Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

Effect of gold on catalytic behavior of palladium catalysts in hydrodechlorination of tetrachloromethane

Magdalena Bonarowska [a], Zbigniew Kaszkur [a], Dariusz Łomot [a], Michał Rawski [b], Zbigniew Karpiński [a,c,*]

[a] Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01224 Warszawa, Poland
[b] Faculty of Chemistry, Analytical Laboratory, Maria Curie-Skłodowska University, Plac Marii Curie-Skłodowskiej 3, PL-20031 Lublin, Poland
[c] Faculty of Mathematics and Natural Sciences-School of Science, Cardinal Stefan Wyszyński University, ul. Wóycickiego 1/3, PL-01938 Warszawa, Poland

A R T I C L E   I N F O

A B S T R A C T

Catalytic gas-phase hydrodechlorination (HdCl) of tetrachloromethane was investigated over Au/Sibunit and Pd/Sibunit carbon prepared by impregnation, and Pd-Au/Sibunit carbon prepared by either reductive deposition of Au onto Pd or successive impregnation of Pd/Sibunit carbon with a solution of gold salt carried out at aerobic conditions. The activated (by reduction in H$_2$ at 400 °C) catalysts were characterized in terms of H$_2$ and CO chemisorptions, XRD and (S)TEM-EDS measurements. Presence of smaller (<2 nm) metal particles in 2.8 wt.% Pd/Sibunit (d_{mean} 3.1 nm) evidenced by TEM was not confirmed by XRD and gas chemisorptions. XRD and (S)(TEM)-EDS showed a reasonable quality of Pd-Au alloying in catalysts prepared by reductive deposition. Compared with the monometallic palladium, active carbon-supported bimetallic Pd-Au catalysts (∼0.24 g charges) showed very good activity (conversions up to 92%), resistance to deactivation during ∼70 h runs and high selectivity to nonchlorinated products (up to ∼80%) in the reaction of hydrodechlorination of tetrachloromethane, carried out at 90 °C. However, their behavior greatly depends on the quality of Pd-Au alloying: well mixed Pd-Au particles of Pd-Au maintain a very good catalyst performance, while the increasing presence of small unalloyed Pd particles leads to rapid deactivation. A large part of these small Pd particles can be leached out from such insufficiently homogenized catalystsby dissolution in 10% nitric acid. This treatment, followed by catalyst re-reduction results in the remarkable improvement of catalytic performance, especially the catalyst's stability in a long-term operation. During the reaction, carbon species originating from CCl$_4$ enter palladium (but not PdAu) bulk, leading to the formation of the palladium carbide phase, PdC$_x$, which seems to be less effective in hydrogen activation, and results in massive accumulation of nonreactive deposits containing both carbonaceous as well as chlorine species leading to rapid catalyst deactivation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic hydrodechlorination (HdCl) appears to be one of the most prospective technologies for the utilization of harmful chlorine-containing wastes [1,2]. In contrast to incineration and catalytic burning, HdCl offers conversion of toxic and ozone-depleting substances to more benign while still valuable chemicals. Until recently, HdCl of tetrachloromethane to chloroform carried out in the presence of Pt-based catalysts was regarded as a suitable practice [3–5], but today because of its high toxicity and carcinogenic character CHCl$_3$ is included in the U.S. EPA's Toxic Release Inventory (TRI). Thus, conversion of CCl$_4$ to chlorine-free compounds, i.e. hydrocarbons, appears now a more prospective solution. Compared to platinum, palladium catalysts were found more useful in such a transformation [6–15], however they quickly deactivate on stream [6–9,12–16].

It seems general consensus that small metal (Pt, Pd) particles are less suited for HdCl, both in batch liquid and continuous gas phase operations (Refs. [17–27], for Pd catalysts). Small metal particles strongly deactivate [3,5], especially when they interact with support acidity, becoming electrodeficient [5]. It appears that the more acidic support, the faster catalyst deactivation. In this respect, basic MgO appears a better support than Al$_2$O$_3$, although still is not good, quickly deactivating on stream [8]. In addition, possible transformation of basic supports to respective chlorides during HdCl would lead to catalyst's downgrading, since MgO

* Corresponding author at: Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01224 Warszawa, Poland.
Tel.: +48 3433356; fax: +48 3433333.
E-mail address: zkarpinski@ichf.edu.pl (Z. Karpiński).

turns MgCl$_2$, reducing the surface area [28]. Carbon is the support of industrial choice for a number of reasons, including high specific surface area, availability and stability against corrosion by chlorine-containing species, and, in effect, Pd/active carbon catalysts were intensively investigated. Gómez-Sainero et al. [29] suggested that both electrodeficient and zero-valent species are needed for HdCl of CCl$_4$ on carbon-supported Pd catalysts in gas phase, whereas catalysts with only one of the species ((Pd^{n+} or Pd^0) are inactive. They proposed a dual nature of Pd active sites by the association of both species, reaching a maximum of activity at a Pd^{n+}/Pd^0 ratio close to 1. Other authors were also in agreement with the proposed dual nature of the Pd active sites in HdCl [23,25,30–32]. Concerning the electronic effects, Diaz et al. [25] admit that there are not a clear relationship between dispersion and concentration of electro-deficient palladium species (as judged from XPS), being this parameter markedly more dependent on the considered support and the surface activation than on the metal dispersion itself. Therefore, sources of electrodeficiency of carbon-supported palladium particles would be seen in the extent of Pd interactions with oxygen-containing (acidic) functional groups present on carbons, which were not subjected to a sufficiently rigorous temperature pretreatment, especially in a reducing atmosphere (H$_2$).

Reasons for deactivation of HdCl metal catalysts are at least threefold. First, metal surface chloriding by a liberated HCl product was thought to be an important cause of deactivation [33–36]. Second, perhaps a more frequently evoked cause, considers massive deposition of carbonaceous deposits blocking the active metal sites [37–40]. Third, changes in the metal phase, such a decrease of metal dispersion caused by long-term operation in this highly exothermic reaction, were also suggested to play an important role in the time-on-stream behavior of HdCl catalysts [41]. Finally, a combination of the previously mentioned factors, e.g. chlorination + carbiding, may also be taken into account [42,43]. So far, regeneration of palladium catalysts subjected to HdCl of CCl$_4$ was not very successful, giving only a short-lived or partial recovery, no matter how was carried out (high temperature flushing with inert gas [9,38] or burning post-reaction deposits [43]). This limitation reinforces our determination to develop long-lasting catalysts of HdCl of CCl$_4$.

At this stage of research, modification of an active phase (Pd) appeared to us a better way to improve the HdCl performance than concerns about possible benefits from support selection. So, we decided to modify carbon-supported palladium particles with gold, i.e. to investigate the system which frequently was found to exhibit synergy in the catalytic behavior. Synergistic effects observed for Pd-Au alloys are interpreted by occurrence of two effects: ensemble (geometric) and ligand (electronic) ones. The ensemble effect is a dilution of surface Pd by Au, leading to disappearance of contiguous Pd site ensembles and creation of isolated Pd sites. In their recent review, Gao and Goodman [44] argued that for vinyl acetate synthesis, this effect is responsible for reaction rate and selectivity enhancements via the formation of highly active surface sites, e.g., isolated Pd pairs. The ligand effects occuring via direct charge transfer or by affecting bond lengths, cause the Pd d band to be more filled, moving the d-band center away from the Fermi level. This makes Pd more "atomic like" which binds reactants and products more weakly. For certain reactions, this relieves catalyst deactivation caused by self-poisoning and enhances activity/selectivity. Such effect would explain better resistance to deactivation of Pd-Au alloys. Venezia et al. [45] reported a synergetic effect of gold in Au/Pd catalysts in HDS reactions, seen as a stronger resistance of gold to sulfur poisoning and to the ensemble size change of the alloyed phase. A more relevant for this study improvement of deactivation resistance in HdCl (of mainly trichloroethene) reactions by for gold-supported palladium nanolayers was observed in numerous papers from the group of Wong [46–53]. In the last paper, on HdCl of CHCl$_3$, Au/Al$_2$O$_3$ catalysts modified by deposition

Pd appeared much more active than respective Pd/Al$_2$O$_3$ catalysts, suggesting a close vicinity of Pd (or at least some part of it) and Au. In general, in a majority of Wong et al. papers both ensemble and ligand effects are invoked to describe the superiority of Pd-Au combinations. Wu et al. [54] reported the catalytic behavior of a magnetic core–shell nanocomposite, Fe$_3$O$_4$@SiO$_2$@Pd-Au, which was synthesized by reducing palladium and gold cations previously bound to the amine ligand-modified surface of silica-encapsulated iron oxide (Fe$_3$O$_4$) nanoparticles. The formation of a Pd-Au alloy resulted in an enhanced 4-chlorophenol conversion and better catalyst' stability, whereas the presence of magnetic iron oxide was considered to facilitate catalyst separation from liquid reaction mixture. Pd-Au/Sibunit catalysts were found more selective to CH$_2$F$_2$, desired product in HdCl of CCl$_2$F$_2$ [55]. It should also be mentioned that, due to the possibility of the occurrence of synergistic effects in catalytic behavior, the Pd-Au system maintains an object of continuing interest [56–58].

Modification of palladium (which is generally regarded as an active phase in HdCl reactions) by alloying with other than gold catalytic metals also upgraded the catalytic performance. Golubina et al. showed that iron addition to palladium greatly increases the catalyst's life time and also leads to a better selectivity towards C$_2$–C$_4$ hydrocarbons [59]. Addition of silver or copper to palladium also had a beneficial effect on the catalytic behavior in HdCl of 1,2-dichloroethane, resulting in higher selectivity to ethene (desired product) [60–65]. However, in the case of HdCl of CCl$_4$ such modifications brought about less preferred changes because either the product selectivity was turned towards chloroform and not to preferred hydrocarbons (Pd-Ag, [66]) or the catalyst stability was not good (Pd-Cu, [67]). Interestingly enough, modification of Ni catalysts by Au generated synergistic effects in HdCl of 2,4-dichlorophenol [68].

In this report we present new data on the behavior of active carbon-supported Pd-Au catalysts in HdCl of CCl$_4$. Practical reasons prompted us to investigatethe catalysts under the conditions of (nearly) full CCl$_4$ conversion achieved at possibly lowest temperatures of reaction.

2. Experimental

2.1. Catalysts preparation and characterization

The support was Sibunit carbon [69] in the form of powder (grain size between 10 and 30 μm), washed with a boiling mixture of concentrated HCl and HF purged with redistilled water and dried in an air oven. Its nitrogen BET surface area measured with an ASAP 2020 Micromeritics instrument was 390 m^2/g, BJH pore volume (from desorption branch) was 0.75 cm^3/g, and average pore diameter was ~7 nm. The cumulative micropore volume (Horvath–Kawazoe) was 0.11 cm^3/g, as estimated at relative pressure 0.012, and the median micropore diameter was 0.59 nm.

First, the primary monometallic 2.8 wt.% Pd/Sibunit was prepared by incipient wetness impregnation using an aqueous solution of PdCl$_2$ (analytical grade from POCh Gliwice). An anaerobic sequential impregnation method was used to prepare Sibunit carbon-supported Pd-Au catalysts. The monometallic Pd/Sibunit catalyst was prereduced at 300 °C for 3 h in a special reactor in flowing H$_2$–Ar (300 cm^3/min), then purged in an argon flow at 300 °C for 1 h, cooled to room temperature in Ar, and, finally, immersed in de-aerated redistilled water. The solution was continuously stirred by bubbling argon, at 200 cm^3/min. Then, a de-aerated aqueous solution of ammonium chloroaurate (specpure from Johnson Matthey, England) was slowly introduced into the reactor. The solution was stirred with bubbling argon for the next 20 min. The resulting solid was separated by filtration, washed with redistilled water, and