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THERMAL DECOMPOSITION OF THE $[Pt(NH_3)_4]^{2+}$ COMPLEX IN NaX ZEOLITE: EFFECT OF CALCINATION PROCEDURE

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The effect of the calcination procedure on the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex in a NaX zeolite was studied by mass spectrometry (MS-TPDE) and diffuse reflectance spectroscopy (DRS). The decomposition of the complex took place in two steps. In the first step, under oxygen, the $[Pt(NH_3)_4]^{2+}$ complex was first converted to $[Pt(NH_3)_2]^{2+}$ complex, accompanied by nitrogen release. In the second step, corresponding to the decomposition of the remaining two amine ligands, NO formation was also observed. Under He, the decomposition also occurred in two steps with H_2 liberation. A reaction scheme was proposed for these results.

Keywords: *mass spectrometry, nitrogen oxide, platinum, thermal decomposition, zeolite X*

Introduction

Zeolites are crystalline aluminosilicates presenting a particular microstructure consisting of a regular array of micropores (and sometimes cavities) which makes them extremely suitable for the preparation of well-dispersed metallic clusters.

The preparation of these metallic clusters can be divided into three steps: metal incorporation, calcination and reduction.

The preferred way of introducing platinum into a zeolite is the partial replacement of Na^+ cations (which are originally present) with the addition of $[Pt(NH_3)_4]^{2+}$ cations. Many experiments have been done to work out the best conditions for this ion exchange [1–3].

The next step is the calcination of the exchanged zeolite in order to thermally decompose the platinum complex. Although it is well known that the thermal decomposition of the $Pt(NH_3)_4Cl_2$ salt leads to the reduction of platinum cations to metallic platinum, even in an oxygen-containing atmosphere [4], the behavior of the tetramine platinum complex as a cation in zeolites (solids with negative charges), is not well known.

The processes that occur during the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex in zeolites were less studied [5, 6] and in some aspects it requires further clarification. Particularly, the occurrence of autoreduction should be avoided, since it promotes the growth of Pt particles, resulting in a less disperse material.

The third step is the reduction, which is also affected by the calcination step, since the activation energy for the reduction of metallic cations depends on their location within the zeolite structure and their electronic state, both being determined by the conditions how the complex was decomposed.

The present paper reports the thermal decomposition of $[Pt(NH_3)_4]^{2+}$ complexes placed in NaX zeolite in the presence or in the absence of oxygen.

The combination of mass spectrometry to analyze the gases evolved from the sample during temperature-programmed decomposition (TPDE) with a study of the electronic state of platinum species by diffuse reflectance spectroscopy (DRS) allows the investigation of the influence of the calcination procedure on the nature of the platinum species obtained.

Experimental

Sample preparation

A NaX zeolite provided by IPT (Instituto de Pesquisa Tecnológica do Estado de São Paulo), with a Si/Al ratio of 1.26, was used as starting material.

Sodium ions were partially exchanged by the $[Pt(NH_3)_4]^{2+}$ complex using an aqueous $Pt(NH_3)_4Cl_2$ solution providing a 1% (mass/mass) Pt concentration in the solid. The $Pt(NH_3)_4Cl_2$ solution was added at a constant flow rate under stirring to the zeolite slurry at 353 K. The slurry was filtered and the solid washed until complete removal of chloride ions and dried at 393 K for 24 h. This sample was named to $Pt(NH_3)_4NaX$.

The chemical composition of the sample was determined by atomic absorption spectroscopy.

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Methods

Thermal decomposition (MS-TPDE)

The gases released during the thermal decomposition of the platinum complex were analyzed by on-line mass spectrometry (Dycor/Metek quadrupole spectrometer). The release of ammonia (m/z=15), water (m/z=17 and 18), nitrogen (m/z=14 and 28), nitrogen oxides (m/z=14, 15, 28, 30, 44 and 46), oxygen (m/z=32), hydrogen (m/z=2) and carbon dioxide (m/z=12, 28 and 44) was monitored. Quantification was done by using adequate calibration standards.

The experiments were carried out under a flow rate of 1000 mL min^{-1} g_{cat}^{-1} of an oxygen (5%)/helium mixture or of helium (99.9%), with 100 mg samples and at a heating rate of 5 K min^{-1}.

Diffuse reflectance spectroscopy (DRS)

Diffuse reflectance spectra were recorded by means of a Varian – Cary 5 spectrometer equipped with a diffuse reflectance accessory Harrick Sci and a pre-treatment chamber HVC-DR2.

A spectrum of the original $Pt(NH_3)_4NaX$ sample was recorded at room temperature and the zeolite was then calcined in a 5% O_2/N_2 stream at a heating rate of 5 K min^{-1} up to 473 K, cooled to room temperature, and another spectrum was acquired. The same sample was successively calcined at 503, 540, 573, and 633 K using the same heating rate. Between two successive calcinations the sample was cooled to room temperature and a new spectrum was recorded. The parent NaX zeolite was used as reference.

Results and discussion

Chemical analysis by AAS showed that the Pt content of the $Pt(NH_3)_4NaX$ sample was 1.02% (mass/mass), which is equivalent to the presence of 0.7 platinum atoms per unit cell and, since the platinum complex has 4 amine ligands, to 2.8 ammonia molecules per unit cell.

Figures 1 and 2 show the thermal decomposition of the $[Pt(NH_3)_4]^{2+}$ complex in the $Pt(NH_3)_4NaX$ sample under 5% O_2 and under helium, respectively.

The decomposition of the $[Pt(NH_3)_4]^{2+}$ complex under 5% O_2 took place in several steps. Water was released from 313 to 653 K, with maximum at 403 K and a shoulder at 543 K. For the gases related to the decomposition of the amine ligands (N_2 and NO) the TPDE profile showed three separated peaks. For the first two peaks, only nitrogen was observed and for the latter one, at a higher temperature, only NO was detected. Nitrogen release took place from 473 to 603 K and from 543 to 653 K, with maxima at 540 and 603 K, while NO was released between 663 and 833 K, with a maximum at 746 K.

The amounts of N_2 and NO released are shown in Table 1 (Case A). About 53% of the amine ligands were released in the first step (corresponding to the first peak), indicating that this step could be attributed to the partial decomposition of the $[Pt(NH_3)_4]^{2+}$ complex producing the $[Pt(NH_3)_2]^{2+}$ complex (Eq. (1)).

$$[Pt(NH_3)_4]^{2+} \rightarrow [Pt(NH_3)_2]^{2+}+N_2+3H_2O \qquad (1)$$

The other two peaks correspond to the decomposition of the last two amine ligands (Eq. (2)). The second peak can be attributed to the release of nitrogen formed during this decomposition, while the third one can be tentatively attributed to the release of nitrogen oxide formed in the second step and temporarily adsorbed in the zeolite framework, being liberated at higher temperatures. Independent experiments indicated that this adsorption effectively occurs.

$$[Pt(NH_3)_2]^{2+} \rightarrow Pt^{2+}+0.7N_2+0.6NO+3H_2O \qquad (2)$$

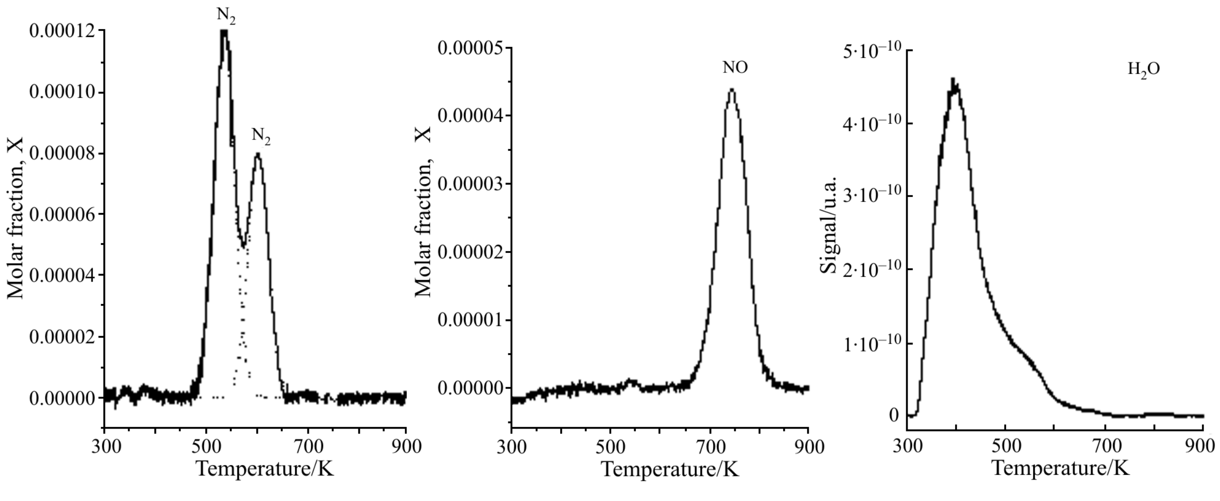

Fig. 1 Temperature-programmed decomposition (5% O_2/He) – of the $Pt(NH_3)_4NaX$

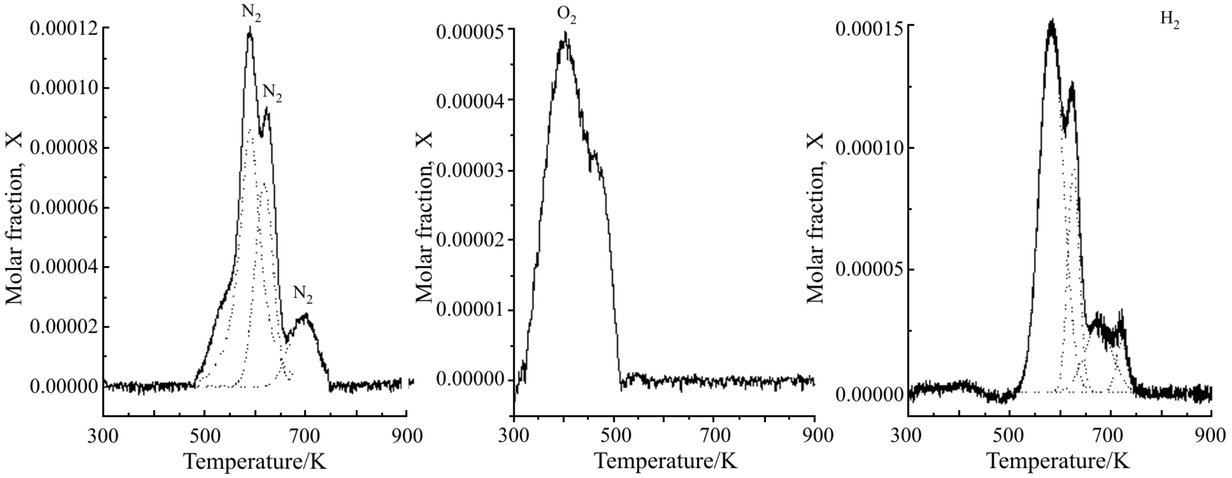

Fig. 2 Temperature-programmed decomposition (He) – of the $Pt(NH_3)_4NaX$

Table 1 Gases liberated during the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex (molecules/unit cell)

Case	1st peak		2nd peak		3rd peak		N_2	NO	Total	NO/	Total
	N_2	NO	N_2	NO	N_2	NO	released	released	NH_3	NH_3	CO_2
A	0.73	–	0.47	–	–	0.38	1.20	0.38	2.78	0.14	7.5
B	0.74	–	0.66	–	–	–	1.40	–	2.80	0	10.3

Carbon dioxide adsorbed in the sample was also released (not shown) in four steps (7.5 moles per unit cell), with maxima at 563, 620, 663 and 720 K. No other species were observed by means of mass spectrometry.

Similarly to what was observed for the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex in an oxygen-containing mixture, its decomposition in helium also occurred stepwise (Fig. 2). Under helium, the decomposition of the $[Pt(NH_3)_4]^{2+}$ complex produced nitrogen and hydrogen. Nitrogen release took place in three temperature ranges: 483–673, 563–673 and 633–753 K, with maxima at 583, 623 and 693 K, respectively. No nitrogen oxide formation was observed, as expected. Again, about 53% of the amine ligands were released in the first step, while the remaining 47% were released at the two last temperature ranges (second step). Water release (not shown, similar profile to that observed for the oxygen-containing decomposition, high interaction with the zeolite, even at high temperatures [7]) was observed from 313 to 713 K, showing a maximum at 403 K and a shoulder at 553 K.

Hydrogen was also released in steps. Two main peaks can be observed together with two minor ones. Quantitative analysis showed that only 55% of the hydrogen atoms of the amine ligands were released as hydrogen molecules. We suggest that the remaining hydrogen atoms were released as water, after reacting with adsorbed O_2 (from zeolite surface).

As observed for the decomposition in an oxygen-containing medium, decomposition in helium also showed carbon dioxide release. The deconvolution of the carbon dioxide signal showed five peaks, not matching the profile observed in the previous case, indicating that oxygen takes an important role in carbon dioxide desorption (actually carbonate-like species decomposition, since NaX zeolites show a large number of carbonate-like species on their surface, as observed by infrared spectroscopy [8] and more recently by DRIFTS [9]).

Besides the gases mentioned, oxygen release was also observed from 320 to 510 K (1.0 moles per unit cell), which supports our suggestion that part of the hydrogen was converted into water due to its reaction with adsorbed oxygen (adsorbed from air).

Figure 3 shows the UV-VIS spectra of the original $Pt(NH_3)_4NaX$ zeolite and after its calcination at different temperatures under 5% O_2/He. Bands below 210 nm can be attributed to charge transfer between *d* orbitals of the transition metal atoms and *p* orbitals of the framework oxygen atoms (not shown in Fig. 3, due to their high F(R) values). The band near 300 nm can be attributed to the d-d transition of electrons of the platinum atoms in $[Pt(NH_3)_4]^{2+}$ [10, 11]. This band can be clearly observed at 503 K, and as a shoulder at 540 K, indicating that even at this temperature part of the $[Pt(NH_3)_4]^{2+}$ complex remains in the zeolite, in complete agreement with TPDE results.

A depression near 240 nm can also be observed until 503 K and it can be attributed to the interaction of platinum and framework oxygen atoms [12]. Then, another band can be observed at 244 nm. This new band appears as a result of the loss of symmetry of the

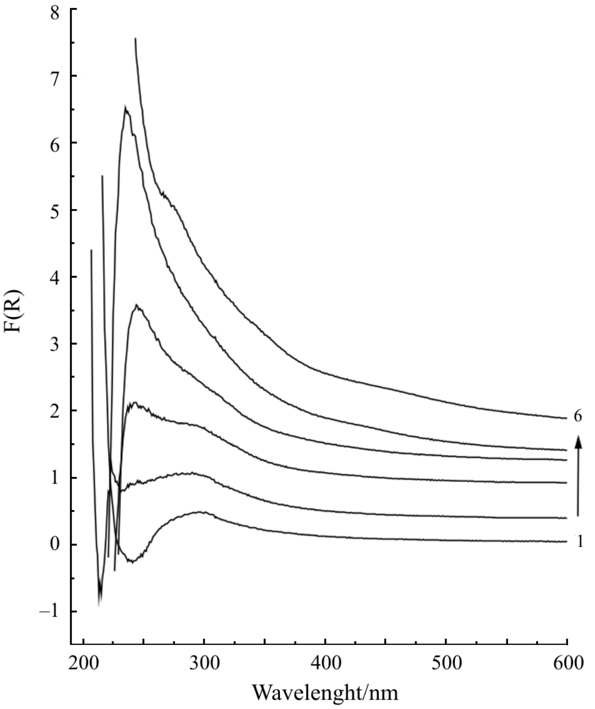

Fig. 3 Diffuse reflectance spectroscopy – $Pt(NH_3)_4NaX$ (1 – at 298 K; 2 – calcined at 473 K, 3 – 503 K, 4 – 540 K, 5 – 573 K and 6 – 633K)

$[Pt(NH_3)_4]^{2+}$ complex, which looses two amine ligands, producing the $[Pt(NH_3)_2]^{2+}$ complex [13], as it has already been observed by mass spectrometry.

At 540 K, the band at 244 nm increases, which is an indication that a larger quantity of the $[Pt(NH_3)_4]^{2+}$ complex was converted to $[Pt(NH_3)_2]^{2+}$ complex (Eq. (3)).

$$[Pt(NH_3)_4]^{2+} \rightarrow [Pt(NH_3)_2]^{2+} + 2NH_3 \qquad (3)$$

At 573 K, only the band at 244 nm can be observed, indicating that the $[Pt(NH_3)_4]^{2+}$ complex was nearly completely decomposed. It can also be observed that the band in the visible region (between 400 and 500 nm) became larger, in comparison to the spectrum taken after calcination at 540 K, suggesting that some platinum oxide was formed, indicating the occurrence of autoreduction [3].

At 633 K, the band related to the $[Pt(NH_3)_2]^{2+}$ complex (at 244 nm) is no more present, indicating the complete removal of the amine ligands. Two shoulders at 274 and 460 nm can be observed, the former being attributed to divalent platinum cations and the latter (a small band, poorly defined) can be attributed to cationic tetravalent platinum species [11, 12, 14, 15].

The divalent platinum cation observed is the result of the removal of the two remaining amine ligands, according to Eq. 4.

$$[Pt(NH_3)_2]^{2+} \rightarrow Pt^{2+} + 2NH_3 \qquad (4)$$

The cationic tetravalent platinum species are related to the occurrence of autoreduction [16, 17]. This process leads to the formation of metallic platinum particles, which are oxidized in the oxygen-containing medium, and then react with hydroxyls (Eq. (5)).

$$Pt^0 \rightarrow PtO_2 \rightarrow [Pt(OH)_2]^{2+} \qquad (5)$$

Conclusions

As observed by diffuse reflectance spectroscopy, platinum atoms in the cationic complex and framework oxygen atoms showed a large interaction, evidenced by the depression at 240 nm. The decomposition of the $[Pt(NH_3)_4]^{2+}$ complex to the $[Pt(NH_3)_2]^{2+}$ complex was observed and the subsequent decomposition of the latter producing divalent platinum cations (≈270 nm), tetravalent platinum species (≈460 nm) and platinum oxide (IV) (increase of F(R) in the visible region) can be clearly seen. The presence of tetravalent platinum (last two species) clearly indicates that the complex decomposition does not happen by the simple removal of the amine ligands, autoreduction also takes place (Fig. 4), although in less extent than in the case of the decomposition of the pure salt, when all the platinum cations are reduced to the metallic state. However, since no significant concentration of protons was observed by infrared spectroscopy [7] we can infer that this phenomenon was not very significant and that the amount of tetravalent platinum was relatively small compared to the amount of divalent platinum.

When the thermal decomposition was monitored by mass spectrometry it became clear that half of the amine ligands of the $[Pt(NH_3)_4]^{2+}$ complex were released at the first step, while the remaining ones were released in another step. When NO was formed in the second step, it was temporarily adsorbed in the zeolite framework [8].

A comparison between the decomposition of the complex in an oxygen/helium medium and in pure helium showed that the decomposition took place at higher temperatures in the latter case. It was also observed that

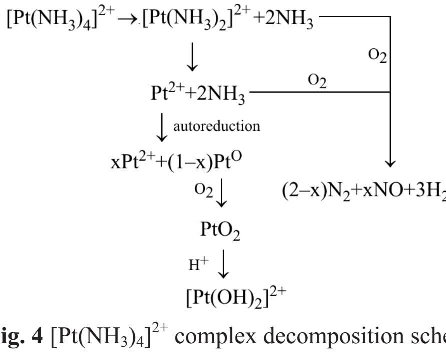

Fig. 4 $[Pt(NH_3)_4]^{2+}$ complex decomposition scheme

for the decomposition in helium, the release of the nitrogen formed in the second step was partially delayed. As a consequence, this second step split into two peaks. The same phenomenon was also observed for the hydrogen release, and it can be attributed to the interaction of the part of the ammonia produced with the zeolite, probably with the Na^+ cations or with the protons formed during autoreduction. When the temperature increases, this ammonia is also decomposed and converted into nitrogen and hydrogen.

In the presence of oxygen, oxidation of ammonia could be observed as soon as the amine ligands were released to the gas phase, resulting the formation of nitrogen, NO and water.

The lower quantity of hydrogen released (in comparison to the total hydrogen amount) for the $Pt(NH_3)_4NaX$ sample indicates that some adsorption or reaction occurred. Since no desorption was observed until 923 K, we can suggest the occurrence of the reaction between hydrogen and adsorbed O_2 accompanied by water formation.

The good matching between the amount of NH_3 liberated (as N_2 and NO) during the MS-TPDE experiments (Table 1) and the value obtained from chemical analysis (2.8 molecules/unit cell) is another evidence that the quantification gave reliable values.

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