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Gas-phase dehydrocyclization of diphenylamine

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Abstract

The gas-phase dehydrocyclization of diphenylamine to carbazole was studied in a fix-bed reactor over Pt and Pd catalysts. Alumina, magnesium oxide and silica were used as supports. The reaction was carried out at a temperature of 560 °C in the presence of hydrogen. Pd catalysts are reasonably active but not selective compared to Pt catalysts which possess very high activity and selectivity. For supporting active metal, proper alumina has advantages compared to silica and magnesium oxide. This is due to its acid sites which accelerate the isomerization step. Though higher loading of Pt has a positive influence on the carbazole formation, at a Pt content higher than 0.6 wt.% this effect is negligible. In the presence of catalyst with 0.6 wt.% Pt deposited on alumina, carbazole is produced with a selectivity of about 90% at a conversion of diphenylamine about 97%.

Keywords: Diphenylamine; Carbazole; Dehydrocyclization; Platinum catalysts; Gas-phase

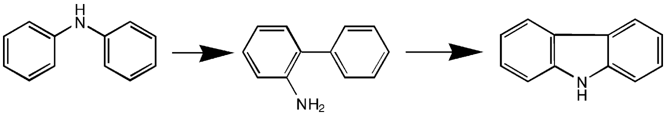
1. Introduction

Carbazole (CB) belongs to the group of important heterocyclic compounds. The main field of its utilization is as an intermediate in fine chemistry, e.g. in the production of insecticides, pigments and drugs [1,2].

Carbazole also easily reacts with acetylene to form *N*-vinylcarbazole which is a good monomer in the production of thin polymer films with good dielectric properties. Derivatives of carbazole (e.g. *N*-vinylcarbazole) are known as challenging compounds to copolymerize with other monomers to form copolymers which have a wide variety of applications in dentistry, optical eyewear, fibre optics, holography and microelectronics [3]. Carbazole-based compounds play a very important role in electroactive and photoactive materials. In organic light-emitting diodes, carbazole derivates are usually used as hosting materials due to their high triplet energy and good hole-transporting ability [4–6].

Carbazole can be obtained from the products made from crude oil or coal [7]. However, carbazole obtained from these nature's sources is usually contaminated with impurities, which are hard to remove due to their similar chemical properties. The purity of this carbazole ranges from 95% to 98%.

For the pharmaceutical industry it is necessary to use carbazole with a purity higher than 98%. There are methods how to prepare carbazole via synthesis, however this way is mostly not interesting for industrial use. According to the patent literature, carbazole can be prepared by dehydrogenation of aromatic amines in the presence of hydrogen over noble metal catalysts in the temperature range 300–600 °C [8–13]. Suitable starting compounds are diphenylamine (DPA), *o*-nitrobiphenyl, 2-aminobiphenyl and various substituted aminobiphenyls or their mixtures. For diphenylamine as a starting compound, following mechanism has been proposed [14]:



The proper heterogeneous catalysts contain Cr_2O_3, Ir, Rh, Pd and Pt. Oxides of Mg, Zn, Al, Si, Ti and Zr serve as carriers.

The objective of this work was to study gas-phase cyclodehydrogenation of diphenylamine to carbazole over metal supported catalysts.

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2. Experimental

2.1. Catalysts preparation

The commercial γ-alumina (Eurosupport Litvinov, Czech Republic) was calcined at 1050 °C for 5, 7 and 10 h. The aluminas obtained were marked as A0 (non-calcined), A5, A7 and A10. Magnesium oxide (surface area 110 m^2/g) was prepared by calcination of $Mg(OH)_2$ (Duslo a.s., Šal'a, Slovakia) at 500 °C for 3 h. The commercial silica (Merck) (surface area 196 m^2/g) was used without treatment. All supports were crushed and sieved to a grain size of 0.315–0.6 mm. Noble metal catalysts containing Pt and Pd were prepared by conventional wet impregnation of 100 g of support with an appropriate volume of aqueous solution (1 wt.%) of H_2PtCl_6 or $PdCl_2$. The loading of metals in the final catalysts was 0.2-1 wt.% Pt or 1 wt.% Pd.

After 1 h of impregnation, water was evaporated at 80 °C and the catalysts dried at 120 °C overnight (Procedure A). Since using this procedure, practically all Cl ions remained in the catalyst [15], after drying, another part of the catalyst was treated with an appropriate volume of aqueous solution of KOH (5 wt.%) according to US Patent 5856516 [16]. During this treatment, the noble metal was precipitated as hydroxide or oxide and fixed to the support. After this procedure, water was evaporated and the catalyst dried as described before (Procedure B). MgO supported catalysts were not treated with KOH solution due to the basicity of the support.

Parts of thus prepared catalysts were stored as prepared and the others were calcined in air (30 ml/min) at 500 °C for 2 h.

2.2. Catalysts characterization

Supports were characterized by XRD (Siemens D5000) using Cu Kα radiation and a Ni filter. Two theta ranges were adjusted to 20–80° with the step of 0.04°. The XRD spectra of supports are shown in Fig. 1. The diffraction peaks were confirmed by JCPDS. The XRD patterns of silica and untreated γ-alumina show the amorphous phase for both of these supports. During the treatment of γ-alumina at 1050 °C (A5, A7, A10), transformation to alpha phase with lower surface area and acidity occurred. After the thermal treatment of $Mg(OH)_2$, characteristic diffraction peaks of MgO were observed. Even after water treatment of MgO followed by drying, no peaks characteristic for $Mg(OH)_2$ were seen.

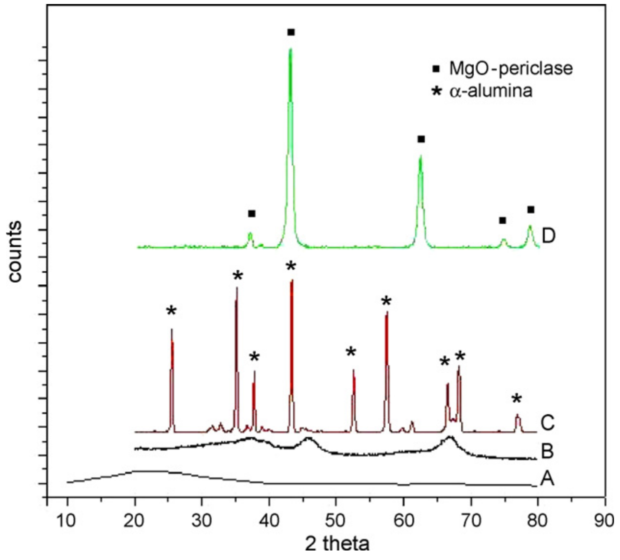

Fig. 1. XRD spectra of supports (A – silica, B – alumina A0, C – alumina A5, A7, A10, D – MgO), (■) MgO – periclase, (*) – α-alumina.

Specific surface areas were measured by Micromeritics ASAP2020 using nitrogen as an adsorptive. The samples were outgassed at 400 °C for 2 h.

Pt dispersion was measured by CO chemisorption at 25 °C using He as a carrier gas. First, samples were reduced under the flow of hydrogen in the temperature range 200–450 °C for 2 h. After reduction, hydrogen was switched to helium and samples were purged at the given temperature for 1 h. The fraction of adsorbed CO dosed into the system in pulses was detected by a thermal conductivity detector (TCD). A CO/Pt ratio of 1 was assumed for the Pt dispersion calculation [17].

The acidity of the catalysts was determined from ammonia TPD measurements in the temperature range 100–600 °C in a nitrogen atmosphere. Measurements were carried out in a conventional flow-type apparatus at a heating rate of 20 °C min^{-1}.

2.3. Catalytic tests

Catalytic runs were carried out in two types of stainless steel fixed-bed reactors, which differ in diameter and length. The reactor (20 mm in diameter and 60 cm in length) was filled with 9 g of the catalyst and the smaller reactor (8 mm ID × 20 cm) with 1.0 g of the catalyst. Practically, the same results were obtained in both reactors. Prior to the reaction, the catalysts were reduced in situ in a flow of hydrogen (30 ml/min) at 200–450 °C for 2 h. Then, the temperature was increased to 560 °C and catalytic tests were performed. DPA was dosed in the form of a solution in aniline (50 wt.%). In the standard experiments, the weight hour speed velocity was 0.1 g of diphenylamine per 1 g of catalyst per hour. The flow of hydrogen (30 ml/min) was measured by a mass-flow meter. The products were collected in an air cooled tube made of stainless steel and the outgas was absorbed in methanol. The products and by-products were analyzed by gas chromatography (Hewlett Packard 5890) using FID and SE 30 column and confirmed by GC/MS techniques. The main by-products are benzene, ammonia and in trace amounts biphenyl, dimethylindoles and other hydrocarbons.

3. Results and discussion

3.1. Palladium catalysts

The palladium catalysts (1 wt.% Pd) were supported on magnesium oxide and alumina prepared by calcination of γ-Al_2O_3 at 1050 °C for 5 h (specific surface area of 30 m^2/g). The dispersion of palladium, measured by CO pulse chemisorption, was 37% in the case of Pd/alumina and only 7% over Pd/MgO catalyst. Similar low dispersion of Pd/MgO (1 wt.%) catalyst