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Preferential CO oxidation over bimetallic Pt–Co catalysts prepared via double complex salt decomposition

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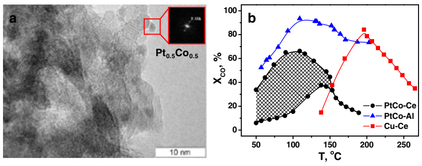
HIGHLIGHTS

- Catalyst preparation via $[Co(H_2O)_6][Pt(NO_2)_4]\cdot 2H_2O$ double complex salt decomposition.
- Close contact between Pt and Co atoms.
- Bimetallic alumina and ceria supported Pt–Co catalysts.
- $PtCo/Al_2O_3$ catalyst exhibited high activity and selectivity.
- Platinum-rich Pt–Co alloy nanoparticles supported over the alumina surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Bimetallic alumina and ceria supported Pt–Co catalysts were prepared via the decomposition of a $[Co(H_2O)_6][Pt(NO_2)_4]\cdot 2H_2O$ double complex salt. Catalysts were tested in CO preferential oxidation (PROX). $PtCo/Al_2O_3$ catalyst exhibited high activity and selectivity. It provided the CO conversion higher than 80% and selectivity above 60% in the temperature interval 90–165 °C at WHSV of 260,000 $cm^3\ g^{-1}\ h^{-1}$ and O_2/CO ratio of 0.6. XRD and TEM analysis indicated the formation of a platinum-rich Pt–Co alloy nanoparticles supported over alumina surface.

1. Introduction

The low-temperature proton-exchanged membrane fuel cell (PEM FC) is an attractive power source for transport and portable applications. One of the promising methods of hydrogen production for application in a PEM FC is the on-board generation from hydrocarbon fuels, such as gasoline, natural gas, alcohols, and ethers through its reforming, followed by the CO water gas shift (WGS) reaction. Typically, the obtained hydrogen-rich gas contains 0.5–2.0 vol.% CO, which poisons the FC anode catalyst and must be removed to a level below 10 ppm. CO preferential oxidation (PROX) is an efficient method for CO removal from a hydrogen-rich gas mixture.

Supported monometallic noble (Pt or Ru), gold and copper–ceria catalysts are reported to be highly active in CO PROX [1–10]. Among supported bimetallic systems proposed for CO PROX, Pt–Co catalysts are one of the most active and could oxidize CO in H_2-rich gas in a wide temperature interval [11–16]. As noted in the most published research articles, these systems demonstrate higher activity compared to respective monometallic catalysts with similar platinum or cobalt loadings.

PROX performance of Pt–Co catalysts in the packed-bed reactors and wall-coated microreactors were studied in several works

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[11–16]. Authors of [13] investigated samples with different cobalt content. The catalyst containing 5 wt.% Pt and 4.5 wt.% Co, that corresponds to Pt:Co atomic ratio of ~1:3, was found to be the most active and selective. XRD analysis showed the presence of Co_3O_4, CoO and spinel $CoAl_2O_4$ phases, no peaks referred to metallic Pt or bimetallic Pt–Co phases were detected, probably due to high Pt dispersion. According to XPS and TPR data, the authors attributed high CO PROX activity and selectivity to the formation of Pt–Co solid solution. The same conclusion was made in recent work [14] on the basis of SAED analysis of catalyst's TEM images, which showed the formation of Pt–Co interphase, probably Pt_3Co intermetallic compound. Kwak and co-workers [12] demonstrated that sodium additive to the Pt–Co/Al_2O_3 catalysts inhibited the interaction between cobalt and alumina, resulting in the suppression of the formation of the surface cobalt spinel species. As a result, sodium promoted the formation of the Pt–Co bimetallic interphase on the platinum–cobalt catalysts and increased the low temperature CO PROX activity. Komatsu and Tamura [15] investigated the CO PROX performance of silica supported Pt_3Co intermetallic compound, and noted that synergetic effect of Co additive to Pt in CO oxidation reaction could be attributed not only to higher Pt dispersion but also to intrinsic activity increase. They proposed two main reasons for this synergetic effect:

- realization of bifunctional mechanism, when CO adsorption and activation occur over Pt, oxygen activation occurs over Co and reaction proceeds over Pt–Co interface;
- extension of the Pt–Pt atomic distance (geographic effect) and electron transfer from Pt to Co (electronic effect) result in a weaker CO adsorption and accelerated CO oxidation.

Thus, since unmodified Pt/Al_2O_3 catalysts show insufficient CO PROX selectivity [2], it is critically important to provide close contact of Pt and Co atoms for reaching high activity and selectivity of bimetallic Pt–Co/Al_2O_3 catalysts.

Microreactors provide much more efficient approach for realization of on-board or portable hydrogen purification by CO PROX process [4,17–20]. Microchannel reactors are characterized by high heat and mass transfer rates, high surface to volume ratio and small scales. A high rate of heat removal from the thin catalytic film deposited onto the microchannel walls allows near-isothermal operation and thus prevents the side reactions (viz., hydrogen oxidation or reverse WGS), rising selectivity and extending the operational window [17,21,22]. The performance of Pt–Co/Al_2O_3 catalytic coatings in microreactors was investigated in several works [11,13,14]. Kim and co-authors [11] compared performance of CuO/CeO_2 and Pt–Co/Al_2O_3 coated microchannel reactors. The Pt–Co system showed higher activity, but was less selective than the copper-ceria one. A microreactor proposed in work of Yu and co-workers [14] demonstrated selectivity less than 35% at high conversion values. Low selectivity of Pt–Co catalysts could be associated with unselective formation of bimetallic particles over support surface, since without contact with cobalt, monometallic platinum behaves in CO PROX in the same way as Pt/Al_2O_3 catalyst, thereby decreasing the process selectivity. The catalysts were typically prepared by alumina coating sequential incipient wetness impregnation with chloroplatinic acid and cobalt nitrate. The samples were dried and calcined after each impregnation and finally reduced by hydrogen [11,13]. Another method consisted in co-impregnation of alumina with chloroplatinic acid and cobalt nitrate acidic solution [14]. Thus, in both cases there was no specific interaction between Pt and Co atoms providing selective formation of bimetallic particles. Moreover, since alumina surface in acidic medium can adsorb anions on amphoteric hydroxyl groups, formation of highly dispersed monometallic platinum particles could be predominant.

Our aim was to develop the preparation procedure for Pt–Co catalysts providing close contact of Pt and Co atoms over the support surface and appropriate for catalyst washcoat preparation. The proposed approach is based on the decomposition of double complex salts directly on the support surface that provides an effective and simple way to obtain supported alloy nanoparticles. Double complex salts (DCSs) of transition metals – coordination compounds composed of a complex cation of one metal and complex anion of another metal – have a number of advantages as precursors for nanoalloy catalysts:

- complexing metals in a double complex salt are "mixed" on a molecular level that allows one-step formation of alloys and intermetallides (including the meta-stable ones) upon salt decomposition;
- stoichiometry of a precursor complex determines the composition of the polymetallic products;
- possibility to preset exact phase composition and morphology of the alloy nanoparticles by varying the DCS decomposition conditions – temperature and atmosphere (oxidizing, reducing or inert one).

In our previous work [16], we studied $Pt_{0.5}Co_{0.5}$/C, $Pt_{0.5}Co_{0.5}$/Al_2O_3 supported catalysts and $Pt_{0.5}Co_{0.5}$ powder prepared via the decomposition of a double complex salt $[Co(NH_3)_5NO_2][Pt(NO_2)_4]\cdot1.5H_2O$ in hydrogen. The platinum–cobalt powder consisted of the $Pt_{0.5}Co_{0.5}$ unordered solid solution phase with additives of a Pt–Co intermetallic compound and $Pt_{0.9}Co_{0.1}$ alloy phases. Unfortunately, only indirect proofs allowed conclusion on the formation of similar bimetallic particles on support surface; attempts to detect these particles by physicochemical methods appeared unsuccessful.

In present work we report our results on catalyst preparation via the $[Co(H_2O)_6][Pt(NO_2)_4]\cdot2H_2O$ double complex salt decomposition, catalyst characterization and testing in CO PROX; the comparison with Cu/CeO_{2-x} catalyst is given as well.

2. Experimental

2.1. $[Co(H_2O)_6][Pt(NO_2)_4]\cdot2H_2O$ preparation

$K_2[Pt(NO_2)_4]$ (1.00 g) was dissolved in 10 ml of water, then equimolar amount (0.80 g) of $Co(ClO_4)_2\cdot6H_2O$ was added. The solution was cooled to 0 °C and kept for 1 h. The obtained deposit of $KClO_4$ was separated on a glass porous filter and washed out with ice water, acetone and ether. After boiling out in air, large crimson crystals were obtained. Since the product readily lost water upon staying in open air, it was left in the mother liquor and stored in a cup under Parafilm cover.

2.2. Catalyst preparation

The ceria support with a BET surface area of 100 $m^2\,g^{-1}$ was prepared by calcination of $Ce(NO_3)_3\cdot6H_2O$ at 400 °C for 2 h in air.

Bimetallic Pt–Co catalysts were prepared by incipient wetness impregnation of support materials (γ-Al_2O_3 (commercial) with S_{BET} = 200 $m^2\,g^{-1}$, and CeO_2) with the required quantities of $[Co(H_2O)_6][Pt(NO_2)_4]\cdot2H_2O$ aqueous solutions. Then the samples were dried overnight at room temperature. Afterwards the catalysts were reduced in hydrogen stream at 400 °C for 4 h.

The Cu/CeO_2 catalysts was prepared by incipient wetness impregnation of ceria with the required quantity of an aqueous solution of $Cu(NO_3)_2$, then dried at 110 °C in air, and calcined at 400 °C in air for 2 h.