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Editor's choice paper

Effect of oxidative pre-treatment on hydrogen spillover for a Ni/SiO_2 catalyst

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ABSTRACT

The chemisorption and hydrogenating properties of Ni/SiO_2 catalysts prepared by the hydrazine method then calcined at 400 °C with various times were investigated. Metal dispersion and activity in benzene hydrogenation increased with increasing calcination time whereas desorbed amounts of hydrogen significantly decreased. Dilution of a calcined sample by the support led to a sharp increase of both hydrogen storage by the support and catalytic activity. Metal dispersion and hydrogen storage capacity influenced the reaction mechanisms of hydrogenation of benzene which, therefore, is believed to occur on the metal phase or/and on the support by the hydrogen spillover mechanism. The metal active phase would be composed of an ensemble of metallic and oxidized nickel species.

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1. Introduction

In a previous paper we reported results on H_2 chemisorption and hydrogenating properties of metallic nickel nanoparticles supported on silica of low surface area [1]. The catalysts were prepared by reduction in aqueous hydrazine. The activity in benzene hydrogenation and hydrogen storage of the support depended on the metal loading and thermal treatments. Remarkably, after calcination in air then re-activation in H_2 atmosphere, the catalysts became more active but stored less hydrogen than the as-prepared catalysts. The results obtained were explained using the hydrogen spillover mechanism [2,3]. Since then this mechanism has been critically revisited by Prins et al. [4,5] and Choi et al. [6,7]. These authors report more subtile explanations on the nature of the spillover phenomena and particularly for metal catalysts supported over non reducible oxides.

For Prins et al. [5] the surface diffusion of hydrogen species by the spillover mechanism is not possible with non reducible oxides (e.g. MgO, SiO_2, zeolite) because the H-spiltover species are strongly bonded to a metal particle and only moderately to a non reducible support. As a result these species cannot be implied in the hydrogenation of unsaturated molecules unless the oxide contained defects or carbon deposits [8]. As to Choi et al. [6], they defined the conditions where the hydrogen spillover concept does hold with non reducible support oxides. The model catalyst was Pt particles encapsulated in a zeolite framework where the respective dimensions of the metal particles and zeolite pores allowed selective diffusion of H_2 over various organic molecules. As a result the observed catalytic activities could be unambiguously attributed to catalytic reactions via H spillover at the external surface of the zeolite. The occurrence of H spillover also requires the presence of abundant surface hydroxyls.

Effect of calcination on the spillover effect have been reported for metal catalysts supported on non reducible oxides. For Cęckiewicz and Delmon [9], calcination enhances the spillover effect in the hydrogenation of benzene over $Pt/\gamma\text{-}Al_2O_3$ diluted with the support because it removes the carbon impurities deposited on the catalyst surface. Contrary to that Vannice and Neikam [10] did not observe the spillover effect in the hydrogenation of benzene over Pd/Al_2O_3 catalysts diluted with the support and pre-calcined. For the authors, the spillover effect, when claimed for benzene hydrogenation, would be due to carbon impurities which allow the diffusion of surface H-species [5]. Miller et al. [11] reported that the amounts of hydrogen desorbing at high temperature over Pt/SiO_2 (Al_2O_3, zeolites) decreased after a thermal treatment in air. However, the hydrogen molecules were not ascribed to spillover effect

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but to H-species incorporated in the support during the catalyst preparation.

These new insights on the spillover phenomena [4–7] prompted us to confirm and re-examine our previous results on the effect of calcination on catalytic activity. Moreover, effect of calcination on the surface and catalytic properties of metal catalysts prepared by a chemical method has not been reported to our best knowledge. Such investigation would enlarge the knowledge of the role of calcination on the reactivity of metal supported catalysts [12,13]. A Ni^0/SiO_2 catalyst, prepared by the hydrazine method, was calcined at 400 °C with various times. For each sample, the degree of reduction by O_2 adsorption, H_2 adsorption, H_2 temperature programmed desorption (H_2-TPD) and activity in benzene hydrogenation were evaluated. One sample was diluted by the support and similarly investigated.

2. Experimental

2.1. Catalyst preparation

Nickel acetate tetrahydrate (99.0%, Fluka) and aqueous hydrazine 24–26% (_99.0%, Fluka) were used as received. The silica support (Chempur, 99.99%, 15 $m^2\,g^{-1}$ and grains of 325 mesh) was pretreated in air at 500 °C for 10 h before use. The catalyst precursor was prepared by impregnating at room temperature a suspension of silica in a solution of nickel acetate, evaporating at 80 °C in vacuum then drying at 100 °C. The solid precursor was introduced in a solution of hydrazine and heated up to 70 °C. The black solution obtained was cooled, filtered and washed with ethanol. The resulting filtrate was dried under vacuum and stored under argon. The final solid contained 1%Ni.

2.2. Catalyst characterization

The nickel composition of the catalyst was determined on a Varian AA1275 atomic absorption spectrophotometer. The XRD patterns I(θ) were recorded at a classical θ/2θ diffractometer using Cu K_α radiation.

Chemisorption experiments were carried out with a sample of 0.1 g on a pulse chromatographic microreactor equipped with the catharometric detector of a microchromatograph (AT M200, Hewlett Packard) fitted with molecular sieve columns and MTI software. The utilized gases were purchased from Air Liquide. Oxygen traces were eliminated from argon (99.995%) and hydrogen (99.995%) by using a manganese oxytrap (Engelhardt). Diluted H_2 and O_2 in argon and synthetic air were used as received.

Each sample was pre-treated with H_2 pure (100 mL min^{-1}/2 h/300 °C), purged under argon atmosphere (100 mL min^{-1}/2 h) and cooled to room temperature. After that, gaseous hydrogen (100 ppm in argon) was injected in the reactor every 2 min until saturation of the sample. Then, the hydrogen saturated sample was purged at room temperature under argon for 2 h, a time after which no hydrogen (<1 ppm) was detected in the exit gas. It was subsequently submitted to a TPD under same gas (50 mL min^{-1}) with a heating rate of 7.5 °C min^{-1} up to 800 °C.

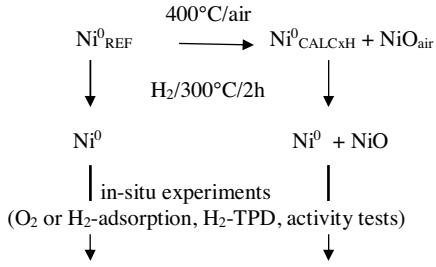
O_2 chemisorption was used to evaluate the degree of reduction of calcined samples, according to the literature data [14]. After calcination each sample was submitted to same H_2 heat treatment as above, cooled to room temperature, purged then flowed with gaseous oxygen (150 ppm of O_2 in helium) every 2 min until saturation.

2.3. Catalytic tests and kinetic study

The gas-phase hydrogenation reaction was carried out in a quartz fixed-bed reactor after activation under hydrogen as described above for chemisorption studies. The catalytic tests were conducted with a sample of 0.1 g and a feed gas of 1% C_6H_6/H_2 and total rate flow of 50 mL min^{-1} at various temperatures. The catalyst was cleaned in a hydrogen flow (50 $cm^3\,min^{-1}$) for 30 min after each test. The reactant and product analysis were conducted on line using a Hewlett-Packard 5730A FID gas chromatograph equipped with TCEP (2 m, 1/8 in) and Sterling (3 m, 1/8 in) columns.

Conversion was determined by crossing the reaction temperature and, after each temperature, the catalyst was cleaned in a hydrogen flow (50 $cm^3\,min^{-1}$) for 30 min.

The kinetic study was performed at 100 °C with a catalyst sample of 0.025 g. The catalyst was flowed with 1% C_6H_6/H_2 + He as a reactant mixture (100 $cm^3\,min^{-1}$). Helium (99.999%) was used as received from Air Liquide. The reaction products were analyzed as described above and the conversion was maintained below 3%.



Scheme 1. Overall protocol of the catalysts studies.

2.4. Study of the effect of calcination on catalyst reactivity

The freshly prepared catalyst was calcined at 400 °C/air (flow rate of 50 mL min^{-1} with a heating rate 7.5 °C min^{-1}) for various times and stored under argon. Notation was Ni^0_{REF} and Ni^0_{CALCxH} for as-prepared and calcined samples respectively, where xH represents the time of calcination in hours. Oxidized nickel was denoted as NiO_{air}. Due to contamination of nickel by moisture during handling, all samples were submitted to in situ standard hydrogen pre-treatment (see above) before chemisorption and catalysis experiments. The overall protocol of the study is reported in Scheme 1.

We underline that after the hydrogen pre-treatment, the reference sample contained Ni^0 only whereas the calcined samples comprised both Ni^0 and NiO species. This means that in each sample Ni^0 is the sum of residual metallic nickel (not oxidized by the 400 °C/air treatment) plus that due to the partial reduction of NiO_{air} during the standard hydrogen pre-treatment.

3. Results and discussion

3.1. Degree of reduction of nickel

In our previous study [1] XRD experiments evidenced the pattern of the Ni^0 phase in a reference Ni/SiO_2 catalyst where the metal content was of 3%. After calcination at 250 °C/2 h, this signal was still present with a lower intensity due to oxidation of metallic nickel. As to the signal of the expected nickel oxidized phases, it was not detected: absence of NiO species was ascribed to formation of amorphous phases. We assumed same mechanisms in the present study with the 1%Ni catalyst. Variation in the proportions metallic/oxidized phases was determined chemically.

The degree of reduction was measured by O_2 chemisorption. It decreased monotonously with the time of previous exposure to air (Table 1). The obtained samples were partly oxidized, reduced and unreduced nickel particles coexisting in various proportions.

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