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Impact of dopant metal ions in the framework of parent zirconia on the *n*-heptane isomerization activity of the Pt/WO_3-ZrO_2 catalysts

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ABSTRACT

Selected Pt/WO_3-ZrO_2 catalysts, promoted by Al, Si and Fe metal ions and isomorphously substituted into the zirconia framework, were studied and compared with their undoped equivalents as catalysts for C_7 isomerization. They were characterized by XRD, UV–vis and TPD-TPR techniques. A mechanism was proposed for the positive dopant effect on the catalyst activity.

1. Introduction

Zirconia-based materials represent a promising and intensively studied subject because of their specific electronic structure and acidic properties [1–6]. They have broad applications ranging from high-temperature ceramics [7] to sensor technology [8]. Doped zirconia has been successfully used as a solid electrolyte in fuel-cells [9], as a modern luminescent material [10], and/or as a thin-layer substrate in semiconductor devices [11,12]. Heterogeneous catalysis is an important area of application for zirconia-based materials. Since Hino and Arata [13,14] discovered WO_3-ZrO_2 as a strongly acidic material that isomerizes *n*-paraffins, a large amount of research has been devoted to the analysis of this solid material. Classical preparation routes typically start from amorphous $Zr(OH)_4$, which is further impregnated with tungstate or other metal precursors, and finally calcined at high temperatures (700–800 °C). This results in the formation of strongly acidic materials [15,16] with varying crystallinity and various types of WO_x species, depending on the calcination conditions. Platinum is usually introduced during the final stage of the catalyst preparation. Pt is generally thought to play a role in the dissociation of molecular hydrogen present in the feed and/or in the hydrogenation of olefinic intermediates. A large number of studies have been devoted to the analysis of changes in the zirconia surface during the above high-temperature calcination step. During high-temperature calcination, the surface area decreases as individual crystal phases are formed, in both monoclinic and tetragonal zirconia structures. There have been numerous studies on the use of metal ions and/or other modifiers in the zirconia framework, and the effect of such modifiers is mostly associated with surface stabilization [17]. Several examples have been reported, of the modification of WO_3-ZrO_2 catalyst in different stages of its preparation, by doping with various metals and/or metal ions, e.g., Al [18–20], Fe [21], Mn [22], Ga, In [23] or Cr ions, and/or a combination thereof [24–30].

This work was performed to study the influence of addition of dopant ions on the properties of the Pt/WO_3-ZrO_2 catalyst used for isomerization of *n*-heptane. This study focuses on the impact of the dopant on the structure of zirconia, i.e., on the formation of individual crystal phases and their surface properties, including surface area, acidity and formation of WO_x species during calcination of the material. Further, an attempt is made to elucidate the relationships among these characteristics and their relevance for the catalytic activity in *n*-heptane isomerization.

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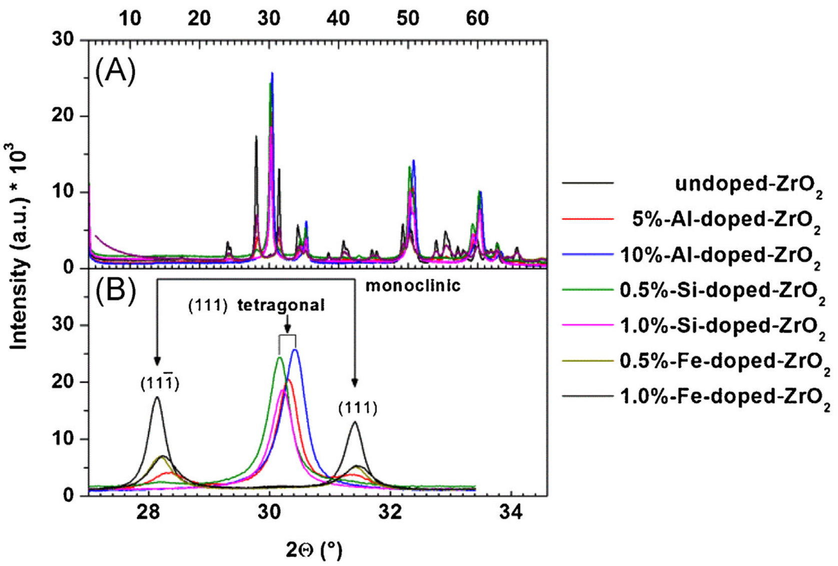

Fig. 1. (A) The diffractograms of parent zirconia materials, undoped and doped with Al, Si, Fe ions (calcined at 700 °C for 3 h in an air stream, i.e., ZrO_2 phases); and (B) These diffractograms in detail, in the range 27–33.4°. The tetragonal (~30.3°) and monoclinic (~28.2°, 31.5°) reflections used for phase evaluation are indicated here.

Table 1
The N_2-BET surface area of undoped and dopant-modified ZrO_2 samples (calcined at 700 °C) and their crystal phases.

Dopant Modification	WO_3 (wt.%)	Monoclinic/Tetragonal Phases	Surface Area (m^2/g) 700 °C
Pure zirconia	0	0.93/0.07	14.8
Pure zirconia	18	0.10/0.90	63.3
5 mol% Al	18	0.37/0.63	38.0
10 mol% Al	18	0.16/0.84	44.0
0.5 mol% Si	18	0.18/0.82	54.4
1.0 mol% Si	18	0.13/0.87	51.3
0.5 mol% Fe	18	0.90/0.10	28.0
1.0 mol% Fe	18	0.90/0.10	41.0

2. Experimental

2.1. Materials preparation

The pure, undoped parent $Zr(OH)_4$ was prepared by precipitation of a $ZrOCl_2{\cdot}8H_2O$ solution by ammonia as follows: the aqueous $ZrOCl_2{\cdot}8H_2O$ solution (4.5 g $ZrOCl_2{\cdot}8H_2O$ in 50 ml H_2O) was precipitated by direct drop-wise addition of concentrated ammonia to pH ~ 10 under vigorous stirring. The product was then filtered, washed and dried at 105 °C.

A similar procedure was used for the preparation of metal-doped hydrous zirconium hydroxides Me/$Zr(OH)_4$; an aqueous $ZrOCl_2{\cdot}8H_2O$ solution containing the appropriate amount of dopant metal ions was precipitated by drop-wise addition of concentrated ammonia up to pH ~ 10. Thus, e.g., 0.25 g of $Al(NO_3)_3{\cdot}9H_2O$ was added to the initial $ZrOCl_2{\cdot}8H_2O$ solution for preparation of 5%-Al-doped-ZrO_2; or 0.1 g of ~36 wt.% solution of $NaSiO_3/H_2O$ was used for preparation of 0.5%-Si-doped-ZrO_2; while 30.6 mg of $Fe_2(SO_4)_3{\cdot}5H_2O$ was used for preparation of 0.5%-Fe-doped-ZrO_2. All other conditions and procedures were similar to those described above for the preparation of pure $Zr(OH)_4$ samples.

The WO_3-ZrO_2 materials were prepared by impregnation of the obtained $Zr(OH)_4$ samples with the required amount of aqueous solution of $(NH_4)_6H_2W_{12}O_{40}$ (Fluka) to achieve 18 wt.% WO_3 in the final WO_3-ZrO_2 (calculated with respect to the initial parent material, regardless of the dopant concentration and/or mass loss during the calcinations). The products were separated by filtration, washed and dried overnight at 105 °C, and finally calcined in a flow of dry air (heating rate 0.7 °C min^{-1}) at a temperature of 700 °C for 3 h. Pt was introduced into the calcined solids prior to the catalytic reaction, via impregnation by a H_2PtCl_6 solution to yield 1.0 wt.% of Pt in the target material.

2.2. Materials characterizations

XRD diffractograms of the prepared solids were recorded on an Xcalibur PX enhanced diffractometer (Oxford Diffraction, U.K.) using CuKα radiation with wavelength 1.54 Å in the 2θ range 4–70° with a step of 0.0167°. The results were evaluated using XPERT-PRO instrument software.

The BET specific surface area was determined from the N_2 adsorption isotherms measured at 77 K (at liquid N_2 temperature) on an ASAP 2010 apparatus (Micromeretics, U.S.A.).

Temperature-programmed reduction by hydrogen (H_2-TPR) was performed on an AMI-200 apparatus (Altamira Instruments, Inc., U.S.A.). The samples (typically 100 mg) were first treated in a U-shaped quartz reactor in a stream of synthetic air at 450 °C for 3 h and then cooled to room temperature. The H_2-TPR experiment was then performed in the same reactor in a mixture of hydrogen (9.44 vol.%) in argon, at a flow rate of 30 cm^3 min^{-1} and with a temperature increase of 10 °C min^{-1}. TCD was used as a detector of H_2-consumption. The quantitative analysis was performed using peak areas, where calibration was performed by the H_2 pulse technique with 5 pulses.

The acidity of the prepared solids was monitored by temperature-programmed desorption of ammonia (NH_3-TPD) using the same apparatus (AMI-200, Altamira Instruments, Inc., U.S.A.). The samples (again typically 100 mg) were first pre-treated in hydrogen at 250 °C for 1 h, followed by ammonia adsorption at 100 °C from a stream of 3.95 vol.% ammonia in helium.