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Hydrogenation of synthetic PYGAS—Effects of zirconia on Pd/Al_2O_3

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Abstract

Pd-based catalysts supported on ZrO_2 and $xZrO_2/Al_2O_3$ ($x = 0$, 10 and 20 wt.%) were prepared and characterized by X-ray diffraction, diffuse reflectance spectroscopy, temperature programmed reduction and chemisorption of H_2. Catalysts were evaluated via hydrogenation of a model mixture representative of pyrolysis gasoline, containing styrene, 1,7-octadiene, 1-octene and dicyclopentadiene in a batch reactor operated at 30 bar and 60 °C. The Pd/Al_2O_3 catalyst presented the higher metallic dispersion and hydrogenation activity. In spite of the occurrence of reduction at high temperatures and no H_2 consumption at room temperature, the catalyst Pd/ZrO_2 presented the lowest dispersion, ascribed to the weak Pd–ZrO_2 interaction. The initial hydrogenation rate of styrene was the highest as compared to that of other components. The results suggest that hydrogenation of 1,7-octadiene to octane occurs via series reaction, with 1-octene as intermediate.

Keywords: Pyrolysis gasoline hydrogenation; Pd; ZrO_2

1. Introduction

Pyrolysis gasoline (PYGAS) is a typical sub-product of high temperature naphtha pyrolysis [1,2]. PYGAS is unstable due to the presence of unsaturated compounds, such as mono and di-olefins, in addition to styrene, that are gum agents. The classical process to stabilize PYGAS is via catalytic hydrogenation of these reactive species, developed in two steps [2]. In the first step, the selective hydrogenation of mono-olefins, di-olefins and styrene is carried out, using Pd or nickel catalysts supported on alumina (Al_2O_3) and mild temperature and pressure conditions [3]. The second step occurs over catalysts like cobalt molybdate supported on Al_2O_3 in order to remove sulfur and additional olefins hydrogenation using more severe conditions [4]. According to new environmental regulations in order to reduce the content of aromatic hydrocarbons in gasoline, recently, the hydrodearomatization of pyrolysis gasoline has received great attention [5,6].

Styrene hydrogenation in particular has been studied with Pd and Ni catalysts using mild conditions [2,7–13]. This process has been used as model reaction to represent PYGAS hydrogenation because it is one of the less reactive components to be hydrogenated [7]. According to Nijhuis et al. [7], the reaction initially proceeds via a zero order in styrene and changes to a first order when complete conversion is being approached for Pd/Al_2O_3 catalysts, as predicted by the Langmuir–Hinshelwood kinetic model.

In the last years, zirconium oxide has been largely used as support in catalysts for many reactions, such as hydrocarbons hydrogenation, methanation and methane reforming [14–16]. The specific behavior of zirconia (ZrO_2) in these reactions is ascribed to its high thermal stability, presence of acid and basic surface sites and oxygen storage capacity. However, ZrO_2 has low surface area, typically about 50 m^2/g, comparing unfavorably with other conventional supports, such as Al_2O_3 and SiO_2 (100–600 m^2/g), and is more expensive. Thus, the dispersion of ZrO_2 over such oxides is an attractive option, allowing obtaining the properties of ZrO_2 with high surface area and mechanical stability of Al_2O_3 or silica [17].

Preparation and characterization of ZrO_2/Al_2O_3 systems have been studied [18–20]. Damyanova et al. [18] reported that the monolayer of ZrO_2 over Al_2O_3 is formed in the range 13–17 wt.% ZrO_2, resulting supports with the following textural

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properties: $S_{BET} \sim 180\ m^2/g$ and pore volume $\sim 0.50\ cm^3/g$. However, few works have reported the use of ZrO_2/Al_2O_3 systems to support metallic particles. Dealing with Pd catalysts, there are not results in the opened literature. Souza et al. [21–23] prepared $Pt/ZrO_2/Al_2O_3$ catalysts with 1–20 wt.% ZrO_2 and observed that surface coverage of ZrO_2 on Al_2O_3 increased up to 10 wt.% of ZrO_2, falling above this concentration, due to the nucleation of ZrO_2 crystallites. The introduction of ZrO_2 in the Al_2O_3 surface occurs due to the formation of Zr–O–Al bonds, which strength decrease with the ZrO_2 content. The stronger Lewis acid sites decrease comparing to the weak ones when increasing the ZrO_2 content. The low acidic character of ZrO_2 increases the activity to dehydration and dehydrogenation reactions due to the reduction of cracking and coking side reactions [15,18,19].

Pd/ZrO_2 catalysts have been used in hydrogenation reactions, although few studies have been reported. Shen et al. [24] compared Pd catalysts in different supports in the CO hydrogenation. The activity and selectivity were distinct, depending on the supports characteristics. Higher CO conversions over Pd/ZrO_2 were ascribed to the presence of cationic Pd species formed through the metal–support interaction. In other study [16], the Pd/ZrO_2 system showed higher activity in the hydrogenation of phenol than other supports (MgO or Al_2O_3).

No references were found on the use of Pd/ZrO_2 catalysts for hydrogenation of styrene or PYGAS. The aim of this work was the development of Pd catalysts supported on ZrO_2/Al_2O_3, with different ZrO_2 loadings. These catalysts were tested in the hydrogenation of a mixture representative of PYGAS, containing styrene, 1,7-octadiene, 1-octene and dicyclopentadiene. The influence of reaction parameters (pressure and temperature) was evaluated.

2. Experimental

2.1. Preparation of supports and catalysts

Supports based on ZrO_2/Al_2O_3 were prepared in a rotatory evaporator by wet impregnation of an aqueous solution of zirconium acetate hydroxide ($Zr(C_2H_3O_2)_{1.4}(OH)_{2.6}$, Aldrich) and γ-Al_2O_3, considering 15 cm^3 of solution per gram of support, followed by calcination under dry air flow at 550 °C for 4 h. Supports presented 10 and 20 wt.% ZrO_2.

Zirconium oxide was prepared by addition of a 10% zirconium acetate hydroxide solution to a 5 M NH_4OH solution with pH control [25]. After digestion for 72 h at 90 °C, the precipitate was filtered, washed and calcined at 500 °C for 12 h (1 °C/min) with dry air flow.

Catalysts were prepared by dry impregnation with an aqueous solution of $PdCl_2$ (Acros) on γ-Al_2O_3 (Engelhard), ZrO_2, 10 wt.% ZrO_2/Al_2O_3 and 20 wt.% ZrO_2/Al_2O_3, yielding 1 wt.% Pd. After impregnation, the catalysts were dried at 120 °C for 16 h and calcined under dry air flow at 550 °C for 1 h.

2.2. Characterization

The elemental analysis of zirconium in the ZrO_2/Al_2O_3 supports and Pd in the catalysts was performed by X-ray fluorescence (XRF), using a Rigaku RIX 3100 equipment.

Specific surface areas (S) and pore volume (PV), calculated as 4 V/S_{BET}, were measured with a Micromeritcs Model ASAP 2000 equipment, using N_2 at -196 °C. Samples were outgassed for 18 h at 300 °C before the measurement of N_2 adsorption.

X-ray diffraction (XRD) measurements were carried out with the calcined samples and supports, using a Rigaku Miniflex diffractometer (voltage: 30 kV and current: 15 mA), equipped with a copper tube ($\lambda = 1.5405$ Å) and a graphite monochromator, operated in the step-scan mode 0.05° 2θ per step and counting for 2 s per step.

Diffuse reflectance spectroscopy (DRS) analyses were done on a Varian Cary 5 UV–vis–NIR spectrophotometer equipped with a Praying Mantis diffuse reflection device (Harrick^{TM}). Spectra were taken with the calcined catalysts, in the range of 200–800 nm. Supports were used as references.

Temperature programmed reduction (TPR) with H_2 used a quartz U-tube reactor with an on line thermal conductivity detector (TCD). Catalysts (0.5 g) were dried at 150 °C for 1 h under argon flow (AGA, 99.99%) and reduced with 1.6% H_2/Ar flow (30 cm^3/min) from 25 to 500 °C (10 °C/min). After reduction, samples were outgassed under argon flow at 500 °C for 30 min, cooled to 70 °C and then H_2 chemisorption measurements were performed. The amount of irreversible adsorbed H_2 was measured using the frontal method.

2.3. Hydrogenation of a model mixture

Hydrogenation tests were carried out in a batch reactor (Parr Instruments, Inc.) with a volume of 160 cm^3. Before each run, the catalyst (10 mg) was reduced with high purity hydrogen (AGA, 99.9999%) at 30 cm^3/min for 2 h under 130 °C (10 °C/min). After reduction, the reactor was cooled to the designed reaction temperature under H_2. A mixture (100 cm^3) of toluene (82.9% v/v), 1,7-octadiene (6.0% v/v), 1-octene (1.8% v/v), styrene (8.5% v/v) and dicyclopentadiene (DCPD, 0.8% v/v) was transferred to the reactor under inert atmosphere. This mixture was previously prepared and stored with molecular sieve in a refrigerator. Concentrations of mixture components were determined from typical pyrolysis gasoline composition [26]. The stirrer was set to 600 rpm and the pressure was increased by the introduction of H_2 in the reactor. Liquid samples were taken at regular intervals during 3 h and analyzed using a Hewlett-Packard gas chromatograph (HP6890 Plus) equipped with a column HP 1 (60 m) and FID detector.

3. Results and discussion

3.1. Catalysts' characterization

Table 1 shows the textural characterization of supports. Addition of ZrO_2 over Al_2O_3 caused an almost linear reduction on the surface area and pore volume of ZrO_2/Al_2O_3 in