



Influence of the support on the selective ring opening of methylcyclohexane and decalin catalyzed by Rh–Pd catalysts



Silvana A. D'Ippolito^a, Catherine Especel^b, Laurence Vivier^b, Stéphane Pronier^b, Florence Epron^b, Carlos L. Pieck^{a,*}

^a Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

^b Université de Poitiers, CNRS UMR 7285, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), 4 rue Michel Brunet, TSA 51106, 86073 Poitiers Cedex 9, France

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ABSTRACT

Rh–Pd catalysts supported on Al₂O₃, SiO₂ and SiO₂–Al₂O₃ (SIRAL 40) were studied for methylcyclohexane (MCH) and decalin ring opening reactions. It was found that the Rh/Pd atomic ratios were similar to the theoretically expected one and the metal dispersion values varied between 30 and 50%. On bimetallic catalysts supported on Al₂O₃ and SiO₂, Pd and Rh were present mainly in the form of monometallic particles, whereas a heterogeneous distribution constituted of large Pd particles and small bimetallic ones were observed on SIRAL 40. Total and Bronsted acidities followed the order: SIRAL 40 » Al₂O₃ > SiO₂. Al₂O₃ supported catalysts were the most suitable for MCH ring opening, while the opening of decalin was favored by using SiO₂–Al₂O₃ (SIRAL 40). The catalysts supported on SiO₂ produced mainly dehydrogenated compounds. The higher total and Bronsted acidities of SIRAL 40 series had a great impact on the opening of bicyclic naphthenes, whereas the metal function of the catalyst and the hydrogenolytic activity of Rh had a major role during MCH reaction. Using bimetallic catalysts in the MCH reaction decreased the formation of cracking and dehydrogenated products, and the selective formation of RO products could be optimized by tuning the working temperature.

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1. Introduction

LCO (Light cycle oil) is a waste stream from the bottom of the fluid catalytic cracking (FCC) unit that is used for heating and is added to heavy fuel to adjust its viscosity [1]. Due to the increasing diesel demand, an interesting application would be to combine the LCO fraction to the diesel pool. However, the LCO characteristics are very different from the diesel fuel specifications. Therefore, the LCO fraction must be subjected to major changes. The content of sulfur and nitrogen can be reduced by conventional hydrotreating [2] and the polycyclic aromatic by hydrogenation to improve the cetane index (CI). However, this improvement is not sufficient and it is necessary to open the naphthenic rings [3,4]. The CI increases considerably when decalin is converted to linear or monobranched paraffins. The selective ring opening (SRO) of naphthenes is a very complex chemistry, largely depending on the operating conditions and characteristics of the catalyst system [5].

The support has a strong influence on the SRO reaction because the interaction with the metallic particles can change their elec-

tronic properties and the presence of acid sites can significantly change the chemistry of the process [6]. The zeolites with larger pore size, such as HY, are considered as among the most suitable supports for this purpose. In general, the use of zeolites of large pore size favors the ring opening reaction, limiting the deactivation due to coke deposits [7–9]. Also the size of the crystal [10], the number and distribution of the strength of Bronsted acid sites [10,11] are important parameters for obtaining ring opening (RO) products. Santana et al. reported in a study devoted to ring opening of decalin and tetralin that Pt/HY is more effective than HY without metallic promoters [12]. Pt in Pt/USY bifunctional catalysts significantly increases the rate of isomerization and thus the formation of ring opening products compared to monofunctional USY catalysts. It has been shown that the addition of Pt to acidic materials reduces the strength of Bronsted acid sites and significantly improves the isomerization and ring opening of decalin [13]. The use of zeolites can lead to non-selective cracking (undesirable side reactions) and pore constraints issue steric impediments [7,12,14,15].

The opening reaction of C₆ naphthenes is enhanced by the use of bifunctional catalysts [16–19]. This can be explained considering that on the acid function of the catalyst takes place contraction of C₆ ring to C₅ one, which is easier to open on the metal function [4,18,19]. Kustov et al. [20] studied Pt, Rh, Ru and Ni catalysts

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.

E-mail address: pieck@fiq.unl.edu.a (C.L. Pieck).

supported on alumina and silica for ring opening (RO) of cyclohexane in conditions close to the industrial ones. It was observed that Rh catalysts have higher activity and inhibit the dehydrogenation reaction as compared to the Pt catalysts. Other authors [13,21] also proposed and studied Rh-based catalysts for the reaction of SRO due to their large hydrogenolytic capacity. Metals such as Pt, Pd, Ir, Ru and Rh supported on Al_2O_3 were observed as active and selective for RO of methylcyclopentane to C_6 paraffins [22,23].

It was reported that the hydrogenolytic activity follows the order: $\text{Pt} < \text{Rh} < \text{Ir} < \text{Ru}$ [24,25]. Over bifunctional catalysts, characterized by the presence of acidic sites and a hydro-dehydrogenating function, the reactions occur via carbenium ions, i.e., β -scission and isomerization. Do et al. [5] pointed out that decalin ring opening is catalyzed both by the acid function through β -scission and by the metal via dicarbene mechanism leading to highly isomerized products.

The research has begun with noble metal catalysts supported on mesoporous silica-based materials [7,26]. In this type of bifunctional catalysts the acid function allows the contraction of the ring, and then the metal sites more easily produce hydrogenolysis of C–C bonds. The silica–alumina mixed phases contain not only silica–alumina, but also pure silica and aluminum groups which exhibit strong Bronsted acid sites with strengths comparable to that of zeolites [27]. The concentration of Bronsted acid sites can be adjusted by varying the silica content [28]. This support is presented as an alternative to zeolites that commonly lead to excessive cracking activity.

In previous works [29,30], we studied the influence of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the Rh–Pd content on the ring opening of methylcyclohexane and decalin using silica–alumina as support. In line with this research, this work studies the influence of the support (Al_2O_3 , SiO_2 and $\text{Al}_2\text{O}_3\text{--SiO}_2$) on the properties of Rh and Pd monometallic and Rh–Pd bimetallic catalysts. The objective is to optimize the metal/acid functions for favoring the selective opening of the rings of methylcyclohexane and decalin.

2. Experimental

2.1. Catalysts preparation

$\gamma\text{-Al}_2\text{O}_3$ (Cyanamid Ketjen CK-300, pore volume = $0.5 \text{ cm}^3 \text{ g}^{-1}$, $\text{Sg} = 180 \text{ m}^2 \text{ g}^{-1}$), SiO_2 (SIL, pore volume = $0.31 \text{ cm}^3 \text{ g}^{-1}$, $\text{Sg} = 130 \text{ m}^2 \text{ g}^{-1}$) and $\text{SiO}_2\text{--Al}_2\text{O}_3$ provided by Sasol (SIRAL 40, 60.7 and 39.3 wt% of Al_2O_3 and SiO_2 , respectively; pore volume = $0.9 \text{ cm}^3 \text{ g}^{-1}$, $\text{Sg} = 514 \text{ m}^2 \text{ g}^{-1}$) were used as support. Previously, they were calcined at 450°C for 4 h ($10^\circ\text{C min}^{-1}$, air, $60 \text{ cm}^3 \text{ min}^{-1}$). Rh and Pd were added by a common coimpregnation 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 total metal charge of 1 wt%. For the bimetallic catalysts, the Rh/Pd atomic ratio was 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. Drying was completed in a stove at 120°C overnight. Finally, the samples were calcined in flowing air ($60 \text{ cm}^3 \text{ min}^{-1}$) at 300°C for 4 h and reduced under flowing H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$, 500°C , 4 h). The monometallic catalysts were named Pd1 or Rh1/support while the bimetallic catalysts were named Rx/support, Rx corresponding to the Rh/Pd atomic 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 of the sample in an acid solution and dilution. Chlorine contents of catalysts in their final state, i.e., after activation, were measured with the Charpentier–Volhard method, in which the sample was dissolved in concentrated sulfuric acid and Cl ions precipitated with silver nitrate solution. Excess silver solution was back titrated with a thiocyanate solution to give the amount of chlorine on the original sample.

2.3. Temperature programmed desorption of pyridine

This test was used for measuring the amount and strength of the acid sites. Samples of 200 mg were impregnated with an excess of pyridine. The samples were then rinsed and the excess of physisorbed pyridine was eliminated by heating the sample in a nitrogen stream at 110°C for 1 h. Then the temperature was raised at a rate of $10^\circ\text{C min}^{-1}$ to a final value of 700°C . To measure the amount of desorbed pyridine, the reactor exhaust was connected to a flame ionization detector. The error associated to the peak position and areas has been determined to be of about 7% [31].

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

The equipment used was described previously [29]. The catalyst (50 mg) was pretreated in situ, by reduction with H_2 ($60 \text{ cm}^3 \text{ min}^{-1}$, 450°C , 1 h). The sample was then cooled in N_2 ($30 \text{ cm}^3 \text{ min}^{-1}$) to the reaction temperature adjusted in order to have small conversion values to avoid secondary reactions. Then the feed from the saturator was injected. The reagent partial pressure and flow rate were 20.9 kPa and 15.2 mmol h^{-1} , respectively. The error associated to the test of 33DM1B isomerization was determined by calculating the variance of the conversion in a set of seven experiments (variance = 6.5%).

2.5. H_2 chemisorption

This technique was used in order to estimate the metallic accessibility of the Pd, Rh and Rh–Pd particles on the surface of the catalyst. The sample (100 mg) was reduced at 500°C ($10^\circ\text{C min}^{-1}$, H_2 $30 \text{ cm}^3 \text{ min}^{-1}$) for 1 h. Then argon ($30 \text{ cm}^3 \text{ min}^{-1}$) 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 Pd or Rh surface atom (H/Pd and H/Rh) equal to 1.

2.6. Transmission electron microscopy (TEM) measurements

TEM measurements were performed on a JEOL 2100 electron microscope operating at 200 kV with a LaB_6 source and equipped with a Gatan ultra scan camera. The powder was ultrasonically dispersed in ethanol, and the suspension was deposited on an aluminum grid coated with a porous carbon film. Average particle sizes were determined by measuring at least 100 particles for each sample analyzed, from at least five different micrographs. The particle size distribution was obtained from TEM pictures calculating the surface average particle diameter from $d = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$. Microanalysis of Pd and Rh was carried out by energy dispersive X-ray spectroscopy (EDX) in the nanoprobe mode.

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