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Hydrodechlorination of carbon tetrachloride over PtNaX zeolite: Deactivation studies

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Abstract

Platinum-containing NaX zeolite showed high activity and high methane selectivity in the hydrodechlorination of carbon tetrachloride. The catalyst showed fast deactivation. To identify the possible causes of deactivation, the fresh and used catalysts were studied by thermogravimetric analysis, X-ray diffraction, thermoprogrammed oxidation, infrared spectroscopy and diffuse reflectance spectroscopy. The results indicate that the deactivation is probably caused by the attack of the HCl produced during the reaction to the zeolite structure forming an amorphous aluminosilicate. The HCl adsorption can also be pointed as a cause for deactivation. It is worthy to mention that no coke formation (oligomers) was observed, which is not consistent to some other observations made for other platinum-containing catalysts.

Keywords: Hydrodechlorination; Deactivation; Zeolite X; Platinum; Carbon tetrachloride

1. Introduction

The chlorinated hydrocarbons are pollutants which cause great concern because of their high toxicity and carcinogenicity. Carbon tetrachloride is a versatile chemical used as a reagent and as a solvent in the chemical industry and is produced in high amounts as a by-product of many chlorination processes. The concern about this compound is becoming more pronounced, since its production is far exceeding its needs. Beyond the fact that it is carcinogenic and toxic both to humans and to the environment, it persists in water and soil and it can reduce the ozone layer [1]. Its use was prohibited in developed countries since 1996.

Thus, from both economic and environmental points of view, the development of efficient methods for the elimination of these compounds is needed. Nowadays, three methods are proposed for the destruction of chlorinated hydrocarbons residues: thermal combustion [2], catalytic combustion and catalytic hydrogenation [3]. The most conventional technique, the thermal combustion, is an energy-consuming process that produces secondary chlorinated pollutants, such as dioxins. The catalytic combustion is also an energy-consuming process and produces secondary chlorinated pollutants due to partial oxidation, such as CO, Cl_2 and $COCl_2$. Catalytic hydrogenation over noble metals, such as Pd [4–11] and Pt [3,7,8,11–14] in a large variety of supports, such as Al_2O_3, SiO_2, carbon and MgO presents great economic potential due to the low reaction temperature required (generally below 500 K) and the production of useful and/or harmless products, such as chloroform and methane, without the production of the pollutants mentioned for the other two methods. This method is also known as hydrodechlorination. A great challenge is the development of active and stable catalysts for this reaction, since it is reported that catalysts show rapid deactivation, which disencourages its use in a commercial process.

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The causes for the deactivation of the hydrodechlorination catalysts are not totally understood. Some authors [15,16] attribute the deactivation to the poisoning due to the HCl formed in the reaction. Other possible cause is coke formation, which would cover the catalyst surface, blocking the access of the reagents to the metallic sites.

Choi et al. [13] observed surface carbon deposition over Pt/MgO catalyst in the hydrodechlorination of carbon tetrachloride and suggested that the oligomers (C_2 and heavier) formed by dimerization were the precursors of the coke. Although they have attributed the deactivation to coke deposition, they also observed intense modification of the catalyst, with the conversion of part of the MgO phase into a $MgCl_2$ phase. That should have also contributed to rapid deactivation. Weiss et al. [17] verified a high initial activity for a Ni-Y catalyst, which quickly decreased. The authors also attributed the deactivation to oligomers accumulation in the cavities of the zeolite, since this catalyst presented high selectivity for heavier compounds.

In this work, a platinum-containing zeolite NaX was employed in the carbon tetrachloride hydrodechlorination. The catalyst showed high activity with complete removal of chlorine from carbon tetrachloride leading to preferential formation of methane. In spite of these promising results, fast deactivation was observed. The present work intends to identify the causes of the deactivation of the Pt/NaX catalyst in the carbon tetrachloride hydrodechlorination.

2. Experimental

2.1. Sample preparation

A NaX zeolite provided by Instituto de Pesquisa Tecnológica (IPT, Brazil), with a silica alumina ratio (SAR) of 2.4, was used as starting material. Powder X-ray diffraction showed good cristallinity and absence of any diffraction line not assigned to a NaX zeolite.

Sodium ions were partially exchanged by the $[Pt(NH_3)_4]^{2+}$ complex using a $Pt(NH_3)_4Cl_2$ aqueous solution to give a Pt concentration of 1% (w/w) in the solid. The $Pt(NH_3)_4Cl_2$ solution was added at a constant flow rate under stirring to a 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. The calcination was carried out under oxygen flow (99.9% purity, 1000 ml min^{-1} $g_{cat}{}^{-1}$) at a heating rate of 5 K min^{-1} up to 633 K.

2.2. Reaction conditions

The catalytic tests were performed in a fixed-bed microreactor at atmospheric pressure for up to 24 h time-on-stream. Reaction temperatures used ranged between 373 and 413 K, space velocities ranged between 5000 and 32,000 L kg^{-1} h^{-1} (by varying the hydrogen flow), whereas the H_2/CCl_4 molar ratio was kept constant at 9. The H_2/CCl_4 ratio was obtained with a saturator coupled to a condenser that was kept at 290 K using a thermostatic bath. In order to avoid condensation, all lines of the experimental unity were heated. Before the catalytic tests, the samples were dried under N_2 from room temperature to 633 K (2 h) at a heating rate of 5 K min^{-1}. They were then reduced under H_2 flow from room temperature to 773 K (2 h) at a heating rate of 5 K min^{-1}. Hydrocarbons were analyzed by on-line FID gas chromatography (CP-Sil-5CB column). Following the end of the test, the used catalyst was cooled to room temperature and removed from the reactor for further analysis. All catalytic tests were repeated three times to assure reproducibility. Preliminary experiments indicated that no diffusional limitations were present within the range of operating conditions.

2.3. Characterization

The chemical composition of the sample was determined by atomic absorption spectroscopy using a Perkin-Elmer spectrometer model AAS 1100B.

The calcined sample, previously dried at 633 K, was analyzed by temperature-programmed reduction (TPR) carried out in a microflow reactor operating at atmospheric pressure under H_2 atmosphere (1.6% H_2/Ar) in the range 257–823 K, using a heating rate of 8 K min^{-1} and keeping at 823 K for 30 min. The outflowing gases were accompanied by on-line mass spectrometry using a Balzers quadrupole spectrometer (model PRISMA-QMS 200). The consumption of hydrogen ($m/z = 2$) was monitored and quantified.

Thermogravimetric studies and derivative thermogravimetric studies were conducted in a Rigaku thermobalance model TAS 100 with a TG 8110 accessory. Around 10.0 mg of the material was heated from room temperature to 923 K at 10 K min^{-1} under 5% O_2.

The sample used in the test at 393 K with a space velocity of 9000 L kg^{-1} h^{-1} was oxidized in a flow of 5% O_2/He (TPO) in the range 298–1173 K using a heating rate of 5 K min^{-1}. The outflowing gases were analyzed by on-line mass spectrometry.

X-ray powder diffraction patterns were recorded in a Rigaku X-ray generator diffractometer with a graphite monochromator using Cu Kα radiation and varying 2θ values from 2 to 90°.

The catalyst samples were also analyzed by infrared spectroscopy in a FTIR Perkin-Elmer 2000 spectrometer with a resolution of 4 cm^{-1}. Before analysis, each sample was evacuated at 473 K for 2 h.

UV–visible spectra were recorded in a VARIAN - Cary 5 spectrometer equipped with an accessory for diffuse reflectance (Harrick Sci) and a pre-treatment chamber model HVC-DR2. The NaX zeolite was used as reference for the PtNaX catalyst.

H_2 chemisorption (Micromeritics ASAP 2900 C) and transmission electronic microscopy (JEOL 2010 microscope) were used to determine metal particle size and

dispersion for the sample reduced under H_2 at 5 K min^{-1} up to 773 K (2 h). For TEM analyses, sections with thickness around 80–90 nm were obtained with a microtome. The particle size as given by TEM was taken from various micrographs. About 700 particles were examined for each sample and the average diameter, assuming spherical particles, was determined from Ref. [18].

$$d = \frac{\sum n_i \times d_i^3}{\sum n_i \times d_i^2} \quad (1)$$

where n_i is the number of particles with diameter d_i.

Dispersion and particle size were related by [19]:

$$d = \frac{1}{D}. \quad (2)$$

3. Results and discussion

The Pt content was close to the nominal value of 1% (w/w). The X-ray diffraction patterns confirmed that none of the preparation steps (ion exchange, calcinations and reduction) had significant effect on the cristallinity of the zeolite.

3.1. Carbon tetrachloride hydrodechlorination reaction

The results from the catalytic tests indicate that both conversion and catalyst stability were dependent on the reaction conditions. The catalytic performance of the samples is shown in Fig. 1 for a space velocity of 9000 L kg^{-1} h^{-1}, reaction temperatures from 373 to 413 K and H_2/CCl_4 molar ratio of 9. The results indicate that the better reaction condition (temperature of 413 K) was also the better condition observed by Choi et al. [13] for platinum catalysts supported over MgO.

The influence of the space velocity was also evaluated for the PtNaX catalyst at 393 K and for a constant molar ratio H_2/CCl_4 of 9. The space velocity was varied from 5000 to 32,000 L kg^{-1} h^{-1} (Fig. 2). It can be observed that the increase of the space velocity was followed by a larger deactivation.

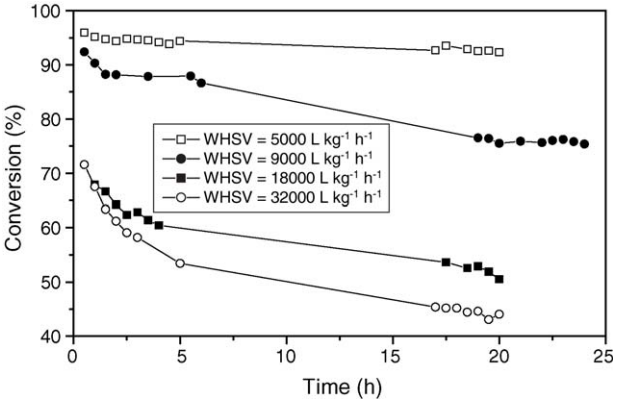

Fig. 2. Effect of WHSV on the conversion of carbon tetrachloride (H_2/CCl_4 molar ratio of 9 and reaction temperature of 393 K).

Although the conversion was very dependent on the reaction conditions, the same was not observed for the selectivity, which remained almost constant for all conditions tested. Neither the time-on-stream nor the space velocity affected the selectivity to methane and to $CHCl_3$ (Figs. 3 and 4). The high selectivity observed to CH_4 was higher than that which is reported in the literature for this reaction over other catalysts, reaching values around 80%. This high selectivity to CH_4 can be assigned to the stronger electron-deficient character showed by small platinum particles, as the particles usually obtained in zeolite supercages. This behavior can be ascribed to an intrinsic size effect or to a metal–support interaction [20,21]. It is important to point out that from the environmental point of view, methane is a much less toxic product and therefore is more interesting than $CHCl_3$ or other chlorinated products.

Weiss et al. [3] observed substantial amounts of C_2 produced over NiY zeolite and this behavior was attributed

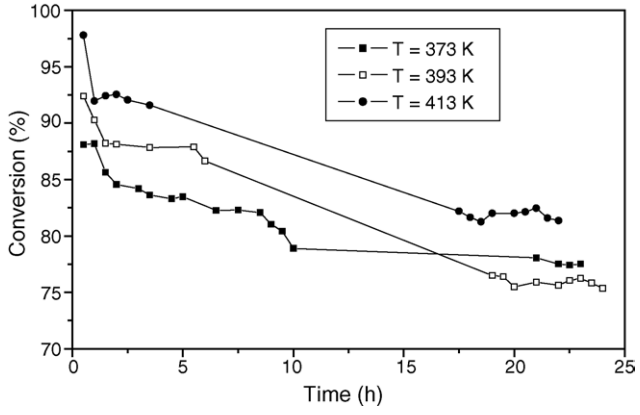

Fig. 1. Effect of reaction temperature on the conversion of carbon tetrachloride (H_2/CCl_4 molar ratio of 9 and WHSV of 9000 L kg^{-1} h^{-1}).

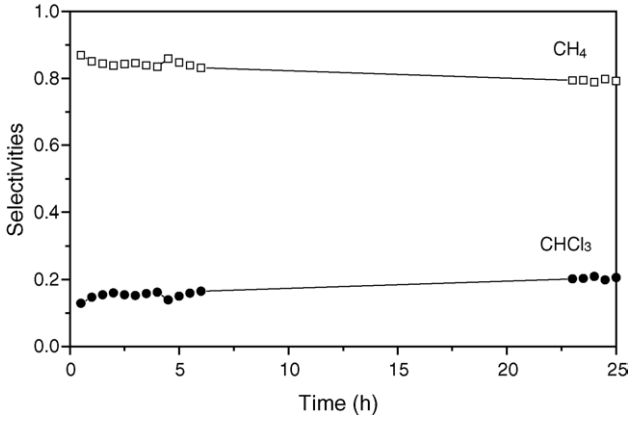

Fig. 3. Product selectivities as a function of time-on-stream (H_2/CCl_4 molar ratio of 9, WHSV of 9000 L kg^{-1} h^{-1} and reaction temperature of 393 K).

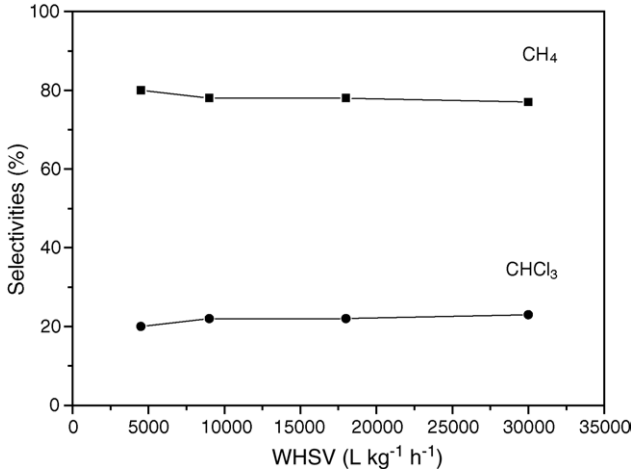

Fig. 4. Effect of WHSV on the product selectivities (H_2/CCl_4 molar ratio of 9 and reaction temperature of 393 K).

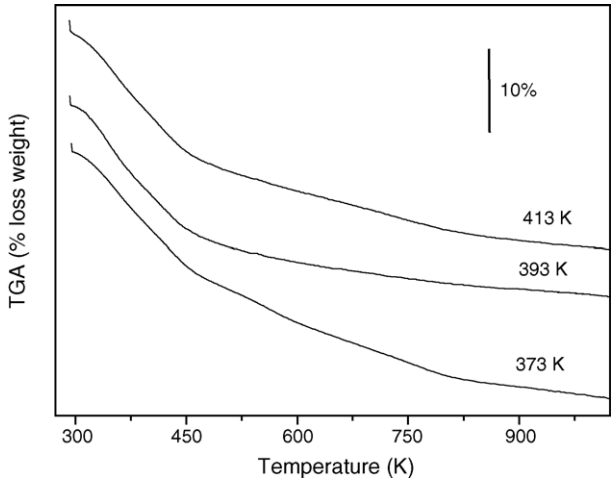

Fig. 5. Thermogravimetric analysis of the catalysts used at different reaction temperatures (H_2/CCl_4 molar ratio of 9 and WHSV of 9000 L kg^{-1} h^{-1}).

to the zeolite acidity. Since PtNaX is less acid than NiY, a lower production of C_2 or even its complete absence should be expected, as indeed observed.

3.2. Temperature-programmed reduction

The TPR profile of the calcined catalyst indicated that all Pt atoms were completely reduced before 633 K. It also let clear that platinum divalent cations were the predominant species before reduction, indicating that autoreduction was not significant during calcination [22–24]. This, in turn, favors the formation of smaller metal particles [22–24].

3.3. H_2 chemisorption and TEM

The results obtained from H_2 chemisorption and TEM indicate an average particle size of 2.8 and 3.1 nm, corresponding to a dispersion of 35 and 32%, respectively [25]. The particle size distribution was already published [25].

3.4. Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analysis

Figs. 5 and 6 show the thermogravimetric and derivative thermogravimetric profiles of the PtNaX catalyst used at different reaction temperatures in the carbon tetrachloride hydrodechlorination reaction.

The loss observed below 473 K is related to water removal from the catalyst. It is assumed that water was adsorbed from ambient air during storage between the catalytic test and the thermogravimetric analysis due to the hygroscopic character of the NaX zeolite.

Further heating led to a uniform loss of weight without the thermal effects associated to coke burning and can be related to the desorption of compounds with increasing adsorption energy or located at different zeolite sites. The nature of these adsorbed species will be further discussed using the TPO results.

Although many authors [5,13,15] suggested that catalyst deactivation for the carbon tetrachloride hydrodechlorination is due to coke deposition (mainly oligomers) on the catalyst surface, coke was not detected for any of the reaction temperatures used in the catalytic tests (absence of a significant exothermic peak in the DTA profile - not shown).

So, in the case of this study, deactivation cannot be attributed to the formation and deposition of coke on the catalyst surface.

3.5. Temperature-programmed oxidation (TPO)

A sample of used catalyst (reaction temperature of 393 K and space velocity of 9000 L kg^{-1} h^{-1}) was submitted to

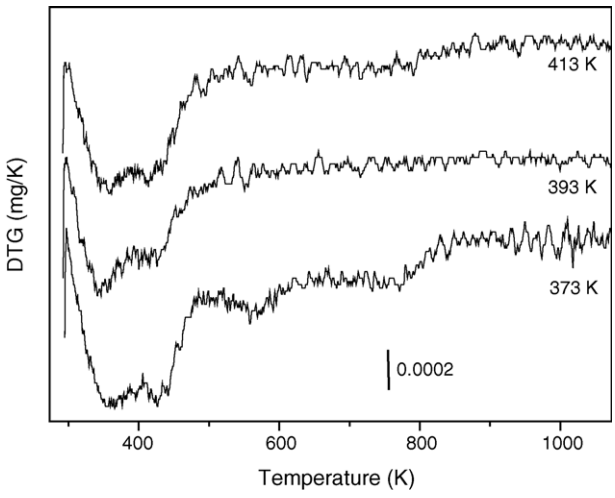

Fig. 6. Derivative thermogravimetric analysis of the catalysts used at different reaction temperatures (H_2/CCl_4 molar ratio of 9 and WHSV of 9000 L kg^{-1} h^{-1}).

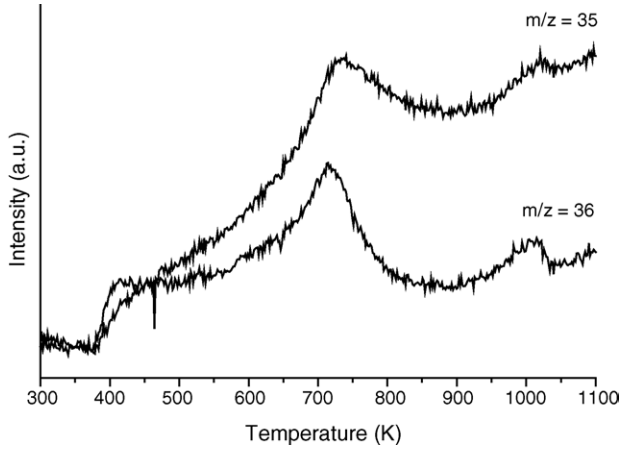

Fig. 7. Thermoprogrammed oxidation of a used catalyst (H_2/CCl_4 molar ratio of 9, reaction temperature of 393 K and WHSV of 9000 L kg^{-1} h^{-1}).

TPO under 5% O_2. Besides water release, HCl desorption (m/z = 35 and 36) took place from 393 to 1173 K, showing peaks at 730 and 1010 K (Fig. 7). Other signals were also observed for m/z equal to 48 and 50. For m/z = 48, two peaks with maxima at 480 and 670 K were observed, while a peak at 880 K was observed for m/z = 50. They can be attributed to the desorption of traces of chlorinated hydrocarbons.

3.6. X-ray diffraction

The XRD pattern of the NaX zeolite is shown in Fig. 8a. The sharp reflections are characteristic of the well crystallized NaX zeolite [26]. No other phase was detected.

After reaction (Fig. 8b), most of the NaX reflections disappeared. However, other reflections related to another crystalline phase appeared. This phase was identified as sodium chloride (NaCl) [26] and the parameter a (cubic symmetry) was calculated using the lines corresponding to the crystallographic planes (2 0 0), (2 2 0), (2 2 2) and (4 2 0) as 5.64 Å (Unit cell program) [27], which agrees with the data available for NaCl [26]. Since for the run at 5000 L kg^{-1} h^{-1}, the amount of HCl produced is significantly lower than that produced in the run at 9000 L kg^{-1} h^{-1}, it is reasonable to expect that the destruction of the structure in the former case was lower. This is in accordance with its higher stability.

The NaCl was formed by the reaction between the HCl produced during the reaction and the zeolite framework, promoting the almost complete destruction of the zeolite structure. It is suggested, therefore, that the zeolite has been transformed into an amorphous aluminosilicate, being this the probable cause of the deactivation of the catalyst. Choi et al. [13] also observed that MgO was converted into $MgCl_2$ after carbon tetrachloride hydrodechlorination over Pt/MgO. However, they claimed that deactivation was due to coke deposition.

3.7. Infrared spectroscopy

Fig. 9 shows the infrared spectra in the hydroxyl region of the PtNaX catalyst. Fig. 9a shows the spectrum of a sample that was heated under nitrogen flow from room temperature to 633 K. Fig. 9b shows the spectrum of that sample reduced under hydrogen flow until 773 K. Finally, Fig. 9c displays the spectrum of a used catalyst tested at 393 K.

The bands present in the region between 3200 and 3500 cm^{-1}, before reaction, can be attributed to the presence of adsorbed water [28], not removed during the drying step. The band at 3688 cm^{-1} can be attributed to the interaction of water with the cations present in the zeolite [28]. The bands at 3585 and 3658 cm^{-1} are associated to the hydroxyl groups present in the sodalite cavities and in the supercages, respectively. It can be seen that reduction had a small effect on these hydroxyls. After reaction, it was observed that all bands in the region of the hydroxyls disappeared.

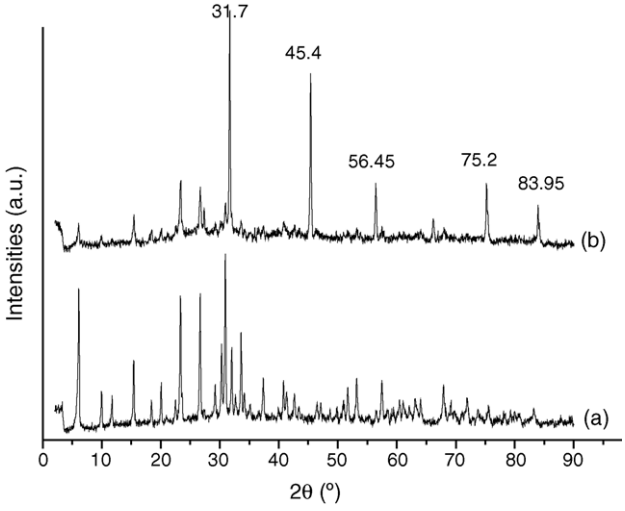

Fig. 8. X-ray diffractograms for PtNaX catalyst before (a) and after (b) carbon tetrachloride hydrodechlorination reaction (H_2/CCl_4 molar ratio of 9, reaction temperature of 393 K and WHSV of 9000 L kg^{-1} h^{-1}).

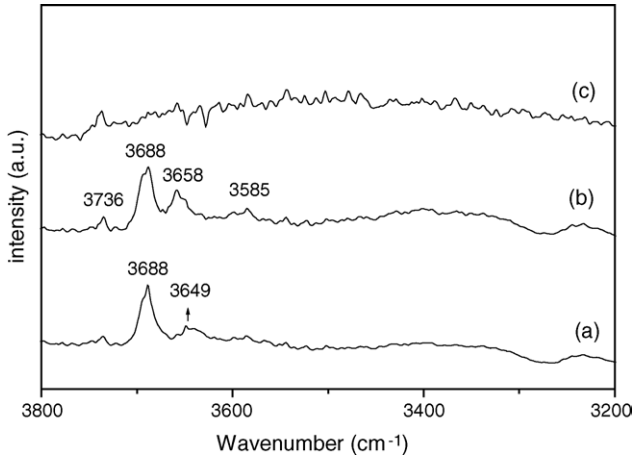

Fig. 9. IR spectra of the PtNaX catalyst in the hydroxyl region: dried at 633 K (a), reduced at 773 K (b) and used on the carbon tetrachloride hydrodechlorination reaction (c) (H_2/CCl_4 molar ratio of 9, reaction temperature of 393 K and WHSV of 9000 L kg^{-1} h^{-1}).

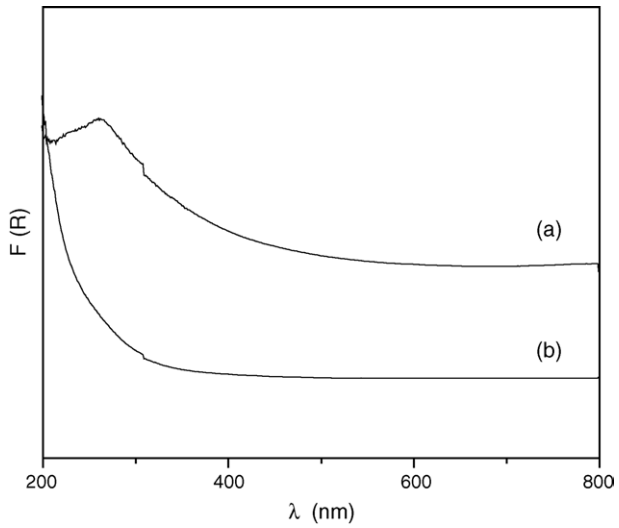

Fig. 10. Diffuse reflectance spectra at room temperature of the PtNaX catalyst before (a) and after (b) carbon tetrachloride hydrodechlorination reaction (H_2/CCl_4 molar ratio of 9, reaction temperature of 393 K and WHSV of 9000 L kg^{-1} h^{-1}).

This result is in agreement with the X-ray diffractograms, indicating that the zeolite framework was destroyed during reaction.

3.8. Diffuse reflectance spectroscopy (DRS)

Fig. 10 shows the DRS spectra of sample PtNaX calcined at 633 K (adequate temperature for the removal of amin ligands) before and after reaction at 393 K and for a space velocity of 9000 L kg^{-1} h^{-1}).

A peak around 260 nm was observed in the spectrum of sample PtNaX after calcination and exposure to air. This band can be attributed to the presence of the tetraaquoplatinum(II) complex generated by adsorption of water from air by the sample, which restored the square planar symmetry of platinum (d^8) lost when the amin ligands were removed during calcination.

After the carbon tetrachloride hydrodechlorination reaction, the spectrum did not show any peak, which is consistent with the presence of metallic platinum formed during the reduction carried out before reaction. The metallic platinum was not oxidized by ambient air (the analysis was not realized in situ due to the corrosive character of the reaction), which suggests that due to the collapse of the framework and the formation of NaCl and a amorphous aluminosilicate phase, the platinum particles were enclosed, thus, preventing their oxidation to PtO_2 (absence of shoulder or peak around 400 nm).

4. Conclusion

The PtNaX catalyst showed high activity and selectivity to methane in the carbon tetrachloride hydrodechlorination reaction. Its stability strongly depends on the reaction conditions. The catalyst exhibited fast deactivation in most of the studied conditions. Thermogravimetric and derivative thermogravimetric analysis indicated the absence of coke and the presence of other adsorbed species. TPO coupled with mass spectrometry indicated that HCl and some traces of chlorinated hydrocarbons were adsorbed on the catalyst. It was also observed the almost complete destruction of the zeolite framework with the formation of amorphous aluminosilicate and NaCl. From these results, one may claim that the most probable cause of deactivation is the destruction of the initial catalyst structure as a consequence of the attack by the HCl formed along the reaction. The adsorption of HCl on the active sites is probably a less important deactivation factor.

Acknowledgement

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