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Journal of Molecular Catalysis A: Chemical 242 (2005) 81–90

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Study of nickel catalysts supported on Al_2O_3, SiO_2 or Nb_2O_5 oxides

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Received 13 June 2005; received in revised form 14 June 2005; accepted 7 July 2005
Available online 2 September 2005

Abstract

We have studied nickel classical catalysts supported on Al_2O_3, SiO_2 and Nb_2O_5 oxides, using simple (SIM) or EDTA-double impregnation (DIM) methods. Non-classical catalysts were obtained by pretreatment of the SIM or DIM nickel precursors in aqueous hydrazine at 353 K. The catalysts were characterized by H_2-adsorption, H_2-TPR, isopropanol decomposition and FTIR measurements. They have been tested in the gas phase hydrogenation of benzene. The results obtained show that the support surface acidity order was: $SiO_2 < Al_2O_3 < Nb_2O_5$. The catalysts exhibited various nickel species due to the existence of various metal–support interaction strengths. As a consequence, the reducibility, surface or hydrogenating properties changed as a function of the nature of the support or method of preparation. The best performances were obtained with the silica support which seemed to interact less with the nickel. The metal–support interactions are highest when niobium oxide is used as the matrix. Ni impregnated on niobia was not active at all, due to very strong metal–support interactions. The interaction of aqueous hydrazine with the catalyst in the reduction conditions was examined. It was shown that hydrazine formed stable complexes with nickel, whereas it adsorbed on the support with a strength depending on the nature of the oxide.

Keywords: Nickel; Catalyst; Support; Double impregnation; Benzene hydrogenation

1. Introduction

The activity and selectivity of a supported metal catalyst are strongly influenced by the amount of metal, the size of dispersed metal particles, the preparation method and the support composition [1–3]. To improve the catalyst activity and its durability, it is necessary to obtain a well-dispersed active phase in the catalyst [4]. Several methods can be applied to obtain highly dispersed metals on the support surface [5]. Supported metal catalysts are commonly prepared by metal salt impregnation. If the support is microporous, it will imbibe a solution of a metal salt; drying, calcination (optional) and reduction will generate small metal particles. The classical method of the support impregnation results in obtaining small metal crystallites but only at very low metal contents in the catalyst [6]. It is also possible to obtain small metal crystallites by co-precipitation, but such catalysts are very difficult to reduce [7].

Supported nickel catalysts are most effectively prepared through the optional combination of high dispersion and metal loading. Small metal particles may be formed on the surface of the support to which they are more or less firmly anchored, and on which they are effectively separated from each other. The average distance between the particles will depend on the metal content, the particle size and the surface area of the support [8].

Nickel catalysts were prepared by the double impregnation method (DIM) [9,10]. Previous findings and literature data allow to conclude that this preparation method is suitable for producing well-dispersed nickel/alumina-supported catalysts [9–12]. In DIM, there are two stages, one by one. The first one is the impregnation of inorganic support by H_2Na_2EDTA solution and then (after drying) impregnation by solution containing active metal ions. In contrast to the classical simple impregnation method (SIM) [13], in DIM preparation procedure the carrier is preliminarily “activated” (modified) by

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doi:10.1016/j.molcata.2005.07.013

EDTA introduced by impregnation and dried; the following preparation steps are the same as in SIM [14]. Modification of the support using impregnation by H_2Na_2EDTA has influence on the way of metal bonding, which is added in the next stage of preparation. It changes the concentration of metal in catalyst and decreases average nickel crystals size. Application of H_2Na_2EDTA on the stage of preparation favored high active phase dispersion.

Presence of the EDTA adsorbed on the support surface assures homogenous distribution of the metal ions. The effect of the presence of EDTA is particularly visible in the low and average concentrations of metal ions. As the concentration of metal is increasing in impregnation solution, participation of favorable interaction EDTA–ion is gradually decreasing, which is caused by accelerated adsorption in support pores and the increase of the interactions between metal ions and hydroxyl surface groups [15].

Conventional supported metal catalysts are prepared by in situ reduction of a metal salt. The catalytic activity of the metal particles is strongly influenced by their size and shape [1,2,16–19]. However, it is often difficult to control the morphology of the final material, notably for impregnated catalysts [16–23]. An alternative method to obtain supported catalysts with well-defined metal particles is the preparation of supported catalysts from metal colloids.

Metal nanoparticles research has recently become the focus of intense work due to their unusual properties compared to bulk metal. The reason for such avid research arises from the drastic increase of the surface to volume ratio to such an extent that the material properties are determined much more by the surface atoms than by the framework atoms, with the result that the physical and chemical properties of the particles differ considerably from those of bulk solids [3–8]. They hold promise for use as advanced materials for electronic, magnetic, optical and thermal properties [9,10] and have also been applied in heterogeneous catalysis [7,24–27]. The chemical route for the preparation of such materials is of particular interest since it allows a better control of the structure at the microscopic level [28–40]. The chemical methods have generally involved the reduction of the relevant metal salt in the presence of a stabilizer such as linear polymers [6,41–44], ligands [44,45], surfactants [40,46–48], tetraalkylammonium salts [49,50] or heterogeneous supports [51–53] which prevent the nanoparticles from agglomerating.

Recent works have pointed out the interest of working in aqueous medium as a practical solution for the future in homogeneous and heterogeneous catalysis [54]. This prompted us to undertake a study of nickel nanoparticles obtained by reduction of nickel salts in aqueous medium and stabilized on a silica support of low surface area. The surface properties of the obtained catalysts were tested in gas phase hydrogenation of benzene.

Hydrazine was used because recent studies showed that it is a good reducing agent in aqueous medium for noble and transition metals ions [53,63–65]. As to the silica support, it is known not to give rise to nickel mixed oxides and to allow a better approach of the particle size effect in the behavior of supported nickel catalysts. Moreover, generally speaking, nickel-supported catalysts have been concerned with high surface area supports and nickel loading higher than 5 wt%. Also, the use of silica of low surface area and low nickel loading in the preparation of nickel based catalysts was expected to give rise to an important contribution to the existing corpus of literature on Ni/SiO_2 systems [20]. We were also encouraged in this way because preliminary results showed that, in aqueous medium, the nickel reduction process was enhanced in the presence of low surface area silica, whereas silica of high surface area tended to inhibit it.

In spite of the high number of studies published in the past decades, an increasing attention is paid to the hydrogenation of aromatics because of the stringent environmental regulations governing their concentration in diesel fuels [55–58]. Benzene hydrogenation has been chosen as the model aromatic feedstock [59,60]. This reaction has also been used as model reaction in heterogeneous catalysis by metals where metal–support interactions are involved [58–62].

In this paper, we show how the different methods of preparation change the properties of metal containing catalysts supported on different oxides. We have been working on nickel catalysts supported on Al_2O_3, SiO_2 and Nb_2O_5 oxides. The catalysts were characterized by hydrogen chemisorption, H_2-TPR technique, isopropanol decomposition and FTIR measurements. They have been tested in benzene hydrogenation. The catalysts were prepared with 1% Ni loading, using nickel acetate as precursor. The supported precursors were prepared by simple or double impregnation methods. Classical catalysts were obtained by calcination in air at 773 K, then reduction under hydrogen flow at 773 K. Non-classical catalysts were obtained by reduction of the precursor in aqueous hydrazine at 353K, then treated under hydrogen flow at 673 K (2 h) for activation. The study was carried out with catalysts of 1% Ni content because stronger metal–support interactions were expected to occur than for catalysts with greater nickel contents [1,2,15].

2. Experimental

2.1. Preparation

2.1.1. Classical catalysts

$H_2Na_2EDTA \cdot 2H_2O$, $Ni(CH_3COO)_2$, alumina, silica and hydrated niobium oxide were purchased from POCH (99.9%), Fluka (99.0%), ALFA Johnson Matthey Company (99.97%), Ventron (99.8%) and CBMM (99.97%), respectively. The supports were dried at 363 K for 1 h before the impregnation procedure.

For the SIM, the appropriate quantity of the support was poured over nickel acetate 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}) and