

Ni-supported Pd nanoparticles: a new catalyst for low-temperature ammonia cracking

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ABSTRACT

Ammonia cracking is a method used in the treatment of flue gases from coal or biomass gasification or for hydrogen generation in chemical or related industries. It is an important issue in hydrogen economies. As a carbon-free compound, ammonia provides a potential source of ecological fuel for mobile and stationary power generation, especially for fuel cells, where CO impurities are unacceptable. However, more efficient catalysts are needed for new technologies in this area. Herein, we report a new nanometallic catalyst for ammonia cracking at temperatures well below 500°C. We have discovered that supporting Pd nanoparticles (Pd NPs) directly on Ni grains provides an active and durable catalyst for this reaction. We also report a new, facile and scalable wet chemical method for supporting Pd on Ni; in this method, Pd NPs initially supported on SiO₂ were placed in contact with Ni grains to yield, after a final SiO₂ digestion, a Pd/Ni unalloyed contact.

Keywords: Bimetallic nanocatalysis, oxidation, Sonogashira coupling, Au nanoparticles, Ni-supported nanoparticles

1 INTRODUCTION

Nanocatalysts are extremely sensitive toward structure differentiation, and their activity and selectivity depend not only on nano-metal and support type but also on size, shape, and composition [1]. Thus, optimization of such materials is an open issue. In fact, more efficient catalysts are still being sought to run the reactions with higher yields and higher selectivity under mild conditions. Other important problems to be addressed include reducing the fraction of noble metals, facilitating the catalyst separation, improving reusability, and reducing contamination of the final products. Probably the widest application gained Au nanoparticles (Au NPs) which catalyze a variety of reactions [2-7]. As they tend to agglomerate, they are usually supported on carriers to form more stable catalytic systems. Generally, Au NPs are available on a variety of supports, from carbon-like graphite to inorganic materials.

Basically, the first should be wettable by apolar reagents and solvents, while the latter should be wettable by polar ones. Wettability, and consequently catalyst availability for the reactants, is of crucial importance for the reaction progress; e.g., recently oxidation of cyclohexene and D-glucose over nano-Au/SiO₂ in water has been compared. In this reaction, polar polyhydroxyl D-glucose complying with this polar SiO₂ support and a polar solvent (H₂O) reacted smoothly at room temperature, whereas nonpolar cyclohexene violating the polarity rule needed the addition of surfactants to react efficiently [8].

2 BIMETALLICS FOR NANOCATALYSIS

Recently, we developed a new method for transferring SiO₂-supported nano-metals to a variety of supports [8-10]. We optimized this procedure using SiO₂ supported Au NPs, e.g., we prepared bimetallic nano-Au or Pd supported on Cu or Ni grains, to test their performance in a variety of reactions, including oxidation or Sonogashira coupling [9-10]. We tested for the first time the efficiency of SiO₂-, Cu-, and Ni-supported Au in deep glycerol oxidation in a diluted and viscous H₂O₂/H₂O liquid phase. Acetic acid (AA), the C2 oxidate, was preferentially formed in such a system. High conversion (100%) and AA yields (90%) were observed for the sol-gel SiO₂-supported Au in diluted solutions. Although with the increase of glycerol concentration in the viscous liquid phase these values decreased to ca. 40% (conversion) and 20% (AA yield), the addition of acetonitrile improved the AA yield to ca. 40%, while the surfactants were found to be capable of a many-fold enhancement of the catalyst activity at the room temperature highly-viscous liquid phase. High performances were also observed for the bimetallic Au/Cu and Au/Ni catalysts obtained by nano-Au transfer; however, these catalysts were destroyed during the reaction by the Cu or Ni leaching effect.

A copper supported nanopalladium catalyst obtained by an innovative method of nanoparticle transfer from the intermediate carrier SiO₂ to the target Cu carrier was a highly efficient and selective catalyst, giving as much as quantitative conversion in a series of Sonogashira reactions. Comparisons with other Pd systems, especially Pd/SiO₂,

indicated substantial advantages for this novel catalytic system. X-Ray photoelectron spectroscopy (XPS) studies of the prepared Pd/Cu catalyst revealed the development of a PdO species in the Pd/Cu system and illustrated for the first time the importance of the resulting Pd/PdO/Cu system for efficient Sonogashira coupling [10].

During this study we investigated possible applications of Ni supported Pd NPs.

3 RESULTS AND DISCUSSION

Ammonia cracking is a method used in the treatment of flue gases from coal or biomass gasification or for hydrogen generation in chemical or related industries. It is an important issue in hydrogen economies. As a carbon-free compound, ammonia provides a potential source of ecological fuel for mobile and stationary power generation, especially for fuel cells, where CO impurities are unacceptable. However, more efficient catalysts are needed for new technologies in this area. Herein, we report a new nanometallic catalyst for ammonia cracking at temperatures well below 500°C. We have discovered that supporting Pd nanoparticles (Pd NPs) directly on Ni grains provides an active and durable catalyst for this reaction. We also report a new, facile and scalable wet chemical method for supporting Pd on Ni; in this method, Pd NPs initially supported on SiO₂ were placed in contact with Ni grains to yield, after a final SiO₂ digestion, a Pd/Ni unalloyed contact.

This method provides interesting capabilities for the potential production of industrial catalysts where relatively low-cost Ni, e.g., in the form of wire meshes, provides not only a catalytic moiety but also a flexible catalyst support. This discovery is significant because hydrogen production from ammonia [11] appears to be a difficult problem. Ammonia decomposition is a complex process that proceeds through stepwise dehydrogenation ($\text{NH}_3 \rightarrow \text{H} \rightarrow \text{NH}_2 \rightarrow \text{H} \rightarrow \text{NH} \rightarrow \text{H} \rightarrow \text{N}$) and yields H and N, which recombine to H₂ and N₂, respectively. Although the binding energy of the nitrogen should be sufficiently strong for dehydrogenation, it should not be too high to block the recombination step [12-15].

Among potential catalysts for this process, Ru has been observed to be the most active; [16] however, *the effects of the Ru particle size and shape can be very difficult to elucidate, and a simultaneous comparison of these factors is almost impossible* [17].

In Figure 1 we presented representative SEM and TEM images of the Pd/Ni catalyst.

Hydrogen productivity of the new catalyst [nanoPd/Ni (1% Pd)] if compared with the literature data showed the evident advantage of the new system.

In Figure 2 we illustrated temperature efficiency of the system.

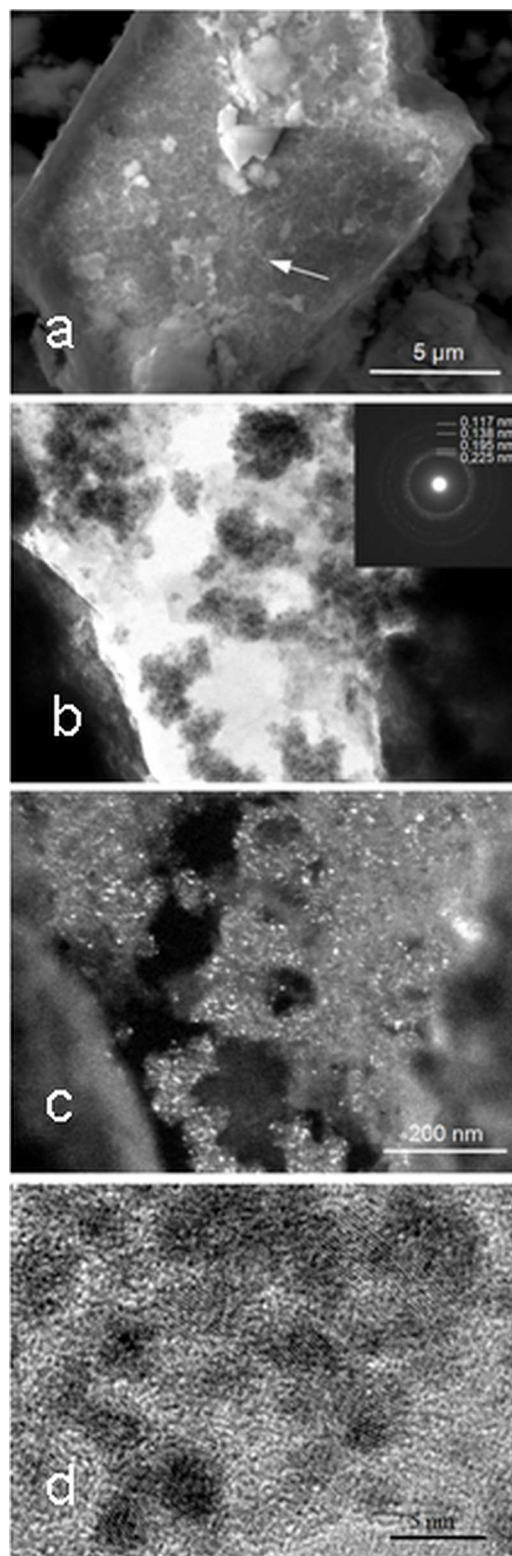


Figure 1: Representative SEM and TEM images of the Pd/Ni catalyst. a - SEM image of the Pd NPs aggregates on the Ni surface; b, c - TEM bright- and dark-field images of the Pd nanocrystalline aggregates on the Ni surface; d - HRTEM image of the Pd NPs with diameters less than 5 nm on the Ni surface.

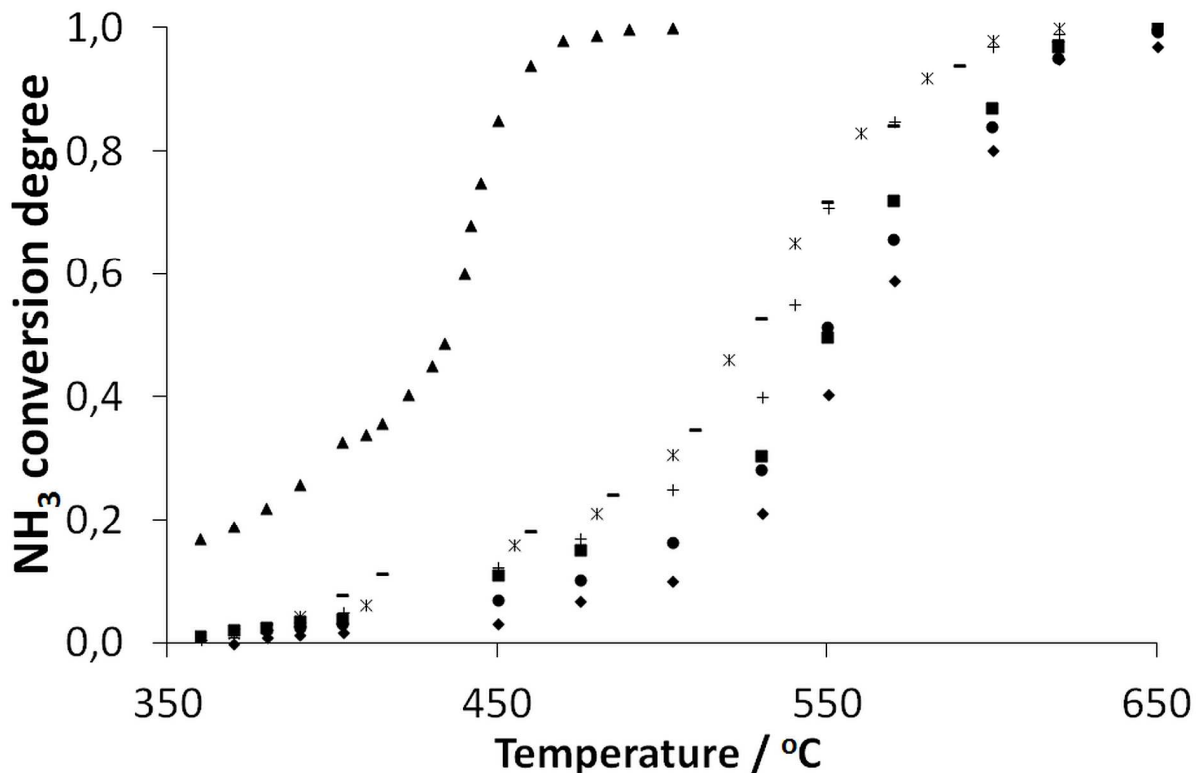


Figure 2: Ammonia conversion on the Pd/Ni catalyst (triangles) compared with that on the analogously processed control Ni carrier (black squares), unprocessed Ni (circles), PdO (crosses), SiO₂ (dashes), Ni/SiO₂ (diamonds) and Pd/SiO₂ (asterisks) at a flow rate of 2 dm³/h.

4 EXPERIMENTAL

4.1 Preparation of metal NPs on sol-gel silica

The series of metal/silica nanocatalysts were prepared according to the procedure optimized. The carrier is obtained using the Stöber method with tetraethyl orthosilicate (TEOS), which is added to a mixture of ethanol and water with an aqueous ammonia solution.

A mixture was sonicated, then concentrated, dried, and reduced under hydrogen at 500 °C. In a typical procedure, 800 mL of anhydrous ethanol and 135 mL of 25 wt.% solution of ammonia were mixed with 78 mL of deionized water. After 10 min of stirring 60 mL of tetraethyl orthosilicate was added to the reaction mixture which was next stirred for 3 h at room temperature. The colloidal silica suspension was centrifuged, placed in an ultrasound bath and stirred for 90 min. A solution containing, e.g., gold precursor (0.07 g 40% (wt.%) chloroauric acid for 0,1% Au/SiO₂) in deionized water (8 mL) was added dropwise

into the obtained carrier, i.e., colloidal silica, and mixed in an ultrasound bath for 30 min. Next, it was dried at 60–90 °C for about 12 h in dark, ground and sieved. The reduction was conducted in an oven under hydrogen at 500 °C for 4 h.

4.2 Preparation of bimetallics

Bimetallic catalysts were prepared using a novel facile approach involving the transfer of nanoparticles from the intermediate carrier, i.e., SiO₂, to the target carrier. The general method includes several steps. The target carrier i.e., Cu or Ni, (0.99 g) and Au (Pd) NPs of a low polydispersity deposited on the intermediate carrier i.e., 1,0% Au/SiO₂, (1.00 g) were suspended in deionized water (100 mL) under mechanical stirring and sonication. After 10 minutes of vigorous stirring sodium hydroxide (40 mL 40% w/w) was added to the suspension and stirring was continued for 4 h at 80 °C, whereupon the suspension was allowed to stand for about 18 h until the suspended solids sedimented. The suspension was centrifuged and the supernatant was decanted, the precipitate was washed five

times with deionized water and centrifuged again to achieve neutral pH of the supernatant. Precipitate was washed with deionized water, centrifuged and supernatant was removed. The obtained catalyst was dried in an electric dryer to a constant weight at 110 °C.

The resulted preparations of silica and bimetallic catalysts were examined by X-ray photoelectron spectroscopy (XPS) using PHI 5700 spectrometer with monochromatized AlK α a radiation. Alternatively, the samples were suspended in ethanol, sonicated for 15 min and the resulted materials were deposited on carbon adhesive tape for the preparation of the samples for TEM analyses. The transmission electron microscopy (TEM) images of the resultant composites were obtained on a JEOL 2000 FX operating at 200 kV or high resolution (HRTEM) JEM 3010 microscopes (both with EDS systems for chemical composition microanalysis). The scanning electron microscopy (SEM) JSM6480 or a PHILIPS XL 30 was used for morphology investigation of composite powders.

The energy-dispersive X-ray fluorescence (EDXRF) analysis was performed on the Epsilon 3 spectrometer (Panalytical, Almelo, The Netherlands) with a Rh target X-ray tube with 50 μ m Be window and max. power of 9W. The spectrometer is equipped with thermoelectrically cooled silicon drift detector (SDD) with 8 μ m Be window and resolution of 135 eV at 5.9 keV. The system is also equipped with five primary filters that can be selected to improve measuring conditions for determined elements. The quantitative analysis of Au or Pd/SiO₂, Pd/Cu or Pd/Ni catalysts was performed using Omnian software based on fundamental parameter method.

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