Available online at www.sciencedirect.com

ScienceDirect

Journal of Colloid and Interface Science 317 (2008) 166–174

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Study of Ni–Ag/SiO_2 catalysts prepared by reduction in aqueous hydrazine

R. Wojcieszak, S. Monteverdi, J. Ghanbaja, M.M. Bettahar *

UMR 7565, Catalyse Hétérogène, Faculté des Sciences, Université Henri Poincaré, Nancy-I BP 239, 54506 Vandoeuvre-lès-Nancy Cedex, France

Received 21 June 2007; accepted 13 September 2007

Abstract

We have studied bimetallic Ni–Ag (Ni + Ag = 1 wt%) catalysts supported on crystallized silica and prepared by aqueous chemical reduction with hydrazine at 353 K. Two protocols of reduction were used. Prepared catalysts were characterized by means of XRD, TEM, STEM, H_2 chemisorption and H_2-TPD. Their catalytic activity was studied in the gas-phase hydrogenation of benzene. The most important feature of the results obtained is the synergistic effect between Ni and Ag which led to improvement of dispersion and reactivity of nickel in the presence silver for precipitated catalysts. Silver is inactive in the test-reaction. Precipitated bimetallic catalysts give rise to total conversion from 373 K, a temperature at which conversion hardly reaches 30% for the impregnated catalysts. Dispersion and activity pass through a maximum of monotonically decrease with precipitated and impregnated catalysts, respectively. Deactivation was observed for bimetallic catalysts, particularly with precipitated samples. These results could be explained by the mechanism of metal reduction in the hydrazine media. As a result, various Ni–Ag species formed where Ni and Ag phases were separated clusters or interacted as heteroatomic groupings on the carrier surface. These grouping would be responsible of the high performances of the precipitated catalysts.

Keywords: Supported bimetallic catalysts; Nickel; Silver; Silica; Hydrazine; Benzene hydrogenation

1. Introduction

Nanoparticles of transition or noble metals have attracted much attention because of their unusual properties compared with the conventional polycrystalline materials. Whereas in the macromolecular solid, surface atoms contribute only a relatively small fraction of the total number of metal atoms, the nanoparticles contain almost all surface atoms [1]. It follows that such atoms have lower coordination numbers than in the bulk and as a consequence are expected to exhibit greatly enhanced activity to all manner of substrates [1]. The synthesis of metal nanoparticles has been focus of numerous studies in the last decade. Some very successful techniques have been developed for producing gold [2–4], silver [5–7], nickel [8–12], platinum [13], copper [14] and other materials as nanoparticles.

Recently, increasing interest has been shown in preparing metal alloys such as Au/Pd [15], Au/Pt [16], Fe/Ni [17], Ni/Cu [18,19] and Ni/Ag [20–23]. It has been demonstrated that even with small particles bimetallic clusters are vastly superior to their monometallic counterparts [1,15].

Nickel supported catalysts are widely used in heterogeneous catalysis due to their high hydrogenating properties. Many parameters determine its catalytic activity in hydrogenation processes. The activity strongly depends on the nature of the support which may modify the properties of the active phase. The extent of metal–support interaction and support acidity seems to play a crucial role in complex chemistry of nickel supported catalysts [24–27]. Silver supported catalyst is considered as an excellent catalyst in epoxidation and oxidation reaction [28,29]. However, it is not active in the hydrogenation processes. Nevertheless, incorporation of silver to palladium catalysts improves the hydrogenation properties. It was shown that incorporation of silver into palladium catalysts increases their selectivity in the acetylene hydrogenation [30].

Hydrazine is a powerful strong reductant widely used in various chemical operations. A series of striking results has been obtained where hydrazine is used as a reducing agent for the production of finely divided metals [31–36]. Degan and Macek [35] used hydrazine as a reducing agent to prepare nickel powders in the submicrometer size range from nonaqueous solu-

---

* Corresponding author.
E-mail address: mohammed.bettahar@lcah.uhp-nancy.fr (M.M. Bettahar).

0021-9797/$ – see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2007.09.031

tions of nickel salts. The rate and yield of the reaction were both enhanced at higher reaction temperatures but were limited by the relatively low boiling point of water. Nickel powders with mean particle sizes ranging from 0.1 to several µm and with up to 99.8% purity were obtained by this method. Nickel et al. [36] studied the production of a silver colloid by reduction with hydrazine as a support for highly sensitive surface-enhanced Raman spectroscopy. The reduction of aqueous silver nitrate by hydrazine dihydrochloride in weakly alkaline solution results in a polydisperse colloid that is stable for many months without addition of stabilizing compounds. The average size of the predominantly spherical particles depends on the initial concentration of silver ions and ranges from 40 to 70 nm in diameter.

Our group has undertaken a systematic study of nickel metal nanoparticles supported on crystallized silica of low specific surface area, prepared by reduction of nickel acetate by hydrazine in aqueous media [34]. It was shown that the morphology of the particles formed changed with the reduction condition and metal loading. The particle shape obtained influenced their surface and catalytic properties. Incorporation of copper in nickel also gave rise to changes in the particles morphology and surface properties [37]. Indeed, nickel was found in a whisker-like shape in monometallic Ni/SiO_2 and as a film of low density in bimetallic Ni–Cu/SiO_2. The Ni particle size is lower than 2 nm in both cases. The copper phase is in the shape of facetted particles in the mono or bimetallic systems with a mean particle size of about 25 nm. The metal dispersion as determined by hydrogen adsorption decreased with the copper content due to Ni–Cu interactions. The amounts of hydrogen incorporated in the catalysts during a previous hydrogen heat treatment changed with the copper content for the same reason.

In the present paper we report the study of 1% nickel–silver supported catalysts prepared by the chemical reduction with hydrazine. Different concentrations of Ag and Ni have been used. Crystallized silica was used as the support for Ni–Ag active phase. The catalysts were characterized by means of XRD, TEM and H_2 adsorption/desorption studies. They were tested in the gas phase hydrogenation of benzene.

Catalytic studies on supported bimetallic Ni–Ag systems have not received much attention. The scarce data reported interestingly show that silver improves the reducibility and the stability of the nickel active phase [38,39]. However, these results are at variance with that reported for unsupported NiAg systems. Indeed, only metastable NiAg alloys have been observed in specific conditions [21,22]. These alloys give rise to phase separation and reformation of Ni and Ag particles with time on stream [21]. Our study aimed to re-investigate this system in preparation conditions not reported before, namely the hydrazine media and using silica as a support. For comparison with previous studies, we used a silica support of low surface area [34]. These studies showed that a silica support of high surface area does not allow nickel reduction in the hydrazine media. Reduction is favoured with basic rather than acidic supports [40].

2. Experimental

2.1. Catalysts

Nickel acetate solution ($Ni(CH_3COO)_2 \cdot 4H_2O$) and silver nitrate solution ($AgNO_3$) were purchased from Fluka ($\leqslant$99.0%) and Prolabo ($\leqslant$99.0%), respectively. Silica was purchased from Chempur ($\leqslant$99.0%, 15 $m^2\,g^{-1}$). Hydrazine water solution (24–26%) was purchased from Merck ($\leqslant$99.0%).

Two series of catalysts were prepared.

The first one included materials denoted as IC (Impregnated Chempur) catalysts which were prepared by classical wet impregnation method then reduction in a hydrazine solution. The silica support (5 g) was poured over nickel acetate and silver nitrate solution with the appropriate concentration. After filtration and 15 min of rotation under vacuum, the mixture was heated and evaporated for 1 h. The solid obtained was dried at 383 K for 1 h. The nickel acetate and silver nitrate concentrations in the solution were calculated to obtain the following Ni–Ag ratios: 1.00% Ni, 0.90% Ni–0.10% Ag, 0.75% Ni–0.25% Ag and 0.50% Ni–0.50% Ag, 1.00% Ag.

After impregnation, the catalysts were reduced with hydrazine solution as follows. The preparation was performed under argon atmosphere (flow rate = 100 $cm^3\,min^{-1}$) in a 3 necked reaction flask of 110 cm^3 dipping in a water bath. The reaction flask was fitted with a reflux condenser and a thermocouple for the control of the reaction temperature and connected to a gas microchromatograph (Agilent G2890A) for the analysis of the gases evolved during the reduction process. A suspension of the supported nickel precursor (5 g of impregnated sample in 60 cm^3 of water) was stirred for 20 min at room temperature. The reaction mixture was slowly heated from room temperature up to 353 K. Then 10 ml of 24–26% aqueous hydrazine in excess (>99% Fluka) was added. The pH of the solution was 10–12 and remained almost constant. Reaction was stopped after 4 h. After reduction the solid was filtered and dried in air at 353 K for 5 h. Note that, after impregnation then drying at 383 K in air, no metal ions were detected in the reaction media when a suspension of the precursor was stirred for 20 min.

The second set of catalysts denoted as PC (Precipitated Chempur) was prepared by simultaneous introduction of appropriate concentration of nickel acetate, silver nitrate and 5 g of silica in 60 cm^3 of distilled water in the 3 necked reaction flask. The reactant mixture was heated to 353 K and then 10 cm^3 of hydrazine was added. Reduced precursors precipitated on the support. Reaction was stopped after 4 h. The obtained solid was filtered and dried in air at 353 K for 5 h.

2.2. Characterization of physico-chemical properties

XRD patterns were recorded with a classical $\Theta/2\Theta$ diffractometer using Cu$K\alpha$ radiation. The electron microscopy images were obtained with a Phillips CM20 STEM microscope after placing a drop of the catalyst suspension on the carbon coated copper grid. X-ray microanalysis chemical compositions were determined using energy dispersive X-ray spectroscopy (EDXS). EDXS spectra were recorded by means of an EDAX