Kinetics of the CO + NO Reaction over Rhodium and Platinum–Rhodium on Alumina

II. Effect of Rh Incorporation to Pt

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The effect of Rh on the kinetics of the CO + NO reaction on Pt/Al$_2$O$_3$ has been investigated using a fixed bed flow reactor at 300°C under atmospheric pressure with initial CO and NO partial pressure ranges of 1.05×10^{-3} to 14.7×10^{-3} atm. The kinetic performances of Rh/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$ catalysts have been interpreted on the basis of two kinetic models which assume competitive adsorptions of NO and CO or noncompetitive adsorptions of the reactants. The former model can correctly fit experimental data both on Rh and Pt–Rh. But the model with noncompetitive adsorptions seems preferable for Pt–Rh/Al$_2$O$_3$ for reasons developed in this paper. The equilibrium adsorption constants of NO are similar on Rh/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$ while those of CO are similar on Pt/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$ which shows that NO preferentially adsorbs on Rh and CO on Pt on Pt–Rh/Al$_2$O$_3$ in agreement with previous results of Van Slooten and Nieuwenhuys (16). It has also been found that adsorbed NO on Rh probably dissociates on a Pt site on the bimetallic Pt–Rh catalyst. N$_2$O is the major N-containing product on Rh/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$. In addition, the selectivity for the formation of N$_2$O is similar on these two catalysts; it is also insensitive to reaction conditions (P$_{NO}$, P$_{CO}$, and temperature). All these observations would emphasize the fact that NO is coordinated to Rh. The selectivity of Rh/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$ is controlled by a bimolecular reaction (NO$_{ads}$ + N$_{ads}$), yielding either N$_2$ or N$_2$O. It differs from what is observed on Pt/Al$_2$O$_3$ since the rate of the recombination of two adsorbed N atoms cannot be neglected on Pt alone as shown in the previous paper of this series. © 1998 Academic Press

INTRODUCTION

Catalytic converters are currently used to control NO$_x$ emissions in particular from mobile sources as automotive exhaust gases. The catalysts used in this technology contain a mixture of platinum and rhodium with a weight ra-

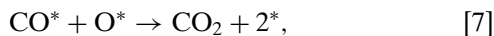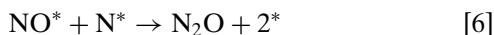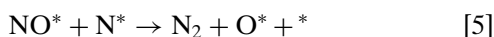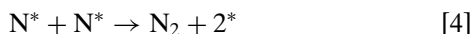tio varying between 5 and 10 (1, 2), and sometimes with palladium.

There is presently a general agreement to consider that Rh addition significantly improves the activity of supported Pt and Pd catalysts for the reduction of NO by CO. Several investigations on the adsorption of NO over well-defined Rh (111) (3), Pt (111), and Pd (111) surfaces (4, 5) have shown that NO dissociates more easily on Rh than on the two other noble metals. A similar adsorption behaviour towards NO has also been mentioned when rhodium is incorporated to polycrystalline Pt catalysts.

The catalytic behaviour of bimetallic catalysts is usually connected to the procedure used for their preparation since interactions between two metals can take place during this step. Consequently the bimetallic catalysts can sometimes exhibit a catalytic behaviour which differs from that observed for the individual metals. To illustrate these two considerations one can mention a paper of Ng *et al.* (6) in the CO + NO reaction on a Pt$_{10}$Rh$_{90}$ (111) alloy catalyst. These authors suggested that Pt and Rh would preserve their intrinsic adsorption properties. Consequently a change in the catalytic performance of Pt$_{10}$Rh$_{90}$ (111) compared to that of Rh (111) would be mainly ascribed to a dilution effect of Pt on the activity of Rh atoms rather than an electronic effect. However Ng *et al.* (6) do not exclude this latter effect. Other investigators also found an intermediate activity for various Pt–Rh alloyed catalysts between those of Pt alone and Rh alone (7, 8). However, in some cases, synergistic effects, due to alloying have been reported in the literature (9–11). Such a behaviour has been attributed to interactions between platinum and rhodium. They can modify the electronic properties of the whole surface atoms and consequently their intrinsic adsorption properties. Such modifications can further induced a decrease in the TWC activity. Despite the detrimental effect of alloying, the existence of such alloys is typical on TWCs in real operating conditions, at high temperature (12–14). A better

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understanding of the role of Pt and Rh in the active phase is an important preliminary step either for optimizing the surface composition of bimetallic catalysts or modelling the surface reactions which take place during the CO + NO reaction.

Kinetics is an important tool to clarify both the mechanism involved in such reactions as well as the role of the active phases. The following mechanism for the CO + NO reaction was earlier established for various monometallic Pt catalysts deposited on γ alumina, chromium carbide Cr_3C_2, and silicium nitride Si_3N_4 (15),

$$NO + {}^* \Leftrightarrow NO^* \qquad [1]$$

$$CO + {}^* \Leftrightarrow CO^* \qquad [2]$$

$$NO^* + {}^* \rightarrow N^* + O^* \qquad [3]$$

$$N^* + N^* \rightarrow N_2 + 2^* \qquad [4]$$

$$NO^* + N^* \rightarrow N_2 + O^* + {}^* \qquad [5]$$

$$NO^* + N^* \rightarrow N_2O + 2^* \qquad [6]$$

$$CO^* + O^* \rightarrow CO_2 + 2^*, \qquad [7]$$

where * denotes a vacant adsorption site.

The rate expression,

$$r_{CO} = \frac{k_3 \lambda_{NO} P_{NO}}{(1 + \lambda_{NO} P_{NO} + \lambda_{CO} P_{CO})^2}, \qquad [8]$$

was derived, assuming: (i) competitive adsorptions of NO and CO on one kind of active site; (ii) the dissociation of adsorbed NO (Eq. [3]) as rate determining step; (iii) adsorbed NO and CO as the most abundant species on the active surface which assumes that N_{ads} and O_{ads} are very reactive. k_3, λ_{NO}, and λ_{CO} are the specific rate constant for the dissociation of NO and the adsorption equilibrium constants for NO and CO, respectively.

In this study we have investigated the role of rhodium addition on the kinetics of the CO + NO reaction by using the mechanism previously selected for Pt. Here two alternative assumptions have been made concerning CO and NO adsorptions. It has been successively assumed that CO and NO adsorb competitively on the same sites: CO is preferentially adsorbed on Pt and NO on Rh as proposed by Van Slooten and Nieuwenhuys (16) after an IR study of CO and NO adsorption on a Pt–Rh/SiO$_2$ catalyst.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

The support used for the catalyst preparation was γ-Al$_2$O$_3$ (100 m^2 g^{-1}). This material was impregnated with aqueous solutions of hexachloroplatinic acid and of rhodium trichloride. The concentrations of these metallic salts were adjusted in order to yield 1 wt% Pt and 0.2 wt% Rh. The experimental procedure used for the preparation of Pt–Rh/Al$_2$O$_3$ was the conventional coimpregnation. After drying at 120°C, the precursors were calcined at 450°C, then reduced in flowing hydrogen at 500°C for 2 h. The metal dispersion was calculated from hydrogen chemisorption measurements. The values obtained were 0.55, 0.93, and 0.64 respectively for the dispersions of Pt/Al$_2$O$_3$, Rh/Al$_2$O$_3$, and Pt–Rh/Al$_2$O$_3$. According to X-ray photoelectron spectroscopy measurements, Rh and Pt deposited on γ-Al$_2$O$_3$ were mainly stabilized in a metallic state. The surface composition of the supported bimetallic Pt–Rh/Al$_2$O$_3$ catalyst estimated from XPS data was approximately of 33% Rh metal atoms and 66% Pt metal atoms, close to the global composition of the metal phase.

The catalysts were in powder form with grain size of 80 μm.

2. Catalytic Testing

The experimental setup has been previously described in detail (15). Catalytic testings were performed in a fixed-bed flow reactor. Helium used as the carrier gas (99.995%) was supplied by *Air Liquide*. NO and CO highly purified (99.9995%) were supplied by *Alphagaz*. Prior to the admission of gases in the reactor, water and oxygen traces were trapped on a molecular sieve *(Interchim)* and an oxygen trap *(Alltech)*, respectively. The effluents were analysed by a chromatograph HP 5890 series II equipped with a thermal conductivity detector. The different products and reactants were separated on two concentric columns (CTR1) supplied by *Alltech*. The experimental conditions used for the CO + NO reaction were: 0.023 to 0.2 g of catalyst mixed with 0.1 to 0.8 g of α-Al$_2$O$_3$. The global flow rate was adjusted between 10 and 15 L h^{-1}, and the space velocity ranged from 25×10^3 to 327×10^3 h^{-1}. The initial partial pressures were ranged from 5×10^{-3} to 14.7×10^{-3} atm for CO and from 1.05×10^{-3} to 7×10^{-3} for NO (1 atm $\cong$ 10^5 Pa).

Because of the very high activity of Rh at 300°C, kinetic experiments on Rh/Al$_2$O$_3$ were performed in differential flow reactor conditions by recycling the outlet gas mixture (recycling rate 1800 L h^{-1}) in order to avoid external diffusion limitations. With this high speed recirculation a slight pressure increase of about 0.2 atm was observed.

Before reaction all the catalyst samples were reduced again in flowing hydrogen (3 L h^{-1}) at 500°C for 7 h, then outgassed under flowing nitrogen at 400°C.

The conversion of CO by reaction with NO, T_{CO} was calculated using Eq. [9], where T_{N_2} and T_{N_2O} are the

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conversion of NO into N_2 and N_2O, respectively:

$$T_{CO} = T_{N_2} + \frac{T_{N_2O}}{2}. \qquad [9]$$

The specific rates of reactions were calculated according to Eq. [10],

$$r = \frac{D_T T_j}{100m}, \qquad [10]$$

where D_T is the NO or CO flow rate (mol h^{-1}), m is the mass of catalyst (g), and T_j is the initial conversion (%)—j = [CO, NO, N_2O, N_2] obtained after extrapolation of the conversion curves according to the same procedure used in reference (17).

The selectivity for the formation of N_2O (S_{N_2O}) is obtained by using Eq. [11]. r_{N_2} and r_{N_2O} represent the rates of NO transformation into N_2 and N_2O, respectively:

$$S_{N_2O} = \frac{r_{N_2O}}{r_{N_2O} + r_{N_2}}. \qquad [11]$$

RESULTS

As over supported Pt catalysts (15), N_2 and N_2O are the primary N-containing products in the reduction of NO by CO, both on Rh/Al$_2$O$_3$ and on Pt–Rh/Al$_2$O$_3$. An extraprocess of CO_2 formation also occurs on these two catalysts as already observed on Pt catalysts (15). In the following, we will not consider this extra process; we will discuss only on the conversion of CO with NO, T_{CO} (Eq. [9]).

The specific reaction rates for the oxidation of CO by NO at 300°C on Rh/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$ with 5×10^{-3} atm of NO and CO are compared with those previously obtained on Pt/Al$_2$O$_3$ in Table 1. Clearly, the turnover number (TON) is much higher on Rh/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$. Hence, for Pt–Rh/Al$_2$O$_3$, this TON has been calculated assuming that the activity of Pt atoms is negligible and that the surface composition is the same as that of the bulk (which is probably not true). The value obtained, close to 169 CO molec. oxidized by NO per hour per Rh surface atom, is noticeably lower than that of Rh/Al$_2$O$_3$.

TABLE 1

CO Oxidation by NO Over-Supported Monometallic and Bimetallic Pt, Rh Catalysts

Catalysts	Metal dispersion (%)	Specific rate (mol · h^{-1} · g^{-1})	Turnover number [a]
Pt/Al$_2$O$_3$[b]	55	2.3×10^{-4}	8
Rh/Al$_2$O$_3$	94	2.6×10^{-2}	1423
Pt–Rh/Al$_2$O$_3$	64	2.1×10^{-3}	169[c]

Note. T = 300°C, $P_{NO} = P_{CO} = 5 \times 10^{-3}$ atm.
[a] Molec. h^{-1} (surface metal atom)$^{-1}$.
[b] From Ref. (15).
[c] Calculated per surface Rh atom.

TABLE 2

Activation Energies for the CO + NO Reaction on Pt–Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ Catalysts

Catalysts	Activation energies (kcal mol^{-1})				
	CO[a]	NO[a]	N_2[b]	N_2O[b]	CO[c]
Pt/Al$_2$O$_3$[d]	19	22	27	15	—
Rh/Al$_2$O$_3$	43	44	47	43	45
Pt–Rh/Al$_2$O$_3$	28	30	30	29	29

Note. $P_{NO} = P_{CO} = 5 \times 10^{-3}$ atm.
[a] Apparent activation energy for CO and NO conversion.
[b] Apparent activation energy for N_2O and N_2 formation.
[c] Apparent activation energy for the CO oxidation by NO.
[d] From Ref. (15).

1. Influence of Temperature

Experiments were performed at a constant space velocity during the catalytic testing (25000 and 93000 h^{-1} respectively on Pt–Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$). The partial pressures of NO and CO were initially set at 5×10^{-3} atm, whereas the temperature ranged between 229 and 300°C on Rh/Al$_2$O$_3$ and 270 and 300°C on Pt–Rh/Al$_2$O$_3$. The selectivity for the N_2O formation, S_{N_2O}, on Rh/Al$_2$O$_3$ and particularly on Pt–Rh/Al$_2$O$_3$, remains almost unchanged respectively at $63 \pm 1\%$ and about $69 \pm 5\%$, in our temperature range conditions.

The activation energies (E) for the overall transformations of NO and CO for the oxidation of CO by NO and for the formation of N_2 and N_2O on the two catalysts are reported in Table 2, and compared to the values previously obtained on Pt/Al$_2$O$_3$ (15). The energies of activation are substantially higher on Rh/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$. Those on Pt–Rh/Al$_2$O$_3$ are intermediate between the values obtained on the monometallic catalysts. This result is surprising, since, considering the considerably higher rate of reaction on Rh/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$ (Table 1), similar values of energies of activation on Rh/Al$_2$O$_3$ and Pt–Rh/Al$_2$O$_3$ would have been expected. This probably indicates that Pt and Rh do not act separately on the bimetallic catalyst but they probably cooperate in the reaction mechanism.

2. Influence of the CO and NO Partial Pressures

Two sets of experiments were performed at 300°C on each catalyst by varying the initial partial pressures from 1.05×10^{-3} to 7×10^{-3} atm for NO at $P_{CO} = 5 \times 10^{-3}$ atm and from 5×10^{-3} to 14.7×10^{-3} atm for CO at $P_{NO} = 5 \times 10^{-3}$ atm. The space velocity was 25000 and 327000 h^{-1} on Pt–Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$, respectively.

2.1. Partial Orders

The apparent orders have been calculated from linear regression analysis according to a power law expression

TABLE 3

Kinetic Parameters for the CO + NO Reaction on Monometallic and Bimetallic Pt, Rh Catalysts

Catalysts	$10^3 \cdot P_{CO}{}^c$ (atm)	$10^3 \cdot P_{NO}{}^c$ (atm)	m^a	n^a
Pt/Al$_2$O$_3$[b]	5.0–9.0	1.5–5.7	−0.8	0.95
Rh/Al$_2$O$_3$	3.0–13.6	0.5–2.0	−0.32	0.80
	3.0–13.6	2.5–3.25	−0.32	<0
Pt−Rh/Al$_2$O$_3$	3.0–8.0	1.5–5.7	−0.38	0.40

[a] $r = kP_{CO}^m \times P_{NO}^n$.
[b] From Ref. (15).
[c] Residual partial pressures of NO and CO, taking into account the conversion of NO and CO, respectively.

given by Eq. [12],

$$r_{CO} = kP_{CO}^m P_{NO}^n. \qquad [12]$$

The results are reported in Table 3 and compared to those previously obtained on Pt/Al$_2$O$_3$ (15). The orders in CO are negative on all catalysts, which reveals a CO inhibiting effect on the CO oxidation by NO, but to a lesser extent on Pt−Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$. In contrast, the orders in NO are positive on Pt/Al$_2$O$_3$ and Pt−Rh/Al$_2$O$_3$, but in the case of Rh/Al$_2$O$_3$, the rate goes through a maximun at $P_{NO} \sim 2.5 \times 10^{-3}$ atm. A positive order in NO of about 0.8 is obtained from 0.5×10^{-3} to 2.0×10^{-3} atm while it becomes negative with an increase of P_{NO} above 2.5×10^{-3} atm.

2.2. N$_2$O Selectivity

The value of S_{N_2O} at various partial pressures of the reactants are reported in Table 4. The results show that S_{N_2O} can be considered as independent of the NO and CO partial pressures on Rh/Al$_2$O$_3$ and Pt−Rh/Al$_2$O$_3$ at 300°C, taking into account the margin of error. Moreover, it should be mentioned that for both catalysts, in temperature-programmed experiments S_{N_2O} proved to be approximately constant whatever the temperature and the NO conversion, up to about 80–90% of NO conversion.

DISCUSSION

1. Kinetics of the CO Oxidation by NO

1.1. Monometallic Pt/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ Catalysts

CO and NO are considered to adsorb competitively on the same sites as in Refs. (18, 19). If the same assumptions made in the case of Pt/Al$_2$O$_3$ hold for Rh/Al$_2$O$_3$, Eq. [8] can be used. Let us first mention that such an equation allows apparent orders between 1 and −2 in NO and 0 and −2 in CO, depending on the relative values of $\lambda_{NO}P_{NO}$ and $\lambda_{CO}P_{CO}$. The orders in NO and CO reported in Table 3 are within these limits and consistent with Eq. [8]. One has to

mention that the relative values of $\lambda_{NO}P_{NO}$ and $\lambda_{CO}P_{CO}$ are dependent on P_{NO}/P_{CO}, the temperature, and perhaps the nature of the catalyst. Consequently, it is not easy to compare our values for the orders to those previously obtained by other authors on different catalysts and in other operating conditions. However, one can mention that the results in the literature, e.g., rates going through maxima when P_{NO} increases on 0.01 wt% Rh/Al$_2$O$_3$ (20), positive order dependence on NO ($P_{CO} = 0.01$ atm, $T = 227°C$), and about zero-order dependence on CO ($P_{NO} = 0.01$ atm, $T = 227°C$) on Rh (111) (21), or orders in CO about zero at "high" NO pressure (0.01 atm, $T = 350°C$) and negative (−0.29) at lower P_{NO} (10^{-3} atm, $T = 325°C$), together with order in NO about zero at $P_{CO} = 0.01$ atm, 350°C, and positive (0.51) when $P_{NO} \leq 1.3 \times 10^{-3}$ atm, then almost nil for higher P_{NO} at $P_{CO} = 5.3 \times 10^{-3}$ atm and 325°C on Rh (111) (22, 23), are all qualitatively consistent with Eq. [8] and show the importance of the nature of the catalysts and the experimental conditions.

The decrease of the apparent activation energy (47 to 25 kcal mol^{-1}), mentioned by Oh *et al.* (21), when P_{NO} decreases (from 5×10^{-3} to 5×10^{-4} atm with $P_{CO} = 5 \times 10^{-3}$ atm) is also in qualitative agreement with Eq. [8] since $E_{app} = E_0 + \Delta H_{NO} - f(\Delta H_{CO}) - f'(\Delta H_{NO})$ (E_0 is the activation energy of step [3], ΔH_{NO} and ΔH_{CO}, the adsorption enthalpies of NO and CO, are negative since both adsorptions are exothermic) and $f'(\Delta H_{NO})$ decreases when P_{NO} decreases.

TABLE 4

Influence of the Partial Pressures of the Reactants on the Selectivity of Rh/Al$_2$O$_3$ and Pt−Rh/Al$_2$O$_3$ Catalysts in the CO + NO Reaction

	Rh/Al$_2$O$_3$[a]				Pt−Rh/Al$_2$O$_3$[b]		
$10^3 \cdot P_{NO}$ atm	$10^3 \cdot P_{CO}$ atm	NO conv %	S_{N_2O} %		$10^3 \cdot P_{NO}$ atm	$10^3 \cdot P_{CO}$ atm	NO conv %	S_{N_2O} %
2.00	3.00	60.3	67.6	1.50	5.00	28.5	59
2.75	4.55	45.9	71.2	2.50	5.00	28.5	58
3.15	11.0	37.7	72.1	3.50	5.00	16.6	59
2.75	5.58	45.8	71.2	4.50	5.00	13.7	60
2.75	9.00	45.8	68.9	5.00	5.00	13.8	61
3.25	13.6	35.7	69.5	5.60	5.00	12.8	60
3.00	7.17	39.0	69.3	5.00	3.00	16.4	67
2.00	3.00	60.0	67.7	5.00	4.00	15.3	67
0.48	4.30	66.9	69.7	5.00	5.00	13.8	67
3.48	3.40	40.6	68.3	5.00	6.00	12.6	68
1.52	3.40	59.5	69.2	5.00	7.00	10.6	69
1.05	3.75	64.8	70.2	5.00	8.00	10.0	69
0.70	4.10	68.0	70.2				
4.55	3.40	35.1	71.3				
2.00	3.10	59.6	70.7				

[a] $T = 300°C$, mass of catalyst 0.023 g, global flow rate = 15 L · h^{-1}, space velocity = 327000 h^{-1}.
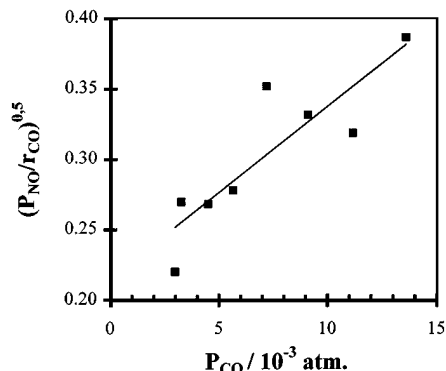[b] $T = 300°C$, mass of catalyst 0.2 g, global flow rate = 10 L · h^{-1}, space velocity = 25000 h^{-1}.

FIG. 1. Plot of $(P_{NO}/r_{CO})^{0.5}$ versus P_{CO} for Rh/Al$_2$O$_3$ in the case of competitive adsorptions of NO and CO; T = 300°C, $P_{NO} = 5 \times 10^{-3}$ atm.

Let us notice that in Ref. (21), Oh et al. reported that, on 0.01 wt% Rh/Al$_2$O$_3$, the rate constant for NO dissociation is much smaller than on Rh (111) and they mentioned the studies of Bell and co-workers (18, 24) and Miyazaki and Yasumori (25) that suggest that for the CO + NO reaction over supported Rh catalysts, the dissociation of NO$_{ads}$ is one of the slowest steps in the reaction sequence, in support of one of the assumptions adopted in this work. Other results of Belton et al. (26, 27) clearly indicate that, on Rh (111), the N atom recombination is not the rate-limiting step in the reduction of NO by CO.

Equation [8] can be linearized according to Eq. [13]:

$$\sqrt{\frac{P_{NO}}{r_{CO}}} = \frac{1 + \lambda_{NO}P_{NO} + \lambda_{CO}P_{CO}}{\sqrt{k_3\lambda_{NO}}}. \qquad [13]$$

Figures 1 and 2 show the plots of $(P_{NO}/r)^{0.5}$ as a function of P_{NO} and P_{CO}, respectively, at constant CO and NO partial pressures on Rh/Al$_2$O$_3$. Linear plots were obtained for this catalyst, taking into account the margin of error of the experimental rates. According to these observations, Eq. [8] correctly fits the CO and NO dependencies of the CO + NO
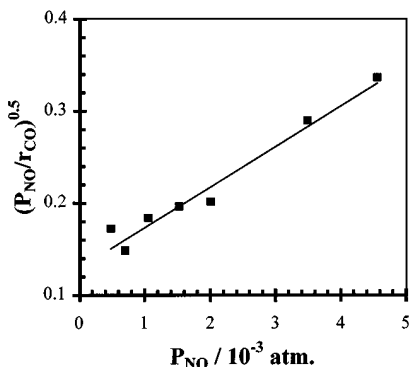

FIG. 2. Plot of $(P_{NO}/r_{CO})^{0.5}$ versus P_{NO} for Rh/Al$_2$O$_3$ in the case of competitive adsorptions of NO and CO; T = 300°C, $P_{CO} = 5 \times 10^{-3}$ atm.

TABLE 5

Kinetic and Thermodynamic Parameters for the Reaction of CO Oxidation by NO over Pt, Rh, and Pt−Rh on Alumina in the Case of Competitive Adsorptions of the Reactants

Catalyst		NO dissociation rate constant		Adsorption equilibrium constants (atm^{-1})	
		$10^3 \cdot k_3{}^a$	$k_3'{}^b$	λ_{CO}	λ_{NO}
Pt/Al$_2$O$_3{}^c$	[a]	8.9	316	127	15
	[b]	11.4	404	121	11
Rh/Al$_2$O$_3$	[a]	245	13409	115	480
	[b]	225	12315	71	472
Pt−Rh/Al$_2$O$_3$	[a]	12.9	285	92	192
	[b]	12.5	276	92	195

Note. Calculation from [a] graphic method, [b] optimization method.
[a] Specific rate constant (mol h^{-1} g^{-1} of catalyst).
[b] Intrinsic rate constant (molec. h^{-1} surf. metal at^{-1}).
[c] From Ref. (15).

reaction rate for Rh/Al$_2$O$_3$. The constants k_3, λ_{NO}, and λ_{CO} can further be estimated from the slopes and intercepts of the straight lines and they are listed in Table 5, together with those obtained in Ref. (15) for Pt/Al$_2$O$_3$. A second set of values has been obtained by using an optimization method, based on the classical least squares method, as explained in Ref. (15).

As seen in Table 5, the comparison between these two sets of values shows some discrepancies in the case of Rh/Al$_2$O$_3$ while the agreement is better for Pt/Al$_2$O$_3$. Let us recall that for the graphic method the pressures of CO and NO are alternately considered as constant. However, only the initial values for P_{CO} (or P_{NO}) are the same, and, since the conversion of CO (or NO) changes, the real partial pressures are not exactly constant. Such slight variations introduce an error on the values of parameters calculated from the slopes and intercepts of the straight lines. Since Rh is consistently more active than Pt (Table 1) the conversions (also the partial pressures) vary in a wider range on Rh/Al$_2$O$_3$ (35 to 67% for NO conversion) than on Pt/Al$_2$O$_3$ (1 to 2% for NO conversion), despite the fact that lower amounts of catalyst were used with Rh/Al$_2$O$_3$ than with Pt/Al$_2$O$_3$ (0.023 g for Rh/Al$_2$O$_3$ instead of 0.2 g for Pt/Al$_2$O$_3$). Consequently the errors on the k_3 and λ values are greater for Rh/Al$_2$O$_3$ than for Pt/Al$_2$O$_3$. On the contrary, the optimization method used the real values of the partial pressures and a greater number of measurements (the two series obtained at P_{CO} and P_{NO} constant). According to this procedure the accuracy on the adjusted parameters, k_3 and λ, should be better. This explains why the agreement between the two methods is not so good for Rh/Al$_2$O$_3$. In such a case the values calculated by the optimization method are probably more accurate.

Accordingly, changes in activity by varying P_{NO} and P_{CO} at 300°C on Rh/Al$_2$O$_3$ can probably be modelled by the dissociative mechanism previously established for Pt/Al$_2$O$_3$ (15). This conclusion is consistent with earlier studies on monometallic Pt and Rh based catalysts (18, 19, 28) which suggest that the dissociation of adsorbed NO limits the CO oxidation by NO.

It is interesting to note, that Pt and Rh, in the monometallic catalysts, mainly differ by λ_{NO} and k_3, which are concerned with NO adsorption and NO dissociation. Both values are considerably higher on Rh/Al$_2$O$_3$ than on Pt/Al$_2$O$_3$. Such a direct relationship between NO adsorption and dissociation (the higher the λ_{NO}, the higher the k_3 value) has already been observed on Pt deposited on various supports and discussed in a previous paper (15). These higher values for k_3 and λ_{NO} are responsible for the higher activity of Rh/Al$_2$O$_3$.

1.2. Bimetallic Pt−Rh/Al$_2$O$_3$ Catalyst

In the case of the bimetallic Pt−Rh/Al$_2$O$_3$ catalyst the situation is more complex because of the presence of the two metals at the surface. Two extreme cases have been examined. In the first one, Pt−Rh/Al$_2$O$_3$ has been treated as a monometallic catalyst; i.e., we have considered only one type of reaction site at the surface of the catalyst. This assumption is supported by the work of Ng *et al.* (6), mentioned in the Introduction, where it is suggested that the primary effect of Pt in Pt$_{10}$Rh$_{90}$ (111) is to dilute Rh which is more active than Pt for the CO + NO reaction. However, they also noticed that the changes in the catalytic performance could be consistent with an electronic modifications of all surface atoms.

The second set of assumptions is suggested by a paper of Van Slooten and Nieuwenhuys (16), where results of an IR study of CO and NO adsorption on Pt−Rh/SiO$_2$ led the authors to the conclusion that CO is preferentially adsorbed on Pt and NO on Rh. This conclusion is well supported by the results of the previous paragraph in this study which have shown that CO is more strongly adsorbed on Pt than on Rh ($\lambda_{CO} = 120$ and 70 atm^{-1} respectively on Pt and on Rh), while the opposite is true for NO ($\lambda_{NO} = 10-15$ and ~480 atm^{-1} respectively on Pt and on Rh). Consequently it seems reasonable to consider that, if Pt and Rh preserve their individual adsorption properties in the bimetallic Pt−Rh/Al$_2$O$_3$ catalyst, CO and NO could be mainly adsorbed noncompetitively on different sites, Pt for CO and Rh for NO. Let us note that, if this hypothesis is valid, the values obtained for λ_{CO} on Pt/Al$_2$O$_3$ and Pt−Rh/Al$_2$O$_3$ should be similar, as well as those of λ_{NO} on Rh/Al$_2$O$_3$ and on Pt−Rh/Al$_2$O$_3$.

1.2.1. Competitive adsorptions of CO and NO.

Application of Eq. [13] to the results obtained on Pt−Rh/Al$_2$O$_3$ at various CO and NO partial pressures give the straight lines in Figs. 3 and 4 and the values of k_3, λ_{CO}, and λ_{NO} in
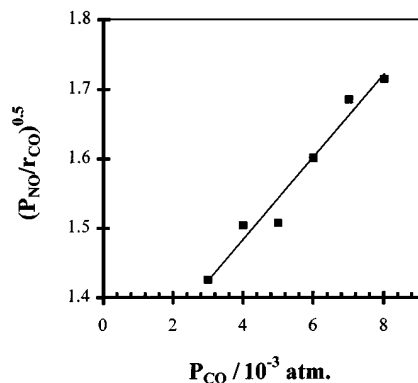

FIG. 3. Plot of $(P_{NO}/r_{CO})^{0.5}$ versus P_{CO} for Pt−Rh/Al$_2$O$_3$ in the case of competitive adsorptions of NO and CO; T = 300°C, $P_{NO} = 5 \times 10^{-3}$ atm.

Table 5. The good agreement between the two sets of values obtained from the graphic and the optimization methods can be noticed.

1.2.2. Noncompetitive adsorptions of CO and NO.

According to the second model, on Pt−Rh/Al$_2$O$_3$, it was assumed that NO is mainly adsorbed on Rh, whereas CO is preferentially coordinated to Pt sites. Consequently, the adsorption reactions can be derived from these assumptions,

$$CO + *' \Leftrightarrow CO^{*'} \qquad [14]$$

$$NO + * \Leftrightarrow NO^*, \qquad [15]$$

where $*$ and $*'$ stand for a Rh and a Pt site, respectively.

The adsorptions of the reactants are supposed to be at equilibrium and the dissociation of adsorbed NO is considered as rate limiting. In the dissociation step the additional vacant nearest-neighbour site can be either one Pt or one Rh site:
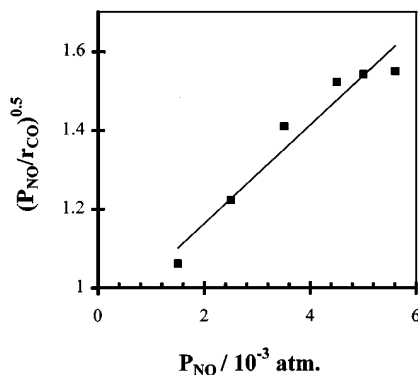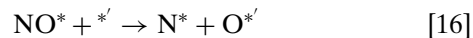
$$NO^* + *' \rightarrow N^* + O^{*'} \qquad [16]$$

FIG. 4. Plot of $(P_{NO}/r_{CO})^{0.5}$ versus P_{NO} for Pt−Rh/Al$_2$O$_3$ in the case of competitive adsorptions of NO and CO; T = 300°C, $P_{CO} = 5 \times 10^{-3}$ atm.

or

$$NO^* + {}^* \rightarrow N^* + O^*. \qquad [17]$$

The following equations can be established from the reactions [16] and [17]:

$$r_{CO} = k_{16}\theta_{NO}(1 - \theta_{CO})$$

$$= \frac{k_{16}\lambda_{NO}P_{NO}}{(1 + \lambda_{NO}P_{NO})(1 + \lambda_{CO}P_{CO})} \quad \text{from step [16]} \quad [18]$$

if the dissociation of NO adsorbed on Rh can occur only with a neighbour Pt site;

$$r_{CO} = k_{17}\theta_{NO}(1 - \theta_{CO}) = \frac{k_{17}\lambda_{NO}P_{NO}}{(1 + \lambda_{NO}P_{NO})^2} \quad \text{from step [17]}$$
$$[19]$$

if it occurs only with a neighbour Rh site;

$$r_{CO} = k_{17}\theta_{NO}(1 - \theta_{NO}) + k_{16}\theta_{NO}(1 - \theta_{CO})$$

$$= \frac{k_{17}\lambda_{NO}P_{NO}}{(1 + \lambda_{NO}P_{NO})^2} + \frac{k_{16}\lambda_{NO}P_{NO}}{(1 + \lambda_{NO}P_{NO})(1 + \lambda_{CO}P_{CO})} \quad [20]$$

if the dissociation can take place on both sites.

k_{16} and k_{17} are the rate constants for the dissociation of adsorbed NO on vacant nearest neighbour Pt and Rh sites, respectively. Clearly, Eq. [19] which is unable to describe the CO partial pressure dependency of the reaction rate can be ruled out. Only Eq. [18] can be linearized, yielding to Eq. [21]:

$$\frac{P_{NO}}{r_{CO}} = \frac{(1 + \lambda_{CO}P_{CO})(1 + \lambda_{NO}P_{NO})}{k_{16}\lambda_{NO}}. \qquad [21]$$

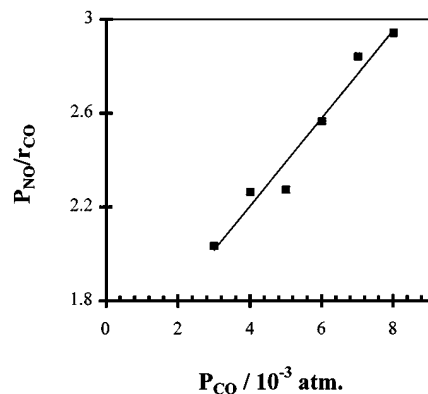Consequently, the kinetic and thermodynamic constants can be calculated either by the graphic method (see Figs. 5

FIG. 6. Plot of P_{NO}/r_{CO} versus P_{NO} for Pt–Rh/Al$_2$O$_3$ in the case of noncompetitive adsorptions of NO and CO; $T = 300°C$, $P_{CO} = 5 \times 10^{-3}$ atm.

and 6) or the optimisation method. On the other hand, the resolution of Eq. [20] can only be achieved by a mathematical procedure. The various constant values are listed in Table 6.

Let us note the acceptable agreement between data obtained from the graphic and optimisation methods. It is noteworthy that the rate constant k_{17} for the dissociation of NO$_{ads}$ with a Rh vacant site is negligible by comparison with k_{16} when NO dissociates on a Pt vacant site. Hence, if the postulated mechanism is valid, the dissociation of NO adsorbed on Rh sites takes place preferably with a Pt neighbour site.

Let us mention that the criteria of validity concerning the values of λ_{CO} and λ_{NO} are met since λ_{CO} is about the same on Pt/Al$_2$O$_3$ (121–127 atm^{-1}) and on Pt–Rh/Al$_2$O$_3$ (122–129 atm^{-1}) and λ_{NO} on Rh/Al$_2$O$_3$ (470–480 atm^{-1}) and on Pt–Rh/Al$_2$O$_3$ (450–500 atm^{-1}).

Consequently both hypothesis are in agreement with our experimental results, but the similarities of the values of λ_{CO} and λ_{NO} on Pt and Pt–Rh, on the one hand, and Rh

FIG. 5. Plot of P_{NO}/r_{CO} versus P_{CO} for Pt–Rh/Al$_2$O$_3$ in the case of noncompetitive adsorptions of NO and CO; $T = 300°C$, $P_{NO} = 5 \times 10^{-3}$ atm.

TABLE 6
Kinetic and Thermodynamic Adsorption Constants for CO and NO on Pt–Rh/Al$_2$O$_3$ Catalysts in the Case of Noncompetitive Adsorptions of the Reactants

Assumptions		NO dissociation rate constants (mol h^{-1} g^{-1})		Adsorption equilibrium constants (atm^{-1})	
		$10^3 \cdot k_{16}{}^a$	$k_{17}{}^b$	λ_{CO}	λ_{NO}
Pt site	[a]	8.47	—	129	449
	[b]	4.74	—	122	505
Either Pt or Rh site	[b]	4.74	0	122	505

Note. [a] from the graphic method; [b] from the optimization method.
[a] Dissociation of NO on a vacant nearest-neighbour Pt site.
[b] Dissociation of NO on a vacant nearest-neighbour Rh site.

and Pt−Rh, on the other hand, together with the IR study of Van Slooten and Nieuwenhuys seem strong arguments in favour of the noncompetitive adsorptions of CO and NO.

At a first glance it may seem surprising that the dissociation of NO_{ads} with a Rh neighbour site would be much slower ($k_{17} \sim 0$) than with a Pt neighbour site (k_{16}), since on monometallic catalysts the rate constant of NO dissociation is much higher on Rh than on Pt. However, this observation, together with the fact that k_{16} on Pt−Rh/Al_2O_3 is smaller than k_3 on Rh/Al_2O_3, whereas the Rh content is similar on both catalysts, could be accounted for by several explanations. First, this could be a consequence of Pt surface enrichment in the bimetallic catalyst. Moreover, Pt and Rh atoms could not be randomly distributed at the surface; for example, Rh atoms could be surrounded by Pt atoms. Another explanation could be found in the well-known structure sensitivity of NO dissociation (21, 29, 30), Rh atoms being segregated in locations (for instance, on some dense planes where they would be highly coordinated), where they would be less reactive. Another possibility is that the neighbour site is composed of n metal atoms. In such a case the probability of finding Pt sites to that of finding Rh sites would be in the ratio $(X_{Pt}/X_{Rh})^n \cong 3^n$ (where X_{Pt} and X_{Rh} are the molar fractions of Pt and Rh).

2. NO Conversion

As far as S_{N_2O} is concerned, it must be mentioned that N_2O is the major primary N-containing product in the CO + NO reaction on Rh based catalysts. Rh/Al_2O_3 and Pt−Rh/Al_2O_3 exhibit a poorer selectivity for the production of N_2 ($S_{N_2O} \sim 70\%$) than Pt/Al_2O_3 ($\sim 50\%$) which emphasizes previous observations made by Hecker and Bell on 5 wt% Rh/SiO_2 (18), by Permana *et al.* (22, 23) on Rh (111), and by Cho *et al.* at low temperature on Rh/Al_2O_3 (31).

Let us note that, on Rh/Al_2O_3 and Pt−Rh/Al_2O_3, S_{N_2O} is insensitive to reaction conditions (temperatures from 230 to 300°C and partial pressures of the reactants), while it has been found to change both with the NO partial pressure and with the temperature on Pt/Al_2O_3 (Ref. (15) and Table 4).

It must be mentioned that on Pt−Rh/Al_2O_3 the values of S_{N_2O}, relative to the part of the experiment when P_{NO} was varied (Table 4), are slightly erroneous because of temporary problems in integrating the N_2 chromatographic peak which was slightly overestimated. The value of S_{N_2O} can be considered as roughly constant throughout the experiment. Moreover, Table 4 clearly shows that the selectivity S_{N_2O} is similar on Rh/Al_2O_3 and Pt−Rh/Al_2O_3 (0.69 ± 0.03). Such a selectivity insensitivity of CO + NO reaction on Rh has already been mentioned on Rh (111) (22, 23) at $P_{NO} = 0.01$ atm.

These observations (same selectivity and similar insensitivity to kinetic conditions for both catalysts) show that Rh governs the selectivity of NO conversion and they provide additional arguments in favour of the hypothesis of preferential adsorption of NO on Rh for Pt−Rh/Al_2O_3, since for both catalysts, NO is adsorbed on Rh and yields one N atom adsorbed on Rh after dissociation. Hence steps [4], [5], and [6] which account for the formation of N_2 and N_2O are concerned only with Rh.

Concerning the rate of NO conversion, it can easily be established (15) that r_{NO}, the overall rate of NO transformation in the CO + NO reaction, is related to that of CO oxidation by NO, r_{CO}, by

$$r_{NO} = r_{CO}\left(1 + \frac{1}{1 + 2r_{N_2}/r_{N_2O}}\right), \qquad [22]$$

where r_{N_2} and r_{N_2O} are the rates of formation of N_2 and N_2O, respectively.

Since the ratio r_{N_2}/r_{N_2O} is related to S_{N_2O}, which is independent of the temperature and of the CO and NO partial pressures, r_{NO} is proportional to r_{CO} for Rh-containing catalysts ($r_{NO} \cong 1.5 r_{CO}$ for Rh/Al_2O_3 and Pt−Rh/Al_2O_3) and obeys for these catalysts the same kind of kinetic expression.

Belton and Schmieg (28) have mentioned similar observations in the CO + NO reaction performed on Rh (111). According to these authors, such an insensitivity of S_{N_2O} to experimental conditions could be explained, assuming that N_2O is formed via step [6] and N_2 via step [4]. In this way changes in θ_N and θ_{NO} due to variations of partial pressure of NO should be balanced by differences in the energies of activation associated to steps [4] and [6]. Clearly, one can discard this interpretation since the activation energies ascribed to the transformation of NO into N_2 and N_2O on Rh/Al_2O_3 and Pt−Rh/Al_2O_3 slightly vary within the margin of error.

According to the proposed mechanism for the CO + NO reaction the rates of N_2 and N_2O production can be expressed by Eqs. [23] and [24],

$$r_{N_2} = k_4\theta_N^2 + k_5\theta_N\theta_{NO} \qquad [23]$$

$$r_{N_2O} = k_6\theta_N\theta_{NO}, \qquad [24]$$

where θ_N and θ_{NO} represent N and NO surface coverages.

Consistently, the selectivity for the formation of N_2O is

$$\frac{r_{N_2}}{r_{N_2O}} = \left(\frac{k_4}{k_6}\frac{\theta_N}{\theta_{NO}}\right) + \frac{k_5}{k_6}. \qquad [25]$$

In an earlier study of the CO + NO reaction on Pt based catalysts (15) by calculating the ratio θ_N/θ_{NO} we have established Eq. [26] relating the ratio r_{N_2}/r_{N_2O} to the NO partial pressure:

$$\frac{4r_{N_2}}{r_{N_2O}} = \left(1 + \frac{k_5}{k_6}\right)\sqrt{1 + \frac{16k_4k_3}{(k_5 + k_6)^2\lambda_{NO}P_{NO}}} + \frac{3k_5}{k_6} - 1.$$

$$[26]$$

On Pt/Al$_2$O$_3$ the ratios k$_4$/k$_6^2$ and k$_5$/k$_6$ have been respectively found equal to 0.25 and 0.30 (15).

Let us note that this expression is valid for competitive adsorptions of CO and NO, hence for monometallic catalysts. In the case of noncompetitive adsorptions, that is probably for Pt−Rh/Al$_2$O$_3$ the expression of r$_{N_2}$/r$_{N_2O}$ becomes

$$\frac{4r_{N_2}}{r_{N_2O}} = \left(1+\frac{k_5}{k_6}\right)\sqrt{1+\frac{16k_4k_{16}(1+\lambda_{NO}P_{NO})}{(k_5+k_6)^2(1+\lambda_{CO}P_{CO})\lambda_{NO}P_{NO}}} + \frac{3k_5}{k_6} - 1. \qquad [27]$$

The fact that r$_{N_2}$/r$_{N_2O}$ hardly changes with P$_{NO}$, both for Rh/Al$_2$O$_3$ and on Pt−Rh/Al$_2$O$_3$, suggests that the terms 16k$_4$k$_3$/(k$_5$ + k$_6$)^{2}λ$_{NO}$P$_{NO}$ and 16k$_4$k$_{16}$(1 + λ$_{NO}$P$_{NO}$)/(k$_5$ + k$_6$)^2(1 + λ$_{CO}$P$_{CO}$)λ$_{NO}$P$_{NO}$ are small on these two catalysts. In such a case Eqs. [26] and [27] are approximated to

$$\frac{r_{N_2}}{r_{N_2O}} \cong \frac{k_5}{k_6}. \qquad [28]$$

Hence the selectivity of NO conversion on catalysts containing Rh is mainly governed by the relative rates of steps [5] and [6] which both involve N and NO adsorbed on Rh. The value of k$_5$/k$_6$ is similar on Rh/Al$_2$O$_3$ and on Pt−Rh/Al$_2$O$_3$ (around 0.45). It must also be mentioned that it is of the same order of magnitude as for Pt/Al$_2$O$_3$ (0.3).

Unfortunately nothing can be said on the relative values of k$_4$ in comparison with those of k$_5$ and k$_6$, since, if the ratio k$_4$k$_3$/(k$_5$ + k$_6$)^{2}λ$_{NO}$ is much lower than 1, this is probably because of both the low value of k$_3$ and the high value of λ$_{NO}$, that is, because θ$_N$ is very low in comparison with θ$_{NO}$, N adsorbed on Rh being very reactive. Consequently, the rate of step [4] is negligible in comparison with those of steps [5] and [6]. This situation is different from that observed for Pt/Al$_2$O$_3$, where the slope of the curve r$_{N_2}$/r$_{N_2O}$ versus 1/P$_{NO}$ and then the ratio k$_4$/(k$_4$ + k$_6$)^2 could be estimated. This is readily explained by the weak NO adsorption on Pt which resulted in a low θ$_{NO}$, hence in a lower ratio θ$_{NO}$/θ$_N$ than for the Rh-containing catalysts, and step [4] can occur at a rate similar to those of steps [5] and [6].

To summarize, the changes of the selectivities in the NO conversion on Pt/Al$_2$O$_3$, Rh/Al$_2$O$_3$, and Pt−Rh/Al$_2$O$_3$ are very much in agreement with the change in the strength of NO adsorption on these metals.

CONCLUSION

The kinetics of the oxidation of CO by NO has been investigated on Pt−Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ at 300°C.

Our results have been interpreted on the basis of a mechanism selected for Pt catalysts which involved CO and NO nondissociative adsorptions and a step of dissociation of adsorbed NO molecule with a vacant-neighbour site as rate determining.

For Pt−Rh/Al$_2$O$_3$, rate expressions have been derived using two models which assumed respectively competitive adsorptions of NO and CO on the same sites or noncompetitive adsorptions of the reactants. Both rate expressions are in agreement with experimental results. But with the second set of assumptions (noncompetitive adsorptions of CO and NO) the value of λ$_{NO}$, the equilibrium adsorption constant of NO on Pt−Rh/Al$_2$O$_3$ is similar to that obtained on Rh/Al$_2$O$_3$, whereas λ$_{CO}$, the equilibrium adsorption constant of CO on Pt−Rh/Al$_2$O$_3$, is comparable to that on Pt/Al$_2$O$_3$, NO is much more strongly adsorbed on Rh than on Pt (λ$_{NO}$ about 500 atm^{-1} against 15 atm^{-1}). Moreover, it has been shown that the dissociation of NO adsorbed on Rh occurs preferably on a Pt vacant-neighbour site.

The conversion of NO gives N$_2$O as the major primary product on both Pt−Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$. This selectivity S$_{N_2O}$ is higher than on Pt/Al$_2$O$_3$. It is similar on Pt−Rh/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ and has been shown to be practically independent of the temperature and of the NO and CO partial pressures, which is another argument in favour of preferential NO adsorption on Rh since, in that case, only Rh is involved in N$_2$ and N$_2$O formations. Another conclusion is that, contrary to what has been observed for Pt based catalysts, N$_2$ seems to be mainly formed via step [5] involving a bimolecular reaction between N$_{ads}$ and NO$_{ads}$, step [4] being slow in comparison with steps [5] and [6] probably because of (i) high NO surface coverage resulting from the very high λ$_{NO}$ value, (ii) low N surface coverage resulting from a very high reactivity of N adsorbed on Rh.

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