


Editorial

Mono- and Bimetallic Nanoparticles in Catalysis

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Introduction

The catalytic applications of supported mono- and bimetallic nanoparticles are wide on the laboratory, pilot plant and industrial scale. Over the last 20 years, the design, synthesis and characterization of metal nanoparticles have been the focus of attention in heterogeneous catalysis due to specific surface, electronic and structural properties, as well as a large surface-to-volume ratio [1]. In the nanoscale size range, metal particles undergo a transition from metallic to atomic properties, leading to unique electronic and catalytic properties that differ from their bulk phases. A bright example is catalysis using gold, which was opened up only in 1987 when Haruta's research group succeeded in the preparation of isolated Au NPs of the size below 7 nm on the surface of metal oxides [2] and received wide recognition 15 years later after the publication of detailed results on the preparation of supported Au NPs by Louis's research group alongside others [3]. Moreover, the size of nanoparticles (average size and particle size distribution) was shown may not only enhance catalytic activity, but also changes the process direction and the major reaction products. For example, it was shown [4] that a decrease in the size of isolated palladium NPs to 3.5 nm improved specific catalytic activity in the hydrogenation of 2,4,6-trinitrobenzoic acid sodium salt to triaminobenzene, whereas the reaction over the catalyst with large Pd NPs (the average size of 15 nm) resulted in the non-aromatic cyclohexane-1,3,5-trione trioxime and further hydrogenation was suppressed. In ethanol dehydrogenation, the selectivity of acetaldehyde and ethyl acetate can also be tailored by the Cu NP size; namely, the small particles of about 2.7 nm favor acetaldehyde formation [5], while particles larger than >10 nm benefit the ethyl acetate production [6].

Another way to improve the catalytic activity and selectivity of supported metal NPs is the modification of the surface of primary metal NPs with a second metal or metal oxide, as well as the synthesis of bimetallic NPs with the alloy, intermetalide, core-shell and other structures. Bimetallic NPs have found wide applications in catalysis and have become a prevailing concept in catalyst development. The combination of precious metals with non-noble ones in bimetallic NPs can lead to different structures and different types of interactions. It was recently shown that the combination of gold in ultra-low amounts (<0.1% wt) with FeO_x NPs supported on CeO₂ can provide the selective oxidation of glycerol to glyceric acid with a high yield, while monometallic Au and Fe catalysts were almost not active in the reaction [7]. Pt-Zn intermetalide NPs showed high activity and selectivity in acetylene semihydrogenation due to the weak π -bonding of ethylene with the Pd-Zn-Pd surface, excluding the further hydrogenation of a double bond [8].

A number of research papers and reviews on various subjects of advanced nanocatalyst preparation have already been published in 2021–2023. Particular interest is paid to precise synthesis on the atomic scale [9–12]. Supported bimetallic nanoparticles can be prepared in controllable ways depending on the required particle size, chemical composition, spatial distribution of the two metals, morphology and potential applications. In the recent years, besides nanocatalysts, single-atom catalysts (SACs) based on precious metals have been developed and successfully used in heterogeneous catalytic reactions [13]. The coexistence



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of nanoparticles and single-atom sites (SAS) offers another promising approach to improve the catalytic performance of nanocatalysts [14]. For example, a catalyst comprising both Ir nanoparticles and Ir single-atom sites exhibited excellent performance in the hydrogen oxidation reaction and CO electro-oxidation reaction [15]. The coexistence of Fe NPs and Fe single-atom sites in the catalyst on N-doped carbon resulted in increased catalytic activity and selectivity in the aerobic oxidation of primary amines to imines compared to both the Fe single-atom and the nanoparticle catalysts [16]. A similar effect was observed for TiO₂-supported Pd catalyst in the hydrogenation of methylacetophene [17]. Anchoring single-site oxide promoters can be successfully used for selective regulation in nitroaromatic hydrogenation over Au NPs [18]. The stable single-atom active sites on the surface of bimetallic nanoparticles can be prepared using galvanic replacement, sequential reduction and impregnation methods or generated via adsorbate-induced segregation [19]. The application of the SAC approach considerably decreases the amount of expensive precious metals and enhances catalytic activity, thus making the catalytic process more economical and sustainable.

The study of both monometallic and bimetallic catalysts, especially with low loadings of active components, is sometimes a tricky issue. The electronic states of the elements in small NPs can be distinguished using non-trivial methods such as EXAFS or NAP XPS, which is also applied in situ [20,21], and DRIFTS methods combined with DFT calculations [22,23]. However, these methods are not routine and even require the use of international synchrotron centers. Therefore, understanding the action mechanism of SAC and low-loaded mono- and bimetallic catalysts is still a big problem that creates a gap in obtaining catalytic systems with tuned properties.

In this Special Issue, we want to address the importance of the controllable synthesis of supported nanocatalysts and show how their properties influenced their catalytic activity. The combination of two metals or a metal and metal oxide opens a wide range of different structures and types of interactions between the two components, which, in turn, governs the application of the obtained systems in a variety of reactions as follows: partial and complete oxidation, selective hydrogenation, electro- and photocatalysis. Studies on the structure of the catalyst are one of the main topics of this issue, and the use of modern methods can give unique results in understanding the catalytic behavior of systems.

Selepe et al. [24] proposed a straightforward and cost-effective strategy for the preparation of the electro-catalysts comprising highly dispersed monometallic Pd NPs or bimetallic Pd–Sn alloy NPs supported on amorphous carbon nanofibers with cylindrical shape-like morphology via the chemical reduction method with ethylene glycol as the reducing agent. The improvement of the electrochemical performance in both methanol and ethanol electro-oxidation was revealed for the Pd–Sn catalyst compared with the Pd and conventional catalysts, which are associated with a synergistic effect via alloy formation and modifying the Pd atom arrangement using Sn, thereby promoting oxidation through a dehydrogenation pathway. Moreover, the simultaneously formed SnO₂ generates abundant OH species, which affords an increase in the rate of the oxidative removal of carbon monoxide intermediates from Pd sites, thus enhancing the stability of the catalyst. Both methanol and ethanol are recognized as promising forms of fuel for direct alcohol fuel cells used as power sources for mobile, stationary and portable applications.

Saraev et al. [25] explore the important phenomena of nanoscale active component evolution under the reaction conditions. In situ extended X-ray absorption fine structure (EXAFS) spectroscopy was used for studies of 3% Pd/Al₂O₃, 3% Pt/Al₂O₃ and bimetallic (1% Pd + 2% Pt)/Al₂O₃ catalysts examined in the total oxidation of methane in a temperature range of 150–400 °C. The mono- and bimetallic Pd and Pt catalysts were prepared via the incipient wetness impregnation of γ -alumina using a solution of palladium and/or platinum nitrates with glycine, whose addition led to the formation of Pt(Pd)–glycine complexes, resulting in highly dispersed the noble metal NPs over the support surface. In all initial catalysts, a “core–shell” structure of NPs was observed, in which the metallic core was covered by an oxide shell. The Pt and bimetallic Pd–Pt NPs were shown to be more

stable against the sintering processes than Pd NPs. The “core–shell” structure for the Pt and bimetallic Pd–Pt NPs was stable in the temperature range of 150–400 °C, while the metallic core of Pd NPs was reversibly oxidized at temperatures above 300 °C and reduced to a metallic state with the decrease in the reaction temperature.

Smirnova et al. [26] investigated the local structure of Pd₁ single sites on the surface of relatively large Pd₁In₁ intermetallic NPs of the size 10–30 nm supported on α-Al₂O₃ with the combination of experimental and theoretical methods, i.e., CO-DRIFT spectroscopy and DFT calculations. The preparation procedure of the incipient wetness impregnation of α-Al₂O₃ by an aqueous solution of Pd and In nitrates followed by a reduction with molecular hydrogen was made possible to avoid the formation of monometallic Pd NPs. The results of CO-DRIFTS revealed only linear CO adsorption on PdIn nanoparticles as indicated by two CO stretching vibration bands at 2065 and 2055 cm^{−1}, corresponding to CO adsorption on (111) and (110) facets of PdIn NPs. DFT results also showed that multipoint CO adsorption on the surface of Pd atoms, which is featured for Pd NPs, was hindered both on the (110) PdIn facet due to the large distance between neighboring Pd atoms (3.35 Å) and on the (111) facet because adjacent Pd atoms were located below the surface plane.

Authors also traced the temperature-induced changes in the bulk and surface structure of alumina-supported PdIn intermetallic NPs using in situ XAFS and DRIFTS of adsorbed CO [27]. TEM studies exhibited how morphology and a relatively narrow size distribution in the range of 2–6.5 nm for the supported NPs was essentially preserved after oxidative treatment at 250 °C, although the mean particle diameter decreased slightly from 5.1 nm to 4.2 nm. It was shown using EXAFS that even at ambient conditions upon contact with oxygen, the intermetallic PdIn compound, which was formed by a reduction with hydrogen at 500 °C, partially decomposed with the formation of In oxide species.

Kirichenko et al. [28] developed a novel type of bimetallic catalyst in which the surface of metal NPs was modified with another metal oxide. Cr₂O₃/Pd/TiO₂ and Cr₂O₃/Pd/SiO₂ catalysts were prepared using a redox method based on the catalytic reduction of CrO₄^{2−} to Cr³⁺ via H₂ adsorbed on Pd NPs under ambient conditions that could be performed in the two following steps or in a “one-pot” regime. This method allows small CrOx–Pd NPs with an average size < 3 nm to be obtained. The selective deposition of Crⁿ⁺ species onto the Pd surface was confirmed via the FTIR–CO study and TPR–H₂. Intensive hydrogen consumption from −90 to −40 °C using the Cr₂O₃/Pd/TiO₂ system was observed for the first time for Pd-containing catalysts. Cr₂O₃/Pd/TiO₂ catalysts showed much higher activity and selectivity in the semi-hydrogenation of phenylacetylene compared to the monometallic Pd/TiO₂ sample under ambient conditions.

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