Isomerization of Cyclohexene: Effect of Number and Type of Acid Sites

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Introduction

Cyclohexene (CHE) conversion has been used as a probe reaction for isomerization and hydrogen transfer over a variety of acid catalysts [1]. This model reaction has been especially suitable [2], since it allows the simultaneous determination of the catalyst's capability to promote skeleton isomerization and hydrogen transfer reactions. From a practical standpoint, it is important to evaluate the hydrogen transfer tendency of FCC active phases, since this bimolecular type of reaction leads to an enhanced coke formation and to a reduction of the octane number of the gasoline fraction [3].

In this work we examine different solids acids with varying textural properties and acidity, either Brönsted and/or Lewis, using supported SO_4^{2-} and $[PW_{12}O_{40}]^{3-}$ (PW) anions, to illustrate their use as catalysts through their activity and selectivity in the CHE skeletal isomerization process, a reaction that requires the presence of strong surface acid sites.

Materials and Methods

Four acid catalysts: (*i*)ASO_4 (sulfated alumina), (*ii*) 25PW/Z, (*iii*) 25PW/Z* (PW on fresh or calcined* ZrO_2 and (*iv*)ZrO_2, calcined for 4h at different temperatures were used. The detailed preparation procedure has been described elsewhere [4, 5]. Furthermore and as a comparison, γ–Al_2O_3 and acid-form Zeolite-Y (PQ Zeolites BV) catalysts were also studied. The isomerization of CHE was carried out in a fixed-bed microreactor, flowing a mixture of CHE and He (CHE/He = 0.045) on 0.1 g of catalyst. The gas products were analyzed on-line on a gas chromatograph, using a 50 m long, 0.20 mm i.d., DB-1 column. The textural properties of the catalyst were determined by means of nitrogen adsorption- desorption isotherms in an Autosorb-1 equipment from Quantachrome and the type and amount of acid sites was determined by FTIR of pyridine adsorption.

Results and Discussion

The main physicochemical characteristics of the different solids are shown in Table 1. In the case of Al_2O_3 catalysts (γ-Al_2O_3 and ASO_4) an improvement in the SA and the quantity of acid sites were observed when SO_4^{2-} was incorporated in the structure of Al_2O_3. A similar effect occurs in ZrO_2 (Z), as it presents a SA of 132 m^2/g and when impregnated with PW, the SA increases to 181 m^2/g. This can be due to the fact that Keggin anions hinder the structural transformation of ZrO_2, favoring the formation of a less ordered structure with higher SA. The two different forms of ZrO_2, either fresh or calcined (Z or Z*) affect the acid site generation, 30PW/Z* presented 357 μmol py/g while 30PW/Z presented 247 μmol py/g.

Tabla 1. Textural properties and total acidity of the solids

Catalyst	S A (m^2/g)	Total acidity (μmol py/g)[a]
γ-Al_2O_3	205	203
ASO_4	317	320
Z*[b]	132	180
25WP/Z	181	247
25WP/Z*	132	357
Zeolite-Y	780	NA

[a]Total acidity at T= 100°C; [b] Z*:Calcined ZrO_2

The incorporation SO_4^{2-} and $[PW_{12}O_{40}]^{3-}$ anions in the indicated supports, improves their textural properties and enhances their acidity and hence their catalytic activity in the isomerization of CHE, as shown in Table 1 and 2. The presence of Lewis acid sites mainly favors the formation of MCPEs, while the Brönsted acid sites favor the selectivity toward MCPA, DIM and others. This reaction is attractive as a reaction model for the diversity of products obtained where the selectivity depends on the quantity, strength and type of acid sites.

Tabla 2. Conversion, rate and selectivity in the CHE reaction @ 250°C.

Catalyst	X_{CHE} (%)[a]	r x 10^{-6} (mol/g s)[b]	MCPEs	MCPA	CHA	C_6H_6	DIM
γ-Al_2O_3	0.5	0.2	40.0	0.0	29.0	31.0	0
ASO4	17.0	12.0	97.0	2.0	0.0	0.0	0.5
Z*[c]	21.0	9.0	2.0	0.0	7.0	30.0	60.0
25PW/Z	24.0	10.0	73.0	17.0	0.0	0.1	6.0
25PW/Z*	26.0	11.0	81.0	1.0	0.0	3.6	11.0
Zeolite-Y	41.0	28.0	50.0	34.0	8.0	0.3	3.4

[a]Taken after 3 min of reaction, [b]Rate of reaction, [c]Z* (ZrO_2 calcined previously). MCPEs, methylcyclopentenes; MCPA, methylcyclopentane; CHA, cyclohexane; C6H6, benzene and DIM, dimers.

Significance

Isomerization of CHE can be used to distinguish Lewis or Brönsted acid sites in close to real application conditions.

References

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