Formation of Pd-group VIII bimetallic nanoparticles by the “water-in-oil” microemulsion method

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Abstract: Pd-M bimetallic catalysts (M = Au, Pt, Ru, Ir) were synthesized by the “water-in-oil” microemulsion method. Physicochemical (XRD, XPS, SEM, HRTEM, EDS) and electrochemical methods were applied to characterize the structure, morphology and surface properties of the catalysts. It is suggested that nucleation processes are mainly responsible for the metal particle formation. The segregation is most pronounced in the PdAu and PdPt systems, resulting in a surface enrichment with Pd and Pt, respectively, whereas the PdRu and PdIr systems exhibit practically homogeneous microstructure. It has been shown that these microstructure-induced surface effects are related to the catalytic properties in the cinnamaldehyde hydrogenation reaction.

Keywords: microemulsion, bimetallic nanoparticles, cinnamaldehyde hydrogenation

1. Introduction

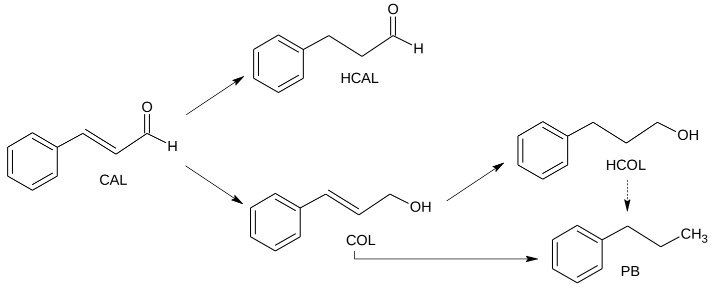
The bimetallic nanoparticles-containing catalysts have received considerable attention because of the significantly improved reactivity relative to their monometallic components. The procedure of preparation is a key factor determining morphology and surface properties of bimetallic particles including concentration and arrangement of metal components within the first few atomic layers. Commonly applied the co-impregnation method produces bimetallic particles of a broad size distribution and the high temperature treatment needed to obtain the alloy structures further facilitates particles aggregation. Alternatives are the colloid-based procedures, allowing a better control of the nanoparticles size and composition, among them the reverse “water-in-oil” microemulsion (w/o) method. In the present work, carbon-supported Pd-based bimetallic catalysts are synthesized by the single-microemulsion procedure. Metal particles are prepared by directly adding the reducing agent ($NaBH_4$) as a powder to the metal salts dissolved in microemulsion. The PdM/C catalysts, where M = Au, Pt, Ru, Ir of 2 wt % metal loading and a Pd/M molar ratio of 10/1 have been prepared. Their monometallic counterparties have been synthesized according to the procedure described in our previous work[1]. The aim of studies was to find out the effect of metal type on the size and microstructure (metal segregation) of bimetallic particles[2].

2. Experimental

In the present work, carbon-supported PdM bimetallic catalysts (where M = Au, Ir, Ru, Pt) with the 2 wt % and a Pd/M molar ratio of 10/1 are synthesized by the single-microemulsion procedure. Metal particles are prepared by directly adding the reducing agent ($NaBH_4$) as a powder to the metal salts dissolved in microemulsion. Their morphological and structural characteristics are determined by XRD, XPS and electron microscopy (SEM, TEM, HRTEM). Surface properties of the PdM particles including Pd and M surface fractions and ability to hydrogen sorption/desorption are characterized by CV measurements. Catalytic tests are performed to gain more insights into PdM surface prosperities in particular a role of metal type in modification of Pd reactivity.

3. Results and discussion

The microscopic results show that the metal particles in mono- and bimetallic catalysts are almost monodisperse and well distributed on the carbon support. The average size of monometallic particles is dependent on the metal type and increased from Ir to Au. Roughly proportional increase of the monometallic particles size with the metal heat of metal sublimation (ΔH_S) from Ir through Ru, Pt and Pd to Au was determined. It is suggested that nucleation process is mainly responsible for the metal particles formation at these preparation conditions. On the other hand, a commonly considered difference in the reduction potential of metal components seems to be less significant for the process of bimetallic particles formation. The size of all bimetallic PdM-0.1 particles is smaller than that of corresponding monometallic counterparts (Pd, Ir, Ru, Pt). The PdM particles differ in the extent of metal components surface segregation. Segregation is evident for the PdAu-0.1 (Pd-rich surface) and PdPt-0.1 (Pt-rich surface) systems. On the other hand, metal components segregation is very weak in the PdRu-0.1 and PdIr-0.1 systems, both showing nearly homogenous alloy microstructure. These microstructure-induced surface effects are confirmed by catalytic performance of PdM-0.1/C for the cinnamaldehyde hydrogenation (Scheme 1).



Scheme 1. Reaction pathways for the hydrogenation of cinnamaldehyde (CAL)

This reaction is chosen as a test reaction, since the properties of catalyst surface, such as the type of active metal as well as its neighbourhood play a vital role in the activity/selectivity pattern[2].

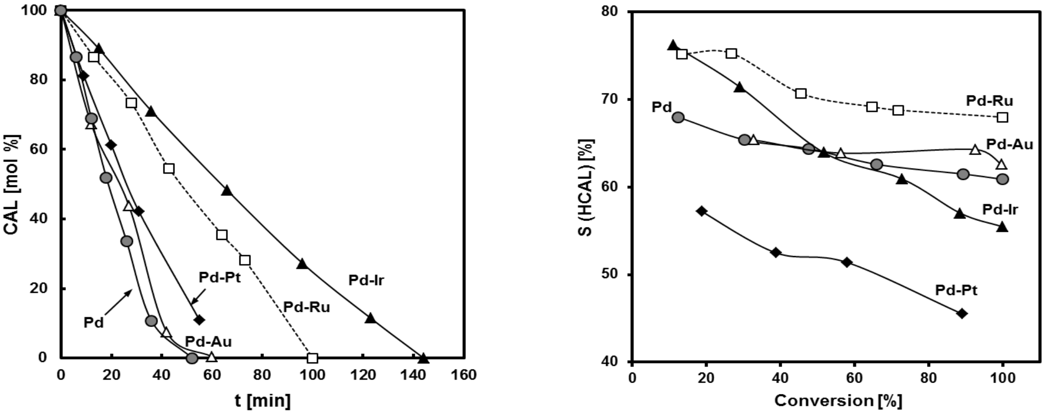


Figure 1. Hydrogenation of CAL in the presence of Pd/C and PdM/C catalysts

The obtained results (Fig. 1) corresponds well with the morphological and surface composition properties of the PdM particles. The enhanced selectivity to C=O hydrogenation characteristic for the Pt and Ir-surface is observed on the PdPt-0.1/C and PdIr-0.1/C catalysts with relatively rich Pt or Ir surface fraction. The PdAu-0.1/C and PdRu-0.1/C display selectivity similar to that of Pd, explained by a very low Au surface fraction and Ru reactivity towards C=C hydrogenation.

4. Conclusions

It is suggested that nucleation process is mainly responsible for the metal particles formation at these preparation conditions. On the other hand, a commonly considered difference in the reduction potential of metal components seems to be less significant for the process of bimetallic particles formation.

References

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2. T. Szumełda et al., Coll. Surf. A: Phys. Eng. Asp. 529 (2017) 246

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