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**RESEARCH PAPER** 

# Dehydrocyclization of Diphenylamine to Carbazole over Platinum-Based Bimetallic Catalysts

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**Abstract:** Gas phase dehydrocyclization of diphenylamine (DPA) to carbazole over monometallic and bimetallic 0.4 wt% Pt-based catalysts in a fixed bed reactor was studied in the presence of hydrogen at a temperature of 550 °C. Alumina and carbon supported Pt catalysts showed very high initial activity (> 95%). The selectivity for carbazole over carbon supported Pt catalysts was slightly lower. Doping of the catalyst with potassium led to an increase in the selectivity for carbazole by 15%. Bimetallic Pt-Sn catalysts prepared by co-impregnation were less selective than catalysts prepared by successive impregnation. The selectivity for carbazole over bimetallic Pt-Sn catalysts prepared by successive impregnation was 75%, but their activity decreased with increased Sn loading. Highly active and reasonably selective catalysts were Ir-doped bimetallic Pt-based catalysts. The conversion of diphenylamine over Pt-Ir catalysts was above 98% and the selectivity for carbazole was nearly 55%, while the lifetime was much longer.

Key words: diphenylamine; carbazole; dehydrocyclization; platinum; tin; iridium; bimetallic catalyst

Carbazole (CB) belongs to a group of heterocyclic compounds with increasing fields of utilization developed during the last decade. Insecticides, pigments, drugs [1,2], polymers [3], dentistry, holography, microelectronics [4], and organic light emitting diodes [5] are areas where carbazole and its derivatives have been utilized. Carbazole can be obtained from crude oil and coal [6]. However, the utilization of such carbazole can be problematic due to contamination by impurities with similar properties. For fine chemicals manufacture, carbazole with a purity > 98% is required.

There is not much data on carbazole synthesis in the literature. According to the patent literature, carbazole can be synthesized by the dehydrogenation of aromatic amines in the presence of hydrogen over supported noble metal catalysts [7–9] based on Pt, Ir, Rh with loadings of 0.1–2.0 wt%:



The common way of metal loading onto the support is by impregnation. Suitable supports are oxides of Al, Zn, Mg, and Si. Carbazole can be also obtained by non-catalyzed cyclization of 2-aminodiphenyle (500–800 °C) in the presence of air. However, this produces many byproducts, mainly tars [8].

In our previous studies [10,11], Pt catalysts were found to be the best for carbazole synthesis, but further catalyst development was needed to maximize the yield of carbazole and prolong the lifetime of the catalyst. The literature revealed that carbon supported Pt catalysts are efficient for dehydrogenation reactions [12]. Much data are available for alumina and carbon supported bimetallic catalysts consisting of platinum as the primary metal, and rhenium, iridium, or tin as the second metal that gave improved activity and selectivity in many reactions [13,14]. In Pt-Sn catalysts, the main effects due to Sn introduction is increase in catalyst stability, decrease of the rate of deactivation, change in selectivity, and inhibition of hydrocracking and coke deposition on the catalyst [15]. Iridium deposition into a Pt catalyst led to the destruction of coke

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precursors by hydrogenolysis [16,17]. Moreover, in a hydrogen atmosphere, iridium can remove coke deposits [18]. In the present work, platinum based bimetallic catalysts for the dehydrocyclization of diphenylamine (DPA) to CB were studied.

# 1 Experimental

## 1.1 Catalyst preparation

In our previous study [10],  $\gamma$ -alumina calcined at 1 050 °C for 5 h was found to be a suitable support for the dehydrocyclization of diphenylamine.  $\gamma$ -Alumina (Eurosupport Litvínov, Czech Republic) was calcined under these conditions to give an  $\alpha$ -phase of 30 m<sup>2</sup>/g specific surface area. This was crushed and sieved to a grain size of 0.315–0.6 mm. For comparison of the support, activated carbon Gac 1240 supplied by NORIT was used. Since carbon can contain metals, the carbon support was treated with HNO<sub>3</sub> solution (10 wt%) for 24 h and subsequently washed with deionised water to pH 7 to prevent their potential influence [19].

Monometallic catalysts containing Pt were prepared by the conventional wet impregnation method. The support (10 g) was added to an appropriate volume of an aqueous solution of  $H_2PtCl_6$  with the concentration to give a Pt loading of 0.4 wt%. After 1 h of impregnation at room temperature, the catalysts were dried at 80 °C and then at 120 °C overnight. These catalysts were denoted as PtA (A for alumina) and PtC (C for NORIT active carbon). The catalyst prepared with HNO<sub>3</sub> treated carbon as support was marked as PtC\*.

The positive effect of potassium addition on the Pt catalyst described in our previous study [10] was also applied to the PtC catalysts. The PtC catalysts after drying were doped with an appropriate volume of aqueous solution of KOH (5 wt%) [7]. After this procedure, water was evaporated and the catalyst dried as before (the catalyst was denoted as PtCK).

Bimetallic catalysts were prepared by co-impregnation and successive impregnation. The co-impregnated Pt-Sn catalyst

was prepared by dissolution of an appropriate amount of  $H_2PtCl_6$  and  $SnCl_2 \cdot 2H_2O$  in acetone (with the concentration to give 0.4 wt% Pt and 0.4 or 1.0 wt% Sn in the catalyst) and then 10 g of support (alumina) was added to this solution. After 1 h of impregnation at room temperature, the catalysts were dried at 40 °C and then at 120 °C overnight. The catalysts were denoted as  $PtSn_{0.4}$  and  $PtSn_{1.0}$ .

The Pt-Ir catalysts were prepared by co-impregnation using hexachloroplatinic acid ( $H_2PtCl_6$ ) and hexachloroiridic acid ( $H_2IrCl_6$ ). The concentration of the impregnation solution was adjusted to give a loading of 0.4 wt% Pt and 0.1 wt% Ir. The procedure of Pt-Ir catalyst preparation was the same as for the monometallic catalysts. The catalysts were marked PtIrA (alumina support) and PtIrC (carbon support).

The Pt-Sn bimetallic catalysts prepared by successive impregnation were prepared using the following procedure. To the appropriate amount of 1 mol/L HCl solution of  $SnCl_2 \cdot 2H_2O$ was added 10 g of alumina. The obtained slurry was left to stand at room temperature for 1 h and then it was heated at 80 °C and finally placed in an oven at 120 °C overnight. To the dried catalyst was added the solution of hexachloroplatinic acid and the obtained slurry was treated as before. The concentration of impregnation solutions was adjusted to give the loadings of 0.4 wt% Pt and 1 wt% Sn. The same procedure was used for the preparation of similar catalysts but the Pt metal was impregnated first. The catalysts were denoted as SnPtA and PtSnA, where the order of the metals denoted the order of metal introduction onto the support (alumina). The catalysts with their characteristics are listed in Table 1.

### 1.2 Catalyst characterization

The specific surface area of the support was measured with a Micromeritics ASAP 2020 using nitrogen. Prior to the measurement, the sample was outgassed at 400 °C for 2 h.

The Pt dispersion was measured by CO chemisorption. The measurement was performed at 25 °C using He as carrier gas.

Catalyst <sup>a</sup>	Metal	Metal loading	Specific surface area	Acidity	Dispersion (%)		DPA conversion <sup>c</sup>	CB selectivity <sup>c</sup>	TOF
		(wt%)	(m <sup>2</sup> /g)	(mmol/g)	Fresh	Deactivated	(%)	(%)	$(10^{-3})$
PtA	Pt	0.4	30	0.225	59.0	10.6	99.0	75.1	8.41
PtC	Pt	0.4	1150	N/A	72.5	12.3	98.8	58.5	6.83
PtC*	Pt	0.4	1150	N/A	66.8	12.6	97.4	57.9	7.31
PtCK <sup>b</sup>	Pt	0.4	1150	N/A	64.3	13.1	98.5	74.2	7.67
PtSn <sub>0.4</sub>	Pt-Sn	0.4 + 0.4	29	0.225	32.2	_	91.4	28.1	14.22
PtSn <sub>1.0</sub>	Pt-Sn	0.4+1	28	0.208	28.4	_	73.7	31.5	13.00
SnPtA	Pt-Sn	1+0.4	26	0.196	29.9	_	61.4	75.7	10.29
PtSnA	Pt-Sn	0.4+1	26	0.201	25.7	_	46.9	75.7	9.14
PtIrA	Pt-Ir	0.4	30	0.225	51.2	12.6	98.6	53.4	9.65
PtIrC	Pt-Ir	0.4	1150	N/A	54.3	16.2	99.0	55.7	9.13

Table 1 Physicochemical properties of the catalysts and their catalytic performance for dehydrocyclization of DPA to CB

<sup>a</sup>Catalysts prepared by impregnation.

<sup>b</sup>Catalyst doped with KOH.

°Reaction conditions: 550 °C, hydrogen flow 30 ml/min, WHSV 0.1 g/(g·h).

The catalysts (100 mg) were reduced in a flow of hydrogen at 400 °C for 2 h. After reduction, hydrogen was replaced by helium and the catalyst was purged at the same temperature for 1 h. CO was dosed into the system as pulses (0.5 ml). Typically, 3–5 pulses were required for saturation. The fraction of non-adsorbed CO molecules was detected by a thermal conductivity detector (TCD). The adsorbed CO amount was calculated from the consumption of the peaks. A CO/Pt ratio of 1 was used for the calculation of Pt dispersion [20]. Since the reaction temperature was 550 °C, the catalysts were reduced at this temperature and chemisorption measurements were carried out as described above and compared with those at 400 °C. The differences in dispersion values were negligible.

Since carbon has an electrostatic charge, measurements with He as carrier gas were not reproducible. For the carbon supported catalysts, chemisorption measurements were carried out in a hydrogen atmosphere. The temperature was raised to 400 °C at a rate of 10 °C/min. After treatment at 400 °C for 2 h, the catalyst was cooled in hydrogen to 25 °C. Subsequently, CO pulses of 0.5 ml were injected into the carrier gas (H<sub>2</sub>) [21–23]. Typically, 3–5 pulses were required for saturation.

Support acidity (for alumina) was determined from ammonia temperature-programmed desorption measurements (TPD) in the temperature range 100–600  $^{\circ}$ C in a nitrogen atmosphere. Measurements were carried out in a conventional flow apparatus at a heating rate of 20  $^{\circ}$ C/min.

DTA-TG measurement using a SHIMADZU DFG60 was employed to study oxidation of the deactivated catalysts. Analyses were carried out under an oxygen atmosphere (flow rate 50 ml/min). The samples of 2–3 mg were placed onto standard aluminium pans and heated to 500 °C (heating rate 10 °C/min).

#### 1.3 Catalytic tests

Catalytic tests were carried out in a stainless steel fixed-bed reactor. Prior to the reaction, the catalyst was reduced in a flow of hydrogen (30 ml/min) at 400 °C for 2 h. Then, the temperature was increased to 550 °C and catalytic tests were performed. DPA was dosed in the form of a solution in aniline (50 wt%). 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 flowmeter. The products were collected in an air cooled tube made of stainless steel and the product gas was absorbed in methanol. After 6 h on stream, the experiment was stopped for sampling and continued the next day starting with the reduction of the catalyst. The products and byproducts were analyzed by gas chromatography (Hewlett Packard 5890) using FID and a SE 30 column and confirmed by GC/MS. The main byproducts were benzene, ammonia, and trace amounts of biphenyl, dimethylindoles, and other hydrocarbons.

DPA conversion and CB selectivity were calculated as DPA

conversion =  $(m(DPA_d) - m(DPA_p))/m(DPA_d)$  and CB selectivity =  $m(CB)/(m(DPA_d) - m(DPA_p))$ , respectively, where DPA<sub>d</sub> is the weight of DPA dosed into the reaction and DPA<sub>p</sub> is the weight of DPA in the product (unconverted DPA).

# 2 Results and discussion

#### 2.1 Monometallic catalysts

The physicochemical properties of the catalysts are presented in Table 1. Catalysts based on the carbon support showed a higher dispersion of the active metal. This may be attributed to the higher specific surface area of the carbon. The influence of the acidity of the supported catalysts on diphenylamine dehydrocyclization was discussed in our previous paper [10].

The catalytic results obtained over the monometallic catalysts are shown in Fig. 1. From the comparison of the activity and selectivity of the carbon supported catalysts, it was obvious that the treatment of the carbon support with HNO<sub>3</sub> solution (residual metals removal) had no influence on catalyst performance. The conversion of DPA decreased with time on stream, but the conversion was still > 80% after 5 d. A similar trend was observed with the alumina supported catalysts, but these catalysts were more selective. The selectivity for carbazole on the carbon supported catalysts after 6 d of testing decreased from 60% to 45%. Over the alumina supported platinum catalyst, the selectivity was 70% and decreased slightly to 65%. A positive effect on the activity and selectivity of the carbon supported catalysts was due to the doping of the catalyst with potassium (PtCK catalyst). Using this catalyst, DPA conversion of after 8 d of testing remained more than 85% while the selectivity for carbazole decreased from 75% to >50%.

As compared to the PtC catalysts, the selectivity improvement was 15%. A positive effect of potassium was also observed in our previous experiments with alumina supported catalysts [10]. The effect of potassium on the selectivity improvement can be explained by a weak interaction of potassium with platinum [24] or by structural changes and changes in electronic properties [25]. Juan-Juan et al. [26] ascribed changes in the structure of the metal in the presence of potassium to the modification of metal-support interactions and consequently, the reducibility of the metal species. A similar behavior of potassium was also observed by other authors [27,28]. Since potassium is a good catalyst for carbon gasification [29,30], it cannot be excluded that the increase of the potassium/metal ratio decreased the rate of coke deposition [26].

#### 2.2 Bimetallic catalysts

As seen from the results summarized in Table 1, bimetallic



Fig. 1. Dehydrocyclization of DPA to CB over monometallic catalysts at 550 °C.

Pt-Sn catalysts prepared by co-impregnation were active (conversion of DPA 91.4% and 73.7%) but their selectivity for the desired product was low at 30%. The increase of the tin loading negatively influenced the activity of the catalyst. In contrast, the catalysts with the same Pt/Sn ratio prepared by successive impregnation gave very high selectivity but their activities were relatively poor (conversions of DPA were only 45% - 60%). A decrease in catalyst activity with increasing tin loading was also observed in other types of reactions [31]. It is probable that at higher tin loadings, tin gets spread on the support and cover the alumina [32]. The alumina surface tin species would decrease the amount of active alumina sites responsible for catalyst activity. It is known that the adding of tin to a Pt/alumina catalyst prevented Pt particles from sintering [32], which resulted in more active metal sites available for reaction and decreased the amount of carbon deposited on the metallic phase. Lieske and Volter [33] have shown that the addition of tin to platinum catalysts led to the formation of more mobile coke precursors, which can more easily migrate to the alumina to leave more platinum sites coke-free.

A very positive effect on the performance of the Pt-based catalysts was the doping of the catalysts with iridium. Using the same Pt/Ir atomic ratio and procedure of preparation, bimetallic Pt-Ir catalysts supported on thermally treated alumina and activated carbon were prepared and tested. As seen in Table 1, despite the enormous difference between the specific surface areas of the alumina and carbon support, the overall dispersions of the metals over these supports were similar. As was observed in our previous work [10], the specific surface area did not have a significant influence on the catalyst performance.

The results of the catalytic tests using Pt-Ir alumina and carbon supported catalysts are shown in Fig. 2. From the dependences of the conversion of DPA and the selectivity for carbazole versus time on stream, it is clear that the presence of iridium very positively influenced the lifetime of both catalysts tested. Over the alumina supported Pt-Ir catalyst, the conversion of DPA remained more than 98% during 9 d of testing. The selectivity for carbazole after 9 d decreased from the initial 53% to 30%. The lifetime of this catalyst was prolonged almost twice in comparison to the monometallic Pt/alumina catalyst. Even better results were obtained with the carbon supported Pt-Ir catalyst. Over this catalyst the conversion of DPA after 18 d remained more than 92% and the selectivity for the desired product varied in the range of 45%-63%. Barbier et al. [34] have proposed that the positive effect of iridium addition to platinum catalysts is related with the hydrogenolysis ability of these bimetallic catalysts. Iridium-doped Pt catalysts have the ability to destroy coke precursors by hydrogenolysis [16,17]. In a hydrogen atmosphere. Ir can destroy even the coke deposits on the surface of platinum [18]. Also, an effect of iridium on the breaking up of large platinum ensembles into smaller ones, which gave less coking has been reported [35].

#### 2.3 Deactivation of the catalysts

After catalyst testing, samples of deactivated catalysts were taken and CO chemisorption measurements were carried out to evaluate the active metal dispersion. As seen from Table 1, the effect of metal dispersion on the catalyst performance showed a nonlinear dependence. Over carbon supported catalysts after 6 or 8 d of testing, the conversion of DPA dropped 20% but the



Fig. 2. Dehydrocyclization of DPA to CB over Pt-Ir catalysts at 550 °C.

metal dispersion decreased from the initial 64%–72% to 12%– 13%. On the other hand, a significant decrease in Pt dispersion caused a decrease of selectivity for carbazole of only 15%. The nonlinear Pt dispersion dependence was more obvious in the case of the alumina supported catalysts. After 7 d of testing, the conversion of DPA decreased by 15% and the selectivity only by 5% despite a sharp decrease in Pt dispersion (from 59.0% to 10.6%). A similar nonlinearity between Pt dispersion and catalysts performance was observed also in our previous experiments [10]. The explanation of this phenomenon and comparison with other studies is difficult due to a lack of information on other types of chemical reactions. In the literature, only data from model dehydrocyclization reactions can be found.

The study of deactivated Pt-Ir catalysts revealed that the metal dispersions were comparable to those of the monometallic catalysts. Thus, we conclude that the modification of the properties of the metal phase by doping with iridium gave a decrease in the deactivation of the metal phase, resulting in a significant increase in catalyst lifetime.

Since catalyst deactivation can be related also with coke formation, DTA-TG measurements were used to study the carbonaceous deposits formed on the catalysts during the catalytic reaction. DTA-TG curves of PtA and PtIrA catalysts are shown in Fig. 3. In the case of Pt catalysts supported on activated carbon, the support itself starts to burn at 300 °C, which makes DTA-TG analysis impossible. Thermograms of coked samples of alumina supported catalysts (coke content 8%-10%) exhibited two distinct coke oxidation temperature regions corresponding to the metal and support sites, in agreement with those observed by Barbier [36]. The 250-300 °C region consisted of coke deposited on metal sites, which were oxidized at lower temperatures. This type of coke has a low molecular weight and low density, hence it occupies more volume and block more active sites by being more extended [37]. The 400–450 °C region corresponded to the oxidation of condensed/polymerized coke species, which were oxidized at higher temperatures. This type of coke accumulated over support sites [38] and blocked the acid sites resulting in the decrease of the activity of PtA catalysts. However, iridium-doped Pt catalysts exhibited a high activity as reported above. We assumed that over the Pt-Ir catalysts, iridium contributed to the very high DPA conversion due to its ability to catalyze hydrogenolysis reactions.

In the TG curves, it can be seen that the TG curve for the spent PtA catalyst exhibited an almost linear decrease, which suggested that the weight loss (approximately 8%) was uniform and consequently the amounts of coke on metal and support sites were approximately the same. In contrast, the TGA curve of the PtIrA catalyst weight loss (11%) exhibited a larger decrease at 320 °C, when the oxidation of condensed coke species started. The loss of weight in the 250–320 °C region was 4%, which showed that 36% of the coke were on metal sites. The rest of the coke (64%) were located on support sites. This suggested that in case of Pt catalysts, coke deposition was random. In case of Pt-Ir catalysts, the deposition of coke was higher over support sites and left more metal sites available for dehydrocyclization, which resulted in prolonged catalyst lifetime.



Fig. 3. DTA-TG profiles of deactivated catalysts.

# 3 Conclusions

Monometallic platinum catalysts supported on thermally treated alumina and activated carbon give high conversions of diphenylamine and good selectivities for carbazole. Doping the catalyst with potassium increased the selectivity for carbazole. The activity and selectivity of bimetallic Pt-Sn catalysts depended on the method of their preparation. Highly active and selective platinum-based catalysts were obtained by doping with iridium. The presence of iridium prolonged the lifetime of the Pt-Ir catalyst several times. There was not much difference in the nature of the coke on Pt and Pt-Ir spent catalysts.

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