

Phosphated Zirconia as Promoter of *n*-Hexane Isomerization

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Introduction

A variety of physicochemical properties, such as acidic and basic behavior, reducing and oxidizing characteristics, thermal resistance capacity, etc. [1], make zirconia and excellent material for many industrial applications. The addition of oxo-anions (SO_4^{2-} and WO_4^{2-}) gives more stability, inhibiting zirconia sintering and the tetragonal to monoclinic phase transformation. It also produces a material which can catalyze reactions demanding high acid strengths, such as alkane isomerization [2,3]. The first zirconia promoter used was SO_4^{2-} ion and the use of alternative promoters is an interesting field of research. Phosphate ion (PO_4^{3-}) may be one of them. In this area, literature is poor, reporting only a few attempts to incorporate PO_4^{3-} ion to zirconia and its applicability in some reactions such as methanol and dimethyl carbonate synthesis [4], benzylation and esterification [5]. Catalytic behavior of phosphated zirconia also has been reported for 1-butene isomerization at 150°C [6]. Many papers have reported how SO_4^{2-} ion has modified the structure, specific area, acid and catalytic properties on zirconia, however, little works has been done to identify if PO_4^{3-} ion produces similar effects on this material. For that, this work proposes to investigate the effect of the phosphate ion and calcination temperature over physicochemical properties of zirconia, testing the resulting catalysts in the *n*-hexane isomerization.

Materials and Methods

Zirconia and phosphated zirconia (ZrO_2 and $\text{ZrO}_2\text{-PO}_4^{3-}$) were synthesized from hydroxylated zirconium [$\text{Zr}(\text{OH})_4$] obtained by sol-gel method as described in literature [7], followed by ion exchange of OH^- by PO_4^{3-} with a H_3PO_4 2 N solution. The amount of PO_4^{3-} ion was maintained in 15 wt%. The hydroxides were dried at 120°C for 24 h and finally calcinated in an air atmosphere at 400, 500 and 600°C for 3 h. In order to evaluate the catalytic activity of the materials in the *n*-hexane isomerization, these were impregnated by incipient wetness with a solution of diammine-dinitrito-platinum [$\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$]. The doped oxides with the metallic agent (0.5 wt% of the platinum) were calcined at 400°C. The materials were characterized by thermal analysis, nitrogen physisorption, X-ray diffraction, infrared spectroscopy, NH_3 temperature-programmed desorption, and the *n*-hexane isomerization took place at 250°C, atmospheric pressure and WHSV = 3 h⁻¹.

Results and Discussion

Table 1 shows a positive effect on the physicochemical properties of the catalytic supports after $\text{Zr}(\text{OH})_4$ impregnation with the doping agent (H_3PO_4). Phosphate zirconium oxides remained thermically stable after calcination. It was observed that the doping agent (PO_4^{3-}) remained firmly attached to the zirconium oxide surface, inhibiting the particle growth

and delaying the syntherization of the material and the apparition of the monoclinic phase, obtaining mesoporous and nano-crystalline materials (crystallite size 1.0-6.5 nm) with high specific areas (210-329 m²/g) and tetragonal structure defined for the calcination temperature of 600°C. Also, with the incorporation of the doping agent, the total acidity of the material increased specially the amount of strong acid sites being this type of sites the most abundant in the acidified samples. Acidity developed by the materials was adequate to catalyze the *n*-hexane isomerization with conversions around 40% and selectivities toward isomerization products above 80%.

Table 1. Characterization and catalytic activity of ZrO_2 (Z) and $\text{ZrO}_2\text{-PO}_4^{3-}$ (ZP)

Material	Area (m ² /g)	Crystalline phase	Crystallite size (nm)	Total acidity (μmol NH ₃ /g)	X _T <i>n</i> -C ₆ (%)	Selectivity Isom. (%)
Z400	144	T (+), M (-)	4.3	1234	n.d.	n.d.
Z500	73	T (+), M (-)	6.9	970	n.d.	n.d.
Z600	18	M	16.2	472	11	37
ZP400	329	A	1.0	2725	44	79
ZP500	256	A	1.1	2292	40	84
ZP600	210	T	6.5	2170	34	95

- Bulk structure: A = amorphous, T = tetragonal, M = monoclinic
- Isomerization products: *i*-C₅, 2,2-DMB, 2-MP, 3-MP, 2,4-DMP, 3-MH

Conclusions

In this work it can be concluded that the system $\text{ZrO}_2\text{-PO}_4^{3-}$ exhibits an interesting behavior as an isomerization catalyst due to improved physicochemical properties of ZrO_2 , which ones were a result of the PO_4^{3-} ion incorporation on its surface.

Significance

The development of these materials has been essentially made by the modification of well known acid compounds, in order to obtain new catalytic supports with controlled structure and high reactivity. Such materials can find application in many areas of catalysis.

References

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