Influence of the Brønsted acidity, SiO$_2$/Al$_2$O$_3$ ratio and Rh–Pd content on the ring opening: Part I. Selective ring opening of decalin

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The influence of the Brønsted acidity, SiO$_2$/Al$_2$O$_3$ ratio and Rh–Pd content on the ring opening of decalin was studied. Rh- and Pd-based monometallic and bimetallic catalysts were prepared by impregnation on three commercial SiO$_2$/Al$_2$O$_3$ supports (SIRAL 5, 20 and 40). The catalysts were characterized by TPD of pyridine, X-ray diffraction, H$_2$ chemisorption, isomerization of 3,3-dimethyl-1-butene (33DM1B) and selective ring opening (SRO) of decalin. It was found that the support acidity is strongly influenced by the SiO$_2$/Al$_2$O$_3$ ratio, the SIRAL 40 being more acid. The metal accessibility has the following order: supported catalysts on SIRAL 40 > SIRAL 20 > SIRAL 5. The incorporation of Rh and/or Pd modifies the conversion and the product distribution on decalin reaction. The support acidity has a strong influence on the conversion and product distribution on the decalin reaction at 350 °C. SIRAL 5 series have low selectivity to RO and high selectivity to dehydrogenated compounds. On the other hand, SIRAL 40 series lead to the highest yield to cracking products of the three studied series. Catalysts with Rh/Pd atomic ratios equal to 2 and monometallic Rh1 supported on SIRAL 40 are the most active and selective catalysts to ring opening products.

1. Introduction

Petroleum refining industry needs more capacity to cope with an increasing demand of high quality fuels, with low aromatic, sulfur and nitrogen content and higher cetane number (CN). CN is the key parameter for diesel fuels to secure a proper combustion quality which leads to a lower level of NOx and particulate matter emissions [1]. The lowering of S and aromatic contents in fuels has been traditionally achieved using well known hydrotreating and hydrocracking technologies [2]. The selective ring opening (SRO) of naphthenic molecules is an alternative route for the valorization of several products resulting from catalytic reforming and cracking processes [3–5], due to the hydrogenation of aromatic compounds followed by a selective opening of the obtained naphthenes to paraffins allowing to improve notably the fuel quality. It is known that normal paraffins increase the CN of fuels [6]. Research works on SRO have mainly dealt with reactions of one-ring molecules despite the fact that two-ring molecules are more

important to diesel chemistry. These are abundant in light cycle oil (LCO), an fluid catalytic cracking (FCC) residue commonly upgraded by hydrotreating in order to contribute to the diesel pool. The SRO of bicyclic naphthenes such as decalin is very important in the processing of LCO; the CN significantly increases when decalin is converted into linear or monobranched paraffins. Two main reaction types occur during the catalytic ring opening (RO) process. A first possible reaction type is the rupture of C—C bonds attached to naphthenic rings, associated with a decreasing in mean molecular weight of products. On the other hand, the main desired reaction, i.e. SRO, does not significantly affect the resulting molecular weight due to the internal nature of C—C ring bonds.

Decalin ring opening reaction can proceed by acid or metal mechanisms as reported in detail by Resasco et al. [7]. On the other hand, Mostad et al. proposed that the decalin cracking is initiated by hydride abstraction [8,9]. The support acidity is particularly important for the opening of compounds having more than one ring, such as decalin [10]. Zeolites are a special kind of useful acid supports for this purpose. Corma et al. studied the conversion of decalin on zeolites of different pore sizes and found that the pore size and channel topology have a strong influence on diffusion and adsorption, and therefore on the product distribution [11]. Zeolites with

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large-sized pores (USY, beta, mordenites) as ring opening catalysts are more selective to RO products as compared to middle pore size ones; consequently, this parameter is very important in RO catalysis [11]. Zeolites of larger pore size, such as HY, are considered as one of the most appropriate supports for ring opening catalysts [12,13]. The zeolite crystal size [14] and the number and strength distribution of the acid sites [11,15] are important parameters for ring opening activity and selectivity. Kubicka et al. [15,16] found an important influence of acidity in the SRO of bicyclic naphthenes, the presence of Brønsted sites is required for ring opening and isomerization. Santikunaporn et al. [17] studied the contraction and ring opening of decalin and tetralin and found that the Pt/HY catalysts are more effective than HY catalysts without metal promoter. The addition of Pt to USY zeolites was also found to greatly increase the rate of isomerization and therefore the formation of ring opening products. For these bifunctional metal–acid catalysts, the formation of ring opening products increases with the proximity between the Pt and the acid sites and also with the increase of the metal/acid ratio [18].

Amorphous silica–alumina (ASA) may replace advantageously zeolites, which often lead to excessive cracking activity, as carriers for bifunctional metal–acid catalysts. ASA supports contain not only silica–alumina mixed phases, but also pure silica and aluminum clusters [19]. They present strong Brønsted acid sites; with strength comparable to that of zeolites but in much lower concentration, which can be adjusted by varying the silica content [20]. It has been widely reported that the SiO_2 increases acidity of silica–alumina support improving catalyst performance particularly for deep hydrodesulfuration (HDS) of diesel fuel [21]. Nassreddine et al. [22,23] demonstrated that ASA supports provide a good ring-opening and contraction selectivity to iridium for tetralin hydroconversion in the presence of sulfur. It was shown that the most active and selective Ir/ASA catalyst for tetralin conversion was the one with 40% of silica in the support, which presents the highest Brønsted acidity.

In this work, the influence of the Brønsted acidity of the support on the selective ring opening of two-ring naphthenic compounds was studied. Mono and bimetallic Pd–Rh catalysts supported on SiO_2–Al_2O_3 with different SiO_2 contents (SiO_2 = 5, 20 and 40 wt%) and different atomic Rh/Pd ratios were used. Decalin was taken as model molecule.

2. Experimental

2.1. Catalysts preparation

Three commercial SiO_2–Al_2O_3 supports provided by Sasol (SIRAL 5, SIRAL 20 and SIRAL 40) were used as support. Previously, they were calcined at 450 °C for 4 h (10 °C min^{-1}, air, 60 cm^3 min^{-1}). Rh and/or Pd were added by a common impregnation method. An aqueous solution of HCl (0.2 mol L^{-1}) was added to the support and the system was left unstirred at room temperature for 1 h. Then an aqueous solution of RhCl$_3$ and/or PdCl$_2$ (Sigma–Aldrich) was added in order to have a 1 wt% of total metal charge. For the bimetallic catalyst, the Rh/Pd atomic ratio was x = 0.5, 1 and 2. The slurry was gently stirred for 1 h at room temperature and then it was put in a thermostated bath at 70 °C until a dry solid was obtained. The drying was completed in a stove at 120 °C overnight. Finally, the samples were calcined in flowing air (60 cm^3 min^{-1}) at 300 °C for 4 h and reduced under flowing H$_2$ (60 cm^3 min^{-1}, 500 °C, 4 h). The monometallic catalysts are named Pd1/Sy or Rh1/Sy, while the bimetallic are named Rx/Sy, where Sy is the support (SIRAL) and y is the weight percentage of SiO_2. In the case of the bimetallic catalysts, R corresponds to the Rh/Pd atomic ratio and x is the value of this ratio.

2.2. Measurement of the Pd and Rh contents

The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) after digestion in an acid solution and dilution.

2.3. Temperature-programmed reduction (TPR)

The tests were performed in an Ohkura TP2002 apparatus equipped with a thermal conductivity detector. At the beginning of each TPR test the catalyst samples were pretreated in situ by heating in air at 400 °C for 1 h. Then they were heated from room temperature to 700 °C at 10 °C min^{-1} in a gas stream of 5.0% hydrogen in argon (molar base).

2.4. X-ray diffraction

The analysis was performed with a Shimadzu XD-D1 diffractometer. Diffraction patterns were recorded using Cu Kα radiation filtered with Ni in the 10–60° range at a scan rate of 2° min^{-1}, operating at 30 kV and 40 mA.

2.5. H$_2$ chemisorption

This technique was used in order to estimate the metallic accessibility of the Pd–Rh bimetallic particles on the surface of the catalyst. The sample (100 mg) was reduced at 500 °C (10 °C min^{-1}, H$_2$ 30 cm^3 min^{-1}) for 1 h. Then argon (30 cm^3 min^{-1}) was made to flow over the sample for 2 h at 500 °C in order to eliminate adsorbed hydrogen. Finally the sample was cooled down to 70 °C in argon and calibrated pulses of H$_2$ were injected into the reactor (HC1). These pulses were sent until the sample was saturated. After flushing the system with argon during 30 min, a second set of pulses was injected (HC2). The difference HC1 − HC2 allows one to estimate the metallic accessibility considering the stoichiometry between a hydrogen atom and a surface Pd or Rh atom (H/Pd and H/Rh) equal to 1.

2.6. Temperature-programmed desorption of pyridine

The amount and strength of the acid sites of the catalysts were assessed by means of temperature programmed desorption of pyridine. An amount of 200 mg of the catalyst to be tested were first immersed in a closed vial containing pure pyridine (Merck, 99.9%) for 4 h. Then the vial was open and excess pyridine was allowed to evaporate in a ventilated hood at room conditions until the surface of the particles was dried. The sample was then loaded into a quartz tube microreactor and supported over a quartz wool plug. A constant flow of nitrogen (40 mL min^{-1}) was made to flow over the sample. A first step of desorption of weakly adsorbed pyridine and stabilization was performed by heating the sample at 110 °C for 1 h. Then the temperature was raised at a rate of 10 °C min^{-1} to a final value of 700 °C. The reactor outlet was directly connected to a flame ionization detector.

2.7. Isomerization of 3,3-dimethyl-1-butene (33DM1B)

The reaction was performed in a microreactor of U shape (length = 20 cm, diameter = 0.6 cm). The feed was generated by passing a nitrogen stream through a saturator contactor containing the liquid reagent and immersed in an ice bath at 0 °C. The catalyst (50 mg) was pretreated in situ by reduction with H$_2$ (60 cm^3 min^{-1}, 450 °C, 1 h). The sample was then cooled in N$_2$ (30 cm^3 min^{-1}) to the reaction temperature, which was changed in order to have small conversion values to avoid secondary reactions. It was fixed at 100, 150 and 200 °C for SIRAL 40, 20 and 5, respectively. Then the feed