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Bimetallic systems of mesoporous ordered silica supports and noble metals nanoparticles

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This paper describes of preparation and characterization of new bimetallic materials based on platinum/silver, platinum/palladium and palladium/silver systems of nanoparticles supported on mesoporous ordered silica composite. In all investigated materials unusual ammine complexes of noble metals ($[Pt(NH_3)_4]Cl_2$, $[Ag(NH_3)_2]OH$ and $[Pd(NH_3)_4]Cl_2$) were used as nanoparticles sources. Bimetallic materials were synthesized by one-pot procedure or post synthesis modification via impregnation method with metal precursors on surface of mesoporous ordered silica. The obtained materials were characterized by various techniques including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), nitrogen physisorption and FTIR/PAS spectroscopy.

Proposed system of noble metal nanoparticles allows determining subtle changes in the interaction between metallic phases and porous carrier with particular emphasis of spectroscopic properties. In the current study, we have attempted to relate the synergistic effect of components for understanding relationships between type of noble metal ammine complexes as metal precursors and final material properties. We found that significant interactions occur between supported metals and relatively inert mesoporous ordered silica. What is more, noble metal crystallites in bimetallic systems exhibit different sizes depending on the kind of metal source. Such a difference in sizes of individual components may be responsible for lack or presence of interactions between metal nanoparticles and solid support. Specific distribution of platinum nanoparticles on the support surface and their very small sizes in Pt,Ag/SBA-15 systems causes intrinsic electron deficiency due to the interactions between a small platinum crystallite and the silica surface. The possible interaction effect between palladium and the silicon atoms was also observed. This indicates that the metal-support effect should be considered during designing and production of new functional materials, models of catalysts and adsorbents.

1. Introduction

Nanoscience is one of the fundamental technologies of the current century and become a major part of future technological solutions and our live. Over the last decade, the design, synthesis and detailed characterization of nanomaterials became important issue because of the enormous demand for new functional materials. High ordered mesoporous materials with noble metals ions and nanoparticles attract the attention in designing catalysis and modern materials [1–3]. The ordered mesoporous materials are often modified to improve their desired properties by addition of noble metals or metal oxides. The presence of highly dispersed metal particles is advantage in obtaining new functional materials and active catalysts as well as functional materials for biomedical applications due to their biocompatibility and well-defined structure [4–6]. Such systems link the useful properties of solid carrier like high surface area, uniform pore size and ordered pore structure with size-related properties of microscopic particles [7,8]. Moreover, modern catalysts many times are supported on bimetallic or trimetallic configuration of noble metals and nanoparticles and the important feature of this solution is synergetic effect generated by two or more types of constituents as well as unique properties of new composites which are sometimes quite different in comparison with their individual counterparts [9,12]. Among them, Pd, Pt

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and Ag atoms are widely used owing to their activity in catalysis, also in the context of industrial applications [13]. Some examples include the following instances: the preparation of uniform and well-distributed Ag-Pd nanobimetallic colloidal particles supported on organically modified aminosilicate [14], the synthesis of nanobimetallic particles of Au–Pd, Au–Ag, and Au–Pt in organically modified silicates systems [15], preparation of silver–palladium nanoparticles in supercritical carbon dioxide [16] and finally the description of the mechanisms of nucleation and growth of Ag–Pd bimetallic clusters [17]. Of course a lot of other work relates to this topic [18–23]. It was also confirmed that the addition of another atom to platinum catalysts, significantly improves the activity of the catalytic system by the protecting of the surface functionality [24,25]. The latest reports concern about preparing bimetallic palladium–silver nanoparticles supported on reduced oxide graphene. Such new hybrid system exhibited good electrochemical catalytic activity for alcohols electro-oxidation process [26]. Among the new catalytic materials, noble and transition metal particles supported on mesoporous ordered silica were proposed for reaction of catalytic combustion of acetonitrile [27]. Though significant progress has been achieved in designing and obtaining the functional products, more precise explanation of the interaction between components is required to achieve confidence to final multi-component materials. This class of structures is important due to unique properties generated by combination of components, their sizes and possible interactions [28–36]. On the other hand the catalytic performances of supported noble metal ions or nanoparticles are directly related with nature and properties of support and its surface [37]. Surface layers and supported molecules, without any doubt, determine the final properties of nanostructures [38,39]. Despite the fact that surface of nanoparticles is so important, it should be underlined that nanoparticles are never produced in equal sizes. Even very uniform nanoparticles with regard to sizes and properties may have different surface properties and these differences may have an impact on their applications. For meeting the needs of actual researches, there has been an important problem of noble metal nanoparticles interaction with biological and catalytic systems. Only precise characterization of nanostructures is helpful in understanding the nature and fundamentals of nanomaterials. Estimation the strength and type of interactions of metal particles with support surface is significant for catalytic solutions [40,41]. They can alter the properties, efficiencies and selectivities of chosen materials [42–44]. Very important is the fact that the presence of interactions causes the final product completely different than anticipated during their designing. Among many types of new composites, the noble metal/silica composites are willingly used as the test systems as well as composites with high potential for application [45–48]. Still, one of the significant problems is the nature and intensity of interactions that may exist between support and metal nanoparticles [49]. Tauster et al. [50] defined a strong metal-support interactions (SMSI) between noble metals and TiO_2 as the support. In that early work, the authors proposed the formation of chemical bonds between the supported noble metals and titanium cations or atoms and the formation of intermetallic compounds. Partial electron transfer as a model of metal-support interaction for small platinum clusters supported on Y zeolite was observed in literature [51,52]. Strong and rare interactions between metal and support atoms were defined by R. Lamber et al. [53]. They observed that heating procedure of the palladium/silica system in a hydrogen atmosphere might lead to chemical metal/support interaction and growth of Pd_2Si phase. Similarly, the intermetallic Pd–Si interaction was identified in our previous work. It was found that some part of palladium atoms is able to form the chemical bonds with silicon during simple preparation procedure of monometallic model of catalyst [54]. In this work, highly dispersed noble metal particles on mesoporous ordered silica were prepared in terms of bimetallic systems. Mesoporous ordered silica (SBA-15) was used as a support materials due to high surface area, ordered structure of mesopores and high thermal and chemical stability. The presence of two types of porosity (micro and mesopores) with very narrow pore size distribution gives possibility of simultaneous incorporation crystallites of one type of metal in pores of the support (for example small particles of platinum) and second one outside the porous system if they reveal the size differences. Such system may exhibit positive catalytic properties.

The proposed systems of noble metal nanoparticles allow to determine subtle changes in the interactions between metallic phases and porous carrier in bimetallic systems. The precise definition of possible behavior of the active phases in the catalyst model may have important implications in catalysis and surface science. The measurement of the binding energy of atoms made by X-ray photoelectron spectroscopy may be applied to analyze the crucial surface properties of new materials and composites.

2. Experimental

2.1. Materials

Triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Mw = 5800), tetraethyl orthosilicate (TEOS, 98%), tetraammineplatinum(II) chloride hydrate (98%) were all purchased from Sigma–Aldrich. Tetraamminepalladium(II) chloride monohydrate (99.9% metals basis, Pd 39% min.) was purchased from Alfa Aesar GmbH & Co KG (Germany). Diamminesilver (I) complex $[Ag(NH_3)_2]^+$ was prepared as follows: silver nitrate (0.3 mol L^{-1}) was mixed with sodium hydroxide aqueous solution (1.25 mol L^{-1}) for receiving brown precipitate of Ag_2O. Silver(I) oxide was separated from solution, washed with distilled water and dissolved in 2.63 mL of concentrated (25%) ammonium hydroxide All solutions were prepared with deionized water.

2.2. Preparation of SBA-15 support

SBA-15 support was prepared on the basis of procedure proposed by Zhao et al. [55,56] and described in details in our previous work [57]. The synthesis route was carried out at constant temperature (35 °C in the case of synthesis mixture and 95 °C during aging step). Mesoporous support was made by dissolution of copolymer template (4 g) in the mixture of 30 mL of deionized water and 120 mL of HCl (2 mol/l). Next 9.12 g of tetraethyl orthosilicate was dropped and the mixture was maintained at 35 °C for 24 h under stirring. The solution and precipitate was loaded into an autoclave and heated at 95 °C for 48 h. Finally material was calcined at 550 °C for 4 h with 3 °C/min heating rate in muffle furnace under an air-atmosphere.

2.3. Preparation of bimetallic composites

For impregnation of SBA-15 by noble metal ions, calcined SBA-15 (0.5 g) was immersed in aqueous solution (10 mL and pH = 8.0) of one type or mixture of noble metal ammine complexes from the group of $[Ag(NH_3)_2]^+$, $[Pt(NH_3)_4]^{2+}$ or $[Pd(NH_3)_4]^{2+}$ ions (Table 1). Firstly, the mixtures were kept in an ultrasonic bath for 1 h and secondly left overnight in static conditions. Products were recovered by filtration and dried under an air atmosphere in 100 °C. Samples B10 and B11 were prepared similarly to pure SBA-15 support sample. The metal ions were added to the synthesis mixture before TEOS addition.