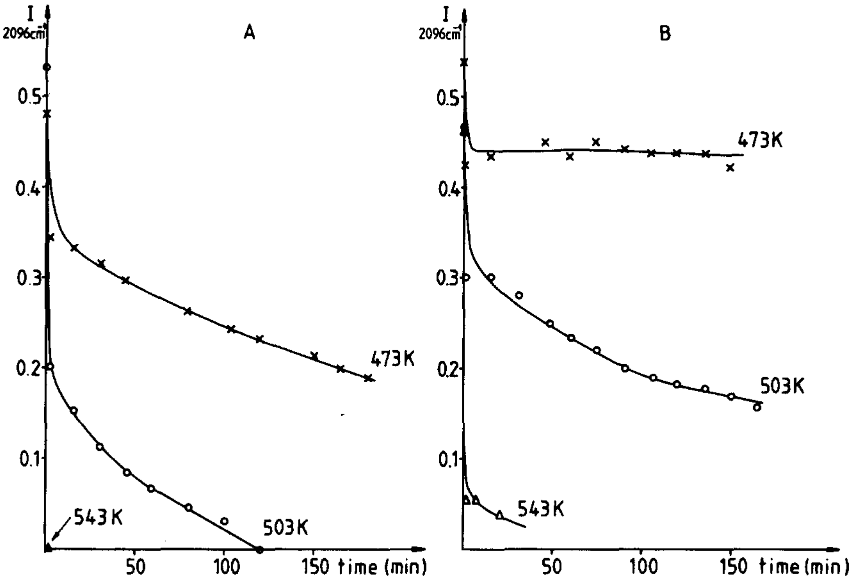

Fig. 6. The effect of NO on the intensity changes of the CO bands observed on 1% Pt-1% Rh/Al_2O_3 (T_R = 573 K) at different temperatures: (A) intensity of the 2096 cm^{-1} band in 10 Torr CO and (B) intensity of the 2096 cm^{-1} band in 1 Torr NO + 10 Torr CO.

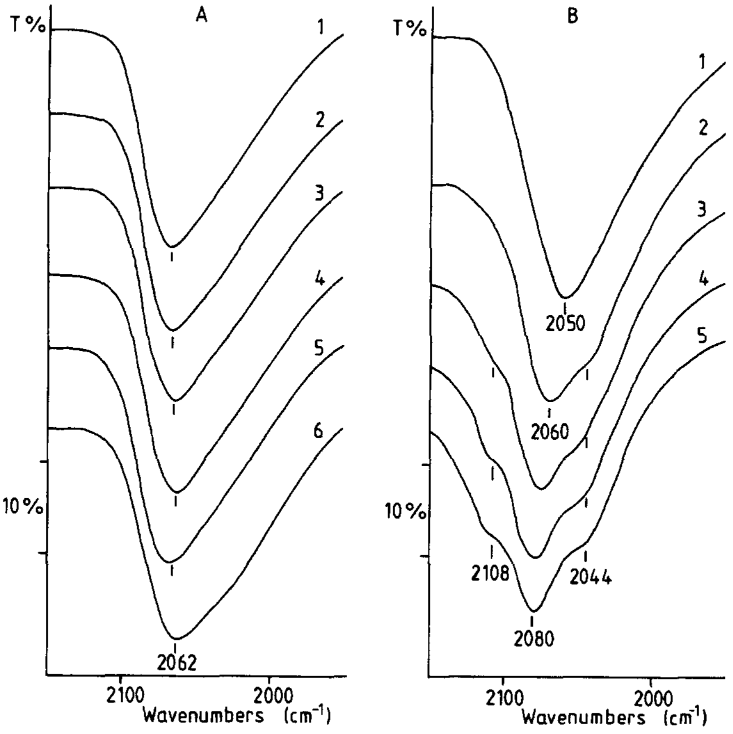

Fig. 7. Spectral changes at 300 K of 1% Pt-1% Rh/Al_2O_3 (T_R = 573 K) in (A) 10 Torr CO and (B) 5 Torr NO + 10 Torr CO. (A): (1) after CO treatment (10 Torr) at 543 K for 1 min and evacuation (spectrum taken at 300 K); and 10 Torr CO for (2) 1 min; (3) 90 min; (4) 180 min; (5) 240 min and (6) 19 h. (B): (1) after CO treatment (10 Torr) at 543 K for 1 min and evacuation (spectrum taken at 300 K); and 5 Torr NO + 10 Torr CO at 300 K for (2) 1 min; (3) 30 min; (4) 60 min and (5) 90 min.

which was sufficient to the complete transformation of $Rh^1(CO)_2$ to Rh_x–CO, the sample was degassed at the adsorption temperature and cooled to room temperature. IR spectrum showed only the linearly bonded CO absorbing at 2062 cm^{-1}. Introducing 10 Torr of CO in the cell the development of the dicarbonyl bands did not occur even after 19 h (Fig. 7A). In the case of a fresh Pt-Rh/Al_2O_3 catalyst ($T_R = 1073$ K) the gem-dicarbonyl appeared even after 2–3 h (Fig. 1A). From the comparison of Fig. 1A and Fig. 7A we can conclude that the reactivity of Rh_x cluster was significantly reduced. Similar features were observed for Rh/Al_2O_3 samples [10]. In the explanation of this feature we considered the size of Rh crystallites, the consumption of OH groups and the deposition of carbon and we came to the conclusion that the surface carbon produced in the CO dissociation is primarily responsible for the lack of reactivity of Rh_x cluster towards CO. The dissociation of CO on Rh/Al_2O_3 proceeds to detectable extent at and above 473 K [14].

In an other experiment 5 Torr NO + 10 Torr CO was added at 300 K to Pt-Rh/Al_2O_3 treated with CO at 543 K for 1 min and evacuated. As the spectra depicted in Fig. 7B show, weak spectral features due to gem-dicarbonyl could be observed even after 1 min, which grew in intensity with the time. These results suggest that NO promotes the oxidative disruption of even the less-reactive Rh_x clusters formed in CO-induced agglomeration, too.

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