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Influence of hydrothermal aging on the catalytic activity of sulfated zirconia

Mariana Busto [a], Kiyoyuki Shimizu [b], Carlos R. Vera [a,*], Javier M. Grau [a], Carlos L. Pieck [a], Miguel A. D'Amato [a], M.T. Causa [c], M. Tovar [c]

[a] Instituto de Investigaciones en Catálisis y Petroquímica -INCAPE- (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina
[b] Council for Science and Technology Policy, Cabinet Office (AIST-MITI), 3-1-1 Kasumigaseki, Chiyoda-ku, Tokyo 100-8970, Japan
[c] Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, Av. Ezequiel Bustillo 9500, 8400 San Carlos de Bariloche, Argentina

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ABSTRACT

The use of reflux aged zirconia gel in the synthesis of sulfated zirconia catalysts for isomerization of short paraffins and isomerization-cracking of long paraffins was assessed. It was found that reflux aging greatly improved zirconia textural properties. The growth of the monoclinic phase was greatly suppressed and the initial area and sintering resistance were increased. The specific surface area of reflux aged material with no sulfate was almost 75 $m^2 g^{-1}$ after calcination at 800 °C. Sulfate promotion of aged materials further increased the tetragonal/monoclinic ratio and the area of sulfated catalysts was 220 $m^2 g^{-1}$ after calcination at 600 °C.

Impregnation of reflux aged materials with sulfate produced materials which had very low activity in isomerization of *n*-butane. The effect of aging was explained in terms of a dissolution-precipitation process that eliminated specific sites of the gel that were responsible for much of the activity of the final catalyst. In the case of the hydroisomerization-cracking of long paraffins the effect was less deletereous partly due to the higher reactivity of this feedstock.

1. Introduction

Oxoanion promoted zirconia catalysts have outstanding properties of conversion of short paraffins at low temperature with high selectivity to branched isomers. Currently Pt/SO_4^{2-}–ZrO_2 and Pt/WO_3–ZrO_2 are the basis of commercial C_5–C_6 virgin naphtha isomerization process like the Par-Isom (UOP) and EMICT (Exxon-Mobil) ones. New formulations are constantly tried to improve their activity and selectivity for new applications [1,2]. As for any other catalyst the improvement of the textural properties of oxoanion promoted zirconia catalysts is an important issue. It is known that common oxoanions like sulfate and tungstate produce a textural promotion and the catalysts have a preferential presence of the tetragonal structure, while the sintering resistance and the total area are higher than those of pure zirconia after calcination at high temperatures [3–5]. This is true only when the calcination does not produce the decomposition of the adsorbed oxoanion layer. At temperatures higher than 650–700 °C sulfate decomposes and the zirconia support sinters rapidly into the monoclinic form [6]. Sintering decreases the available surface area to negligible values in this process. At temperatures lower than those of decomposition the temperature needed for the obtention of maximum activity is also sufficiently high to decrease the area to small values. For SO_4^{2-}–ZrO_2 (SZ) calcination at 600–650 °C yields catalysts with 100–120 $m^2 g^{-1}$ and in the case of WO_3–ZrO_2 (WZ) calcination at 800 °C decreases the final area to 20–60 $m^2 g^{-1}$. A higher specific surface area translates into a higher activity per unit volume and reactor sizes can be decreased in new process designs or the production can be increased in reactor revamps.

Another textural property that can be improved for the benefit of some processes is the mesoporosity. In the case of sulfated zirconia the pore structure spans both the micropore and mesopore range. Though the microporosity contributes to a great extent to the total available surface this area sometimes cannot be reached due to mass transfer limitations. This is the case when bulky molecules are involved in the reaction. Moreover if micropores are in the way of a wider pore inner volume the access to other wider pores is also restricted.

Stabilization of the tetragonal phase seems to be another important issue because oxoanion promoted monoclinic zirconia is catalytically less active for many acid-catalyzed reactions, like *n*-butane isomerization and dehydration of 2 octanol [4,7]. Completely amorphous catalysts are also inactive. Additional

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* Corresponding author.
E-mail address: cvera@fiq.unl.edu.ar (C.R. Vera).

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textural improvements in oxoanion promoted zirconia catalysts could be obtained by adopting different synthesis methods for the zirconia gel. Some encouraging results have been found for tungsten-zirconia and sulfated zirconia obtained by the promotion of zirconia aerogels. These aerogels have a very high initial surface that is produced by supercritical drying [8–10]. Mesoporous zirconias produced by cogellation with molecular templates have also been produced [11,12] but their structure is brittle and collapses during calcination at relatively low temperatures. Additional stabilization of the gel pore structure could also be achieved by incorporating surface or bulk dopants into sulfate or tungsten-zirconia. In many cases when a marked enhancement of the sintering resistance or the microporosity are obtained this is in detriment of the catalytic activity, as it happens with silica addition [13–15]. New methods of improving the textural properties should be found that do not affect the catalytic properties of oxoanion promoted zirconia catalysts [16,17]. These should produce a greater noticeable increase in surface area, sintering resistance and tetragonal/monoclinic ratio beyond that produced by the surface oxoanion promoter itself. In this work we report our results on the use of hydrothermally aged zirconia for the preparation of SO_4^{2-}-ZrO_2 catalysts. The influence of reflux aging on textural properties and catalytic activity for isomerization of *n*-butane and hydroisomerization-cracking of *n*-octane were assessed.

Hydrothermal aging is a rather old technique for the improvement of the texture of the gel of precipitated hydroxides. Aging is thought to be related to a process of simultaneous dissolution and precipitation which favors the growth of “neck structures” in the gel network. During the process the support dissolves from regions of positive curvature and redeposits at regions of negative curvature reinforcing the hydrogel network [18]. This lattice refining removes brittle structures and a more homogeneous network is produced. SEM images of materials aged in aqueous medium or in molten salt baths reveal a “cheese” like structure [19]. Our study is concentrated on zirconia gels reflux aged at strong basic pH values because in this condition the stabilization of the tetragonal active phase seems to be complete and sintering resistance is very high [20].

2. Experimental

2.1. Catalyst preparation

2.1.1. Zirconia gels

Reflux aged $Zr(OH)_4$ was prepared from $ZrOCl_2{\cdot}8H_2O$ (Strem Chem., 99.9985%). A solution of the salt (0.4 M in Zr^{4+}) was allowed to drip over an ammonia solution (5 M NH_4OH, with a volume of 2 times that of the dripping solution) and under constant stirring. The freshly precipitated gel was gently refluxed for 120 h at about 100 °C in a rotating Büchi evaporator heated by an oil bath. Successive cycles of decantation-washing (15–20) were then performed. They were considered enough for the elimination of the ammonium and chloride ions. Then the gel was filtered and dried at 110 °C overnight (sample Z^{AG}). For another batch of zirconia reflux aging was eliminated and the gel was only kept overnight at room temperature. After washing, filtering and drying, a reference non-aged batch of zirconia was obtained (sample Z). The portion of these solids (Z^{AG} and Z) were fired at three different temperatures (500, 600 and 800 °C) in static air in a muffle oven.

2.1.2. Sulfated catalysts

They were prepared by wet impregnation. The dried samples (Z, Z^{AG}, dried at 110 °C) were dipped in a 1N H_2SO_4 solution for 2 h ($10\ ml\ g^{-1}$). After sulfation all catalysts (SZ and SZ^{AG}) were calcined at 500 °C, 600 °C and 800 °C for 3 h in static air in a muffle oven.

2.1.3. Pt/SO_4^{2-}–ZrO_2 catalysts

The sulfated zirconia gels, either aged or non-aged, were impregnated with an aqueous solution of chloroplatinic acid (Strem Chem., 99.9%) using the incipient wetness technique (addition of a volume of solution equal to the catalyst pore volume). The time of impregnation was 6 h. The samples were then dried at 110° overnight and calcined at 500 °C in flowing air for 2 h. The volume and concentration of the impregnating solution were adjusted to get a 1% Pt in the final catalyst (Pt/SZ and Pt/SZ^{AG}).

2.2. Catalyst characterization

2.2.1. Sulfur content

It was measured in a LECO CS444 carbon and sulfur analyzer using direct combustion and infrared detection.

2.2.2. Platinum content

It was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after digesting the samples.

2.2.3. X-ray diffraction measurements (XRD)

The XRD measurements were performed in a Shimadzu XD-1 diffractometer with Cu Kα radiation filtered with Ni. Spectra were recorded in the 20–65° 2Θ range and scanned at a rate of $1.2°\ min^{-1}$.

2.2.4. Textural properties

They were measured in a Belsorp 28 SA nitrogen adsorption apparatus. The specific surface area (Sg) was measured by the BET method and the pore distribution by the D–H (Dollimore and Heal) method.

2.2.5. Raman

Laser Raman spectra were recorded in a Spectramax equipment having a NEC Ar ion laser (514.5 nm) and operating with a laser power of 40–50 mW. The detector was a CCD Yobin Yvon HR320 with a Hg baseline of $1122.74\ cm^{-1}$ and a slit of 25 μm.

2.2.6. Temperature-programmed reduction (TPR)

Tests were performed in an Ohkura TP2002 S apparatus equipped with a thermal conductivity detector. The samples were heated from room temperature to 750 °C at $10\ °C\ min^{-1}$ in a reducing gas stream (5% H_2 in Ar, of $45\ ml\ min^{-1}$).

2.2.7. Temperature-programmed oxidation (TPO)

Tests were carried out in an apparatus with intermediate methanation and with detection by flame ionization (FID). The catalyst sample was heated from room temperature to 700 °C at $12\ °C\ min^{-1}$ in an oxidizing gas stream ($30\ ml\ min^{-1}$, 2.3% O_2 in N_2).

2.2.8. Temperature-programmed desorption (TPD) of probe molecules

Acidity was measured by adsorption of pyridine. The adsorption was performed in a glass equipment. The adsorbed amount was assessed by light absorption in the infrared region (1400–1600 cm^{-1} range). The measurements were performed in a Nicolet Avatar 360 FT-IR spectrometer. Self supported circular wafers (2 cm diameter, 50 mg) of the catalysts were used and they were vacuum treated in a cell with NaCl windows. Residual pressure was less than 1 mTorr. Additional experiments of temperature programmed desorption of pyridine were also performed. 200 mg of the catalyst were first immersed in a closed vial