

Synthesis, characterization and catalytic activity of zirconia promoted with tungstophosphoric acid

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Introduction

In spite of zirconia is an acid catalyst, its activity is very weak to catalyze processes that require a strong acid strength such as isomerization of hydrocarbons. However, this possess strong acid sites when oxoanions are incorporated on its surface (SO_4^{2-} , PO_4^{3-} , WO_6 , etc.) being active their sites for the type of reaction indicated [1-6]. In this work is presented the synthesis of modified zirconia with tungstophosphoric acid. The purpose of this synthesis was to increase the acidity of zirconia with the introduction of the modifier mentioned above and at the same time decrease the disadvantages that heteropolyacids present in the solid-gas reactions (low thermal stability and surface area).

Materials and Methods

The preparation $\text{Zr}(\text{OH})_4$ was carried out by the sol-gel method dissolving zirconium *n*-butoxide in 1-butanol taking place the hydrolysis and condensation of this by the addition of a low dropping water/1-butanol solution maintaining a pH = 8 during the synthesis. Later, the gel was aged for 72 hours and dried at 120°C for 24 hours. Impregnation of zirconium hydroxide with the heteropolyacid (HPA) took place using the wet incipient technique adding the necessary amounts of an alcoholic solution that contained the HPA to obtain a 15 wt% of the acid agent present in the support. The modified hydroxides were dried at 120°C for 24 hours, calcined afterward in a dynamic air atmosphere at 400, 500 and 600°C for 3 hours. The synthesized materials were characterized by thermogravimetric analysis (TGA-DTA), infrared spectroscopy (FT-IR) as well as by ammonia thermoprogramed desorption (TPD-NH₃). Materials obtained were impregnated with 0.5 wt% of Pt in order measure to their catalytic activity in the isomerization of *n*-pentane at 250°C, 1 atm and WHSV = 3 h⁻¹.

Results and Discussion

Thermal analysis indicate that $\text{ZrO}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ was thermally stable up to 900°C losing weight attributed to water desorption and solvents used during the synthesis. On the other hand, the heteropolyacid lost water around 70 and 200°C presenting an exothermic change at 600°C due to the decomposition of its Keggin structure (Figures 1 and 2). The FT-IR spectra show bands around 1080, 970, 867 and 795 cm⁻¹ corresponding to P=O, W=O bonds and two bonds types W-O-W which identify the presence of the heteropolyanion in zirconia showing also the characteristic band of the hydroxyl groups (3400 cm⁻¹) which were reduced by the calcination temperature effect, parameter or synthesis variable which affects as well the characteristic bands that identify crystalline zirconia (762, 578 and 532 cm⁻¹). Results from ammonia thermoprogramed desorption indicate that the total amount of acid sites of ZrO_2 was increased when HPA was deposited on its surface. Nevertheless, it is important to mention a decrease in

the acidity due to the calcination temperature which can be related with a possible dehydroxylation of the sample. Acidity developed by the materials was appropriate to catalyze the isomerization reaction of *n*-pentane with significant conversions and selectivities being the hydrocarbon conversion above 30 % and selectivities toward isopentane around 95 %. No deactivation was detected along the 180 minutes reaction (Table 1).

Figure 1

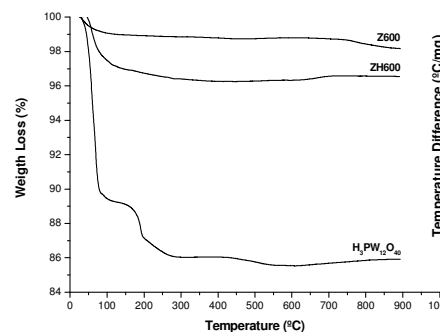


Figure 2

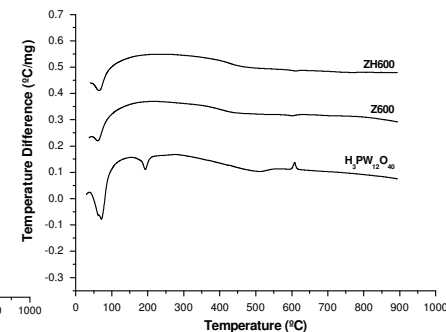


Figure 1-2. Gravimetric and differential thermal analysis for $\text{H}_3\text{PW}_{12}\text{O}_{40}$, ZrO_2 and $\text{ZrO}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$.

Table 1. Nomenclature, acid and catalytic properties of ZrO_2 , $\text{ZrO}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$.

Material	$T_{\text{calcination}}$ (°C)	Acid agent	Total acidity ($\mu\text{mol NH}_3/\text{g}$)	% X_T <i>n</i> -pentane	% Selectivity		
					<C ₅	<i>i</i> -C ₅	>C ₅
Z400	400	---	1234	---	---	---	---
Z500	500	---	970	---	---	---	---
Z600	600	---	472	---	---	---	---
ZH400	400	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	2130	48	2	94	4
ZH500	500	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	1520	39	3	94	3
ZH600	600	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	1020	30	2	95	3

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