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Spent automotive three-way catalysts towards C—C bond forming reactions

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ABSTRACT

Spent automotive three-way catalysts, containing Rh, Pd and Pt nanoparticles supported on oxide-based ceramic materials, catalyze the Heck cross-coupling of iodobenzene with butyl acrylate and unsaturated alcohols at 140 °C. Under Suzuki reaction conditions, biphenyl was formed with high yield when the same catalysts were applied. Successful hydroformylation of 1-hexene was performed in the presence of PPh_3. The catalytic activity of spent automotive three-way catalysts was compared with that of airborne matter collected in the city of Wrocław.

1. Introduction

The amount of platinum group metals (PGMs) in atmosphere and in soil has increased in recent years, mainly as a result of the worldwide application of catalytic converters in motor vehicles [1–10]. Catalytic converters are widely used today to decrease the level of pollutants such as CO, NO_x, and unburned hydrocarbons (HCs) emitted with exhaust gases from combustion engines [11,12]. The active components of automotive catalytic converters consist of PGMs, such as Pd, Pt, and Rh, supported on ceramic material coated with Al_2O_3 and other metal oxides (CeO_2, ZrO_2). Palladium and platinum are active in the oxidation of CO and HCs to CO_2 and H_2O, whereas rhodium catalyzes the reduction of NO_x to N_2. Besides a very beneficial effect of automotive catalytic converters on the environment, especially the atmosphere, some negative aspects of their application should also be considered. Thus, PGMs in the form of nanoparticles may be released from the catalytic converter during car operation and accumulated in dust and subsequently in water and soil [13–15]. Moreover, spent catalytic three-way converters can be classified as hazardous waste materials, which is why the development of efficient and cheap methods of PGM recovery is very important [16–19]. In this context, it is also very important to recognize the catalytic activity of waste PGMs present in road dust and to estimate the catalytic activity of spent automotive catalysts which may find application in other catalytic reactions. For example, it has been demonstrated that scrap catalytic converters efficiently catalyze the hydrogenation of various alkenes [20] and show activity in VOC combustion [21]. Thus, it could also be possible to use spent catalytic converters not only as a source of PGMs but also as active catalysts for organic reactions.

The aim of the studies presented in this paper was to estimate the catalytic ability of (a) airborne particulate matter and (b) spent automotive three-way catalysts that have been used for a period of 6 years or more for the purification of exhaust gases. We applied these materials without any special pretreatment as catalysts for C—C bond forming reactions to test their catalytic potential. Aryl halides were used as substrates in the model C—C bond forming reactions. It is important to point out that the presence of aryl halides as wastes in water or soil should be seriously considered today. Consequently, knowledge about the catalytic activity of waste PGMs towards aryl halides might be useful in anticipation of possible transformations of aryl halides in the environment.

Usually, C—C cross-coupling reactions are catalyzed by palladium compounds, both organometallic complexes and Pd(0) nanoparticles [22–31]. In most cases these catalysts are not only specially prepared but also stored in an inert atmosphere before use. In this context, it was interesting to check whether PGM-containing wastes could compete in catalytic activity with carefully designed species.

Chemical deactivation or poisoning of the spent three-way catalysts is an important factor to consider. The properties of such double-use catalysts, which were first employed as a part of gasoline-powered vehicle emission control systems, and then engaged as the catalysts of C—C coupling reactions, might be much

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