Pt-Mg-Ir/Al$_2$O$_3$ and Pt-Ir/HY zeolite catalysts for SRO of decalin. Influence of Ir content and support acidity

Silvana A. D'Ippolito, Laura B. Gutierrez, Carlos R. Vera, Carlos L. Pieck *

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

ARTICLE INFO

ABSTRACT

Pt-Ir/HY and Pt-Mg-Ir/Al$_2$O$_3$ catalysts were studied and tested in the reaction of ring opening of decalin. The acidity of the alumina support was modified by addition of 3% Mg and the acidity of the zeolite by ion exchange with NH$_4$Cl. The Pt content of the catalysts was fixed at 1% (mass basis) while the Ir content was adjusted between 0.1 and 0.6%. The catalysts were characterized by temperature programmed reduction, temperature programmed desorption of pyridine and FTIR of adsorbed CO. They were further tested with the reactions of cyclohexane dehydrogenation, cyclopentane hydrogenolysis and n-C$_5$ isomerization.

It was found that the Pt-Ir/HY catalyst was substantially more acid than Pt-Mg-Ir/Al$_2$O$_3$. Increasing the Ir content produced an increase of the hydrogenolytic activity and a decrease of the dehydrogenating activity of both catalysts. The n-pentane isomerization reaction results revealed that in the case of the alumina catalyst increasing the Ir content promoted both the catalyst stability and the cracking selectivity to C$_5$ isomers. The opposite was found for the Pt-Ir/HY zeolite catalysts. The zeolite supported Pt-Ir catalysts performed better for decalin ring opening than those supported on alumina. Higher Ir content favored the formation of ring-opening products in all cases.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Selective ring opening (SRO) has been presented as a means of improving the quality of diesel fuel by increasing its cetane number (CN) and decreasing its density. The CN of naphthenic molecules is increased by converting rings into alkyl chains. 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 LCO (light cycle oil), a residual stream from the bottom of the fluid catalytic cracking (FCC) unit, commonly upgraded by hydrotreating in order to contribute to the diesel pool. Even in two-ring molecules the opening of only one ring does not lead to a substantial increase in the CN. Therefore for CN enhancement the opening of the second ring is crucial. Highly selective catalysts are needed for SRO of naphthenes since the cracking of C—C bonds of tertiary carbons should be involved if mainly linear products are to be obtained. Branched products have low CN [1].

Ring opening occurs by hydrogenolysis over certain noble metals [2] but proceeds more effectively on bifunctional catalysts [3]. It has been found that alumina supported metals such as Pt, Pd, Ir, Ru and Rh supported on Al$_2$O$_3$ are active and selective for

ring opening of methylcyclopentane to C$_6$ paraffins [2,4]. McVicker et al. [5] emphasized the high activity and selectivity of Ir/Al$_2$O$_3$ catalysts for the ring opening of alkyl substituted cyclopentanes and bicycle C$_5$ naphthenes. When the acid function of the support is combined with the high hydrogenolytic activity of a noble metal, such as iridium, the resulting bifunctional catalyst is found to have an enhanced performance for SRO of naphthenes to alkanes [5]. The support acidity is essential for the opening of compounds having more than one ring, such as decalin, but not for compounds such as cyclohexane that can be opened using monofunctional metal catalysts [6]. Zeolites are a special kind of useful acid supports for this purpose. In this case the pore size and channel topology have a strong influence on diffusion and adsorption and hence on the final activity and selectivity for ring opening. Corma et al. [7] studied the conversion of decalin on zeolites of different pores sizes. HY, a big pore zeolite, is considered as one of the most appropriate supports for ring opening catalysts [7,8]. The zeolite crystal size [9] and the number and strength distribution of the acid sites [10,11] are important parameters for ring opening activity and selectivity. Kubicka et al. [11,12] determined that the acidity plays a very important roll in the SRO of bicycle naphthenes. Santikunaporn et al. [13] studied the contraction and ring opening of decalin and tetralin and they found that the Pt/HY catalysts are more effective than HY catalysts without metal promoter. The addition of Pt to USY zeolites is also found to greatly increase the rate of isomerization and therefore the formation of ring opening products. For

---

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.
E-mail address: pieck@fiq.unl.edu.ar (C.L. Pieck).

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 [14].

Special classes of SRO catalysts are those based on two or more noble metals, such as Pt and Ir. For these systems the method of deposition of the metal is of crucial importance because a high metal-metal interaction is needed in the final catalyst for getting the desired modulation of the metal function properties.

Whereas classical coimpregnation and successive impregnation techniques lead to an unpredictable deposition of the two metals, other methods have been developed to favor the metal-metal interaction, such as the redox reactions in aqueous phase [15]. In this sense most works on Pt-Ir SRO catalysts focus their attention on catalysts prepared by common impregnation methods. Practically no works deal with SRO catalysts prepared by catalytic reduction. This preparation method has been previously reported to produce a strong interaction between the metals in naphtha reforming bimetallic catalysts [16–18]. A strong Pt–Ir interaction is known to enhance the hydrogenolysis reaction [19]. Pt-Mg-Ir(x)/Al$_2$O$_3$ catalysts prepared by catalytic reduction have been reported to have a strong interaction between Pt and Ir as confirmed by the presence of a Pt–Ir solid phase by electron diffraction [20]. Some patents propose that the addition of Mg has a beneficial effect on the performance of supported metal catalysts [21,22] though there is little information about this effect in the open literature.

The objective of this paper is to study the influence of the content of Ir, a metal with high hydrogenolytic activity, and the support acidity, on the SRO activity and selectivity of supported Pt–Ir catalysts. Decalin is used as a model naphthene molecule while HY zeolite and alumina are used as supports. Their acidity is modified by the addition of Mg (alumina) or the ion exchange with NH$_4$Cl (Y zeolite).

2. Experimental

2.1. Catalysts preparation

Pt–Mg/Al$_2$O$_3$ was prepared using an alumina supplied by Ketjen (CK-300, 200 m^2 g^{-1}, 0.55 cm^3 g^{-1}). This support was crushed and sieved in order to keep particles sizes between 35 and 80 mesh. Then it was calcined in flowing air at 500 °C for 4 h. Pt was 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 H$_2$PtCl$_6$ (Sigma–Aldrich, 0.038 M) was added. 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. The amount of the impregnating solution was adjusted in order to obtain 1.0 wt% Pt in the final catalyst. The Pt/Al$_2$O$_3$ catalyst was then calcined in flowing air at 300 °C for 4 h and cooled down to room temperature in nitrogen. A Mg doped of lower acidity was obtained by impregnation of Pt/Al$_2$O$_3$ with a solution of Mg(NO$_3$)$_2$·6H$_2$O. The volume and concentration of this salt solution were adjusted to obtain a 3 wt% Mg on the final catalyst. Impregnation was performed by immersing the Pt/Al$_2$O$_3$ sample in the Mg solution and leaving the system unstirred for 1 h at room temperature. Then the slurry was dried in a thermostated bath at 70 °C until a dry solid was obtained. This solid was heated in a stove at 120 °C overnight. This Pt-Mg catalyst was finally calcined (air, 60 cm^3 min^{-1}, 300 °C, 4 h) and reduced (H$_2$, 60 cm^3 min^{-1}, 500 °C, 4 h) in a fixed bed reactor. A heating rate of 10 °C min^{-1} was employed for all heating steps. The Mg–Ir(0.6)/Al$_2$O$_3$ catalyst was made by the same procedure using an H$_2$IrCl$_6$ (0.08 M) solution instead of the H$_2$PtCl$_6$ one. The impregnation order was also changed. Mg was impregnated first and Ir last.

Pt-Mg-Ir(x)/Al$_2$O$_3$ catalysts were prepared by the catalytic reduction method using the Pt-Mg/Al$_2$O$_3$ catalyst as base support. Pt-Mg/Al$_2$O$_3$ was first reduced (H$_2$, 60 cm^3 min^{-1}, 1 h, 300 °C, 10 °C min^{-1}) and then cooled down to room temperature in hydrogen. Then a degassed H$_2$IrCl$_6$ solution with the appropriate concentration was poured into the reactor. The catalyst-solution slurry was mildly stirred for 1 h while bubbling hydrogen (300 cm^3 min^{-1}). Then the solution was drained and the catalyst was placed in a fixed bed, dried at 100 °C (hydrogen, 12 h, 60 cm^3 min^{-1}, 2 °C min^{-1} heating rate) and reduced at 500 °C (hydrogen, 2 h, 60 cm^3 min^{-1}, 2 °C min^{-1} heating rate). The Ir concentration of the impregnating solution was varied in order to obtain 0.1, 0.3 and 0.6 wt% Ir on the final catalysts. A total transfer of Ir from the solution to the catalyst was assumed. This was confirmed by ICP chemical analysis of the spent solution. The final catalysts were named Pt-Mg-Ir(x)/Al$_2$O$_3$ (x: nominal Ir content).

Pt-Ir(x) catalysts were prepared using a non-commercial NaY zeolite base support (Si/Al = 3.16, provided by the Petrobras R&D Center, CENPES). This zeolite was exchanged with an aqueous solution of NH$_4$Cl 2.2 M for 2 h at room temperature and with mild stirring. The solid was then filtered, repeatedly washed with distilled water and dried in an oven at 120 °C overnight. The dried solid was then calcined in air (2 h at 500 °C, heating rate 2 °C min^{-1}). The Si/Al ratio of the thus obtained material was 3.7 as measured by ICP chemical analysis. Pt and Ir were added by a common wet impregnation technique using H$_2$PtCl$_6$ and H$_2$IrCl$_6$ aqueous solutions. Pt and Ir monometallic catalysts were prepared by one-step impregnation and Pt-Ir by one-step coimpregnation. The metal concentration of the solutions was regulated in order to obtain the desired metal contents (Pt: 1.0 wt%; Ir: 0.1, 0.3 and 0.6 wt%). After the impregnation of the metals the samples were oven dried at 120 °C, calcined in dry air (3 h, 300 °C) and reduced in hydrogen (2 h, 300 °C). The thus obtained catalysts were named Pt-Ir(x)/zeolite (x: Ir mass content).

2.2. 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 °C min^{-1} to a final value of 650 °C. To measure the amount of desorbed pyridine the reactor exhaust was connected to a flame ionization detector.

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. Fourier transform infrared (FTIR) absorption spectroscopy of chemisorbed CO

FTIR spectra of adsorbed CO were obtained in order to study the effect of Ir deposition on the properties of the metal function. The spectra of chemisorbed CO for the prepared catalysts were recorded within the wavenumber range of 4000–1000 cm^{-1}. A Shimadzu Prestige-21 spectrometer with a spectral resolution of 4 cm^{-1} was used. Spectra were recorded at room temperature and self-supported wafers with a diameter of 16 mm and a weight of 20–25 mg were used. The experimental procedure was as follows: