



Modification of silica with NH_4^+ agents to prepare an acidic support for iridium hydrogenation catalyst



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ABSTRACT

The inert SiO_2 was modified with basic or slightly acidic aqueous solutions of ammonium compounds in order to impact acidic properties to its surface. The obtained silica samples were used as supports for iridium catalysts (1 wt%). The influence of the support acidity on the activity of iridium catalyst for toluene hydrogenation was examined. The acidity of the modified SiO_2 was estimated by means of temperature-programmed desorption of ammonia (NH_3 -TPD) and FT-IR spectra of adsorbed pyridine. It has been found that the sample treated with the basic solution had a higher total acidity, however, the sample modified with the acidic solution had a higher contribution of strong Lewis acid sites. The acidic solution-treated sample had also a higher number of silanol groups compared to the parent SiO_2 (FT-IR data). The activity of iridium catalysts supported on the modified samples (particularly that on the acidic solution-treated SiO_2) for toluene hydrogenation was higher than that of the catalyst supported on unmodified SiO_2 . The obtained results bring to conclusion that catalytic activity for toluene hydrogenation is influenced by the contribution of strong Lewis acid sites and the content of silanol groups rather than by total acidity.

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1. Introduction

Hydrogenation processes are broadly applied worldwide both for the large scale production of various chemical compounds and for the synthesis of fine chemicals [1,2]. Environmental legislation imposed a reduction in the aromatic content in engine fuels and this resulted in an increased attention to searching for more efficient catalysts for hydrotreating processes. Supported noble metal catalysts are widely used for a variety of catalytic hydrogenation reactions. For example, Pd and Pt supported catalysts exhibit excellent activity for the hydrogenation of unsaturated bonds like $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$, while supported Ru, Rh and Pd catalysts show high activity for the hydrogenation of aromatic hydrocarbons [3]. In the platinum metal group, iridium is known to be active for selective hydrogenation of α,β -unsaturated aldehydes [3–6], toluene hydrogenation [7,8] and NO reduction [9–11]. There is some literature information on the application of alumina-supported iridium catalysts to hydrogenation of monoaromatics [12,13]. Vannice et al. observed enhanced activity for hydrogenation of monoaromatics

over noble metal catalysts supported on acidic supports [14,15]. The authors have shown that the overall conversion of aromatics over the noble metal/acid catalysts comes from two kinds of sites: one is the well-known noble metal active center, and the other is an acid site on which the adsorbed aromatics can be hydrogenated with the activated hydrogen spillover from metal centers.

Kitamura et al. [16] has shown that treatment of zeolites, especially siliceous zeolites with a MFI structure, with aqueous solution of ammonium salts and at least one basic compound (aqueous ammonia solution, alkylamines, allylamines or alkylammonium hydroxide) generates their catalytic activity in the Beckmann rearrangement reaction. The FT-IR analysis of the samples modified by this way indicated the formation of H-bonded silanol defect groups of different kind with low acidity [17,18].

This work was aimed at determining the influence of SiO_2 support acidity on the efficiency of the resulting iridium catalysts for toluene hydrogenation. To the best of our knowledge, no data are available on such a modification of silica followed by its use as iridium catalyst support for hydrogenation. Amorphous silica was chemically modified with aqueous basic (NH_4OH and NH_4NO_3) or slightly acidic (NH_4Cl) solution and then thermally treated at 823 K. Taking into account the influence of the acid function of supports on the activity of such bifunctional catalysts, the characterization of

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the supports and catalysts was performed using classical characterization methods for evaluating both the acid functions of supports (temperature-programmed desorption of ammonia and pyridine adsorption-desorption followed by FT-IR) and the hydrogenating properties of catalysts (e.g. H₂ chemisorption, temperature programmed reduction with hydrogen). Iridium catalysts supported on unmodified and modified SiO₂ were compared. The impact of acidity of supports on the activity of iridium catalyst was assessed in the reaction of toluene hydrogenation.

2. Experimental section

2.1. Preparation of supports and catalysts

2.1.1. Supports

Amorphous SiO₂ (silica gel, Polish Chemicals Reagents, Inc.) was activated by thermal treatment in air at 823 K for 3 h (denoted as SiO₂-0) followed by the modification with basic or acidic solutions of ammonium salt. The basic treatment was performed according to the procedure described by Kitamura et al. [16] with some changes. The original SiO₂ sample (5 g) was treated with a mixture of aqueous ammonium nitrate solution (7.5 wt%, 20 g) and aqueous ammonia solution (25 wt%, 30 g) (denoted as SiO₂-B). The acidic modification was performed using 1M NH₄Cl solution. The sample (1 g) of activated silica was mixed with 100 cm³ of the NH₄Cl solution (the resulting sample was labeled as SiO₂-A). In both cases, the mixture of silica and aqueous solution of ammonium salt was stirred under reflux at 333 K for 1 h. The procedure was repeated twice. After the treatment, the samples were filtered, washed with deionized water and then dried at 383 K and calcined in air at 823 K for 3 h.

2.1.2. Supported iridium catalysts

Silica samples, both parent one and those treated with basic or acidic solutions of ammonium salt, were impregnated with the methanolic solution of tetrairidium dodecacarbonyl (Ir₄(CO)₁₂, 98%, Aldrich). The iridium content was 1 wt%. The catalysts dried at 373 K for 24 h were denoted as Ir/X-D (X stands for SiO₂-0, SiO₂-A or SiO₂-B; D – for dried catalyst).

2.1.3. Activation of catalysts

Prior to the measurements by transmission electron microscopy, as well as before the measurements of hydrogen chemisorption and low-temperature nitrogen adsorption-desorption, each precursor-impregnated support was placed in a porcelain boat and reduced in hydrogen flow (99.99%, Linde, 50 cm³·min⁻¹). At the beginning, the system was flushed at room temperature with argon (150 cm³·min⁻¹, 99.99%, Linde) which was then replaced with hydrogen (150 cm³·min⁻¹). After 30 min, the hydrogen flow was reduced to 50 cm³·min⁻¹ and the temperature ramp (10 K·min⁻¹) started. After reaching the setpoint (673 K), the catalyst precursor reduction was continued for 2 h. Then the catalyst was cooled down to the room temperature in hydrogen flow. The last step consisted in flushing the sample with argon for 15 min.

The catalysts were labeled with the code Ir/X (X = SiO₂-0, SiO₂-A or SiO₂-B).

2.2. Characterization of supports and catalysts

2.2.1. Determination of surface area, pore volume and pore diameter

Textural characterization of the supports calcined at 823 K and the catalysts reduced at 673 K was conducted by the low-temperature (77 K) nitrogen adsorption-desorption using a sorptometer ASAP 2010 manufactured by Micromeritics. Prior to the

measurements of adsorption-desorption isotherms, the samples were outgassed at 623 K for 4 h. The surface area was calculated by Brunauer-Emmett-Teller (BET) method and the total pore volume and average pore radius were determined using the Barrett-Joyner-Halenda (BJH) method. The microporosity was estimated using the t-plot method.

2.2.2. Determination of metal content

Iridium content in catalysts reduced at 773 K for 2 h was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Varian Vista-MPX spectrometer.

2.2.3. Transmission electron microscopy

Transmission electron microscope (TEM) images were recorded on a Hitachi HT7700 microscope operating at accelerating voltage of 100 kV. They were used for the estimation of Ir particle size, as well as for elemental analysis with the help of energy dispersive X-ray spectroscopy EDS/TEM. The materials studied were deposited on nickel grids coated with a carbon film. The average particle size was calculated from 100 particles using the following formula [12]:

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where: d stands for particle size and n is the number of particles.

2.2.4. FT-IR spectra

The Fourier transform infrared spectra (KBr and self-supported wafers) were recorded with a Bruker Tensor 27 spectrometer. The acidity of the supports was estimated using pyridine as a basic probe. The samples were pressed under low pressure into a thin wafer and placed in a vacuum cell. Then they were outgassed at 673 K for 2 h, followed by pyridine adsorption at room temperature. The desorption was carried out for 30 min at each of the following temperatures: 373, 474 and 573 K. The spectra were recorded at room temperature and then normalized to the same weight (1 g).

2.2.5. Temperature-programmed desorption of ammonia (TPD-NH₃)

The TPD-NH₃ measurements of acidity were performed in a flow reactor. In the typical experiment a sample (~40 mg) was heated in He (99.999%, Linde) at the rate of 10 K·min⁻¹ up to 773 K and then maintained at this temperature for 0.5 h. Afterwards, it was cooled down to 393 K and saturated with ammonia for 0.5 h. The physically adsorbed NH₃ was removed by purging with helium flow at 393 K for 1 h. The TPD-NH₃ analysis was carried in the range of 373–873 K with a heating rate of 10 K·min⁻¹. The desorbed NH₃ was detected by a TCD analyzer. All TPD-NH₃ profiles presented in this work were normalized to the same sample weight (1 g).

2.2.6. Temperature-programmed reduction with hydrogen (TPR-H₂)

Measurements of temperature-programmed reduction with hydrogen (TPR-H₂) were carried out on a PulseChemisorb 2705 (Micromeritics) instrument. Dried metal precursor-impregnated supports were reduced in the flow of 10 vol% H₂-Ar (99.999%, Linde) at the flow rate of 30 cm³·min⁻¹. The measurements were conducted in the temperature range from 313 to 1123 K at a linear temperature ramp of 10 K·min⁻¹. All TPR-H₂ profiles presented in this work were normalized to the same sample weight (40 mg).

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