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Application of silica-supported Ir and Ir-M (M = Pt, Pd, Au) catalysts for low-temperature hydrodechlorination of tetrachloromethane

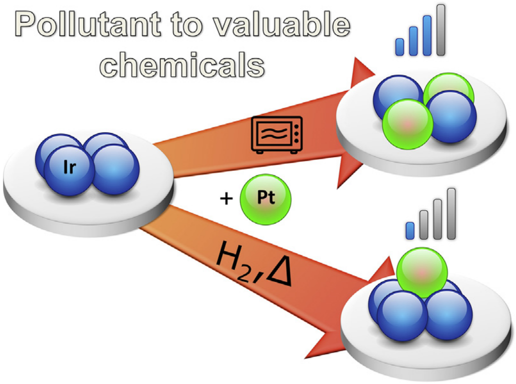
Magdalena Bonarowska [a], Krzysztof Matus [b], Anna Śrębowata [a], Jacinto Sá [a,c,*]

[a] Institute of Physical Chemistry Polish Academy of Sciences, Warsaw 01-224, Poland
[b] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Gliwice 44-100, Poland
[c] Department of Chemistry-Ångström, Uppsala University, Uppsala, 751 20, Sweden

HIGHLIGHTS

- Chemoselective hydrodechlorination with iridium-based catalysts
- CCl_4 conversion at low temperature and atmospheric pressure
- Effect of activation procedure (microwave vs thermal with H_2) on catalytic properties
- Production of useful chemicals from toxic waste

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, it is presented a catalytic system for gas-phase hydrodechlorination of tetrachloromethane at low temperature and atmospheric pressure, using iridium supported on silica as parent catalyst. Iridium electronic configuration is suitable to catalyse the hydrodechlorination reactions, however, it has been rarely used in this reaction to date. The catalytic abilities were significantly improved when a second transition metal was added. Catalysts' stability and selectivity to the desired products (i.e. C_1-C_4 hydrocarbons) improved compared to conventional activation in hydrogen when catalysts were activated shortly with microwave irradiation. Microwave irradiation of catalysts favourably influences the homogeneity of the metallic active phase, both in terms of the size of metal crystals and the homogeneity of bimetallic systems. Addition of platinum to the 'parent' iridium catalyst improved its catalytic properties and decreased deactivation. Fresh and spent catalysts were comprehensively characterized using several techniques (BET, CO-chemisorption, XRD, XPS, electron microscopy and mass spectrometry) to determine structure-activity relationships and potential causes for catalyst deactivation. No significant changes in crystalline size or bimetallic phase composition were observed for spent catalysts (with the exception of Ir-Pd catalysts which underwent bulk carbide during the reaction).

1. Introduction

Tetrachloromethane (CCl_4), due to its high toxicity and potentially carcinogenic nature, is currently classified as a hazardous gaseous

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* Corresponding author.
E-mail address: jacinto.sa@kemi.uu.se (J. Sá).

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pollutant. The Montreal Protocol (Montreal Protocol, 1987) restricted CCl_4 emissions to the atmosphere to protect the ozone layer, and diminish the formation of photochemical smog and global warming. For these reasons the production, use and even transportation of CCl_4 have been prohibited, however, CCl_4 remains a significant component in the waste stream originating from the production of chloroform, dichloromethane and other chlorinated organic compounds. Despite stringent limits on CCl_4 production for many years, global observations still suggest large emissions of this pollutant to the atmosphere (Hu et al., 2016) and a number of industrial processes have been suggested as contributors to its persisting emission (US Environmental Protection Agency, 2015; Fraser et al., 2014; Odabasi et al., 2014). Therefore, methods for safe and environmentally acceptable destruction of recovered wastes or stocks of CCl_4 are needed.

Catalytic hydrodechlorination (HdCl) has potential economic and environmental advantages over other methods since it operates at relatively low temperatures and ambient pressure (Bonarowska et al., 2015a), and the final reaction products (dechlorinated hydrocarbons) represent some economic value. The removal of just one chlorine atom from the CCl_4 molecule gives chloroform ($CHCl_3$), which creates fewer environmental problems than CCl_4. Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) for the both compounds are: $ODP_{CCl4} = 1.1$, $GWP_{CCl4} = 1730$, $ODP_{CHCl3} = 0.01$, $GWP_{CHCl3} = 16$ (for ODP and GWP values, the reference compound is from CFC-11, for which the values are 1.0 and 4600, respectively) (Tsai, 2017). Additionally, both CH_4 and $CHCl_3$, show much shorter atmospheric lifetime than CCl_4, 12.4 years and 0.4 years respectively. Therefore, the CCl_4 conversion into methane and less chlorinated hydrocarbons seem to be interesting from the environmental point of view. Additionally, the reaction products of CCl_4 HdCl are less hazardous than those (as $COCl_2$) created with other techniques (e.g. incineration and catalytic oxidation (Hodnet, 2000)). HdCl of CCl_4 to chloroform was widely regarded as a suitable practice however it should be noted that recent studies have shown that chloroform is toxic and possesses carcinogenic properties (Tsai, 2017).

Supported noble metal catalysts, such as Pd, Pt, Rh, Ir, Re, and Ru, are known for catalyzing hydrogenolysis of carbon-chlorine bonds, and they have become the most researched elements for the abatement of toxic chlorinated compounds. It is worth noting that both monometallic (Bonarowska et al., 2010; Dong et al., 2014; Chen et al., 2010) and alloy catalysts (noble metals (Xu et al., 2016) and noble metals mixed with inexpensive ones (Dong et al., 2015; Hina et al., 2016)), or even some more complex catalytic systems, are used (Ming et al., 2017).

Noble metals show significant differences regarding activity, selectivity to desired products, and resistance to deactivation. For example, palladium catalysts exhibit high activity and selectivity to methane in HdCl of CCl_4 but deactivate quickly (Wiersma et al., 1996; Coq et al., 1993; Moore and O'Kell, 1992), while platinum and iridium are particularly selective to single chlorine atom removal (Bonarowska et al., 2010; Reeves et al., 2003). Although iridium shows high resistance to HCl attack and stability under severe reaction conditions, its applications in hydrochlorination reactions are rare. Some discussion on its use can be found in the following publications: hydrodechlorination of CCl_3F (Ordóñez et al., 2001a), CCl_2F_2 (Wiersma et al., 1998) and CCl_4 (Reeves et al., 2003). The latter also examines the dissociative adsorption of CCl_4 on a single crystal Ir(110). Therefore we can recognize that application of iridium catalysts in HdCl of CCl_4 is not fully researched issue.

Gold is considered inactive in the HdCl reactions, but it creates a synergetic effect when used in with Pd, resulting in higher activity and selectivity of the palladium as an active phase and reduction of catalyst deactivation (Bonarowska et al., 2015a; Gao and Goodman, 2012a; Nutt et al., 2005; Pretzer et al., 2013; Bonarowska et al., 2002). The synergistic effects observed in Pd-Au alloys (and other bimetallic systems) in HdCl were interpreted by the occurrence of two effects, namely ensemble (geometric) and ligand (electronic). The ensemble effect dilutes Pd surface by Au, leading to the disappearance of contiguous Pd site ensembles and creation of highly active isolated Pd sites (Gao and Goodman, 2012b). The ligand effect occurring via direct charge transfer or by affecting bond lengths, cause the Pd *d* band to be more occupied, moving the *d*-band centre away from the Fermi level. This makes Pd more "atomic-like", binding reactants and products weaklier. For certain reactions, this reduces catalyst deactivation caused by self-poisoning and enhances activity and/or selectivity (Venezia et al., 2003). In general, both effects are invoked to demonstrate the catalytic superiority of Pd-Au combinations.

Enhanced catalytic properties of bimetallic supported catalysts in HdCl are related to bimetallic homogeneity. However, preparation of well-homogenized bimetallic system remains a real challenge. Impregnation methods resulted in insufficient bimetal homogeneity (Juszczyk et al., 1995) and require high temperature (up to 1173 K) to alloy the metals (Sancier and Inami, 1968; Inami and Wise, 1972). Such temperature led to undesirable metal sintering and/or formation of strong metal-support interactions. More advanced and complicated methods (such as ion exchange method (Lam and Boudart, 1977) or direct redox method (Barbier, 1997)) produce good metal mixing but have not gained popularity, probably due to harder synthesis compared to simple impregnation (Comandella et al., 2016). There is another challenge in obtaining homogeneous bimetallic systems with Ir-Au, Ir-Pd and Ir-Pt catalysts since iridium demonstrates very limited miscibility in bulk with Au, Pd, and Pt, thus hindering alloy formation with randomly dispersed atoms in the crystalline structure (Hansen, 1958).

In recent years, microwave assisted (MW) synthesis has been employed in the preparation of nanosized materials (Luo, 2007; Chen et al., 2005). MW-irradiation provides uniform heating, thus making the nucleation step more homogeneous. We postulate that MW irradiation has a potential to generate more homogeneous bimetallic catalyst formulations from the inset and/or after synthesis (post-synthetic treatment). Rahsepar and Kim (2015) reported the formation of homogeneous Pt-Ru nanoparticles supported on carbon nanotubes from aqueous solution and Berry et al. (2000) improved Pd-Fe/Al_2O_3 catalyst homogeneity (prepared by impregnation) after MW post-synthetic treatment. Moreover, MW–assisted synthesis is considered a sustainable and green approach for the preparation of metals/support systems (Raspolli Galletti et al., 2010).

The literature concerning the influence of activation by microwave irradiation on catalytic properties of HdCl catalysts is rather scarce (Berry et al., 2000; Gopinath et al., 2002; Bonarowska et al., 2018). Thus, in this contribution, we report the impact of MW radiation treatment versus classic thermal treatment in hydrogen flow on HdCl performance for a series of Ir, Ir-Au, Ir-Pd and Ir-Pt catalysts supported on SiO_2. The catalysts were prepared by simple impregnation and their catalytic performance was evaluated in gas phase hydrodechlorination of CCl_4 at low temperature and atmospheric pressure. Practical reasons prompted us to investigate the catalysts under the conditions of (nearly) full CCl_4 conversion. Nevertheless, the catalysts display long-term stability in terms of both activity and selectivity to desired products (i.e. preferably to fully dechlorinated C_1-C_4 hydrocarbons).

2. Experimental section

2.1. Materials

The catalyst support we used was Davison 62 silica gel with 120–200 mesh size. The support was washed with diluted HCl and doubly distilled water, dried at 393 K for 21 h, and finally calcined in air at 723 K for 4 h. Tetrachloromethane (CCl_4) analytical reagent was purchased from POCh–Gliwice and had a purity of 99.9%. The following compounds were used as metal precursors: hexachloroiridic(IV) acid hydrate (ABCRGmbH&Co), ammonium chloroaurate (IV) hydrate (Specpure, JohnsonMatthey Chemicals Ltd), hexachloroplatinic(IV)