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Influence of the precursors kind of catalysts on the course of a denox reaction

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Abstract

Many investigations of the approach to NO removal show that the preparation of catalysts and the precursor type both influence the course of the nitrogen oxide reduction by carbon oxide. Catalytic reduction of NO to nitrogen was carried out over supported platinum and palladium catalysts that were derived from chlorides and nitrates as the precursors. The effect of the kind of precursor and the activation conditions on the performance of Pt and Pd/Al_2O_3 preparation has been studied. The activity was largely dependent not only on the kind of metal support used but also on the precursors. The Pd supported catalyst derived from $Pd(NO_3)_2$ was much more active within 773 K temperature than the catalyst prepared from $PdCl_2$. The activity measurements for the Pt catalysts show that the catalyst prepared from H_2PtCl_6 was more active. The highest activity was revealed by the Pd/Al_2O_3 obtained from nitrates. The kind of metal cation bounded with carboxyls of EDTA and the kind of geometric structure of contact agent are important factors in generating supported catalysts.

Keywords: NO reduction by CO; Pd/Al_2O_3; Pt/Al_2O_3 catalysts; Catalyst precursor type

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1. Introduction

Nitrogen oxide removal is a very important industrial process. The catalytic reduction of nitrogen oxides by carbon oxide may offer an attractive alternative to the other method.

This paper aims at shedding light on the roles of Pd and Pt in the nitrogen oxide reduction by carbon oxide by comparing the activity. Interest in new approaches to NO removal were demonstrated that just as the type of precursor used the preparation of catalysts plays an important role. A detailed description of the problem has been given [1,2] and it was proved that the double impregnation method [3] of obtaining as well as treating catalysts precursors have a great influence on the catalysts' properties. This paper investigates the influence of the precursors of Pt and Pd catalysts on the course of a NO + CO reaction. In the many works concerned with platinum [4,5] and palladium [6,7] as catalysts of denox reactions a lot of attention has been paid to the size of metal crystallites and their arrangement on a surface support. The study of the influence of metal dispersion on the course the discussed reaction has proved that the qualities of catalysts can be modified by the double impregnation method [8,10].

Mallet et al. has shown that the type of precursor of Pt catalysts influences the magnitude of redox potential, which changes under the influence of the size of Pt crystallites [4]. The size of the metal crystallite obtained will depend on many factors: the concentration of metal ions in the impregnation solution, the presence of other ions, the time of exposition and the kind of support [9]. Beyond the preparation method the character of the substance used as a catalyst is also important. The rate of following reaction changes with the kind of catalysts precursor.

We presented the preparation of Pt and Pd contact agent supported over γ-Al_2O_3 and properties of these catalysts using nitrogen oxide conversion as a model reaction.

2. Experimental

The catalysts investigated, i.e. Pt/Al_2O_3 and Pd/Al_2O_3, supported on γ-Al_2O_3 obtained from St. Gobain, France ($S_{\text{total}} = 82.4\,\text{m}^2/\text{g}$), were prepared via following methods:

- Platinum catalysts were obtained by the double impregnation of alumina support. The Al_2O_3 support was exposed

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to activation in 0.1 M EDTA disodium salt solution at the temperature of 343 K for 30 min. After that time the activated forms of the support were dried at 383 K in air for 45 min. Next, the active support was impregnated at 343 K with $Pt(NO_3)_2$ or H_2PtCl_6, respectively.

- Palladium catalysts were obtained by the double impregnation of alumina support too. The Al_2O_3 support was exposed to activation in 0.1 M EDTA disodium salt solution at the temperature of 343 K for 30 min. After that time the activated forms of the support were dried at 383 K in air for 45 min. Next, the active support was impregnated at 343 K with $Pd(NO_3)_2$ or $PdCl_2$ solution, respectively.

All obtained catalysts were calcinated at 773 K for 1 h in air. After calcination in air catalysts were reduced with hydrogen at a temperature of 773 K for 3 h.

3. Methods

The content of platinum or palladium introduced to the catalysts was measured with the X-ray fluorescence (XRF) method in the Department of Analytical Laboratory, Faculty of Chemistry of UMCS. The total surface area of the catalysts was determined from argon adsorption at the temperature of liquid nitrogen by the BET method in a volumetric apparatus ensuring a vacuum of at least 10^{-5} mm Hg. The same apparatus was used for the determination of the active surface areas of the catalysts from the amounts of hydrogen (for Pt catalysts) or carbon monoxide (for Pd catalysts) adsorbed at room temperature. The active surface area was calculated assuming hydrogen binding stoichiometry to be 1:1 and the surface area covered by one hydrogen atom being 8.9 Å^2 [11]. Carbon oxide adsorption was measured assuming the binding stoichiometry to be 1:1 with a carbon monoxide molecule occupying an area of 8.9 Å^2 [12], too. The mean dimensions of the metal crystallites were determined by X-ray line broadening studies over the range 20–44.4°, after Warren, by using a DRON-2 diffractometer employing a Cu Kα radiation source, and also from chemisorption measurements. The average crystallite size was calculated from the results of hydrogen chemisorption from the equation

$$d\,(\text{nm}) = \frac{6 \times 10^4}{S_{\text{Pt,Pd}} \times \gamma_{\text{Pt,Pd}}} \qquad (1)$$

where $S_{\text{Pt,Pd}}$ is the surface area of 1 g of the platinum or palladium catalysts and $\gamma_{\text{Pt,Pd}}$ is the specific gravity of rhodium or platinum (Pt (21.5 g/cm^3) and Pd (12.0 g/cm^3)), assuming that a platinum and palladium crystallite is a sphere. For the calculation of the average particle size of Pt or Pd, 100% metal reduction was assumed.

Measurements of the rates of NO reduction by CO were carried out in a gradientless reactor based on the one described in [10]. All kinetic experiments were carried out in an atmosphere of helium, determining isothermally the relationship between the reaction rate of NO reduction and degree of NO conversion (iso-X) [8,11]. In this way, the functions $r = f(X)$ obtained at $T =$ constant served as a basis for plotting the dependence of the reaction rate for several conversion degree. The reaction was carried out with a NO:CO molar ratio of 1:1 (1500 ppm of NO and 1500 ppm of CO) at a temperature of 773 K. The reaction products were analyzed chromatographically using a Chrompack gas chromatograph with a PC computer as an integrator. The degree of nitrogen oxide conversion was calculated from the equation

$$X_{\text{NO}} = \frac{C^0_{\text{NO}} - C_{\text{NO}}}{C^0_{\text{NO}}} \qquad (2)$$

where C^0_{NO} is the concentration of NO at the inlet (1500 ppm) and C_{NO} the concentration of NO at the outlet.

The reaction rate were calculated using the following equation, valid for a gradientless reactor [10]:

$$r\,(\text{mol/g}_{\text{catal.}}\,\text{h}) = \frac{((C^0_{\text{NO}} - C_{\text{NO}})/C^0_{\text{NO}})F}{W} \qquad (3)$$

where F is the final volumetric rate and W the catalysts weight.

4. Results and discussion

Results obtained from adsorption measurements together with other physicochemical properties of platinum and palladium catalysts are presented in Table 1. To make the task clear, each type of precursor is discussed separately.

The data in Table 1 show that catalysts show great difference either on the metal loading, the active surface or crystallites size.

Fig. 1 show a comparison of activities of Pt/Al_2O_3 preparations obtained from different precursors, i.e. H_2PtCl_6 and $Pt(NO_3)_2$.

Fig. 2 show a comparison of activities of Pd/Al_2O_3 preparations obtained from different precursors, i.e. $PdCl_2$ and $Pd(NO_3)_2$.

The kind of platinum or palladium precursors was established to have a significant effect other catalysts activity. Figs. 3 and 4 show reaction rate of reduction NO on recounted on gram of metal.

In general, the preparations obtained on the basis of platinumchloric acid were more active than those based on platinum nitrate. It was found to have significant effect on the

Table 1
The physicochemical properties of catalysts

Sample (type of precursor)	Metal loading (wt.%)	Active surface area (m^2/g)	Crystallite size (nm)
Pt/Al_2O_3 (H_2PtCl_6)	1.07	5.23	4.9
Pt/Al_2O_3 ($Pt(NO_3)_2$)	1.22	1.21	18.9
Pd/Al_2O_3 ($PdCl_2$)	0.27	1.74	107
Pd/Al_2O_3 ($Pd(NO_3)_2$)	0.30	6.19	26.9

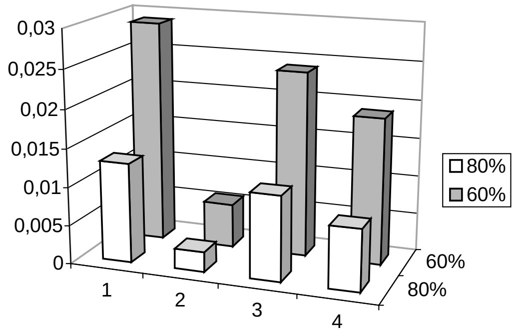

Fig. 1. The rate of a NO + CO reaction over Pt/Al_2O_3 obtained from H_2PtCl_6 (1, 2) and from $Pt(NO_3)_2$ (3, 4) at $T = 773\,K$ and $X_{NO} = 60$ or 80% (1, 3—reaction rate on gram of catalyst ($mol/g_{catal.}\,h$); 2, 4—reaction rate on m^2 surface ($mol/m^2\,h$)).

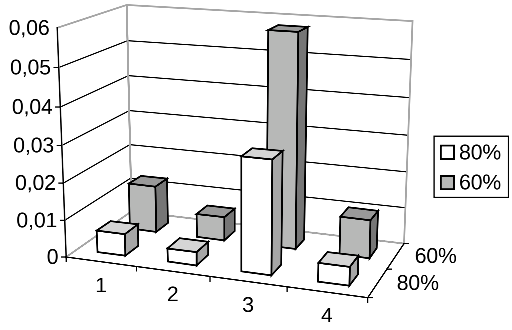

Fig. 2. The reaction rate of a NO + CO reaction over Pd/Al_2O_3 obtained from $PdCl_2$ (1, 2) and from $Pd(NO_3)_2$ (3, 4) at $T = 773\,K$ and $X_{NO} = 60$ or 80% (1, 3—reaction rate on gram of catalyst ($mol/g_{catal.}\,h$); 2, 4—reaction rate on m^2 surface ($mol/m^2\,h$).

activity of the chlorine series preparation for palladium, for which a drastic decrease in activity was noted.

Fig. 5 shows a comparison of activities of the chlorine and nitrate series for both platinum and palladium catalysts at conversion degree 60%.

The catalysts Pd which were obtained from $Pd(NO_3)_2$ show the greater rate on recounted on m^2 or gram of metal in comparison to $PdCl_2$.

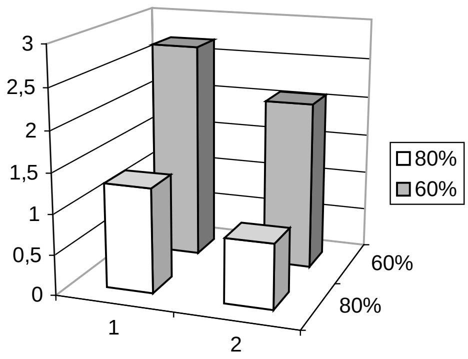

Fig. 3. The rate of a NO+CO reaction in $mol/g_{Pt}\,h$ over Pt/Al_2O_3 obtained from H_2PtCl_6 (1) and from $Pt(NO_3)_2$ (2) at $T = 773\,K$ and $X_{NO} = 60$ or 80%.

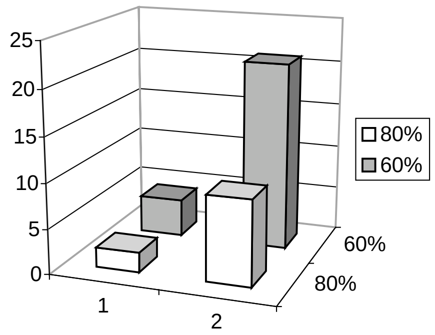

Fig. 4. The rate of a NO + CO reaction in $mol/g_{Pd}\,h$ over Pd/Al_2O_3 obtained from $PdCl_2$ (1) and from $Pd(NO_3)_2$ (2) at $T = 773\,K$ and $X_{NO} = 60$ or 80%.

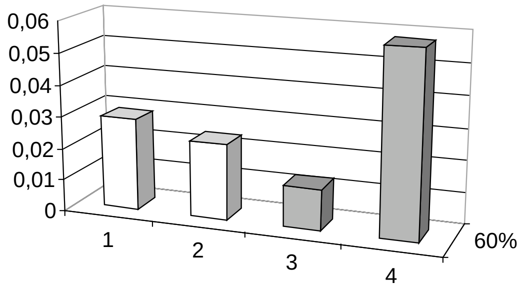

Fig. 5. The rate of a NO + CO reaction in $mol/g_{catal.}\,h$ on Pt/Al_2O_3 (1—obtained from H_2PtCl_6; 2—obtained from $Pt(NO_3)_2$) and on Pd/Al_2O_3 (3—obtained from $PdCl_2$; 4—obtained from $Pd(NO_3)_2$) at $T = 773\,K$ and $X_{NO} = 60\%$.

Then we compare rates of reaction between NO and CO on the Pt and Pd catalysts obtained from NO_3^- and Cl^- precursor we can state that the rate is the biggest for Pd catalysts obtained from $Pd(NO_3)_2$, at nitrogen oxide conversion 60% and in temperature 773 K.

In Table 2 relative rate of reduction of nitrogen oxide by carbon oxide by two kinds of precursor were compared. Value of rate of reaction for both series have shown that the activities of the nitrate series were higher for palladium catalysts.

The results have shown that the preparations obtained on the basis of chlorides have much better catalytic properties for platinum than palladium catalysts.

Analyzing the course of nitrogen oxide reduction on Pt catalysts it is necessary to mention that the bigger rate is obtained on these which were received from H_2PtCl_6.

Table 2
The relative rates of the NO + CO reaction for platinum and palladium catalysts at conversion degree 60%

Precursors	Relative rate of reaction		
	r (mol/g h)Pd/r (mol/g h)Pt	r (mol/m^2 h)Pd/r (mol/m^2 h)Pt	r (mol/g_{Pd} h)/ r(mol/g_{Pt} h)
Nitrate	2.42	0.55	10.05
Chloride	0.44	1.14	1.5

As far as it concerned Pt catalysts obtained from H_2PtCl_6 and $Pt(NO_3)_2$ there were the significant differences in rate counted into gram of Pt, but there were hardly any differences on the m^2 surface or on gram of catalysts. According to the work [13] impregnation solutions including chloride can cause corrosion processes but they are less receptive on the influence of water decreasing metals activity. The catalysts received from $Pt(NO_3)_2$ show more stability in reduction of nitrogen oxide process in examining temperature 773 K and they have more accessible active centers, which was proved by Burch and Millington [14]. Dependence of reaction rate on the conversion nitrogen oxide degree modifies quite differently in case of Pd catalysts. The reaction rate takes a course, which is much better for catalysts obtained from $Pd(NO_3)_2$. The significant differences are obtained from the rate converted into gram of Pd. The causes of that phenomena can be observed in chloride precursors tendentious to come into reactions with surface catalyst and as a result the activity is decreasing. It is proved by the work [15] where the author clam the creation of permanent connections between platinum and chlorine. We should not omit the fact that metals in shape of more dispersion have different qualities than arrangement in the crystallite size more then 5 nm [16] which also changes the course of reaction. The studies have shown that the Pd preparations obtained on the basis of nitrates have much better catalytic properties than those based on chlorides contrary to Pt catalysts.

5. Conclusions

The results presented in paper lead to the following conclusions:

- The course of the reaction between NO and CO depends on the kind of precursors for both catalysts.
- For the platinum catalysts obtained from H_2PtCl_6 as well as from $Pt(NO_3)_2$ insignificant differents in the activity of reduction NO reaction were observed.
- Palladium catalyst obtained from $Pd(NO_3)_2$ show more activity than the catalyst obtained from $PdCl_2$ and both platinum catalysts.

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