

BARBARA KUCHARCZYK*

OXIDATION OF CARBON MONOXIDE OVER MONOLITHIC PLATINUM CATALYSTS DOPED WITH METAL OXIDES

The deposition of NiO, MnO, CeO₂, Co₃O₄ or Fe₃O₄ onto the surface of an Al₂O₃-based wash-coat enhances the activity of the 0.15% Pt/Al₂O₃ catalyst in CO oxidation. The highest activities were found to be those of the 0.15% Pt/0.1% Mn/Al₂O₃ and 0.15% Pt/0.1% Ce/Al₂O₃ catalysts, over which a 100% conversion of CO was achieved at 204 °C and 209 °C, respectively. The activity of 0.15% Pt/Al₂O₃, as well as that of the oxide-doped 0.15% Pt/MO_x/Al₂O₃ (*M* = Ni, Mn, Ce, Co, Fe) catalysts, can be notably increased by using Pt(NO₃)₄ as a Pt precursor instead of H₂PtCl₆.

1. INTRODUCTION

Of the noble metals for CO oxidation, Pt, Pd [1], [2] and Au [3] show the highest catalytic activity, but CO oxidation is also catalyzed by the oxides of the following metals: Co₃O₄, Fe₃O₄, NiO, CeO₂, MnO, CuO and Cr₂O₃ [4]–[6]. The activity of particular oxides in CO oxidation can be enhanced using a mixture of several oxides. The use of mixed oxides, such as CoO_x–CeO₂, CuO–CeO₂ or CuO_x–CeO₂–ZrO₂ [5], [6], containing CeO₂, is regarded as the most advantageous. These catalysts promote a strong interaction of CeO₂ with other metal oxides and thus increase their activity. Also catalysts with Pt deposited onto the surface of CeO₂ (Pt/CeO₂, Pt/CeO₂/γ–Al₂O₃) are found to display a high activity in CO oxidation [7]. The activity of Pd/Al₂O₃ in CO oxidation can be enhanced by depositing Pd onto Mn₂O₃ [8] or CeO₂–ZrO₂ [9].

2. METHODS OF CATALYST PREPARATION AND EXAMINATION

CO oxidation was conducted over cylindrical monolithic catalysts, 26 mm in diameter and 70 mm in length. The catalysts were supported on a heat-resisting,

* Institute of Inorganic Chemistry and Mineral Fertilizers, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. E-mail: barbara.kucharczyk@pwr.wroc.pl

0.05-mm thick 00H20J5 foil covered with an Al₂O₃-based washcoat. The 112 canals/cm² support, together with the deposited washcoat, was calcined at 400 °C for 3 h. The washcoat content in the catalysts amounted to 2±0.1 wt.%. The Al₂O₃ washcoat was covered with the nitrates of Co, Ni, Ce, Fe, Mn and Cu and calcined at 500 °C for 3 h, which allowed decomposing the metal nitrates into the corresponding oxides. 0.15 wt.% Pt was deposited by impregnation onto the support prepared via the above route. Chloroplatinic acid or platinum nitrate (with the addition of an aluminium hydroxide sol of a concentration of 1 wt.% Al₂O₃) was used as a platinum precursor. The catalysts were calcined at 500 °C for 3 h. Their characterization is given in table 1.

Table 1

Characterization of catalysts

Catalyst	Composition of washcoat	Pt precursor	Active metal surface area (m ² /g _{cat.})	Dispersion of Pt (%)	Average size of Pt crystallites (nm)
0.15% Pt/Al ₂ O ₃	Al ₂ O ₃	Pt(NO ₃) ₄	0.21	42.7	26.5
0.15% Pt/0.3% Co/Al ₂ O ₃	Al ₂ O ₃ covered with Co ₃ O ₄	Pt(NO ₃) ₄	0.145	41.9	27.0
0.15% Pt/0.1% Ce/Al ₂ O ₃	Al ₂ O ₃ covered with CeO ₂	Pt(NO ₃) ₄	0.152	47.3	23.9
0.15% Pt/0.1% Ce/Al ₂ O ₃	Al ₂ O ₃ covered with CeO ₂	H ₂ PtCl ₆	0.154	52.0	21.8
0.15% Pt/0.1% Mn/Al ₂ O ₃	Al ₂ O ₃ covered with MnO	Pt(NO ₃) ₄	0.196	46.6	24.3
0.15% Pt/0.1% Mn/Al ₂ O ₃	Al ₂ O ₃ covered with MnO	H ₂ PtCl ₆	0.196	52.9	21.4

Surface composition was analyzed by X-ray photoelectron spectroscopy (XPS), using a SPECS UHV system with a PHOIBOS 100 spectrometer and SpecLab software.

Active metal surface area and Pt dispersion were established by examining the chemisorption of hydrogen at 110 °C with an Autosorb 1CMS Quantachrome. The isotherm of hydrogen chemisorption was determined within the pressure range from 20 to 200 mm Hg, at a chemisorption stoichiometry of H/Pt = 1.

Catalytic activity was tested in the oxidation of 1% CO in air over the monolithic catalysts, using a flow reactor placed in a heater with a programmed temperature increment (heating ramp, 3 °C/min), total gas hourly space velocity (GHSV) being set at 10000 h⁻¹. Inlet and outlet CO concentrations were measured with the following analyzers: MEXA-574GE (Horiba) – the concentration of CO of 0.01–10 vol. %, and Monoxor II (Bacharach) – the concentration of CO of 0–2000 ppm.

3. RESULTS AND DISCUSSION

3.1 CATALYST ACTIVITY IN CO OXIDATION

When H_2PtCl_6 or $\text{Pt}(\text{NO}_3)_4$ is used as a Pt precursor, the activity of the 0.15% Pt/ Al_2O_3 catalyst can be increased via modification of the Al_2O_3 -based washcoat by depositing a layer of the oxides of such metals as Ce, Co, Ni or Fe onto its surface (0.1 wt.% metal by support mass) (figure 1). If the washcoat is doped with CuO, the activity of the 0.15% Pt/ Al_2O_3 catalyst will decrease. Examination of Pt dispersion on the surfaces of the catalysts (Pt precursor: $\text{Pt}(\text{NO}_3)_4$) has revealed an increase in the value of this parameter from 42.7% to approx. 47% and a decrease in the size of Pt crystallites from 26.5 nm to 24 nm, when MnO or CeO_2 was incorporated into the 0.15% Pt/ Al_2O_3 catalyst (table 1). The activity of the catalysts in CO oxidation depends more on the type than on the amount of the metal oxide added (figure 2).

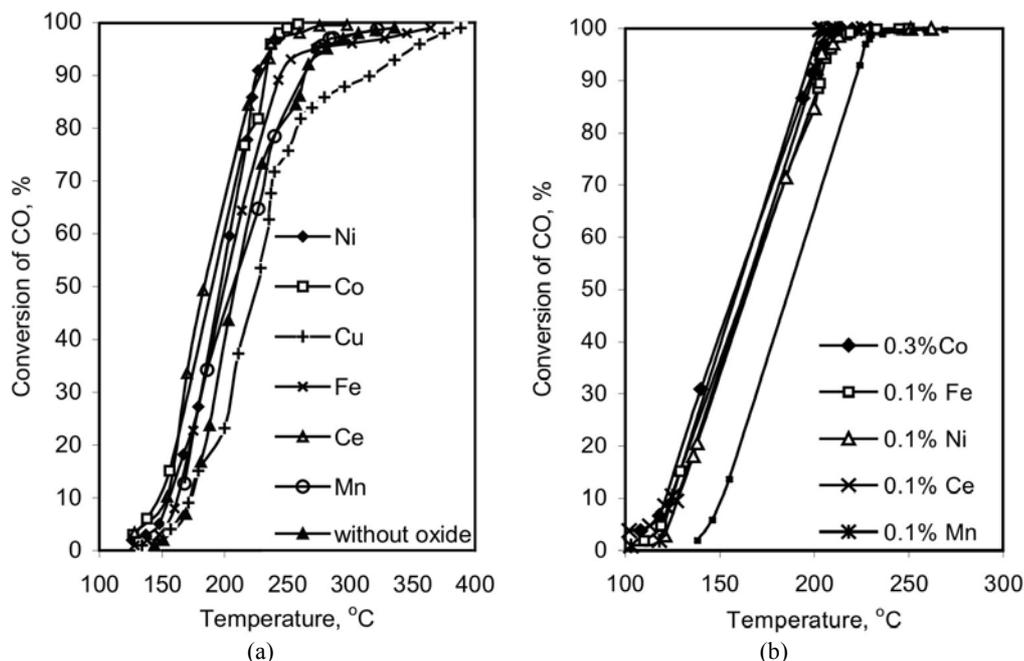


Fig. 1. Conversion of methane over 0.15% Pt/ Al_2O_3 (without oxide) and 0.15% Pt/0.1% M/ Al_2O_3 ($M = \text{Mn}, \text{Ni}, \text{Fe}, \text{Ce}, \text{Co}, \text{Cu}$) catalysts. Pt precursor: (a) H_2PtCl_6 ; (b) $\text{Pt}(\text{NO}_3)_4$

The activities of the 0.15% Pt/ $x\%$ M/ Al_2O_3 catalysts depend on the type of the Pt precursor used. Table 2 shows the temperatures of 99.9% CO conversion over the most active catalysts. Thus, when $\text{Pt}(\text{NO}_3)_4$ was the Pt precursor, all of the catalysts

displayed a notably increased activity in CO oxidation. With H_2PtCl_6 as the Pt precursor, the catalysts showed lower activities despite a slightly higher Pt dispersion on their surfaces (table 1). This is due to the presence of small amounts of chlorine, being poisonous to the catalysts. The chlorine which originated from the Cl-containing Pt precursor has been detected by XPS (figure 3), the chlorine content in the 0.15% Pt/0.1% Mn/ Al_2O_3 catalyst was 0.28 atom. % (XPS). The lowest temperatures of 99.9% CO conversion are those obtained over the 0.15% Pt/0.3% Mn/ Al_2O_3 , 0.15% Pt/0.1% Ce/ Al_2O_3 and 0.15% Pt/0.2% Co/ Al_2O_3 catalysts (table 2).

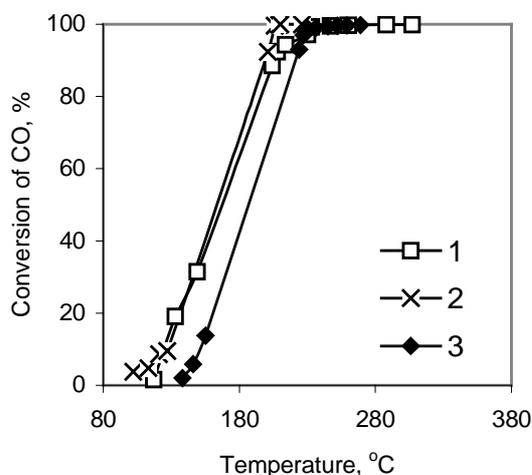


Fig. 2. Catalytic oxidation of CO over 0.15% Pt/x% $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts with different CeO_2 content. CeO_2 content: 1 – 0.25%; 2 – 0.12%; 3 – 0%. Pt precursor: $\text{Pt}(\text{NO}_3)_4$

Table 2

Temperatures of complete CO conversion over 0.15% Pt/0.1% M/ Al_2O_3 catalysts

Catalyst	Conversion of CO (%)	Reaction temperature (°C)	Conversion of CO (%)	Reaction temperature (°C)
	Pt precursor: H_2PtCl_6		Pt precursor: $\text{Pt}(\text{NO}_3)_4$	
0.15% Pt/ Al_2O_3	99.0	336	99.0	236
0.15% Pt/0.1% Ce/ Al_2O_3	99.6	276	99.9	209
0.15% Pt/0.1% Fe/ Al_2O_3	99.8	263	99.9	233
0.15% Pt/0.2% Co/ Al_2O_3	100.0	262	99.9	210
0.15% Pt/0.1% Ni/ Al_2O_3	100.0	285	100.0	251
0.15% Pt/0.1% Mn/ Al_2O_3	98.7	322	100.0	204

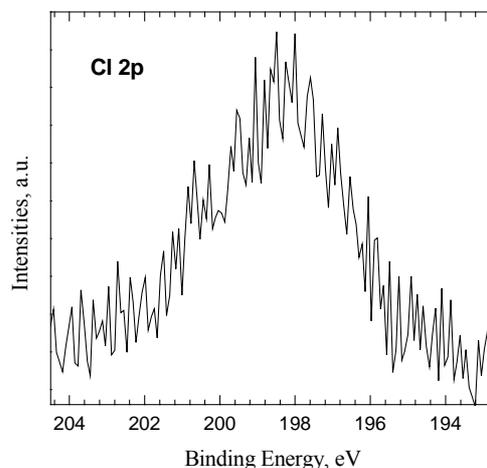


Fig. 3. XPS Cl 2p core level spectra for 0.15% Pt/0.1% Mn/Al₂O₃ catalyst.
Pt precursor: H₂PtCl₆

For the most active catalysts, where Pd(NO₃)₄ was used as the Pt precursor, i. e. for 0.15% Pt/0.1% Mn/Al₂O₃ and 0.15% Pt/0.1% Ce/Al₂O₃, activity tests were conducted during 110-hour oxidation of 1% CO in air. Over the fresh 0.15% Pt/0.1% Mn/Al₂O₃ catalyst, 100% CO conversion was obtained at 204 °C, and its activity did not decrease during the 110-hour run at that temperature. The activity of the 0.15% Pt/0.1% Ce/Al₂O₃ catalyst was also found to be high: after 110 h on stream at 227 °C, the conversion of CO decreased from 100% to 99.5%.

4. CONCLUSIONS

The activity of the 0.15% Pt/Al₂O₃ catalyst for CO oxidation can be enhanced by the deposition of NiO, MnO, CeO₂, Co₃O₄ or Fe₃O₄ onto the surface of the Al₂O₃-based washcoat. The highest activities were found to be those of the 0.15% Pt/0.1% Mn/Al₂O₃ and 0.15% Pt/0.1% Ce/Al₂O₃ catalysts, over which a 100% conversion of CO was achieved at 204 °C and 209 °C, respectively. Their activity did not change during 110 h of 1% CO oxidation in air.

The catalysts show notably higher activities when use is made of Pt(NO₃)₄ with a Pt precursor instead of H₂PtCl₆. This is so because the residual chlorine from the decomposition of H₂PtCl₆ exerts a poisoning effect on the catalysts (XPS).

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UTLENIANIE CO NA MONOLITYCZNYCH KATALIZATORACH PLATYNOWYCH
Z DODATKIEM TLENKÓW METALI

Naniesienie na powierzchnię warstwy pośredniej z Al₂O₃ tlenków: NiO, MnO, CeO₂, Co₃O₄, Fe₃O₄ podwyższa aktywność katalizatora 0,15% Pt/Al₂O₃ w utlenianiu CO. Najwyższą aktywność w utlenianiu CO wykazują katalizatory 0,15% Pt/0,1% Mn/Al₂O₃ i 0,15% Pt/0,1% Ce/Al₂O₃, na których 100% przereagowania CO uzyskano odpowiednio w temperaturach 204 °C i 209 °C. Znaczny wzrost aktywności katalizatora 0,15% Pt/Al₂O₃ oraz katalizatorów 0,15% Pt/MO_x/Al₂O₃ (M = Ni, Mn, Ce, Co, Fe) z dodatkiem tlenków uzyskuje się, stosując jako prekursor platyny Pt(NO₃)₄ zamiast H₂PtCl₆.