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Short Communication

Hydrogenation of 2-methylindole using supported metal catalysts

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ABSTRACT

The hydrogenation of 2-methylindole to 2-methylindoline in toluene was studied at 60 °C and 40 bar hydrogen pressure in a batch mode using a range of carbon, alumina, and zeolite supported metal catalysts were performed in toluene. The results were compared with a more conventional catalytic system containing besides 5% Pt/C also 1.2 eq. of *p*-toluenesulfonic acid in ethanol:water (50:50 v/v). The highest turnover frequency (TOF) was obtained a zeolite supported iridium catalyst.

1. Introduction

Amines are known to be frequently used as starting materials for preparation of pharmaceuticals and agrochemical products [1]. Of particular interests are indolines, which are bicyclic secondary amines consisting of a five membered, nitrogen-containing ring fused to a benzene ring.

Hydrogenation of indoles to indolines is hampered by the resonance-stabilized fused aromatic moiety [2]. Previously, hydrogenation of indoles has been mainly carried out using chiral homogeneous catalysts [3–16], although some heterogeneous catalysts have also been applied [2,17–19].

For instance, Kulkarni et al. [2] studied the hydrogenation of indole to indoline at room temperature and used Pt/C and Pt/Al_2O_3 as catalysts. In particular a variety of combinations of Pt/C with several acids such as trifluoroacetic acid, camphorsulfonic acid, *p*-toluenesulfonic acid, trifluoromethanesulfonic acid, and formic acid was tested with ethanol, methanol, toluene, hexane, 2,2,2-trifluoroethanol and water as solvents. The highest conversion (100%) was obtained using Pt/C, *p*-toluenesulfonic acid and water under 30 bar hydrogen pressure for 3 h with the selectivity being also 100%. Beckers et al. [17] studied hydrogenation of indoles and applied a series of oxide supported mono-, bi-, and trimetallic catalysts. Shaw and Stapp [18] used platinum and rhenium catalysts in the hydrogenation of indoles. Clarisse et al. [19] used Pd/C and hexafluoroisopropanol as solvent in the hydrogenation of indole and indole derivatives. For the hydrogenation of 2-methylindole, the yield of 2-methylindoline was 82% in 1 h at 50 °C and 7 bar.

Heterogeneous catalysts offer obvious advantages over their homogeneous counterparts with respect to easier handling, simple separation and catalyst recycling. In order to enhance the reaction rate in indole hydrogenation, acidic conditions can be used to protonate the indole nitrogen, thereby generating an iminium ion which disrupts the aromaticity [2,3,20]. In the present work, acidic zeolites with and without metals have been used in order to increase the reaction rate in the hydrogenation of 2-methylindole to 2-methylindoline (Scheme 1).

The work was executed within the framework of EU funded POLYCAT project where the authors studied heterogeneous catalytic hydrogen borrowing reaction of 1-(2-aminophenyl)propan-2-ol to 2-methylindoline in one-pot fashion. In addition a two-step approach was explored involving first dehydrogenation-cyclization of 1-(2-aminophenyl)propan-2-ol to 2-methylindole with subsequent hydrogenation to 2-methylindoline.

The current work covers the second part of the latter approach and is based on the hypothesis of the reaction rate enhancement by using acid sites (Brønsted and Lewis). The results are compared with metal catalysts on non-acidic support and with addition of an organic acid.

2. Experimental

2.1. Catalyst synthesis

In this work, commercial catalysts supplied by Degussa were used, namely 5% Pt/C F106 XKYF/W 5%, 5% Pd/C E105 R/W 5%, and 5% Pt/Al_2O_3 F214 VH/D 5%.

Synthesis of Ir-H-Beta-150-IE (SiO_2/Al_2O_3 molar ratio 150) zeolite catalyst was carried out by an ion-exchange method, while Ir-H-Beta-150-IMP was prepared by evaporation impregnation in a rotavapor

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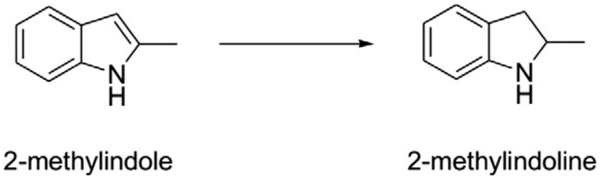

Scheme 1. Reaction scheme for the hydrogenation of 2-methylindole.

using an aqueous solution of iridium chloride. Iridium modified H-Beta-150 zeolite catalyst was dried at 100 °C in an oven and calcined at 400 °C.

NH_4-Beta-150 zeolite (Zeolyst International) was calcined at 400 °C in a muffle oven using a step calcination procedure to obtain H-Beta-150 catalyst. The H-Beta-150 zeolite catalyst was modified with platinum using an aqueous solution of hexachloroplatinic acid (Merck). The modification of H-Beta-150 catalyst with Pt was carried out using evaporation impregnation method in a rotator evaporator for 24 h. The catalyst was recovered after the completion of synthesis, dried at 100 °C and calcined in a muffle oven at 400 °C. The H-Beta-25 zeolite (Zeolyst International) was modified with platinum using a similar procedure as above.

Synthesis of 5 wt.% Pd-H-Beta-25-US catalyst was carried out in the presence of ultrasound. Aqueous solution of palladium nitrate (Merck) and H-Beta-25 zeolite was introduced in a round bottom flask, which was subsequently introduced in an ultrasound reactor connected to ultrasound source [21]. The reaction mixture was subjected to ultrasound irradiation for 4 h, after which it was removed from the ultrasound reactor and connected to the rotator evaporator, where it was rotated for 24 h, followed by evaporation. The Pd modified H-Beta-25 catalyst was recovered from the flask, dried at 100 °C and calcined at 400 °C.

Preparation of Ir-H-Beta-300 catalyst was carried out using an aqueous solution of iridium chloride (Fluka) and H-Beta-300 (Zeolyst International). The preparation of the catalyst was carried out in a rotator evaporator using the evaporation impregnation method. The Ir-modified H-Beta-300 zeolite catalyst was recovered from the flask after evaporation and dried at 100 °C. The calcination of the catalyst was carried out in a muffle oven at 400 °C.

2.2. Experimental procedure

The experiments were carried out in a 300 ml autoclave (Parr instruments) under 40 bar hydrogen pressure (99.999%, AGA). 2-Methylindole was purchased from Aldrich (98%), toluene from J.T. Baker ("Baker analyzed"), ethanol from Altia (99.5%, Etax Aa), and *p*-toluenesulfonic acid from Sigma-Aldrich (≥98.5%). Before the experiment, the catalyst was reduced, in case of Pt and Ir *ex situ* at 400 °C (for 1 h, heating rate 5 °C/min) in hydrogen and for Pd *ex situ* at 200 °C (for 1 h, heating rate 5 °C/min) under hydrogen. The *ex situ* reduced catalysts were also pre-treated *in situ* at 60 °C for 30 min under hydrogen in 70 ml solvent. The reactant and 50 ml solvent was degassed in the bubbling unit for 5 min using hydrogen and then led to the reactor. The stirring rate was 1650 rpm. The reaction time was put to zero and the experiment was started.

Samples were taken at different time intervals and analyzed by a gas chromatograph (GC). The samples were prepared for GC using 0.5 ml of the sample taken from the reactor and to this 0.5 ml of an internal standard, consisting of 0.02 M undecane in toluene, was added. An aliquot of 1 μl of the sample was injected with an autosampler to the GC. The injector temperature was 220 °C and the split ratio 50:1. A Supelco B-Dex-225 column was used with the helium gas flow of 0.9 ml/min. The following temperature program was applied: 130 °C for 60 min and 10 °C/min to 160 °C, where it maintained for 10 min. The flame ionization detector (FID) was kept at 300 °C.

2.3. Catalyst characterization

To determine the metal particle size and dispersion, catalysts were analyzed by CO pulse chemisorption (Autochem 2910, Micrometrics). In these experiments, 0.05–0.1 g of the sample was placed into a quartz U-tube containing silica wool, the tube was inserted to the system and the sample was dried in a stream of helium gas at 50 °C for 30 min. Thereafter, the sample was reduced at the same temperature and time as in the reduction before the experiment in hydrogen, using helium as a carrier gas, after which it was flushed with helium (retained at the reduction temperature) for 1 h, cooled to room temperature, placed on water bath, and subsequently the CO pulses were introduced (10% CO in helium, helium as a carrier gas) until the adsorption was complete. The dispersion was calculated from the amount of CO consumed, assuming the metal:CO stoichiometry to be unity [22].

A PerkinElmer PHI 5400 spectrometer with a monochromatized Al Kα X-ray source operated at 14 kV and 300 W was used in the XPS-analysis of zeolite supported metal catalysts. The pass energy of the analyzer was 17.9 eV and the energy step 0.1 eV. The binding energy calibration was based on the Si 2*p* peak at 103.3 eV. The sensitivity factors used in the quantitative analysis for Si 2*p*, O 1*s*, Ir $4f_{7/2}$, and Ru $3d_{5/2}$ were 0.283, 0.711, 2.402 and 2.208 respectively.

The platinum contents of H-Beta-25 and H-Beta-150 were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Around 50 mg of the catalyst was dissolved using 4 ml aqua regia and 2 ml of hydrofluoric acid in a microwave oven. The dissolved sample was diluted to 100 ml with de-ionized water and further diluted to 1:5, after which it was analyzed.

3. Results and discussion

3.1. Catalyst characterization

According to XPS analysis Ir-H-Beta-150-IE contained 0.3 wt.% of iridium, Ir-H-Beta-150-IMP 0.5 wt.% of iridium, Ir-H-Beta-300 0.7 wt.% of iridium, and Pd-H-Beta-25 1.5 wt.% of palladium. The results for Pt-H-Beta-25 and Pt-H-Beta-150 were not reliable since the platinum and aluminum peaks overlapped. The ICP-AES analysis gave 2.1% of platinum for Pt-H-Beta-150 and 4.5% of platinum for Pt-H-Beta-25.

The results from CO chemisorption are presented in Table 1. The smallest particle size was obtained for 5% Pt/C and 1.5% Pd-H-Beta-25-US with 3 nm. 4.5% Pt-H-Beta-25 had 5 nm particle size. The largest metal particle size was obtained for 0.5% Ir-H-Beta-150-IMP and 2.1% Pt-H-Beta-150 being 7 nm.

3.2. Catalytic activity

The reaction scheme is presented in Scheme 1; the double bond in 2-methylindole is hydrogenated to give 2-methylindoline. A small amount of an unknown byproduct (probably tetrahydro-2-methylindole) with the mass in GC–MS equal 135 was obtained. The results of hydrogenation using supported metal catalysts are shown in Fig. 1. In the literature [2,3], it was stated that addition of an acid is needed to increase both the reaction rate and the yield. Thus, the aim of the present work was to

Table 1
Characterization of the catalysts by CO chemisorption.

Catalyst	Dispersion (%)	Metal particle size (nm)
5% Pt/C	38	3
5% Pd/C	17	6
5% Pt/Al_2O_3	25	4.5
1.5% Pd-H-Beta-25-US	36	3
4.5% Pt-H-Beta-25	21	5
2.1% Pt-H-Beta-150	16	7
0.3% Ir-H-Beta-150-IE	23	5
0.5% Ir-H-Beta-150-IMP	15	7