

Editorial

# Editorial: Special Issue Catalysis by Precious Metals, Past and Future

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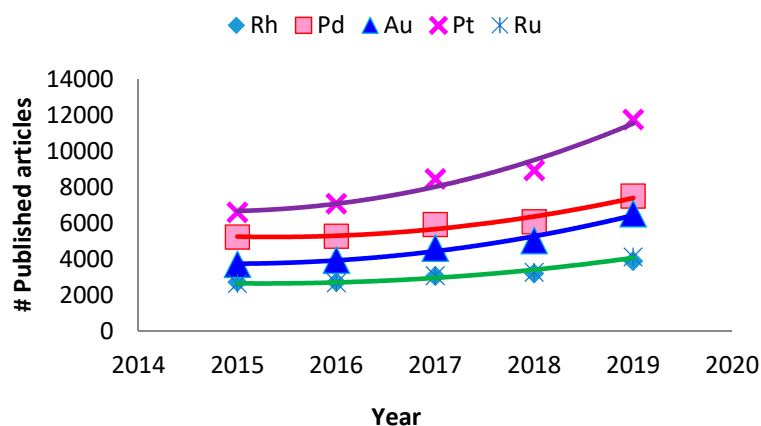
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Precious metal catalysis is often synonymous with diversity and versatility. These metals successfully catalyze oxidation and hydrogenation due to their dissociative behavior towards hydrogen and oxygen, dehydrogenation, isomerization and aromatization, propylene production, etc. The precious metal catalysts, especially platinum-based catalysts, are involved in a variety of industrial processes. Examples include the Pt-Rh gauze for nitric acid production, the Ir and Ru carbonyl complex for acetic acid production, the Pt/ $\text{Al}_2\text{O}_3$  catalyst for the cyclohexane and propylene production, and Pd/ $\text{Al}_2\text{O}_3$  catalysts for petrochemical hydropurification reactions etc. A quick search over the number of published articles in the last five years containing a combination of corresponding “metals” (Pt, Pd, Ru, Rh and Au) and “catalysts” as keywords indicates the importance of the Pt catalysts, but also the continuous increase in Pd and Au contribution (Figure 1).



**Figure 1.** Number of published papers in the last 5 years, search directed on science direct page ([www.sciencedirect.com](http://www.sciencedirect.com)) using combinations of simple keywords relating to corresponding metals (Pt, Pd, Ru, Rh or Au) and catalysts.

An important part of the Pt, Pd and Rh market includes the three-way catalyst (TWC catalyst), although the last research of the last 5 years reflects to a greater extent their participation in more fine chemistry reactions. The growth of the Pd catalyst market is reflected very well in this Special Issue by reports dealing with homogeneous and heterogeneous applications. Hobart, Jr. et al. [1] studied several palladium(II) bis-amino acid chelates for the oxidative coupling of phenylboronic acid with olefins. Despite having modest enantioselectivity, the Pd-complexes present a multiple cross coupling ability of the single substrate, providing a new horizon for the application of palladium organometallic complexes. The heterogeneous palladium catalysis are represented to a greater extent. González-Fernández et al. [2] described Pd/ $\text{Al}_2\text{O}_3$  catalyst activity in the gas phase hydrogenation of C4 alkynols. They found a special relationship between the hydrogenation rate and C-C bond polarity.

The rate increased following the order primary < secondary < tertiary alkynol. The secondary alkynol transformation rate increased due to the preferable ketone formation via double bond migration. Gao et al. [3] carefully designed Pd heterogeneous asymmetric catalyst for the hydrogenation of acetophenone. This strategy allowed the authors to obtain a highly dispersed high-loading catalyst, resulting in an important increase in the enantioselectivity. The ability of Pd/carbon nanotube catalysts to catalyze the dodecahydro-N-ethylcarbazole dehydrogenation reaction was studied by M. Zhu et al. [4]. The catalyst revealed its potential as a stable and well performing catalyst for hydrogen production—5.6 wt.% of hydrogen was maintained after five catalytic cycles. S. P. Samudrala and S. Bhattacharya [5] addressed the near future of the supported Pd catalysts, towards the sustainable synthesis of added value chemicals, specifically the direct hydrogenolysis of glycerol to 1-propanol the exemplified reaction. This study proposed a possible route to convert the biomass-derived glycerol (rest from the biodiesel industry) into useful chemicals. The optimization of catalyst and reaction parameters resulted in around 80% of total propanol yield.

On the other hand, A. Arevalo-Bastante et al. [6] compared the activity of the carbon-supported Pd catalysts to their Pt and Rh homologues in the hydrodechlorination of dichloromethane. The Pd catalyst in this case was taken over by Pt and Rh catalysts due to their higher stability upon sintering and their ability to maintain the active site unaltered during the treatment prior reaction and therefore. X. Auvray and A. Thuault [7] chose the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst to study the effect of microwave pretreatment over precious metal dispersion. The microwave heating was compared to the conventional method of drying and calcination. It was found that microwave heating is only beneficial during drying but the conventional method was necessary to maintain acceptable metal dispersion. J. W. Jung et al. [8] also concentrated on the effect of reduction treatment over bimetallic Pt-Sn catalyst and its behavior in the reaction of propane dehydrogenation. Different Pt-Sn alloys were identified according to the reduction procedure. Well-dispersed Pt<sub>3</sub>Sn alloys were found to allow reaction acceleration together with coke migration and active sites preservation.

Ru was also represented in this Special Issue. M. Nishi et al. [9] designed a series of Cs-Ru catalysts supported on mesoporous carbon for ammonia synthesis. The catalytic results show an important dependence on Ru particle size and reduction behaviour, the latter being especially important to obtain the catalytically active phase metallic Ru with adjacent CsOH species. The ammonia synthesis utility of Cs-Ru catalysts was demonstrated for the first time, using CO<sub>2</sub>-free hydrogen from renewable energy with intermittent operation in Fukushima Renewable Energy Institute (FREA) of AIST, Japan.

The last group of publication involves different gold catalysts for photo and catalytic purposes. O. H. Laguna et al. [10] used Au/TiO<sub>2</sub> catalyst for photodegradation of phenol and CO oxidation. The gold catalysts prepared by photodeposition presented an important photoactivity due to the inhibited titania anatase–rutile transition. However, the prepared catalysts were less active in the gas phase oxidation of CO due to the sintering of the active phase. The importance of preserving gold nanoparticle size appears also to be a key factor in the study proposed by Chenouf et al. [11] where preformed gold colloids were stabilized by polymeric or solid-state protecting agents and immobilized on various ceria based oxides. The catalyst series was employed in two catalytic reactions, one in the gas phase and other in the liquid phase. In both reactions, the use of montmorillonite as a stabilizing agent resulted in very active catalysts due to different metal electronic state.

The review proposed by G. Ferreira Teixeira et al. [12] crowned the Special Issue and revised the role of precious metals in the perovskite photocatalytic and electrocatalytic processes. Silver and gold are the most employed metals to promote perovskites photoactivity, where the future points to the use of metal/perovskite hybrids for pollutants degradation or even for water splitting.

Let us finish as we start: the future of the precious metals is “shiny and resistant”. Although judged expensive and potentially replaceable by transition metal catalysts, precious metal implementation in research and industry shows the opposite. Literally, every year new processes catalyzed by these metals appear, the best example being the important variety of biorefinery reactions or photocatalytic

water splitting. Their versatility reflects their diversity and enlarges their current and future horizons of application.

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