# Activity during reduction of NO by CO over bimetallic palladium–rhodium / silica catalysts

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Received 25 January 1995; accepted 19 July 1995

A study of the activity of bimetallic Pd–Rh catalysts supported on silica in the reduction of NO by CO is presented. The catalysts were prepared by three different methods: (1) Pd and Rh were coimpregnated on the support, (2) Rh was impregnated first and, after calcining, the sample was impregnated with Pd, (3) the monometallic Pd and Rh catalysts were physically mixed. The results showed that the activity of the catalysts prepared by coimpregnation was much lower than that of the other two catalysts.

**Keywords:** NO reduction; CO; palladium–rhodium catalysts

## 1. Introduction

The oxidation of CO (CO–$O_2$ reaction) and the reduction of NO by CO (CO–NO reaction) are important in the three-way catalysts containing supported noble metals that are used for the control of automobile emissions.

The CO–$O_2$ reaction has been studied extensively [1], and has been included as an example of interesting phenomena that occur in non-equilibrium systems, such as transition phases, oscillations and others [2]. The CO–NO reaction, which is important not only because it eliminates NO but also because it inhibits the catalytic oxidation of CO [3], although not as widely studied as the CO–$O_2$ reaction, has received much attention in recent years [4], even in a more theoretical context, as another interesting system of non-equilibrium phenomena [5,6].

Rhodium, which shows a high catalytic activity for the reduction of NO with CO and is therefore a basic constituent of three-way catalysts, has been studied extensively. Special attention has also been given to structural aspects of the catalyst, e.g. the influence of the support [7,8], the effects of promoters added to the system [9], and the addition of other metals such as platinum and palladium [10,11].

In a previous paper from this laboratory [11] aimed at providing an understanding of structural effects such as the influence of alloy formation in the metal concentration on the surface, a study was made of the activity of silica-supported Rh and Pd bimetallic catalysts prepared by different methods on the CO–$O_2$ reaction. Those studies are continued in this paper using the same catalysts and the CO–NO reaction. In addition to the determination of the reaction rate, the calculation of the selectivity of the catalysts toward the formation of $N_2O$ has been included. The selectivity was calculated by direct analysis of the $N_2O$ concentration in the outward flow from the reactor, something that, as far as we can tell, has not been done in other experimental work reported in the literature.

As described earlier [11], the catalysts were prepared by three methods. The first one, described by Del Angel et al. [9], consists in the codeposition of both metals. The second method, described by Oh and Carpenter [7], is that of sequential impregnation, in which there is a lower probability for alloy formation, since the particles of the second impregnated metal find preferentially the surface of the support. Therefore, both metals exist mainly as monometallic crystals on the surface. The third method of preparation consists in physically mixing the monometallic Rh and Pd catalysts.

## 2. Experimental

The first column of table 1 shows the composition and preparation of the mixture while the other two columns present the dispersion values obtained by chemisorption of hydrogen at 60°C, and the ignition temperature. The catalysts were prepared as described previously [11] using silica (Cabosil EH-5) with a BET surface area of 314 $m^2/g$ as the support.

The coimpregnated catalysts (CI) were prepared by impregnating the support simultaneously with Pd and Rh using the incipient wetness impregnation method.

Table 1
Chemisorption of hydrogen (60°C) and ignition temperature

| Sample composition Rh–Pd [a] (%) | Hydrogen (mol/mol metal) | Ignition temp. (°C) |
|---|---|---|
| 100 Rh | 0.29 | 238 |
| 70 Rh–30 Pd CI | 0.32 | 260 |
| 70 Rh–30 Pd SI | 0.42 | 255 |
| 70 Rh–30 Pd PM | 0.27 | 245 |
| 33 Rh–67 Pd CI | 0.37 | 310 |
| 33 Rh–67 Pd SI | 0.30 | 278 |
| 33 Rh–67 Pd PM | 0.24 | 252 |
| 16 Rh–84 Pd CI | 0.25 | 327 |
| 16 Rh–84 Pd SI | 0.31 | 295 |
| 33 Rh–84 Pd PM | 0.23 | 258 |
| 100 Pd | 0.22 | 340 |

[a] CI, impregnated; SI sequentially impregnated; PM, physically mixed.

The salts $RhCl_3$ and $PdCl_2$ were dissolved in the correct quantity of an aqueous solution of HCl (pH = 2). The impregnated support was dried at room temperature for 24 h, and then at 105°C for 12 h. The monometallic catalysts were prepared by the same method.

The sequentially impregnated catalysts (SI) were obtained in two steps. First, the samples were impregnated with pure Rh using the above CI method, and then they were heated at 500°C for 2 h to oxidize the Rh. In the second step, the samples were impregnated with Pd using a solution of palladium acetylacetonate in dichloromethane to avoid dissolving the impregnated Rh. The samples impregnated with both metals were dried in the same way as the CI samples.

The physical mixtures of bimetallic catalysts (PM) were prepared by mixing the 2% monometallic catalysts in the correct amount to yield the same bulk composition as the bimetallic catalysts.

All the catalysts were reduced in hydrogen at 450°C for 5 h, then $H_2$ was desorbed for 2 h at the same temperature, and then the samples were cooled to 25°C. The chemisorption of $H_2$ was carried out in a conventional flow apparatus at 60°C to avoid the formation of hydrides [12], measuring the pulse adsorption (200 μl) of each gas by means of a thermal conductivity detector.

The activity of the catalysts was determined in a plug flow reactor fed with 10% CO, and at a flow-rate of 100 $cm^3/min$, balanced with helium. The catalyst load was 0.3 g, giving a bed thickness of 0.8 cm. The catalyst temperature was measured with a thermocouple inserted in the catalytic bed connected to a recorder. The catalytic reaction rates were obtained in the temperature range of 175–330°C at conversions lower than 5%, and were calculated from the mass balance equation for a differential reactor. The conversion was obtained by analyzing the input and output of the reactor by gas chromatography. The selectivity toward $N_2O$ was determined by measuring directly, by gas chromatography, the amount of $N_2O$ produced during the reaction. A Hayasep Q column (10 feet long and 1/8 inch in diameter) was used, operating at a temperature of 50°C with a He flow of 20 $cm^3/min$, connected to an NWD detector. This column allows the separation of $N_2$, $N_2O$ and $CO_2$, making possible the direct analysis of all the reaction products. The ignition temperature of the catalysts was also determined during temperature-programmed reaction experiments for the reactant concentrations mentioned above, at a heating rate of 5°C/min controlled by a temperature programmer (Eurotherm model 211).

## 3. Results

Fig. 1 shows the activity of the various catalysts in terms of the rate of the CO–NO reaction in moles of NO converted per mole of exposed metal per second.

Fig. 1a shows that, under the experimental conditions described above, the activity of the monometallic Rh catalyst is higher than that of the Pd catalyst at all the

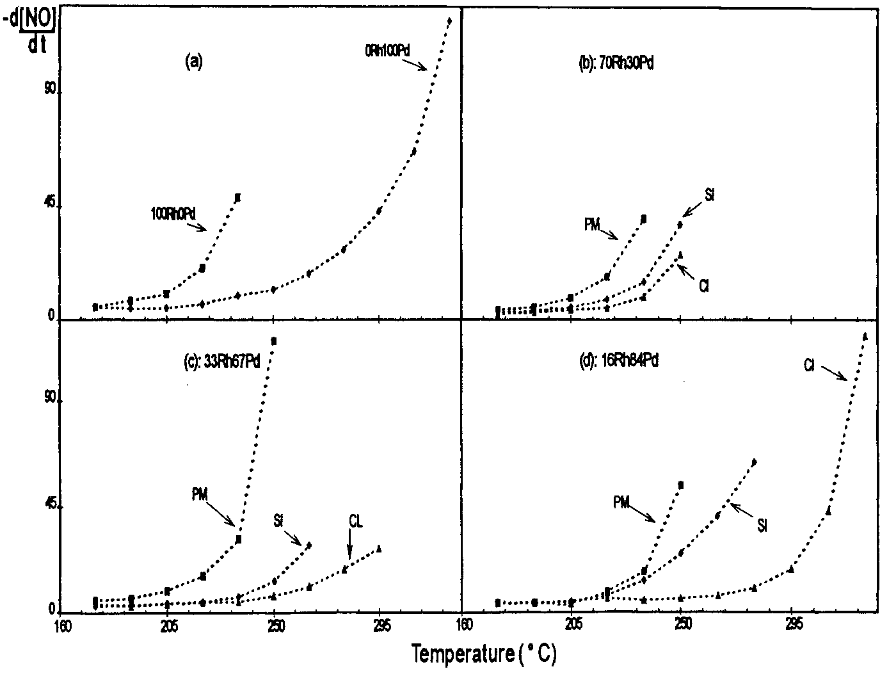

Fig. 1. NO reduction rate $10^3$ (mol/(s mol metal)) of catalysts at different temperatures.

temperatures used. On the other hand, figs. 1b and 1c show that, within the same temperature range, in the bimetallic catalysts the activity of physically mixed preparations (curve PM) is higher than that of the preparations made by sequential impregnation (curve SI), and these, in turn, are more active than the preparations made by coimpregnation (CI). The ignition temperatures are presented in table 1 for all the systems. The results of the selectivity of the reaction toward $N_2O$ ($S_{N_2O}$), calculated from the relation

$$S_{N_2O} = \frac{\text{moles } N_2}{\text{moles } N_2O + \text{moles } N_2},$$

showed, surprisingly, that it did not vary significantly with temperature within the ranges shown in fig. 1, keeping a constant value of about 0.4. This behavior was shown by all the catalysts, regardless of the method used for their preparation.

## 4. Discussion

The activities of the experiments shown in figs. 1a–1d show a behavior similar to that observed recently in this laboratory [11] for the $CO–O_2$ system over the same catalysts. This is interesting because it points to some analogies in the behavior of both systems, related basically to the requirement of a certain probability of finding an important number of superficial Rh atoms that are necessary for the dissociation of oxygen in the CO–$O_2$ reaction and of NO in the CO–NO reaction on the surface. This explains the fact that some situations discussed in theory and simulations, such as reaction windows, phase changes from first to second order between poisoned and active superficial phases, and others of great interest in irreversible thermodynamics that have been studied exhaustively in the CO–$O_2$ system by means of MC simulations and theoretical methods such as that of clusters [2], are now being considered for the CO–NO system [6], the mechanistic complexity of which makes it far more interesting.

The above allows an important part of the explanations given previously for the CO–$O_2$ system to apply also to the CO–NO system. For example, fig. 1a makes it possible for the discussion of the results to refer mainly to the Rh activity in the different catalysts. In figs. 1b–1d two phenomena explain the observed behaviors. The first one refers to the formation of superficial alloys, with the consequent Pd enrichment on the surface of the catalyst. This phenomenon consists in the formation of two phases having different Rh and Pd composition. The Rh-rich phase is located under the Rh-deficient phase, thereby decreasing the catalyst activity. This, as observed by Del Angel et al. [9], occurs at Rh/Pd ratios greater than 0.7 [13]. The second phenomenon refers to the various forms observed for the CO molecules adsorbed on the catalyst, of which two are the most important. The linear form corresponds to one CO molecule per superficial metal atom, and the gem or dicarbonyl form to two CO molecules per metal atom. As pointed out by Dictor [13], and similarly to what happens in the CO–$O_2$ reaction [11], the gem form is less active than the linear form.

The activity sequence for the CO–NO reaction shown in fig. 1b for the catalysts prepared as described, can be explained in the same way as for the CO–$O_2$ reaction [11], since alloy formation with the subsequent surface enrichment with Pd is favored in the catalysts prepared by coimpregnation (CI), but is not possible with physical mixing (PM); in the case of sequential impregnation (SI) an intermediate situation may be assumed.

According to Mose and Gibbens [13], the formation of two phases in the superficial alloys is only observed at high Rh/Pd ratios. The explanation of the superficial enrichment, which is valid for the catalysts with high rhodium concentration (70% Rh–30% Pd), is not adequate for the catalysts of figs. 1c and 1d, in which the high superficial concentration of the less active gem form of CO adsorbed on the catalysts prepared by coimpregnation explains the activity sequences seen in figs. 1c and 1d. This is particularly important in the case of the catalysts with low rhodium composition (16% Rh–84% Pd) since, as commented previously [11], the presence of the gem form is observed especially on single Rh atoms which are important at low Rh proportions in the catalyst.

It is very interesting to consider the explanation given by Del Angel et al. [9] for the low activity of the CO–$O_2$ reaction on catalysts having low superficial Rh density, where the $O_2$ dissociation step, which requires the existence of neighboring

Rh atoms, is hindered. This explanation may be extended to the CO–NO reaction, since it has a similar NO dissociation step and is an alternative explanation of the low activity in the (CI) case of fig. 1d, which is the catalyst having the highest density of single Rh atoms on the surface.

The ignition temperatures reported in table 1 for the various catalysts agree well with the reaction rates observed at temperatures below the ignition temperature: i.e., ignition occurs at lower temperatures in the most active catalysts. Assuming that the mass and heat transfer rates do not vary substantially in the temperature-programmed reduction experiments, then the ignition temperature reflects the activity of the catalyst observed in the experiments at constant temperature, which is actually the case.

The experimentally determined behavior of the selectivity toward the formation of $N_2O$ with the increase in temperature requires a more detailed analysis. According to Oh and Eickel [15], selectivity toward $N_2O$ should decrease gradually as the temperature increases within the 150–300°C temperature range. In our experiments selectivity remained essentially constant in the temperature ranges used. This apparent discrepancy may have different causes. In the first place, our temperature ranges are in general smaller than that of Oh and Eickel [15], and the decrease in the catalyst activity may not be noticeable. Secondly, the experimental conditions of concentration and reactor type used by Oh and Eickel allow operation at high conversion ranges that cannot be achieved in our experiments. To check the above, an experiment was performed using the 2% Rh catalyst and raising the temperature of the reactor beyond the ignition temperature. In this experiment, the selectivity toward $N_2O$ was determined at 300°C when total CO conversion is greater than 90%, and a value of 5% was obtained. This decrease in selectivity actually confirms the trend reported in the literature. However, this result shows that even at that temperature there is a relatively important production of $N_2O$.

It is interesting to note that the increase in the total reaction rate without any variation in the selectivity as temperature increases has been predicted theoretically in work that will be reported shortly [16].

## 5. Conclusions

The activity of bimetallic Rh–Pd catalysts varies significantly with the method of impregnation of the metals in the reduction of NO by CO. The lowest activity was found with those catalysts prepared by coimpregnation of both metals. This low activity can be attributed to the formation of alloys with an enrichment of the surface with Pd and to the presence of the less active dicarbonyl CO. This is similar to what is observed during carbon monoxide oxidation thereby pointing to some analogies in the behavior of both systems, related basically to the requirement of a certain probability of finding an important density of superficial Rh atoms that are necessary for the dissociation of oxygen in the CO–$O_2$ reaction and of NO in the CO–NO reaction on the surface.

## Acknowledgement

The financial support of this work by FONDECYT and DTI (Universidad de Chile) is gratefully acknowledged.

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