Research article

Selective ring opening of decalin on Rh-Pd/SiO$_2$-Al$_2$O$_3$ bifunctional systems: Catalytic performance and deactivation

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ABSTRACT

Ring opening of decalin was studied using Rh-Pd(x) catalysts supported on SiO$_2$-Al$_2$O$_3$, prepared by coimpregnation with a variable total metallic content (x = 1, 1.5 and 2 wt%) while maintaining constant the Rh/Pd atomic ratio (equal to 1). The catalytic performances of these bimetallic systems were compared to those of monometallic Pd and Rh (1 wt%) catalysts. Bimetallic Rh-Pd(x) catalysts were unable to achieve decalin conversion and ring opening selectivity as high as those obtained using the Rh catalyst (~71 and ~67%, respectively, after 6 h reaction time). The principal cause was the reduction of the hydrogenolytic activity and acidity caused by the combination of Pd and Rh. In the case of the bimetallic Rh-Pd(x) samples, an increase in the metal content favored the formation of dehydrogenated products, reduced cracking (by reducing the concentration of strong acid sites) and increased coke deposition during decalin ring opening. Conversely, the Rh catalyst showed less deactivation since its efficient hydrogenolytic character eliminates coke precursors.

1. Introduction

The increase in diesel consumption drives researchers to study the reactions of Selective Ring Opening (SRO) to convert aromatic or naphthenic compounds into linear paraffins, improving the cetane index [1]. The interest to increase the economic value of the Light Cycle Oil (LCO) using SRO is confirmed by the numerous patents referred to the subject [2–9]. The SRO mechanism consists in a saturation of the aromatic rings, followed by isomerization and ring opening reactions, even cracking [10–13]. Ring opening is considered to proceed *via* a direct route (over the metallic sites), or *via* an indirect one where ring contraction products are opened by a bifunctional mechanism. For such a reaction, metallic dispersion and acidity of the catalysts are key parameters affecting their performance. Metals from Group VIII (Rh, Ru, Ir, Pt and Pd) were reported as efficient in terms of activity and selectivity to ring opening when dispersed over acid supports [14–18]. The catalysts used in SRO of decalin and tetralin (model molecules for the LCO) can be classified into: (i) monofunctional solids, mainly zeolites H-Y, H-Beta and H-mordenite [14,19] leading to low yields to ring opening products and high amounts of cracking products, (ii) noble metals on non-acid supports [11,20,21], (iii) bifunctional catalysts characterized by the presence of acid and metal sites. In the latter case, the first publications referred mostly to systems consisting of zeolites

and noble metals such as platinum and iridium [10,14,22–29]. The bifunctional catalysts with noble metals supported on HY zeolite (high acidity) could lead depending on the operation conditions to deactivation by coke formation due to diffusion limitations. For this reason, noble metal catalysts supported on mesoporous oxides were studied [12,30–33].

It has been proposed that the ring opening reaction in presence of bifunctional catalysts begins with the ring contraction from 6 to 5 carbon atoms over acid sites, followed by easier opening of the 5-membered cycle due to the hydrogenolytic activity of the metal [20,34,35]. Selectivity to ring opening and ring contraction products can be tuned according to the ratio between acid and metallic sites, which can be adjusted by varying the nature of the support, the composition of the metallic phase (mono or bimetallic function, metal content and metal particle size) [13]. The importance of acid function on the SRO reaction was reported by several studies [36–38].

In previous works, we reported that the acidity and the Rh/Pd content ratio of Rh-Pd/SiO$_2$-Al$_2$O$_3$ catalysts have a strong influence on the activity and selectivity for the decalin ring opening reaction [39–41]. As the deactivation is a very important factor to be considered in the selection of the best catalysts, we decided to revisit the Rh-Pd catalysts supported on SiO$_2$-Al$_2$O$_3$. The objective of the present study is to evaluate the effect of the metallic and acid functions of Rh-Pd

catalysts supported on SiO_2-Al_2O_3 on both their performances for the selective ring opening of decalin and their resistance to deactivation process. It is important to note that these types of bifunctional catalysts are proposed as a replacement of noble metals supported on zeolites, since these last suffer from excessive cracking and deactivation. Moreover, Taillades-Jacquin et al. reported the use of Rh-Pd catalysts supported on mesoporous aluminosilicate in industrial processes aiming to improve diesel quality by hydrogenation and ring-opening of aromatic components and to increase the thioresistance [31].

2. Experimental

2.1. Catalyst preparation

Commercial SiO_2-Al_2O_3 supplied by SASOL (SIRAL 60 noted S60 containing 57.4 and 42.6 wt% of SiO_2 and Al_2O_3, respectively) with a specific surface area of $489 \, m^2 \, g^{-1}$ was used as support. The calcined support (4 h, 450 °C, air, $60 \, cm^3 \, min^{-1}$) was left for 1 h in HCl solution ($0.2 \, mol \, L^{-1}$) before impregnation, the added solution volume being of $1.5 \, cm^3 \, g_{cat}^{-1}$. The necessary amounts of $PdCl_2$ and $RhCl_3$ precursor salts were added to synthesize the Pd/S60 and Rh/S60 monometallic catalysts containing both 1 wt% metal content, and three Rh-Pd/S60 bimetallic catalysts with 1, 1.5 and 2 wt% as total metal content, keeping a constant Rh/Pd atomic ratio equal to 1. The suspension was gently agitated for 1 h, and then dried at 70 °C until a dry powder was obtained. The catalysts were further dried at 120 °C overnight. Finally, they were calcined (air, $60 \, cm^3 \, min^{-1}$, 300 °C, 4 h) and reduced (H_2, $60 \, cm^3 \, min^{-1}$, 500 °C, 4 h). The bimetallic catalysts were named Rh-Pd (x)/S60, x corresponding to the total metal loading (wt%).

2.2. Pyridine temperature programmed desorption (pyridine TPD)

The acidic function of the bifunctional catalysts was characterized by pyridine TPD. 100 mg of catalyst were impregnated at room temperature with an excess of pyridine, and left in a fume hood to obtain a dry powder by evaporation. A quartz reactor was loaded with the powder and the weakly adsorbed pyridine was eliminated by flowing N_2 ($40 \, mL \, min^{-1}$, 110 °C, 1 h). Then, the temperature was increased up to 750 °C at $10 \, °C \, min^{-1}$ while the amount of pyridine at the reactor outlet was measured by gas chromatography equipped with a FID detector.

2.3. Transmission electron microscopy

The morphology of the catalysts was evaluated by transmission electron microscopy (TEM) on a JEOL 2100 instrument, coupled with energy dispersive X-ray spectroscopy (EDX), according to an experimental procedure previously described [40]. By exploitation of the images with the ImageJ software, mean surface diameters ($d = \Sigma(n_i d_i^3)/\Sigma(n_i d_i^2)$) were determined by measuring at least 600 particles for each analyzed sample, and the metal dispersion was calculated considering spherical particles.

2.4. Dynamic CO chemisorption

This technique was used to measure metallic particle dispersion. It was carried out in a dynamic adsorption equipment, by injecting calibrated CO pulses in the presence of a continuous flow of an inert gas over the sample. First, 75 mg of samples previously reduced after their preparation were reduced again under H_2 at 500 °C ($10 \, °C \, min^{-1}$) for 1 h. Then, N_2 was circulated for 1 h at 500 °C to eliminate all traces of adsorbed H_2. Finally, the samples were cooled to room temperature under N_2 and CO pulses of $0.6 \, \mu mol$ were injected with a 2 min frequency until saturation.

2.5. Cyclopentane hydrogenolysis

The model reaction of cyclopentane (CP) hydrogenolysis was used to evaluate the hydrogenolysis activity of the metal function. The reaction was carried out for 2 h in a fixed bed reactor under atmospheric pressure at 225 °C, using 80 mg of catalyst, and following experimental conditions previously reported [33]. Before the reaction the catalyst was reduced at 500 °C during 1 h (H_2, $36 \, cm^3 \, min^{-1}$).

2.6. Cyclohexane dehydrogenation

The metallic function of the catalysts was also characterized by its activity for the cyclohexane (CH) dehydrogenation performed at 270 °C (with 20 mg of catalyst prereduced *in situ*). The experimental protocol used for this model reaction has been previously described [42].

2.7. Decalin ring opening

An autoclave stainless steel reactor was used to carry out the reaction at 350 °C under a total and constant pressure of 3 MPa (H_2 atmosphere), an agitator speed of 1360 rpm, a decalin volume of $25 \, cm^3$ and 1 g of catalyst. Decalin containing 37.5% of the cis isomer was used as reactant. Before decalin reaction, the catalyst was reduced *in situ* under hydrogen (1 h, 350 °C, atmospheric pressure). The initial reaction time was considered when the agitation was turn-on (immediately after the reaction pressure and temperature were achieved). Diffusion limitations due to mass transfer were negligible (calculated Weisz-Prater module $\Phi = 0.06 \ll 1$). At the end of the reaction run (after 6 h), the reactor temperature was cooled down until room temperature and samplings of liquid mixtures were analyzed in a Shimadzu 2014 gas chromatograph with a Phenomenex ZB-5 capillary column and a FID. The gas phase was analyzed revealing a small C_1-C_4 fraction in agreement with the results reported by Kubička et al. [10]. Product identification was performed through GC-MS in a Saturn 2000 mass spectrometer coupled to a Varian 3800 gas chromatograph using the same GC column.

2.8. Differential scanning calorimetry (DSC)

The analysis of the used catalysts (after 6 h of decalin ring opening reaction) was performed on a Mettler Toledo DSC821e Differential Scanning Calorimeter equipment. The coked catalysts (approximately 10 mg) were heated under air flow ($50 \, cm^3 \, min^{-1}$) from 30 °C until 600 °C ($10 \, °C \, min^{-1}$).

2.9. Temperature programmed oxidation (TPO)

The carbon deposited on the used catalysts was analyzed by TPO experiments, according to the experimental protocol described elsewhere [33].

3. Results and discussion

The total acidity and distribution of the acid strength of the mono and bimetallic catalysts supported on S60 were determined by pyridine TPD. The values obtained for each catalyst (and bare S60 support) are gathered in Table 1, as well as the residual chlorine content present on the activated samples. It was previously reported that the total acidity of the support (S60) was $1559 \, \mu mol$ of pyridine per gram of catalyst, the impregnation with $0.2 \, mol \, L^{-1}$ solution of HCl produced an increase of the total acidity up to $1970 \, \mu mol$ of pyridine per gram of catalyst [32]. This fact points out the importance of the presence of chlorine species on the acidity. In a previous work, we found that the total acidity of the alumina is increased almost three times by the chlorine addition [43]. It was stated that the total acidity of the catalysts is increased by the Cl^- species [44] which can be incorporated by the metal precursors or by