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Hydrodechlorination of CCl_4 over carbon-supported palladium–gold catalysts prepared by the reverse “water-in-oil” microemulsion method

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ABSTRACT

Two series of carbon-supported Pd–Au catalysts were prepared by the reverse “water-in-oil, W/O” method, characterized by various techniques and investigated in the reaction of tetrachloromethane with hydrogen at 423 K. The synthesized nanoparticles were reasonably monodispersed having an average diameter of 4–6 nm (Pd/C and Pd–Au/C) and 9 nm (Au/C). Monometallic palladium catalysts quickly deactivated during the hydrodehalogenation of CCl_4 . Palladium–gold catalysts with molar ratio Pd:Au = 90:10 and 85:15 were stable and much more active than the monometallic palladium and Au-rich Pd–Au catalysts. The selectivity toward chlorine-free hydrocarbons (especially for C_{2+} hydrocarbons) was increased upon introducing small amounts of gold to palladium. Simultaneously, for the most active Pd–Au catalysts, the selectivity for undesired dimers $\text{C}_2\text{H}_x\text{Cl}_y$, which are considered as coke precursors, was much lower than for monometallic Pd catalysts. Reasons for synergistic effects are discussed. During CCl_4 hydrodechlorination the Pd/C and Pd–Au/C catalysts were subjected to bulk carbiding.

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1. Introduction

On account of the ever-increasing concern for environment protection, the safe treatment and detoxification of tetrachloromethane and other organo-chlorinated pollutants has acquired great importance. Several methods, including incineration, biological treatment, photo-catalytic decomposition, and catalytic hydrodechlorination [1–5],

have been proposed for the treatment of chlorinated organic wastes. Among these methods, used for disposal or recycling of chlorinated hydrocarbons, catalytic hydrodechlorination of carbon–chlorine bond (referred to as hydrodechlorination, HdCl) is regarded as the most universal and promising method. HdCl is emerging as a simple, safe and non-destructive alternate technology whereby the chlorinated waste can be converted into hydrocarbons, products of commercial value. Additionally, HdCl operates at low temperatures, so the process is economically viable.

Even though, all Group VIII metals are known for their C–Cl bond cleavage and hydrogenation ability [6], palladium occupies a unique position in this group by virtue of its superior activity and high selectivity towards the desired

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hydrocarbon, i.e. non-chlorine containing, products. However, there are some problems such as the improvement of the stability of Pd catalysts and selectivities to target products, i.e., C₁–C₅ hydrocarbons, remaining to be met. The main drawback for practical application is rapid deactivation of palladium catalysts during H₂Cl of CCl₄ reaction, although they show a very high initial catalytic activity [7–15]. Therefore, the development of new catalysts with highly selective dechlorinating activity and high stability becomes the strategy for the hydrodechlorination of chlorinated hydrocarbons.

As commonly observed in the hydro-treating catalytic reactions, catalytic performance such as activity, selectivity, and resistance towards catalyst deactivation are strongly dependent on the nature of the catalyst. Therefore, various catalyst systems such as noble metals, non-noble metals, and alloy catalysts have been investigated for H₂Cl reactions. It is known that the H₂Cl activity of supported palladium catalysts is affected by many factors: the morphology of metal particles, the nature of the support [16–18] and the presence of a second metal in active phase [19–25].

Bimetallic catalysts are very promising as they feature an interesting catalytic behaviour with respect to monometallic systems [26]. Many bimetallic systems demonstrate enhanced properties in terms of selectivity and activity as well as resistance to poisoning and/or metal sintering. Bimetallic palladium–gold catalysts find industrial application, for instance in the selective hydrogenation of various organic compounds [27], production of vinylacetate [28], hydrodechlorination of chlorofluorocarbons [29] and trichloroethene [30].

The ultimate size of the metal particles and good homogeneity of active metal phase (namely Pd–Au alloy) are essential for improving the catalytic properties of palladium. Our previous results show that for supported Pd–Au catalysts prepared by impregnation techniques a satisfactory extent of Pd–Au mixing was not achieved [23,31]. The reductive deposition of gold to palladium catalysts resulted in a significantly higher, although still not perfect, degree of Pd–Au alloying [32]. Our recent paper [33] deals with similarly prepared carbon-supported Pd–Au catalysts investigated in CCl₄ hydrodechlorination, where attention was focused on the negative effect of alloy inhomogeneity on the catalyst's stability. Although this defect could be largely reduced by removing unalloyed palladium species (by treatment with nitric acid [33]), nevertheless further progress in this research could be made by application of another catalyst's preparation technique which would lead to a still better Pd–Au alloying.

In the present work we decided to prepare palladium and palladium–gold catalysts supported on mesoporous active carbons by the “water-in-oil” reverse microemulsion method [34,35]. In this special method, nanoparticles with precisely defined size are obtained. Nanoparticles are formed by reduction/co-reduction of metal ions present inside nanodroplets of aqueous solution of metal salts stabilized by a surfactant in a non-polar solvent. Proper adjusting of metals ions concentration, concentration and type of reducing agent as well as composition of

microemulsion (especially water to surfactant molar ratio) allow to obtain metal particles precisely predicted in size in a very narrow range (which is difficult to obtain in traditional synthesis routes, e.g., by impregnation). Our recent studies showed that such prepared Pd–Au catalysts are homogeneous and active in the reaction of hydrogenation of cinnamaldehyde [36]. The present work is aimed at the performance of similarly prepared carbon-supported Pd–Au catalysts in the hydrodechlorination of tetrachloromethane. High degree of alloy homogeneity attainable by using the “water-in-oil” reverse microemulsion method should allow us to establish more precisely the activity pattern as a function of Pd–Au composition. Our previous work [33] indicated a number of synergistic effects associated with palladium alloying with Au in H₂Cl of CCl₄, however uncertainty as to the degree of Pd–Au homogeneity did not allow us to render more rigorous relations.

2. Experimental

2.1. Catalyst preparation characterization

Two types of commercial active carbons were used as catalyst's supports: activated pyrocarbon Sibunit (Novosibirsk, Russia) [37] and furnace black Vulcan XC-72 (Cabot Corporation) [38]. Before preparation of catalysts, the active carbon Sibunit was washed with a boiling mixture of concentrated HCl and HF, rinsed with large amounts of redistilled water and dried at 253 K in an air oven for 12 hours. Carbon Vulcan XC-72 was used without any purification. The properties of the supports are given in Table 1. It is evident that the Vulcan carbon is characterized by a larger average size of pores.

The catalysts consisting of the same palladium loading equal to 2 wt% Pd and the growing Au content were prepared by means of the reverse “water-in-oil” microemulsion method according to the procedure described previously [39,40]. In the PdAu/carbon catalysts the molar ratio of Pd:Au ranges were from 95:5 up to 70:30. The monometallic 2 wt%Pd/C (Pd₁₀₀) and 2 wt%Au/C (Au₁₀₀) catalysts (for catalyst notation, Table 2) were also prepared using the same preparation procedure. The reverse micellar solutions were prepared using surfactant dioctyl sulfosuccinate sodium salt (AOT, pure 98%, Fluka) and heptane (pure, Aldrich) as the oil phase. The aqueous solutions of PdCl₂ (99.9% Grade, Johnson Matthey) and

Table 1
Characteristics of active carbons used in this work^a.

Measure	Sibunit	Vulcan XC72
Grain size, μm	~10	0.1–0.3
Surface area (BET), m ² /g	308	228
t-plot micropore area, m ² /g	8	24
Total pore volume (BJH desorption), cm ³ /g	0.890	1.770
Mezopore volume, cm ³ /g	0.841	1.722
H-K micropore volume, cm ³ /g	0.029	0.048
H-K micropore width, nm	0.97	0.74
Average pore width (BJH desorption), nm	5	14

^a The surface areas of the supports, their pore volumes and diameters were determined from desorption isotherms of nitrogen adsorbed at 75 K after evacuation at 623 K for 5 h on ASAP 2020 (Micromeritics, USA).

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