Supported metal nanoparticles for catalytic applications

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Highlights

- Application of the g-C_3N_4 surface as a reducing agent resulted in small metal nanoparticles.
- Such nanoparticles demonstrated high catalytic performance in the electrochemical oxidation of HMF.
- Zeolite supported metal particles as companion catalysts for regeneration of the primary catalyst.
- Decrease in the catalyst regeneration temperature upon the application of Pt and Ru nanoparticles.

1. Introduction

Experimental procedures for the preparation of supported metal nanoparticles typically include impregnation of a support with a suitable metal precursor followed by the reduction of metal ions with a reducing agent ($NaBH_4$, sodium citrate, ethanol, hydrazine, etc.) [1]. Application of graphitic carbon nitride as a support was found to contribute to the formation of small and relatively homogeneous ruthenium nanoparticles (ca. 1.3 – 1.6 nm, reduction of a ruthenium precursor with hydrazine) [2] which can be connected with a stabilizing effect of the carbon nitride surface [3]. We hypothesize here that the surface N-containing species of a suitable support (e.g. g-C_3N_4 as in this case) can serve as a reducing agent to obtain metal nanoparticles with smaller particle sizes due to the high density of N-containing groups uniformly distributed over the support surface.

Contrary to the notion that a catalyst emerges unchanged from a catalytic reaction, most catalysts deactivate over time and require replacement or regeneration. Among the many possible causes for deactivation of solid catalysts [4, 5], the deposition of carbon-containing compounds is a common problem across different feed streams, independent of whether they are sourced from petroleum, biomass, or plastics waste. We propose the new concept of a secondary “companion” catalyst for mild regeneration of a primary catalyst for a given target reaction (Diels-Alder reaction).

2. Methods

Graphitic carbon nitride (g-C_3N_4) prepared via thermal treatment of melamine (525 ºC for 2 h) was applied as a support for Ru, Ni and Co deposition. Metal nanoparticles were prepared using impregnation of the support with corresponding metal chlorides followed by reduction with hydrazine in alkaline solutions (0.1 M KOH) at 80 °C. A similar set of samples were prepared without hydrazine under the same conditions. The prepared samples were tested in the electrochemical oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) in alkaline environments (0.1 M KOH).

As the starting catalyst for the Diels-Alder reaction between 2,5-dimethylfuran and ethylene, a commercial beta zeolite with Si/Al 12.5 (SiO_2/Al_2O_3 25) was used. For the synthesis of regeneration catalysts, the starting zeolite was modified with metals (Pd, Pt, Ru, Ag, Ni, Cu) by ion exchange in solutions of salts of the corresponding metals. The calculated amount of metal deposited on the zeolite was 100 μmol of metal per 1 g of zeolite.

3. Results and discussion

Supported metal nanoparticles prepared without using hydrazine are characterized by smaller particle size and better homogeneity compared to the samples prepared with hydrazine (for instance, 5-9 and 6-30 nm, respectively, for Ni particles). It confirms the hypothesis that the support surface (g-C_3N_4) can serve as a reducing agent itself resulting in smaller and more uniform metal nanoparticles compared to the synthesis using an added reducing agent (hydrazine). The screening of the prepared supported nanoparticles in the electrochemical oxidation of HMF in 0.1 M KOH to FDCA revealed slightly higher or similar electrocatalytic activity for Me-C_3N_4 compared to Me-C_3N_4-N_2N_4. However, a slightly lower metal content in the Me-C_3N_4 (for instance, 7.3% for Ni) than in the Me-C_3N_4-N_2N_4 (8.1% for the Ni sample), indicates higher specific electrocatalytic activity of the sample obtained without an additional reducing agent. Similarly, upon using Ru-C_3N_4, a higher current density is achieved than with Ru-C_3N_4-N_2N_4, which may be due to the smaller size and more homogeneous distribution of metal particles deposited without an additional reducing agent compared to the nanoparticles obtained in the presence of hydrazine.

A set of metal nanoparticles deposited on zeolite Beta-12.5 was synthesized for the application as companion catalysts for the mild regeneration of the primary catalyst (Beta-12.5) for the target Diels-Alder reaction between 2,5-dimethylfuran and ethylene. The application of the supported metal particles does not lead to a decrease in the catalytic activity of the samples in the target reaction, and in the case of platinum and ruthenium it even provides a higher yield of para-xylene (95 and 89% versus 78%, respectively). The use of catalysts doped with Pt^0 or Ru^0, although it leads to a slight increase in coking under the reaction conditions (250 °C), can nevertheless reduce the catalyst regeneration temperature from 550-600 °C to 360-380 °C, i.e. by almost 200 °C.

The content and nature of carbon deposits in the obtained spent catalysts were investigated. The coke in the spent samples is distributed unevenly, and is generated in the form of individual black dots or individual particles with a size of 20 - 40 microns. According to ^{13}C CPMAS NMR the spent samples contain aliphatic and aromatic carbon with the ratio ranging from 1.9 for the initial zeolite to 1 for zeolite catalysts with noble metals. The study of the spent catalysts using XPS indicates predominantly unoxidized carbon deposits and allows us to consider the formed carbon deposits as polyaromatic carbon. Raman spectra of Pd/BEA confirm the presence of a weakly ordered carbon phase and indicate spatial heterogeneity of carbon deposits while preserving the general character of the surface structural motifs in different areas of the sample.

4. Conclusions

Application of the support (g-C_3N_4) surface as a reducing agent resulted in the formation of smaller and more uniform metal nanoparticles in comparison with a traditional reduction of metal precursors with hydrazine. Supported metal nanoparticles demonstrated higher catalytic performance in the electrochemical oxidation of HMF. Application of zeolite-supported metal particles as companion catalysts does not lead to a decrease in the catalytic activity in the target Diels-Alder reaction between 2,5-dimethylfuran and ethylene, and in the case of platinum and ruthenium it even provides a higher yield of para-xylene (95 and 89% versus 78%, respectively). The use of catalysts modified with Pt^0 or Ru^0 can reduce the catalyst regeneration temperature from 550-600 °C to 360-380 °C, i.e. by almost 200 °C.

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Keywords

Metal nanoparticles; reduction; companion catalyst; carbon deposits.