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Study of nickel nanoparticles supported on activated carbon prepared by aqueous hydrazine reduction

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Abstract

Nickel nanoparticles were obtained by the reduction in hydrazine aqueous media of nickel acetate as a precursor supported on activated carbon of high surface area. Classical catalysts using nickel acetate or nitrate were prepared for comparison. The catalysts were characterized by N_2 physisorption, H_2-TPR, H_2-adsorption, TPD, TEM, and XRD, and tested in the gas phase hydrogenation of benzene. Hydrazine catalysts were found much more active in benzene hydrogenation than corresponding classically prepared catalysts. Remarkably, their reactivity is comparable (turn-over frequency of 0.2001–0.2539 s^{-1} at 393 K) to that of Pt classical catalysts supported on activated carbon in the same conditions. Evidence is given for the existence of the hydrogen spillover effect in benzene hydrogenation, not reported before in the literature. As a result of the hydrogen spillover effect, catalysts performances can be explained by a combination of surface metal atom reactivity, metal–support interaction strength, and specific surface area extent. Maximum effect is observed with hydrazine preparation method, for 1% Ni content and nickel acetate as a precursor. Unexpectedly, it was also found that hydrazine preparation increases the specific area of the catalysts.

Keywords: Nickel; Hydrazine; Catalysts; Activated carbon; Hydrogen chemisorption; Benzene hydrogenation

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1. Introduction

The activity and selectivity of supported metal catalysts are strongly influenced by the amount of metal, the size of dispersed metal particles, the preparation method, and the support composition [1,2]. To improve the catalyst activity and its durability, it is necessary to obtain a well-dispersed active phase in the catalyst [3,4]. The chemical species present on the carrier surface interact, more or less, with the metal particles deposited thereon. The metal–support interaction (MSI) is usually stronger when the metal particles are smaller [5]. For the carriers employed in industrial catalysis the intensity of MSI decreases from alumina to silica to active carbon [5]. In the case of highly dispersed materials, the changes in the catalytic activity were related to the combined effects of particle size, surface coverage with adsorbed species, and active site dimension [6].

Conventional supported metal catalysts are prepared by in situ reduction of metal salt. However, it is often difficult to control the morphology of the final material. The control of metal particle nanosize is of the utmost importance for the performance of any industrial catalyst based on supported metals. The synthesis of the metal nanoparticles of uniform shape and high purity has received considerable attention in the past two decades due to their unusual properties compared to bulk metal [7].

The metal nanoparticles are generally produced by the reduction of metal compounds. The number of procedures is fairly large, for example photolytic reduction [8], radiolytic reduction [9], solvent extraction reduction [10], microemulsion technique [11], alcohol reduction [12], chemical reduction in aqueous [13] and nonaqueous [14] media by hydrazine. Hydrazine is a powerful strong reductant widely used in various chemical operations. A series of striking results have been obtained where hydrazine is used as a reducing agent for the production of finely divided metals [15,16]. Degan and Macek [17] used hydrazine as a reducing agent to prepare nickel powders in the submicrometer size range from nonaqueous solutions of

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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.

In the industrial and academic area a great attention is paid to the hydrogenation of benzene, the model aromatic feedstock [18–21]. This reaction has also been used as model reaction in heterogeneous catalysis by metals where metal–support interactions are involved [20–23]. The electronic and structural effects of the MSI influence on the hydrogenation of benzene. This reaction is considered as a structure-sensitive reaction [24,25].

The use of activated carbon (AC) as a catalyst support is increasing due to the advantages it offers as compared to traditional oxides [26]. Cheap and relatively inert material, activated carbon exhibits stability in acidic or basic media, a high surface area and oxygen-containing functional groups. In metal–carbon systems, intense interactions can be promoted and play an important role conditioning both textural properties and reactivity of the catalyst [27]. Metal–carbon interactions attracted much attention [26–30]. In this way, the thermal pre-treatment nature (neutral/reductive/oxidative) may change the surface area or porosity as well the activity or selectivity of the catalyst [27,28]. Carbon atom dissolution in the metal [27,28] may cause the decrease of the catalytic activity through site blockage [27].

Carbon is able to reduce the metal precursor introduced during the catalyst preparation [27,30].

We have undertaken a systematic study of nickel metal nanoparticles supported on silica of low surface area, prepared by reduction of nickel acetate by hydrazine in aqueous media [13,31–33]. The reduction led to metal crystallites of various size and shape according to the conditions of preparation. The shape influenced the surface and catalytic properties of the metal nanoparticles in the hydrogenation of unsaturated molecules.

In the present study we report results on the preparation, the characterization, and the surface and hydrogenating properties of nonclassical catalysts supported on activated carbon. The catalysts were prepared by the chemical reduction with hydrazine in aqueous media using nickel acetate or nitrate as a precursor (1, 5, and 10 wt% Ni). Classical catalysts have also been studied for comparison. The catalysts prepared were characterized by N_2-physisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), H_2-temperature programmed reduction (TPR), and H_2-adsorption and temperature programmed desorption (TPD) techniques. Gas phase hydrogenation of benzene was chosen as a test-reaction. The hydrogen spillover effect in this reaction was also examined.

The aim of this work is to examine the effect of the method of preparation, the nickel content and the nature of metal precursor on the surface, and catalytic properties of Ni catalysts supported on a commercial activated carbon. The results obtained are an original contribution to the literature corpus data on nickel–carbon catalysts and benzene hydrogenation. The method of preparation used is original (hydrazine reduction of Ni^{2+} ions in aqueous media at 353 K) and leads to materials with much better surface and catalytic performances than classical preparation. Moreover, to our best knowledge, the hydrogenation of benzene on nickel catalysts supported on activated carbon has not been reported. The results obtained also give evidence for the hydrogen spillover occurrence in this reaction for the first time for a Ni-activated carbon system.

2. Experimental

2.1. Materials

The active carbon material used was a commercial acid-washed (Merck, ash content $\leqslant 3\%$). A fraction of 40 mesh was used as a support. $Ni(CH_3COO)_2 \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Fluka ($\geqslant 99.0\%$) and Hopkins and Williams Ltd., respectively.

For classical catalysts, the supported precursor was prepared by pouring the appropriate quantity of the support over nickel acetate solution (or nickel nitrate solution) with the appropriate concentration. After 15 min of rotation under vacuum, the mixture was heated and evaporated for 1 h. The obtained solid was dried at 383 K for 1 h (temperature ramp 3 $K\,min^{-1}$). The catalysts were denoted as xNi/AC-A(N) where x, AC, and A(N) refer to nickel content (in wt%), activated carbon support, and acetate (or nitrate) precursor, respectively.

The nonclassical acetate catalysts were prepared under Ar atmosphere according to Ref. [32]. In this method (denoted as H-method), the above supported precursor is reduced in aqueous media according to the following reaction:

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni^0 + N_2 + 4H_2O. \quad (1)$$

The reduction of the supported precursors was performed under an argon flow in a 3 necked reaction flask of 110 cm^3 plunged in an oil bath for heating. The reaction flask was fitted with a reflux condenser, a thermocouple for measurement of the reaction temperature. The exit gases pass through a bubbler equipped with a gas chromatograph for nitrogen analysis. A suspension of the supported nickel precursor was stirred and slowly heated to 353 K in an excess hydrazine solution for 4 h at pH 10–12. After reduction the solid obtained was filtrated off, washed with distilled water and dried. The catalysts were denoted as xNi/AC-AH where H refers to the hydrazine preparation method. The other symbols are the same as described above.

A set of nonclassical acetate catalysts was prepared by simultaneous introduction of nickel acetate and hydrazine at room temperature in a suspension of activated carbon then reducing at 353 K with the same procedure as above. This preparation is denoted as PH-method. The final materials were denoted xNi/AC-APH where PH denotes the procedure of hydrazine reduction used. The other symbols are the same as above.

The nitrate precursor was not reduced by hydrazine even at 373 K for several hours: no gas evolved during the reaction weather it was supported or not.

The activated carbon was also treated in the hydrazine media and dried in the same conditions described above. It is denoted ACH.

No nickel precursor residue was found in the washing solution of the final solid filtrated. This means that all nickel introduced was incorporated into the carbon support.