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Preparation of platinum-on-carbon catalysts via hydrolytic deposition: Factors influencing the deposition and catalytic properties

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ABSTRACT

The deposition of Pt oxide from aqueous chloroplatinate solutions onto carbon supports (activated carbons, carbon blacks, carbon nanofibers) with the aid of Na_2CO_3 and without adding the reductants or wetting agents was studied. It has been revealed that carbons accelerate greatly the hydrolysis of chloroplatinate, and the hydrolytic deposition can therefore interfere with the other preparation methods. Neutral pH was found optimum for heterogeneous nucleation and formation of smaller PtO_x particles. High temperature (80 °C) allowed depositions of 5–30 wt.% of Pt for a short time (1–3 h) but did not affect Pt dispersions (15–90% at surface concentration of Pt 0.5–30 μmol/m^2). The supported particles could be further reduced in the liquid phase with minimal losses of the dispersion (Na-formate as reductant). The heterogeneous nucleation ensured a uniform distribution of Pt particles but provoked particle confinement in narrow pores. The possibility of influencing catalytic properties with the aid of the support, Pt loading and deposition conditions was demonstrated (hydrogenation of cycloalkenes as a model structure-insensitive reaction and oxidation of isopropyl alcohol as structure-sensitive one).

1. Introduction

The carbon-supported Pt catalysts demonstrate remarkable performance in a great variety of chemical processes, and hundreds of scientific papers on properties and synthesis of these catalysts are published every year. The overwhelming majority of the described syntheses are based on reductive deposition of Pt or impregnation of the support with a solution of Pt compound, followed by evaporation of the solvent and reduction in a flow of gaseous reductant [1–4]. A preliminary deposition of oxide species onto the support, being often used with other metals, is very rare in the preparation of Pt catalysts, probably due to the relative inertness of Pt(IV) compounds to hydrolysis.

Several research groups have recently shown, however, that the hydrolytic deposition can be an effective way to highly dispersed Pt/C catalysts. Colloidal particles of PtO_2 and mixed oxides could be obtained through hydrolysis of Pt chloride at 60–100 °C in the presence of betaines [5,6] or polyvinylpyrrolidone (PVP) [7,8]. Reetz and Lopez [9] suggested that the colloidal Pt oxide could be stabilized by hydroxide ions and patented method of obtaining PtO_x/C catalysts in the absence of organic stabilizers, through immobilization of preformed or in situ formed colloidal PtO_x particles at high pH (Li_2CO_3 as the base). Kvande et al. [10,11] attempted the deposition of Pt oxide onto carbon nanofibers (CNFs) under such conditions but found that a large amount of the metal precursor remained in the solution, and Pt loadings could be as low as 1.4 wt.% at the intended value of 20 wt.%; they achieved higher Pt loadings "with a two-step procedure where the precursor solution was initially heated without the presence of carbon". Fang et al. proposed a monotonic increase of pH at the deposition stage and obtained a high loading of Pt oxide with a "urea-assisted" hydrolysis [12,13]; to what extent the smooth changes of pH contributed to the result is not clear, however. Another research group used a "redox-assisted" hydrolysis of Pt(IV) chloride complexes to prepare Pt/C catalysts [14–16], but the expediency of adding the reductant at the hydrolysis stage was not supported by corresponding data.

The previous studies have not addressed the possible influence of the preparation variables on the state and properties of resulting PtO_x particles, and the conditions were not always reported sufficiently in detail. All those studies only concerned an electrochemical application of the Pt/C catalysts obtained (fuel cells), and practically nothing is known regarding the potentialities of the method in the field of traditional catalysis. Reetz and Koch [5] supported Pt oxide colloids on Al_2O_3 and tested the samples in reductive amination; per gram of Pt, the immobilized catalyst was only 5 times more active than bulk PtO_2 (commercial Adams catalyst). Pan et al. [8] tested 1–3 nm PtO_2 colloids (unsupported) in cyclohexene hydrogenation and obtained turnover frequencies

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