Factors influencing the thioresistance of nickel catalysts in aromatics hydrogenation

B. Pawelec [a],*, P. Castaño [b], J.M. Arandes [b], J. Bilbao [b], S. Thomas [c],
M.A. Peña [a], J.L.G. Fierro [a]

[a] *Institute of Catalysis and Petrochemistry, CSIC, c/ Marie Curie, 2, Cantoblanco, 28049 Madrid, Spain*
[b] *University of the Basque Country, Chemical Engineering Department, 644-48080 Bilbao, Spain*
[c] *Fraunhofer Institute for Factory Operation and Automation IFF Magdeburg, Department of Process and Plant Engineering,
Sandtorstrasse 22, 39106 Magdeburg, Germany*

Abstract

Silica–alumina supported nickel catalysts (Ni/ASA) have been modified by the incorporation of electrodonor (Li) or electro acceptor (Pd) elements with the objective of determining the factors controlling the catalyst thioresistance in benzene hydrogenation. The catalysts were tested in benzene hydrogenation (HYD) in the presence of 1-butanethiol (C_4H_9SH 5 ppm of S) and in the hydroconversion of pyrolysis gasoline (PyGas) and compared with zeolite NaY-supported ones. In addition, the catalysts were characterized by variety of techniques (XRD, N_2 adsorption–desorption, TPD-H_2, TPD-NH_3, CO chemisorption, TPR, XPS, FTIR of adsorbed pyridine, TGA–DTA). It was found that the monometallic Ni/ASA catalyst with 24 wt.% of Ni was the most active among the catalysts studied in both benzene hydrogenation (+S) and hydroconversion of PyGas. The data of catalyst characterization suggests that the concentration of both metal and acid sites govern catalytic activity in both activity tests being the catalyst ability for hydrogen adsorption one of the most important factors to be taken into account. In general, it was found that the S-poisoning of the catalysts increased with an increase of the catalyst reactivity and diminished when "refractory-type" coke deposited on the metal sites inhibited the S-compound adsorption. For PyGas transformation, the importance of Pd promotion of the nickel catalysts was confirmed for both hydrogenation and ring-opening reactions.

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1. Introduction

In recent years, there is an increasing demand for benzene reduction in petroleum products, and especially in gasoline, diesel and kerosene [1,2]. The most frequent benzene elimination route is by hydrogenation on transition metal-supported catalysts [2–5]. Unfortunately, those catalysts are very susceptible to poisoning through the small amounts of sulphur present in the feed stream [2–6]. Thus, the challenge is to produce S-resistant catalysts that are highly active for benzene hydrogenation in the presence of S-compounds.

From an economic point of view, Ni-based catalysts are interesting alternatives to noble metal-based catalysts for

hydrotreating reactions [7]. However, the nickel is less tolerant to S-poisoning than noble metals due to the stronger adsorption of S-compounds on nickel [8]. Additionally, the decrease of catalyst thioresistance might occur due to sintering of metal particles induced by decrease in the metal–support interaction and/or by poisoning of the acid sites located on catalyst surface [9]. The effect of the S-poisoning of metallic catalysts on activity and selectivity in hydrogenation reactions has been studied previously [8–12]. For nickel catalysts tested in benzene hydrogenation, Marécot et al. [11] demonstrated that the extent of catalyst deactivation by S-containing compounds depends upon different factors such as the nature of catalyst, the kind of sulphur compound, the reaction conditions and the composition of feed undergoing hydrogenation. It was found that the initial susceptibility of the nickel catalysts to S-poisoning depends on the nature of sulphur compounds of following order: thiophene ≈ thiolate > propane-thiol > hexane-thiol > H_2S [11]. The

* Corresponding author. Fax: +34 915854760.
  E-mail address: bgarcia@icp.csic.es (B. Pawelec).

chemisorption of hydrogen sulphide on various nickel catalysts demonstrated that H_2S not only becomes dissociated but also it quickly develops superficial polysulphides [12].

Certain controversial studies on the effect of alkali promotion on the S-resistance of nickel catalysts have been reported in literature. For example, Guenin et al. [13] reported a decrease in the S-resistance of K-doped Pt/Al_2O_3 catalysts whereas other authors [14,15] observed a large improvement regarding the sulphur resistance of alkali-doped Ni- and Fe-catalysts. This observed discrepancy is caused by the combined effects of electronic modification, site blocking and/or changes in the morphology of metallic crystallites [14]. The electronic modification of metal is induced by the donor nature of the alkali co-metal transferring electrons to the metallic phase [16] whereas geometric modification is due to alkali adsorption on the catalyst surface [17,18]. Thus, depending on the sum of those factors, alkali could be expected to have a positive or negative influence on catalyst thioresistance.

There are studies in which sulphur poisoning of one metal is reduced in the presence of another metal having a higher free energy of formation of the bulk sulphide phases [8]. For example, Bartholomew and Flower demonstrated that the metal oxides in nickel catalysts may provide additional adsorption sites for sulphur atoms [19]. In line with this explanation, Duprez and Mendez [20] and Sepúlveda and Fígoli [21] showed that the presence of a pre-spinelized unreduced $NiO–Al_2O_3$ phase on the catalyst surface may improve nickel thioresistance [20]. This was explained by: (i) electronic effects ($Ni^0–Ni^{2+}$); (ii) geometric effects of the dilution of the nickel surface by unreduced species; (iii) trapping effects of sulphur by Ni^{2+} species [20,21]. Besides alumina, the formation of a spinelized unreduced $NiO–Al_2O_3$ phase is also possible on amorphous silica–alumina (ASA), which has catalytic properties similar to those of zeolites, albeit without zeolite pore restrictions [22]. We are interested in this support material because it has a moderate capacity to disperse noble and semi-noble metals [23] and possesses a greater acidity than conventional alumina [24]. Recently, we reported a study on the thioresistance of an amorphous silica–alumina (ASA)-supported Ni–Pd and tested in the HDS reaction of dibenzothiophene (DBT) [25] in which thioresistance was linked with the specific nickel metal area, which coexists with a certain amount of unreduced Ni^{2+} species.

This report is a continuation of our previous studies on the thioresistance of transition metal catalysts supported on ASA [25]. To shed more light on the effect of electrodonor and electroacceptor elements on the metal/acid balance, as well as on the S-resistance of nickel catalysts, the Ni/ASA catalysts were modified by Li and Pd additives and their activity were compared with those of NaY zeolite-supported nickel catalyst. The catalysts were tested in the hydrogenation of benzene in the presence of 2-butanethiol (accelerated S-poisoning test). Additionally, as Pyrolysis Gasoline (PyGas) is one of the main sources of benzene in the petrochemical industry, the catalytic response of Ni/ASA catalysts in the hydroconversion of PyGas has been evaluated. The information regarding the structure of the calcined, reduced and used catalysts was assessed using

several physico-chemical techniques such as chemical analysis, N_2 adsorption–desorption isotherms at 77 K, X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed desorption of adsorbed hydrogen (TPD-H_2) and ammonia (TPD-NH_3), FTIR spectroscopy of adsorbed pyridine, CO chemisorption, X-ray photoelectron spectroscopy (XPS) and thermogravimetric (TGA) analysis.

2. Experimental

2.1. Catalyst preparation

An amorphous $SiO_2–Al_2O_3$ (ASA) (SMR 5-473; Grace Davison Chemical; 28 wt.% alumina) was selected as support for the catalysts. Prior to Ni-incorporation, this ASA support was calcined in air at 773 K for 3 h. The nickel catalyst containing 25 wt.% of nominal Ni content (referred to hereafter as 24Ni/ASA) was prepared by wet impregnation of ASA with an aqueous solution of $Ni(NO_3)_2 \cdot 4H_2O$ (Carlo Erba, 99%) of appropriate concentration. The ASA support was added to the nickel solution and stirred for 2 h at ambient temperature. Once adsorption equilibrium was reached, water excess was removed in a rotary evaporator. The impregnate was then dried at 383 K in air for 12 h and finally calcined in air at 723 K for 2 h. This catalyst was divided in four aliquots. One of them was re-impregnated with a $Ni(NO_3)_2 \cdot 4H_2O$ solution and the resulting catalyst showed a 33.2 wt.% Ni loading (33Ni/ASA). Another aliquot was sequentially impregnated with a lithium acetate (Fluka, >98%) solution, whose concentration was selected in order to obtain 1 wt.% Li (Li–24Ni/ASA). Finally, another aliquot was re-impregnated with the two $Ni(NO_3)_2 \cdot 4H_2O$ and $Pd(NO_3)_2 \cdot H_2O$ (Fluka, >98%) salts solutions of appropriate concentration to obtain 1 and 40 wt.% of nominal Pd and Ni loading, respectively (Pd–33Ni/ASA), followed by steps described above.

For the sake of comparison with non-acidic catalysts, a 7Ni/NaY catalyst was prepared from NaY (LZ-Y52 Union Carbide; Si/Al = 2.85; Na_2O/Al_2O_3 = 0.9) zeolite by ion-exchange from an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, reagent grade), using a solution-to-zeolite volume ratio of 20:1 at constant temperature (333 K) and under constant stirring for 16 h. After ion exchange, the water excess was slowly removed in a rotary evaporator until dryness. The ion-exchanged sample was air-dried at 383 K for 24 h, and then calcined in air at 723 K for 2 h.

2.2. Catalyst characterization

The chemical analysis of the calcined catalysts was done by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using a Perkin-Elmer Optima 3300DV instrument. The solid samples were treated with a mixture of HF, HCl and HNO_3 at 363 K and homogenized in a microwave oven. The metal content of the catalysts is summarized in Table 1. XRD measurements of the calcined catalysts were performed on a computerized Seifert 3000XRD diffractometer using Cu Kα (λ = 0.15406 nm) radiation and a PW 2200 Bragg–Brentano θ/