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The origin of increased chemoselectivity of platinum supported on magnesium fluoride in the hydrogenation of chloronitrobenzene

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ABSTRACT

A highly active and selective catalyst for the hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) was obtained by supporting platinum on magnesium fluoride. In the above reaction, carried out in a liquid phase at 343 K under 3 MPa H_2, the Pt/MgF_2 catalyst was fivefold more active (apparent rate = 9.26 mol CNB/mol Pt_{surf} s) than the analogous system with Al_2O_3 as a support (apparent rate = 1.83 mol CNB/mol Pt_{surf} s). At the same time its selectivity to o-CAN (96.6%) was higher than that of Pt/Al_2O_3 (79.8%). The FTIR studies of adsorbed nitrobenzene (NB) enabled to determine the adsorption mode via oxygen atoms of nitric group. A model of o-CNB adsorption on the platinum/support interface has been proposed, according to which o-CNB adsorption proceeds on Lewis acid centres located in the vicinity of platinum crystallites which are the centres for hydrogen adsorption and dissociation. The presence of interfacial active sites was additionally proved by FTIR studies of adsorbed carbon monoxide and TPR-H_2 measurements.

1. Introduction

Substituted anilines, including halogenated anilines, are important reagents to the manufacture of a wide variety of drugs, pesticides, pigments and dyes. By way of illustration one can mention *Chlorothiazide*, which is a popular diuretic and a hypertension drug, as well as *Chlorpropham* – a herbicide belonging to the group of growth inhibitors [1].

In the past, chloroanilines were obtained by the Béchamp reduction, however, this method was abandoned for ecological reasons, because it was a source of hazardous iron oxide waste that contained toxic intermediates of the reaction. The Béchamp reduction was replaced by a catalytic method which is less environmentally burdensome, although it is not free of some drawbacks. The most important of them is the easiness at which CNB undergoes hydrodechlorination, which results in the formation of undesirable by-products, mainly aniline [2]. This fact generates serious technological problems and increases production costs associated with the separation and purification of the final product. An ideal solution of the problem would be the application of an active catalyst showing 100% selectivity to chloroaniline. Unfortunately, the catalysts used currently, such as Pt/active carbon, sulphided platinum, palladium and nickel catalysts do not reach 100% selectivity to chloroaniline, particularly at complete conversion of chloronitrobenzene [3]. Hence the interest of researchers in the search for catalysts of possibly highest selectivity. Advantageous effects were obtained by adding dehalogenation inhibitors to the reaction medium, e.g. morpholine, phosphorous acid, amines, etc. [4], as well as by using bimetallic catalysts [5–8] or colloidal nanoparticles [9–12]. Reports were also published, according to which the increase in selectivity and/or activity was achieved by applying new, untypical supports such as γ-Fe_2O_3 [13,14], SnO_2 [15], palygorskite [16], γ-ZrP [17]. The latter approach has stimulated us to investigate properties of another untypical support, namely magnesium fluoride. It is worth to add that recently a rapid increase in the number of papers on MgF_2 and its application to catalysis is observed [18–21]. Magnesium fluoride as a catalyst support was found useful in such reactions as hydrodesulphurization [22–24], hydrodechlorination [25–30], ammoxidation [31], reduction of nitrogen oxides [32,33], Knoevenagel reaction [34], oxidation of CO [35,36], photodegradation of acetone [37], and recently, hydrogenation of chloronitrobenzene to chloroaniline [38,39]. A number of MgF_2 preparation procedures were developed [18,20,40–43] and its detailed characterisation was performed [18–21]. In the present study we have used MgF_2 as a support for platinum. From among metallic, platinum shows the highest activity for the reduction of chloronitrobenzene nitric group, however its selectivity to chloroaniline is relatively low. The application of an appropriate support can result in an increase in the selectivity. The use of TiO_2 [44–46] or γ-Fe_2O_3 [13,14] leads to a considerable rise in the selectivity towards chloroaniline.

The present work was aimed at verifying the usefulness of MgF_2 as a support for platinum catalysts for chemoselective reduction of o-chloronitrobenzene to o-chloroaniline. For comparison purposes,

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a Pt/Al_2O_3 catalyst was employed in the study. Moreover, attempts were made at explaining the high selectivity of Pt/MgF_2 catalyst on the grounds of IR-spectroscopic investigation of adsorbed CO and nitrobenzene as well as TPR-H_2 studies.

2. Materials and methods

2.1. Preparation of supports and catalysts

Magnesium fluoride was obtained by adding small portions of $MgCO_3{\cdot}2H_2O$ to an aqueous solution of hydrofluoric acid until neutralisation followed by acidification with a few additional drops of the acid. The precipitate was then aged at room temperature for a few days under stirring, dried at 353 K and calcined at 673 K for 4 h. After the calcination, MgF_2 was ground to obtain particles of 0.2–0.5 mm in size. Platinum was deposited on MgF_2 by conventional impregnation using an aqueous solution of H_2PtCl_6. The required amount of H_2PtCl_6 was dissolved in water, then contacted with MgF_2 at room temperature for several minutes, followed by evaporation of water. The solid was dried at 353 K, then reduced at 673 K under hydrogen flow for 4 h. The Pt content was 1 wt.%. The catalysts were labelled as Pt–Mg.

Aluminium oxide was prepared by hydrolysis of aluminium isopropoxide. The obtained aluminium hydroxide was washed out of isopropyl alcohol, dried at 383 K for 24 h, then calcined at 823 K for 4 h. The Pt/Al_2O_3 (1 wt.% of Pt) catalyst was prepared in the same way as the Pt/MgF_2 catalyst and labelled as Pt–Al.

2.2. Catalyst characterisation

2.2.1. Surface area

The Brunauer–Emmet–Teller surface areas were determined by N_2 adsorption at 77 K using a Micromeritics ASAP2010 sorptometer. Total pore volume and average pore radius were determined by the Barrett–Joyner–Halenda (BJH) method using a desorption isotherm.

2.2.2. FTIR spectroscopy – CO and nitrobenzene adsorption

Fourier Transform Infrared (FTIR) studies were carried out on a Bio-Rad spectrometer, model FTS 3000MX. The samples, prepared in the form of self-supporting wafers (10 mg/cm^2), were placed in a glass cell equipped with KRS-5 windows. Before FTIR experiments, samples were evacuated *in situ* at 573 K for 1 h at 4×10^{-3} Pa to remove adsorbed water and impurities. Then the samples were cooled down for CO and benzene adsorption at room temperature.

Carbon monoxide was adsorbed at 1.3 kPa and nitrobenzene at 0.7 kPa for 10 min at 298 K. After evacuation, spectra of adsorbed species were recorded with a resolution of 4 cm^{-1}. The FTIR spectrum of a sample before adsorption was used as a subtraction background. Measurements of nitrobenzene chemisorption were carried out for platinum-free supports and for platinum catalysts at 298 K. Spectra shown in Fig. 3 were recorded after evacuation of samples at 323 K for 15 min.

2.2.3. Temperature programmed reduction – TPR-H_2

The measurements were performed on a ChemiSorb 2705 instrument made by Micromeritics. The gases used in the measurements were of high purity. The susceptibility to reduction was measured in a stream of 10 vol.% H_2 in argon. The volume rate flow of the gas mixture was 30 cm^3/min and temperature increased at the rate of 10 K/min. The calibration for the determination of hydrogen consumed was performed by introducing a specified volume of hydrogen (using a sample loop) into the stream of argon.

2.2.4. The determination of metal dispersion by hydrogen chemisorption

Prior to hydrogen chemisorption, samples were pretreated *in situ* to remove adsorbed molecules from the surface of platinum. Samples were evacuated for 15 min at room temperature and next at 673 K for 60 min, followed by reduction in hydrogen flow (40 cm^3/min) at 673 K and evacuated again for 120 min at 673 K. All chemisorption experiments were performed on an ASAP 2010C sorptometer. Chemisorption of hydrogen was carried out at 308 K and the isotherms were determined using 5 different pressures in the range of 12–40 kPa. After first set of pressures (isotherm H_t) the catalyst was evacuated at 308 K for 30 min to remove reversibly adsorbed hydrogen (H_{rev}) and the same procedure was repeated. The difference between adsorbed hydrogen extrapolated to zero pressure value for two isotherms equals to the amount of hydrogen irreversibly bound (H_{irr}).

By assuming that the stoichiometry for hydrogen adsorption on surface platinum atoms (Pt_s) is 1:1, the dispersion of platinum is given by $D = Pt_s/Pt_t = H/Pt_t$ (Pt_t – total number of platinum atoms). Platinum dispersion was calculated from irreversibly chemisorbed hydrogen.

2.3. Catalytic procedure

Hydrogenation of *ortho*-chloronitrobenzene (o-CNB) to *ortho*-chloroaniline (o-CAN) was performed in a liquid-phase at 343 K for 2 h under hydrogen pressure of 3.0 MPa in a 200 cm^3 stainless steel autoclave with a glass tube inside equipped with magnetic stirrer. The autoclave was loaded with 25 mg of catalyst and 50 cm^3 of 0.4 M methanolic solution of o-CNB. Then the autoclave was flushed several times with helium followed by flushing with hydrogen in order to remove air. In each case, the reaction time was 2 h and stirring rate was 1000 rpm. Results of the experiments show that the reaction was conducted in the absence of external mass transport limitations (the stirring rates from 800 to 1000 rpm did not affect the reaction rate). The overall molar CNB/Pt ratio was 15,600. The reaction products were analysed on a gas chromatograph equipped with a capillary column RESTEK MXT-5. Catalytic activity was expressed as a apparent rate (r) in moles of o-CNB reacted per mole of platinum (r_t) or per surface Pt atoms (r_s) (the latter value was determined by hydrogen chemisorption). Catalytic measurements carried out with platinum-free MgF_2 and Al_2O_3 supports proved the inactivity of the supports for the reduction of nitric group of o-CNB.

3. Results and discussion

3.1. Catalyst characterisation

Magnesium fluoride prepared by reacting magnesium carbonate with hydrofluoric acid is characterised by well-developed structure of mesopores as it results from type IV isotherm and H1 hysteresis loop (not shown in this paper). MgF_2 calcined for 4 h at 673 K has BET surface area of about 50 m^2/g and relatively large average pore radius (~10 nm) – Table 1. In the case of the liquid-phase reaction, where processes of mass transfer within catalyst particles play a considerable role, this fact (i.e. large pores) is an advantage. The textural characterisation of MgF_2 used in this study was presented in Table 1.

The impregnation of magnesium fluoride with aqueous solution of hexafluoroplatinic acid, followed by reduction in hydrogen flow (4 h at 673 K), results in a decrease in surface area to 35 m^2/g.

Alumina, one of the most popular supports, was chosen by us as for comparative purposes. After calcination at 823 K we have obtained γ-Al_2O_3 (proved by XRD pattern) of surface area equal to