DEHYDROCYCLIZATION OF DIPHENYLAMINE TO CARBAZOLE OVER PLATINUM CATALYSTS

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The gas-phase dehydrocyclization of diphenylamine (DPA) to carbazole over alumina-supported 0.4 wt.% Pt catalysts in a fix-bed reactor has been studied. The reaction was carried out at a temperature of 550 °C in the presence of hydrogen. All catalysts became well dispersed Pt after in situ reduction. Pt catalysts prepared in the presence of a competitive adsorbate (citric acid) were reasonably active during first hours on stream (DPA conversion higher than 90%). However, later, their activity decreased rapidly, except the catalyst prepared in the presence of a higher concentration of the competitive agent. The same trend was observed for the Pt catalyst prepared by wet impregnation. The activity of the catalysts prepared by a microemulsion technique was very high and stable during testing, the conversion of DPA being higher than 93%. However, the selectivities of catalysts prepared in the presence of citric acid gradually decreased with time on stream (TOS). The initial selectivity of such prepared catalysts for carbazole was about 60%. The same trend was observed for catalysts prepared by microemulsion technique. The highest selectivities, 73%, were obtained over the catalysts prepared by wet impregnation; it dropped after 6 days of testing to about 62%.

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

Carbazole (CB) is a compound of high importance. Though there are only a few literature data about its synthesis[1–6], its utilization covers a wide area. Anticancer drugs, pigments, insecticides, polymers[7,8] and, last but not least, production of OLEDs (organic light emitting diodes) using its good hole-transporting ability and high triplet energy[9–11] can be mentioned.

Crude oil and tar oil are used as an industrial source of CB [12]. However, the purity of such CB is often insufficient for synthesis of fine chemicals due to impurities which can be hardly removed due to their similar chemical properties.

From this point of view, synthetic CB would be of high interest. In the literature, there is little information on the CB preparation by dehydrocyclization of aromatic amines (e.g. diphenylamine (DPA), 2-aminobiphenyl, 2-nitrobiphenyl) over Pt- or Pd-supported catalysts in the presence of hydrogen at 300–600 °C [1–6].

The usual way of preparation of supported catalysts is impregnation with noble metal precursors (e.g. H_2PtCl_6, $PdCl_2$, etc.). In the present paper, modifications of conventional impregnation techniques were used to influence the distribution and the profile of active metal in the resulting catalyst.

The loading of the active metal under the carrier surface was performed by impregnation of a metal precursor in the presence of citric acid. The citric acid ion is known to be adsorbed faster on the alumina surface than the chloroplatinate ion [13]. Thus, the chloroplatinate ions are "forced" to adsorb deeper, under the external alumina surface.

The microemulsion technique was used for finer dispersion of the metal precursor in the impregnating solution, what led to higher dispersion of the noble metal. Several papers dealing with properties of the thus prepared catalysts were published. These consider the influence of the organic solvent used, surfactant type, hydrodynamic conditions, etc. [14–16].

In this paper, a comparison of the above-mentioned methods of catalyst preparation with conventional impregnation is presented for the dehydrocyclization of diphenylamine to carbazole over Pt/Al_2O_3 catalyst (Scheme 1).
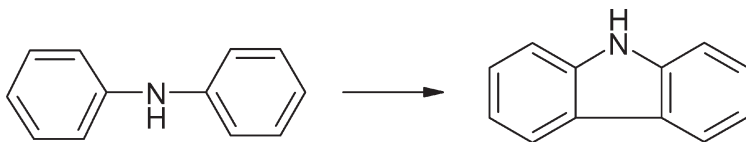
Scheme 1

EXPERIMENTAL

Catalysts Preparation

In our previous study [17], γ-alumina calcined at 1050 °C for 7 h was found to be the best support for dehydrocyclization of diphenylamine. γ-Alumina (Eurosupport Litvínov, Czech Republic) was calcined uder the above conditions affording an α-phase of 30 m^2/g specific surface area. It was crushed and sieved to obtain a grain size of 0.315–0.6 mm. For comparison, untreated γ-alumina with a specific surface area of 197 m^2/g was also used as support.

Metal catalysts containing Pt were prepared by three methods. In the conventional wet impregnation, 10 g of support was added to an appropriate volume of 1% aqueous solution

of H_2PtCl_6 to reach the Pt loading 0.4 wt.% in the catalyst. After 1 h of impregnation, water was evaporated at 80 °C and the catalyst dried at 120 °C overnight. (The thus prepared catalyst is denoted as PT.)

In another method, citric acid was added to the metal precursor solution to eliminate the external surface of the support for chloroplatinate ion adsorption. The acid concentration in solution was 0.1, 0.5 and 1 wt.%. The volume of the H_2PtCl_6 solution was the same as in the previous wet impregnation. After 1 h of impregnation, the catalyst was treated as before. The prepared catalysts were denoted CA0.1, CA0.5 and CA1.0.

The third method of catalyst preparation used the microemulsion technique[14]. Three types of microemulsions (water in oil) were prepared by mixing oil, water and surfactant. As oil, cyclohexanol (COL), cyclohexane (CAN) and heptane (HEP) were chosen, and as surfactant Tween 80 (Merck) was used. The weight ratio oil/water/surfactant was 77.9:20.7:1.4. In the first step, an oil–surfactant mixture was prepared. After addition of water, the mixture was vigorously stirred until a stable emulsion (time of phase separation at least 30 min) was reached. Then, the Pt precursor (in an amount leading to the Pt loading 0.4 wt.%) was added and the mixture vigorously stirred again for 10 min to provide homogenous distribution of the chloroplatinate ions. An evidence of such distribution was the uniform yellowish color of the microemulsion. After addition of the support, the mixture was again vigorously stirred until the yellowish color disappeared, indicating that the Pt precursor was completely adsorbed on the support. After the stirring, phase separation occurred. The oil phase was carefully removed, the water phase filtered and the catalyst washed with an excess of water to remove traces of the surfactant and finally dried at 120 °C overnight. The prepared catalysts were marked COL, CAN and HEP.

Catalysts Characterization

Catalysts were characterized by XRD (Siemens D5000) using CuKα radiation and a Ni filter. Two θ ranges were adjusted to 20–80° with the step 0.04°. The XRD spectra of the catalysts are shown in Fig. 1. The diffraction peaks were confirmed by JCPDS.

The specific surface area of the support was measured with a Micromeritics ASAP2020 using nitrogen as an adsorptive. 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 a carrier gas. The catalysts were reduced in the flow of hydrogen at 400 °C for 2 h. After reduction, hydrogen was exchanged for helium and the catalysts were purged at the same temperature for 1 h. CO was dosed into the system in pulses, the fraction of non-adsorbed CO molecules was detected by a thermal conductivity detector (TCD). The adsorbed CO was calculated as a difference in the consumption between the peaks. The CO/Pt ratio equal to 1 was assumed for the calculation of Pt dispersion[18].

The support acidity was determined from ammonia TPD (temperature programmed desorption) measurements in the temperature range 100–600 °C in nitrogen atmosphere. Measurements were carried out in a conventional flow-type apparatus at a heating rate of 20 °C/min.

The concentration profile of Pt on the support surface was measured with an electron probe microanalyzer JEOL JXA-840A.

Catalytic Tests

Catalytic runs were carried out in a stainless-steel fixed-bed reactor. The reactor (8 mm ID × 20 cm) was filled with 1.0 g of the catalyst. Prior to the reaction, the catalysts were reduced in situ in hydrogen flow (30 ml/min) at 400 °C for 2 h. After reduction, the temperature was increased to 550 °C and 5-h catalytic tests were performed every day. During the night the reactor was cooled down. The next day, reduction of the catalyst was performed and the reaction continued. DPA was dosed as a solution in aniline (50 wt.%). In standard experiments, the weight hour space velocity was 0.1 g of diphenylamine per 1 g of catalyst per 1 h. The flow of hydrogen (30 ml/min) was measured with a mass-flow meter. The products were collected in an air-cooled tube made of stainless steel. The off-gas was absorbed in methanol. The reaction products were analyzed by gas chromatography (Hewlett Packard 5890) and confirmed by GC/MS techniques. The main by-products were benzene, ammonia and biphenyl, dimethylindoles and other hydrocarbons in trace amounts as described in our previous study[17].

RESULTS AND DISCUSSION

Catalyst Properties

XRD measurements were performed to investigate the support phase transformation during the calcination process and noble metal presence. In Fig. 1 is depicted an XRD pattern of the PT catalyst prepared. After calcination, the α-phase of alumina is clearly visible. However, due to the rela-

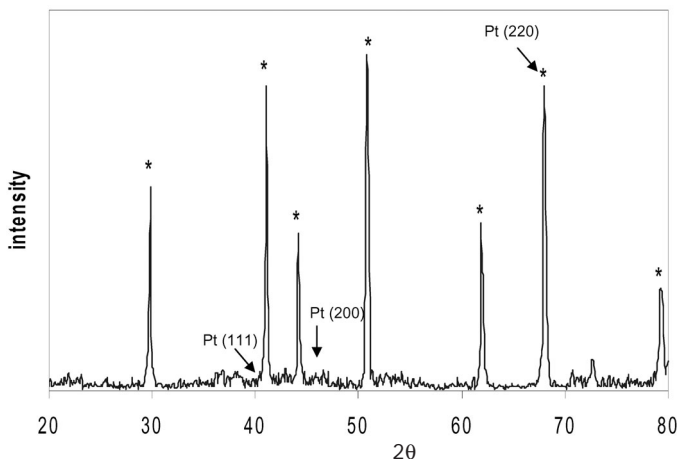FIG. 1
XRD spectra of the fresh 0.4 or 1% Pt/alumina catalyst prepared by microemulsion technique (alumina calcined at 1050 °C for 5 h); * means α-phase

tively low Pt loading and high intensity of alumina main peaks, diffraction peaks of platinum are on the noise level. Therefore, the platinum catalyst supported on uncalcined γ-alumina was investigated. The patterns of such prepared and reduced catalysts are plotted in Figs 2 and 3. The sharp peaks
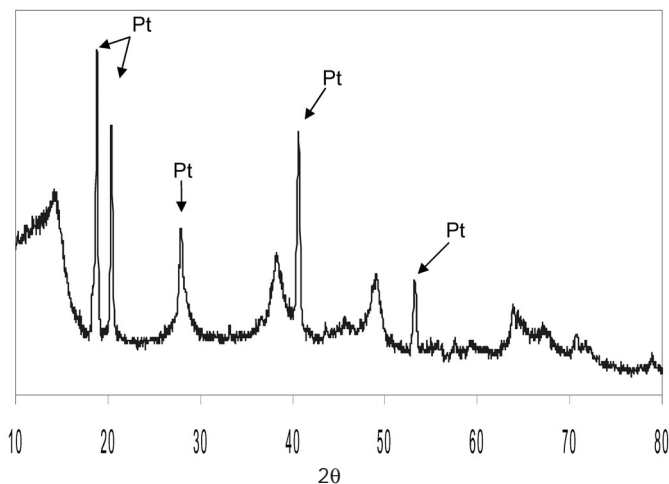

FIG. 2
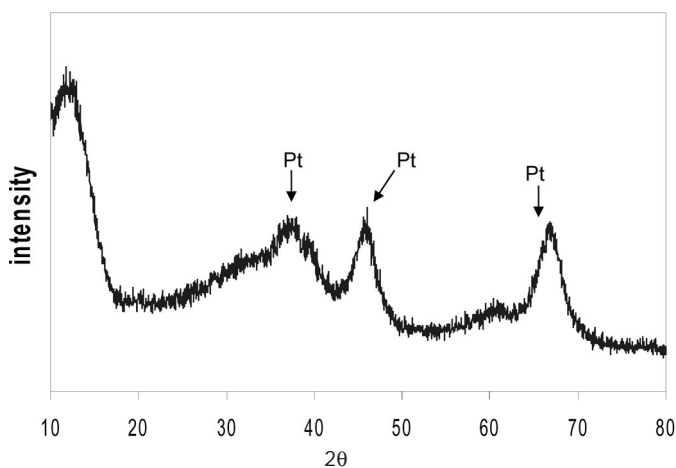XRD spectra of the fresh 0.4% Pt/alumina catalyst (γ-alumina, uncalcined)

FIG. 3
XRD spectra of the 0.4% Pt/alumina catalyst reduced at 400 °C for 2 h (γ-alumina, uncalcined)

in the spectra indicate that in the case of such catalysts, platinum is probably present in form of clusters. After reduction at 400 °C for 2 h in the hydrogen flow, the peaks diminished indicating fine platinum dispersion.

The results of Pt dispersion measurements are listed in Table I. As can be seen, 52–65% dispersions of platinum were reached using the preparation methods.

When citric acid was used for Pt loading, no significant changes in Pt dispersion were observed despite the fact that at least a part of the noble metal should have been deposited under the external surface (egg-white form). Since citric acid acts as a competitive adsorbate[13], a further increase in the amount of citric acid might lead to complete Pt deposition under the external surface.

The implementation of the microemulsion technique in Pt deposition revealed some differences in the resulting Pt dispersion as an influence of the organic solvent used. The use of nonpolar organic solvents (CAN, HEP) leads to a higher-viscosity microemulsion. This may cause the problem of filling the whole surface of the support[14]. The fact is probably the explanation of lower Pt dispersion of PT-CAN and PT-HEP catalysts compared with the PT-COL catalyst (Table I). Cyclohexanol is a polar molecule, so the emulsion is formed easily and its viscosity is low, which leads to good surface accessibility and, consequently, to higher Pt dispersion.

As mentioned above, during overloading of the external surface with citric acid, noble metal deposition occurs under the surface[13]. On the other hand, the use of microemulsion technique leads to Pt deposition mainly on the external surface of the support[14]. To evaluate these suggestions, mea-

TABLE I
Characterization of Pt catalysts

Catalyst	Surface area, m^2/g	Acidity, mmol/g	Pt dispersion, %
PT	30	0.225	56
CA0.1	30	0.225	54
CA0.5	30	0.225	53
CA1.0	30	0.225	52
CAN	30	0.225	56
COL	30	0.225	65
HEP	30	0.225	50

surements were performed using the electron probe microanalyzer. In Fig. 4 are given the relative intensities of Pt for PT-CA0.1, PT-CA0.5 and PT-CA1.0 on the surface of catalyst grains. For comparison, the pattern of the catalyst PT-COL is also depicted. As can be seen, relative intensities of Pt on the external surface of grains decrease at higher citric acid concentrations. This effect is almost negligible in the case of the PT-CA0.1 catalyst, though the concentration of citric acid in solution during preparation is very low and the relative Pt intensity on the catalyst surface is almost the same as in the case of the PT catalyst prepared by wet impregnation without a modifier. The effect of the decrease in the relative Pt intensity on the surface is obvious, particularly in the sample with the highest citric acid concentration (PT-CA1.0), where the average relative intensity of Pt is only about one half compared with the PT-CA0.1 catalyst. On the other hand, the catalyst PT-COL shows an increase in the relative noble metal intensity on the surface of the support. This is in agreement with the paper of Rymes et al.[14] who used the same system and procedure in Pt deposition.

Dehydrocyclization of Diphenylamine

Catalysts prepared by the described procedures were tested for gas-phase dehydrocyclization of diphenylamine to carbazole. In Figs 5 and 6 are given
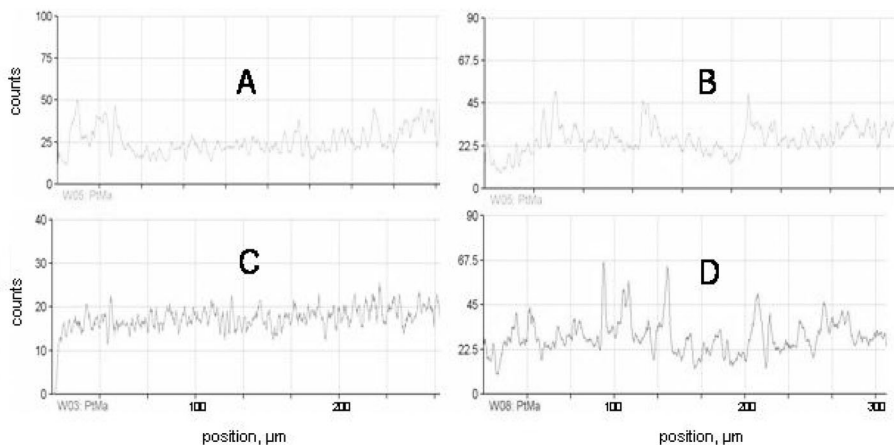

FIG. 4
Relative intensity of Pt signal on the surface of the catalyst grain in the presence of citric acid: **A** PT-CA0.1, **B** PT-CA0.5, **C** PT-CA1.0, **D** PT-COL

the results of conversion of DPA for the catalysts prepared in the presence of citric acid and by the microemulsion technique, respectively. For comparison, the conversion of DPA obtained using the PT catalyst is shown in Fig. 6.

Over catalysts prepared in the presence of low concentrations of citric acid (catalysts PT-CA0.1 and PT-CA0.5 in Fig. 5), a very high conversion of DPA (more than 90%) is obtained in first days of the time-on-tream. This is probably due to the presence of a high number of active sites on the catalyst surface. In the next days, conversion slowly decreases probably due to the Pt sintering and coke formation. The PT catalyst shows a similar trend indicating that low citric acid concentrations during the catalyst preparation do not significantly affect the activity. In the case of PT-CA1.0 catalyst, the conversion of DPA during the first six days changes only negligible. This may be caused by a higher resistance of Pt particles under the support surface to deactivation by the formed coke and sintering. The conversion of diphenylamine is slightly over 90%.
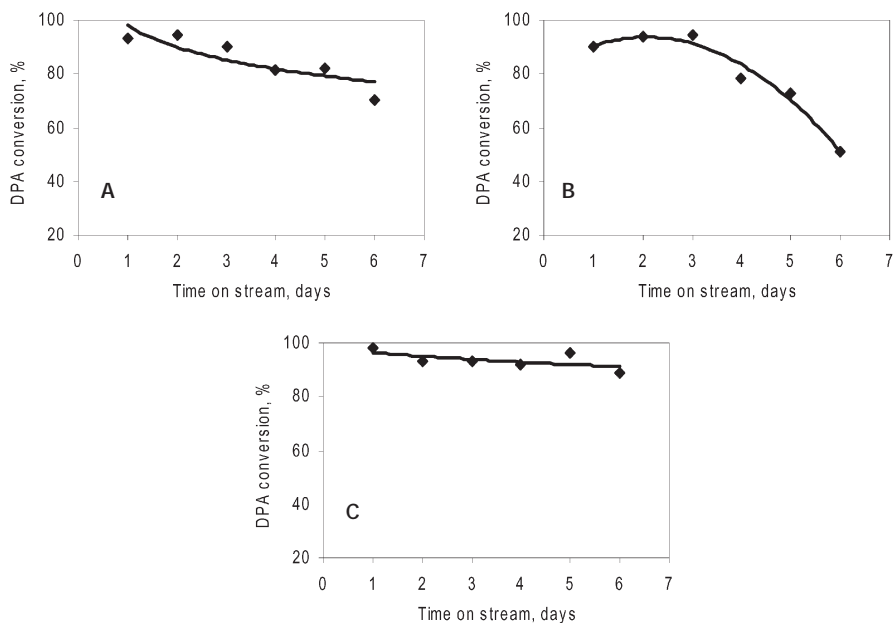

Fig. 5

Time dependence of the activity of Pt catalysts prepared in the presence of citric acid: **A** PT-CA0.1, **B** PT-CA0.5, **C** PT-CA1.0

The platinum catalysts prepared by the microemulsion technique show a very high (>93%) and constant activity during the first five days of time on stream. Taking into account the fact that various oils were used during the microemulsion preparation, there is practically no difference in conversion of the starting compound. However, the noble metal deposited mainly on/near the outer surface of the catalyst grain possesses a higher concentration of active sites resulting in higher conversions compared with the catalyst prepared by classical impregnation (catalyst PT). The catalytic activities of Pt catalysts prepared by the microemulsion technique are in agreement with the published results[14].

A significant effect on the selectivity of dehydrocyclization of diphenylamine for carbazole and its change with the time on stream has the method of preparation of platinum catalyst.

The catalysts prepared in the presence of citric acid do not show any correlation of the selectivity with the concentration of citric acid used in cata-
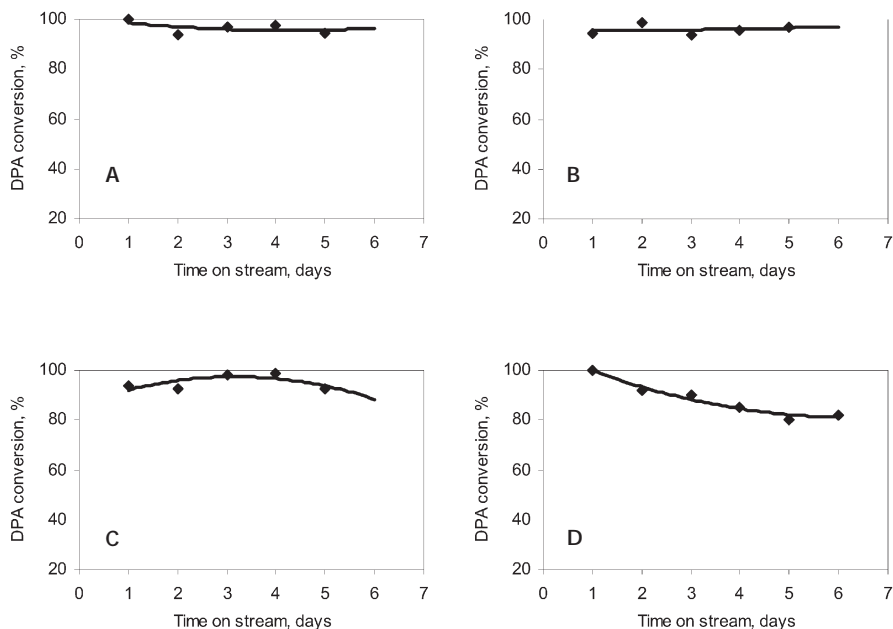

FIG. 6
Time dependence of the activity of Pt catalysts prepared by microemulsion technique: **A** PT-CAN, **B** PT-COL, **C** PT-HEP, **D** PT

lyst preparation (Fig. 7). Different are selectivities in the first hours of catalytic tests and their time dependences. The catalysts prepared in the presence of 0.1 and 1.0 wt.% of citric acid show relatively stable selectivity for carbazole formation. However, the platinum catalyst prepared in the presence of 0.5 wt.% citric acid rapidly deactivates after 4 days of catalytic testing. This is not the result of different dispersion of platinum on the surface of alumina, since all catalysts of this series showe almost the same metal dispersion, 52–54% (Table I).

In comparison with the platinum catalysts prepared in the presence of citric acid, the catalysts prepared using the microemulsion technique are slightly less selective (Fig. 8). Under comparable testing conditions these catalysts lose their selectivity more rapidly. The selectivity of platinum catalysts prepared in cyclohexane/water microemulsion is lost especially rapidly. No more selective is the catalyst prepared in the cyclohexanol/water microemulsion, which contains a very high dispersion of platinum (Table I).
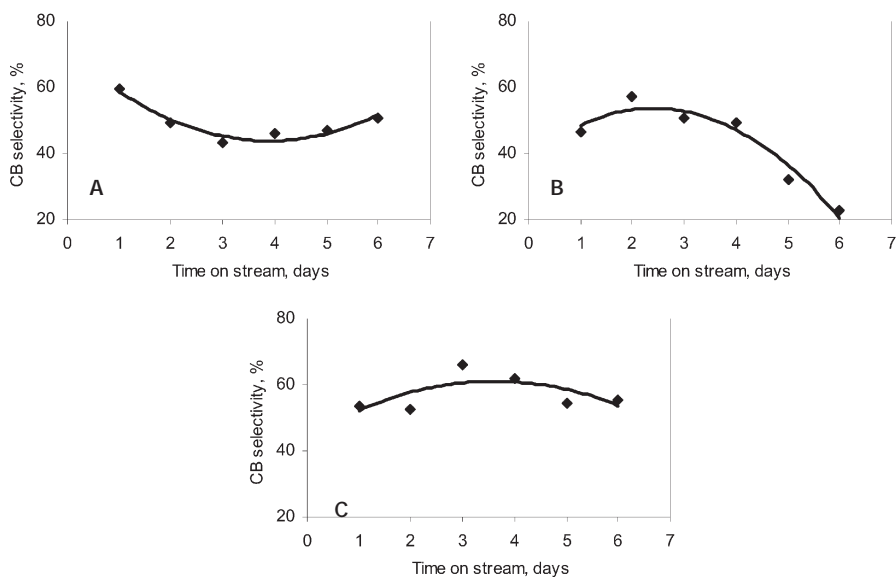

Fig. 7
Time dependence of the selectivity of Pt catalysts prepared in the presence of citric acid: **A** PT-CA0.1, **B** PT-CA0.5, **C** PT-CA1.0

Highly selective is the Pt catalyst prepared by classical wet impregnation. Moreover, the selectivity of diphenylamine dehydrocyclization for carbazole over this catalyst decreases only slightly after six days of testing.

After testing, the dispersion of platinum in the used catalysts was measured by chemisorption. The results suggest that the selectivity drop is associated with a decrease in dispersion of active metal observed in the used catalysts. The Pt dispersion in the used catalysts ranged from 4 to 14%, depending on the catalyst preparation. The catalysts prepared by the microemulsion technique show after six days of testing higher dispersions of platinum (8–14%) than the catalysts prepared in the presence of citric acid by wet impregnation (4–8%). This is surprising since the selectivity drop does not correlate with the decrease in dispersion of platinum. This non-proportionality has not been successfully explained and is the subject of our further study.
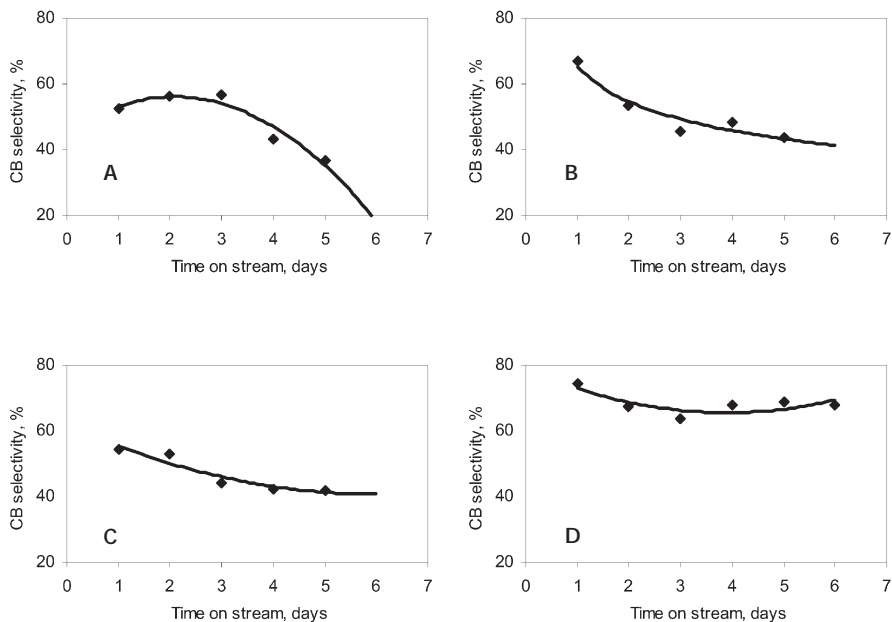

FIG. 8
Time dependence of the selectivity of Pt catalysts prepared by microemulsion technique: **A** PT-CAN, **B** PT-COL, **C** PT-HEP, **D** PT

CONCLUSIONS

The gas-phase dehydrocyclization of diphenylamine to carbazole over various alumina-supported platinum (0.4 wt.%) catalysts in the presence of hydrogen was studied.

The catalysts prepared by wet impregnation and microemulsion techniques after in situ reduction contain well dispersed platinum. They are very active and the conversion of diphenylamine after six days of testing reaches more than 90%. Very active are also platinum catalysts prepared in the presence of citric acid, while its concentration influences the stability of the catalyst to deactivation.

The selectivity of carbazole formation is also strongly influenced by the method of platinum deposition on the support. The highest selectivity for carbazole formation (about 73%) was obtained over the alumina-supported platinum catalyst prepared by wet impregnation. During six days of catalyst testing, the selectivity of dehydrocyclization reaction for diphenylamine decreased by about 10%.

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