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## DEACTIVATION OF $H_3PW_{12}O_{40}/TiO_2$ CATALYST USED IN THE PRODUCTION OF CAMPHENE

Liliana Grzona<sup>a</sup>, Omar Masini<sup>a</sup>, Nora Comelli<sup>a</sup>, Esther Ponzi<sup>b</sup>  
and Marta Ponzi<sup>a\*</sup>

<sup>a</sup>INTEQUI (CONICET-UNSL) 25 de Mayo 384 (5730) V. Mercedes, San Luis, Argentina

<sup>b</sup>CINDECA (CONICET-UNLP) Calle 47 N° 257, La Plata, Buenos Aircs. Argentina

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### Abstract

The deactivation of the  $H_3PW_{12}O_{40}$  (HPW) catalyst supported on  $TiO_2$  used in the isomerization reaction of  $\alpha$ -pinene and its regeneration were studied. The regeneration of the deactivated catalyst was carried out with an air flow at 300 and 500°C, with an ozone-enriched oxygen flow at 150°C and by extraction with solvent and acid treatment. Only the last treatment permitted to recover its activity restoring it in 48% of its initial value.

*Keywords:* Camphene, deactivation, heteropoly acid, isomerization

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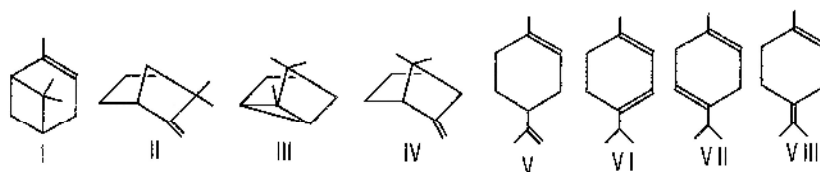
### INTRODUCTION

The catalytic isomerization of  $\alpha$ -pinene produces bi- and tricyclic compounds such as camphene, tricyclene and fenchene and monocyclic compounds such as limonene,  $\alpha$ - and  $\gamma$ -terpinene, terpinolene (Fig. 1).

Among catalysts studied for the isomerization of  $\alpha$ -pinene, mineral clays are found, zeolites and superacid catalysts [1-4]. In particular, our group studied the oxide of sulfated zirconium [5] and sulfated zirconia promoted with Fe-Mn. Deactivation was studied on these catalysts [6] and it was found that the principal deactivation cause was coke deposition.

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\*Corresponding author. E-mail: mponzi@fices.unsl.edu.ar



**Fig. 1.** Principal reaction compounds.

I:  $\alpha$ -pinene, II: camphene, III: tricyclene, IV: fenchene, V: limonene, VI:  $\alpha$ -terpinene, VII:  $\gamma$ -terpinene, VIII: terpinolene

In order to find less aggressive catalysts for the environment, since the used ones up to the present time contain strong mineral acids, in a previous work, HPW catalysts impregnated in different supports were studied. In general acid catalysts suffer a quick deactivation and this limits their uses in industrial applications, for this reason it is important to understand the mechanism responsible for the catalyst deactivation. The deactivation can be produced by formation of carbonaceous residues, phosphotungstic acid (HPW) loss from the catalyst, irreversible adsorption of products and acidity loss or change in the relation between Brønsted and Lewis sites.

The aim of this work is to study the deactivation and regeneration of a HPW catalyst supported on  $\text{TiO}_2$  (HPWTi).

## EXPERIMENTAL

The precursor was prepared by impregnating the titanium oxide with the necessary amount of a HPW solution in ethanol-water so as to obtain 43% of nominal load. Then, it was calcined at  $300^\circ\text{C}$  for 2 h. The  $\alpha$ -pinene isomerization experiments were carried out in a batch reactor with reflux system and magnetic stirring.  $\alpha$ -pinene was loaded in the reactor, it was heated at  $130^\circ\text{C}$ , catalyst was added (1% m/v) and from this moment, the time started to be recorded. The reaction occurred in the course of 1 hour. Periodically, samples of the reaction mixture were removed and analyzed quantitatively by gas chromatography.

Concerning deactivation experiments, sequential tests were done with the same catalyst. A fresh catalyst batch was loaded with the reactant ( $\alpha$ -pinene) to do the first test; then, once the catalyst was separated from the reactant, the second test was began by adding another fresh  $\alpha$ -pinene load.

The regeneration of the deactivated catalyst was performed with a) an air flow (40 mL/min) at two temperatures  $300$  and  $500^\circ\text{C}$ ; b) an ozone enriched oxygen flow (40 mL/min) at  $150^\circ\text{C}$ ; c) by extraction with solvent and acid

treatment. For this last treatment, the deactivated catalyst was placed in a balloon with reflux system with a magnetic bar, ether was added, it was stirred for 2 hours. The solid was separated by filtration and was dried in sand bath at 120°C for 2 hours. The solid so obtained was separated in two portions, and they were exposed to the same previous treatment replacing the ether by nitric acid, HNO<sub>3</sub> 0.1 N was used in a portion and in the other HNO<sub>3</sub> 1 N was employed.

The characterization of carbonaceous deposits formed in the deactivated catalyst was carried out by temperature programmed oxidation (TPO) in a Shimadzu TGA-50 equipment. FTIR spectroscopy was used to characterize acid sites and coke deposition on the catalyst surface by using a spectrophotometer Bruker IFS66 FTIR. The catalyst acidity was determined by measuring isothermally the adsorbed ammonia amount up to no weight variation, in a Shimadzu TGA-50 equipment. The W/Ti ratio was determined by EDAX using a Microscope Philips SEM 505.

## RESULTS AND DISCUSSION

The  $\alpha$ -pinene conversion with the fresh catalyst is 0.42, and with deactivated catalyst is 0.14.

The deactivation can be generated by load loss (lixiviation) of HPW. Studies performed by EDAX show a W/Ti constant ratio for catalyst samples fresh, deactivated and regenerated at 300 and at 500 °C, this indicating that HPW was not lost.

Coke formation during the reaction is considered as a cause of catalyst deactivation [7]. Several types of coke are known: the one that may be removed by heating in oxidizer current is named high boiling hydrocarbon or "soft" coke is eliminated in the range of 170-370°C; polynuclear aromatics or "hard" coke is eliminated in the range of 370-570°C [8].

IR experiments were performed in order to characterize the coke type present in the deactivated catalyst. The spectrum carried out with the fresh catalyst, shows signals between 870 and 1100 cm<sup>-1</sup> corresponding to HPW, a signal at 1625 cm<sup>-1</sup> by water vibration and another at 3440 cm<sup>-1</sup> assigned to the OH groups. In the deactivated catalyst signals found in the fresh catalyst are observed, and also signals at 1370, 1460, 2850 and 2930 cm<sup>-1</sup> appear. The bands 2850 and 2930 correspond to vibrations of -CH<sub>2</sub> and -CH groups connected to aromatic rings. Bands at 1370 and 1460 may be assigned to vibrations of the -CH group in polycyclic aromatics [9].

Figure 2 shows TGA/TPO data for the coke characterization in the deactivated catalyst. A weight loss at 180°C is observed followed by minor losses at 230, 284 and 360°C with a total loss of 11.9% which is attributed to

oft coke and a loss of 1.5 % from 380 up to 500°C attributed to hard coke. According to results of experiments of coke characterization in the deactivated catalyst, temperatures were selected to perform the regeneration.

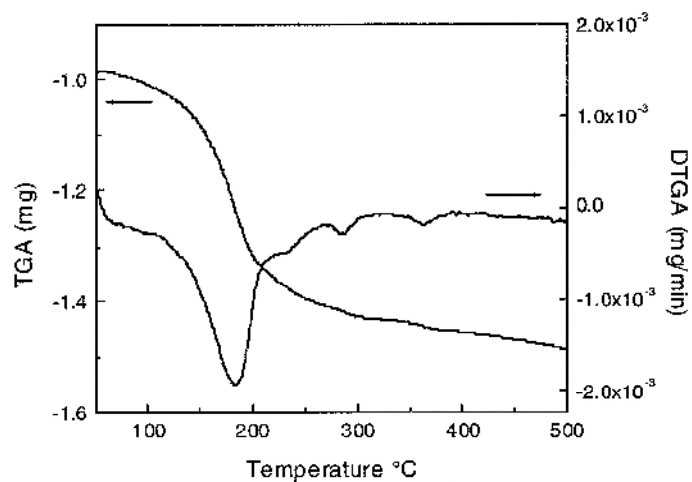


Fig. 2. TPO of deactivated catalyst

The catalyst regeneration was carried out in air at 300°C to remove the soft coke, and at 500°C to remove also the hard coke.

Results of catalytic activity and selectivity in the desired product with these regenerated catalysts are shown in Table I. The conversion for the regenerated catalyst at 300°C (0.07) is lower than the deactivated catalyst (0.14) and the regenerated catalyst at 500°C gives the lowest conversion.

Table 1

Conversion of  $\alpha$ -pinene of regenerated catalyst

Fresh catalyst	Deactivated catalyst	O <sub>2</sub> 300°C	O <sub>2</sub> 500°C	O <sub>2</sub> /O <sub>3</sub> 150°C	Ether and HNO <sub>3</sub> 0.1 N	Ether and HNO <sub>3</sub> 1 N
0.42	0.14	0.07	0.02	0.07	0.20	0.21

Activity result for the regenerated catalyst by O<sub>2</sub>/O<sub>3</sub> at 150°C (Table 1) is very similar to the O<sub>2</sub> regenerated catalyst at 300°C. The catalytic activity is not recovered with treatments in oxidizing atmosphere performed in this work.

Other possible cause of deactivation is the acidity loss. In the adsorption isotherms, the adsorbed ammonia amount was determined in two time intervals 0-5 min and 5-25 min. The first amount is associated with strong sites and the second one with weak sites. Results obtained for catalysts fresh, deactivated and regenerated are shown in Table 2.

**Table 2**  
Acidity of catalysts measured by ammonia adsorption

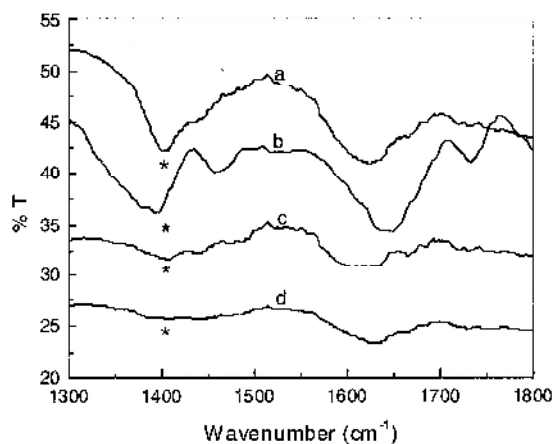
Catalyst	Fresh	Deactivated	Regenerated at 300°C	Regenerated at 500°C
mmol NH <sub>3</sub> /g *	0.36	0.26	0.25	0.00
mmol NH <sub>3</sub> /g **	0.25	0.19	0.27	0.15

\*Adsorption 0-5 min \*\*Adsorption 5-25 min

The total acidity of the deactivated catalyst decreases from 0.61 mmol NH<sub>3</sub>/g in the fresh catalyst to 0.45 mmol NH<sub>3</sub>/g in the deactivated catalyst. With a regeneration at 300°C, strong sites responsible for the catalytic activity are maintained at the same level of the deactivated catalyst, but weaker sites recover the level of the fresh catalyst. With the treatment at 500°C the strong acidity is completely lost and the level of weak sites is lower than in the deactivated catalyst.

In order to better comprehend acid properties of catalysts, complementary experiments were performed. The presence of Brønsted acidity was determined by FTIR of adsorbed ammonia. Results are shown in Fig. 3. The signal at 1400 cm<sup>-1</sup> is observed in all catalysts, fresh, deactivated and regenerated, this indicating the presence of Brønsted acidity. A marked decrease is clearly observed in the signal when the catalyst is regenerated at 300°C, such signal resulting almost imperceptible for the catalyst regenerated at 500°C. These results are coincident with the acidity loss evaluated by ammonia adsorption. Treatments in oxidizing atmosphere were not useful since they were not able to completely eliminate either carbonaceous residues or to regenerate the catalyst acidity.

Extraction results with ether and treatment with nitric acid 0.1 and 1 N are shown in Table 1. It is possible to observe that by means of this treatment the conversion is restored up to 48% from its initial value.



**Fig. 3.** FTIR of catalysts with  $\text{NH}_3$  adsorbed. Curve *a*, fresh catalyst; curve *b*, treated with ether and nitric acid 1 N; curve *c*, catalyst regenerated at  $300^\circ\text{C}$ ; curve *d*, catalyst regenerated at  $500^\circ\text{C}$

As the nitric acid can be generating new active sites on the support, a catalyst was prepared by impregnating  $\text{TiO}_2$  with 0.1 N  $\text{HNO}_3$ . This catalyst did not show catalytic activity in the transformation reaction of  $\alpha$ -pinene tested in the same experimental conditions mentioned above.

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