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Effect of the doping agent nature on the characteristic and catalytic properties of aerogel zirconia catalysts doped with sulfate groups or heteropolytungstic acid

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ABSTRACT

Zirconia catalysts doped with sulfates or heteropolytungstic acid (HPW) prepared by sol–gel method and dried in supercritical conditions of solvent have been evaluated in *n*-hexane isomerization in the temperature range 150–220 °C. Using HPW as dopant, the obtained catalyst is active at 220 °C and selective towards isomers having higher Individual Octane Number, i.e., 2,2-DMB and 2,3-DMB compared with using sulfates as dopant. Based on N2-physisorption, XRD, SEM and TEM analyses, low specific area, particular morphology of grains and the lack of tetragonal ZrO_2 particles reduce the adsorption of *n*-hexane reactant and led to inefficient catalyst throughout the temperature range 150–200 °C. The catalyst doped with sulfur deactivates at $T > 200$ °C since agglomerates of zirconia particles (TEM and SEM results) favor the coke formation. Using HPW, agglomerates of W oxide as well as phosphate groups (revealed by TGA, FTIR, EDX and UV/visible DRS) favor the formation of more valuable isomers at 220 °C.

1. Introduction

There is increasing interest in the environmental protection, which encourage the automobile and petrol industries to develop new catalysts and efficient processes for clean fuel production. Isomerization of linear hydrocarbons to branched ones is a good alternative to improve the quality of fuels [1] by increasing their Run Octane Number (RON) [2,3]. The *n*-hexane isomerization into different branched isomers, e.g., 2,2-dimethylbutane (2,2-DMB), 2,3-dimethylbutane (2,3-DMB) and 2-methylpentane (2-MP) has been extensively investigated in the Laboratory of Materials Chemistry and Catalysis (Laboratoire de Chimie des Matériaux et Catalyse (LCMC)). Catalysts involved are acidic ones, e.g., zirconia doped with sulfate groups and transition metals such as nickel, cerium and chromium [4–9]. Such catalysts have been prepared by sol–gel method and dried either in supercritical condition of solvents or in ordinary condition [4–9] since sol–gel route offers a better control of the homogeneity of the prepared solids as regards to other methods [10–12]. For zirconia based catalysts, the sol–gel method offered the opportunity to introduce in one step zirconium alkoxide, metal precursor and sulfate groups as dopant in order to assure the homogeneity and to control morphological and textural properties of the final materials [13,14].The obtained results showed that aerogels manifest developed textural properties as well as higher acidity. On the other hand, the reactivity of sol–gel derived zirconia depended on several parameters such as the preparation method, the alcogel drying mode and the doping agents (sulfates, tungstates,..) which generates an acidity required in *n*-hexane isomerization [15–18,9].

Though zirconia aerogels doped with sulfate groups are known as suitable for *n*-hexane isomerization, and as such are not definitely commercialized, it would be interesting, at least from the scientific viewpoint, to investigate other dopant agents, e.g., heteropolytungstic acid (HPW) in order to enrich reaction products with isomers having higher Individual Octane Number. Table 1 represents the Research Octane Number (RON) of *n*-hexane as well as each produced isomers [19–21].

In Table 1, it is seen that 2,2-DMB and 2,3-DMB are desired products while 2-MP, having the lower ION, should be avoided.

HPW are reported as efficient dopant in many catalyst formulations and several investigations focused in the isomerization of *n*-pentane and *n*-hexane [22–28]. In this study, we choose to investigate *n*-hexane isomerization in the presence of aerogel zirconia modified either with HPW or sulfates, and follow the contribution of each dopant in the improvement of catalytic

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Table 1
Research octane number (RON) values of reactant and different reaction products (of Ref. [19–21]).

Compound	RON
n-hexane	26
2,2-DMB	93
2,3-DMB	95
2-MP	73

2,2-DMB 2,2-dimethylbutane; 2,3-DMB 2,3-dimethylbutane; 2-MP 2-methylpentane

properties in term of the selectivity toward 2,2-DMB and 2,3-DMB. Different characterization techniques have been employed in order to study the physicochemical properties of the prepared solids. Textural study has been performed by N_2 physisorption at −196 °C, while the stability of materials has been studied by thermal analyses (TGA/TDA). Structural properties have been studied using X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), while the morphology has been evaluated by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). UV/visible Diffuse Reflectance Spectroscopy (UV/visible DRS) has been employed to study the electronic transitions of metals throughout the different catalysts, while the acidity has been evaluated using catalytic isopropanol dehydration.

2. Experimental

2.1. Catalysts preparation

The aerogel sulfated zirconia catalyst was prepared as follows: zirconium (IV) propoxide precursor (Aldrich, 70% in propanol) was dissolved in 1-propanol (Aldrich 99.7%) to order to obtain $[Zr^{4+}] = 1$ M. The solution was maintained under stirring for 1 h at ambient temperature before adding concentrated sulfuric acid (molar ratio $S/Zr = 0.5$). To form the alcogel, the hydrolysis has been performed by adding (dropwise) distilled water (molar ratio $H_2O/Zr = 3$). Once the gel is formed, it is dried in an autoclave under supercritical conditions of 1-propanol ($T = 263.6$ °C, $P = 51$ bar). The obtained aerogel is stored as AZrS, where A stands to Aerogel, Zr is Zirconia and S is the Sulfate dopant. The same way was used to prepare zirconia doped heteropolytungstic acid (HPW) with the same content of dopant and hydrolysis ratio. The obtained solid was denoted as AZrH, where H stands to HPW.

AZrS500 and AZrH500 catalysts were respectively obtained after calcinations of AZrS and AZrH solids under oxygen stream ($30\,cm^3$/min, 1 °C/min) for 3 h at 500 °C.

2.2. Catalysts characterization

N_2 adsorption–desorption at −196 °C were performed with a Micromeritics ASAP 2020 apparatus after outgassing the solids at 200 °C for 3 h. Specific surface area was determined by BET method, microporous volume by *t*-plot method and porous volume is the volume adsorbed at $P/P^\circ = 0.98$. XRD measurements were performed on an X'Pert Pro X-ray diffractometer from PANalytical with CuKα radiation ($\lambda = 1.54060$ Å), generator setting of 40 kV and 40 mA, a scanning speed of 0.05°/min, and a scanning region of 2–70°. The diffractometer was operated at 1.0° diverging and 0.1° receiving slits and a continuous intensity trace was recorded as function of 2θ. Structural data identification was performed using EVA software. TGA and TDA analyses have been performed using a Labsys Evo Thermogravimetric analyzer from Setaram. The thermal treatment was performed under constant air flow ($30\,cm^3$/min) from ambient temperature for up to 1000 °C (10 °C/min). FTIR spectroscopy analysis was performed in the spectral range 400–4000 cm^{-1} using a PerkinElmer XT spectrophotometer, a spectral resolution of 4 cm^{-1} and accumulating 200 scans. The catalyst was mixed with KBr and pressed to obtain a pellet. SEM images were obtained with a Cambridge Instruments Stereoscan 120 at an accelerating voltage of 10 kV. UV/Visible DRS spectra were recorded at room temperature in the range 900–200 nm on a PerkinElmer Lambda 45 spectrophotometer equipped with a diffuse reflectance attachment and $BaSO_4$ as reference material. The DR spectra were converted to the Kubelka–Munk function in order to convert reflectance data into pseudo absorbance. TEM measurements were performed in a JEOL JEM-2000 FX Electron Microscope (200 kV) with an Energy Dispersive X-ray (EDX) Spectroscopy. The catalyst samples were suspended and dispersed by ultrasonic treatment in acetone. A drop of the fine suspension was placed on a copper TEM grid, which was then loaded into the microscope.

The relative acidity of the catalysts was evaluated using the 2-propanol dehydration reaction between 150 °C and 250 °C. Mixture of nitrogen and isopropanol ($P = 20$ Torr) was conducted in a continuous down–low fixed–bed reactor over 100 mg of catalyst. The inlet rate into the reactor was 25 cm^3/min and the gas products were supplied automatically to Alpha M.OOS PR2100 gas chromatography equipped with a HP–innowax column and analyzed by a Flame Ionization Detector (FID). *n*-hexane isomerization was carried out over mechanical mixtures obtained by grinding together during 10 min, an equal weight (100 mg) of the synthesized samples and Pt/Al_2O_3 (0.35 wt.% Pt). Promotion with platinum [29] or other transition metals [30] increases the stability of the catalyst towards deactivation and improves the selectivity towards di-branched isomers according to a metal–acid bifunctional mechanism. Prior the use, Pt/Al_2O_3 was reduced at 400 °C for 5 h under H_2. The mixture (Pt/Al_2O_3 + a synthesized sample) was pretreated under He flow at 150 °C for 30 min then exposed to *n*-hexane stream (20 Torr) diluted with hydrogen (total flow rate: 30 cm^3/min). The hydrogen saturated with *n*-hexane at 0 °C was passed over the catalyst and the results were collected after 5 min. Reaction products were analyzed by online gas chromatography using FID and a 4-m 1/8″ column packed with 10% squalane in Spherosil. The temperature of column was fixed at 70 °C and those of injector and detector are both fixed at 110 °C. Catalytic results were expressed as follows:

$$\text{Selectivity towards the product(i)} : S_i(\%) = \frac{n_i y_i}{\Sigma_i} n_i y_i \times 100$$

where y_i is the mole fraction of product, n_i is the number of carbon atoms in each molecule of reaction product.

3. Results and discussions

3.1. Textural properties

N_2 adsorption–desorption isotherms of AZrS and AZrH solids are presented in Fig. 1(A (a) and (b)).

AZrS solid shows a combination of type II and type IV isotherms, characteristic of a mesoporous material (Fig. 1A (a)), with a H3 hysteresis loop which corresponds to particles with sheet structure [31]. However, the catalyst doped with heteropolytungstic acid manifests the superposition of type I and type II isotherms, according to Brunauer et al. as well as IUPAC classification [32,33], and a small hysteresis (Fig. 1A (b)). Textural properties of prepared solids are shown in Table 1. The pore size distribution curves obtained by BJH method from adsorption branch are presented in Fig. 1(B (a) and (b)).