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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

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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