Selective ring opening of decalin with Pt–Ir/Al$_2$O$_3$ catalyst prepared by catalytic reduction

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ABSTRACT

The reaction of selective ring opening using alumina supported Pt–Ir catalysts with and without Mg addition was studied. The catalysts were prepared by the method of catalytic reduction, having 1 wt% of Pt whereas the Ir content varied in the range 0.1–0.6 wt%. Electron diffraction showed that the method of preparation leads to catalysts with strong interaction between Pt and Ir being observed the presence of a solid phase of Pt–Ir. In the catalysts without Mg no changes in the hydrogenolysis activity was observed as the Ir content increases. However, a decrease both in acidity and dehydrogenating activity was observed. In the Mg containing catalysts, the addition of Ir increases the acidity, the dehydrogenating and hydrogenolytic activity. For the isomerization reaction of n-pentane it was found that the addition of Ir improves the stability of the catalysts and formation of isomers of C$_5$ in both series of catalysts (with and without Mg). The conversion of decalin by ring opening depends on the content of Ir for both studied series.

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1. Introduction

Public and official concern about new energy sources and its environmental impact has steadily increasing in the last decade. Energy providers are continuously seeking for more efficient and clean technologies, with reduced emission of contaminants. According to the European Automobile Manufacturers Association (ACEA) in 2005, sales of diesel cars reached 49.3% in Europe, compared to 14.6% in 1991 due to a lower price of the diesel [1]. 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. In the last years both refiners and research groups have devoted considerable efforts to develop suitable catalytic formulations for selective ring opening of cyclic compounds present in heavy fuels. The lowering of S and aromatic content in fuels have been traditionally achieved using well known hydrotreating and hydrocracking technologies [2]. A reduced particulate emission is achieved through these dearomatization process and also cetane numbers increase significantly. Cetane index (CI) is an important parameter which defines the quality of fuel combustion in motors so high values of CI results in a lower NOx and particulate emissions [3]. The increase

in CI achieved by the hydrogenation of aromatics is not enough due to the relatively low cetane value of the naphthenic produced. This limitation is particularly important for the improvement of high aromatic fractions such as LCO (Light Cycle Oil) from FCC. Ring opening of at least one naphthenic ring is required to achieve the required cetane levels.

Two main reaction types occur during the catalytic ring opening 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 (selective ring opening, SRO), does not significantly affect the resulting molecular weight due to the internal nature of C–C ring bonds. Cyclohexane and methylcyclopentane catalytic ring opening have been used as suitable test reactions in many research works [4]. At least two plausible reaction paths have been proposed: a dicarbene-based mechanism, with molecules perpendicularly adsorbed onto the metal surface, and a multiplet mechanism, with horizontally adsorbed species. In the first case, on highly dispersed Pt a statistical distribution of products is obtained, while in the latter the selective cracking of C–C bonds between two secondary carbon atoms is achieved by Ir, Rh or others. Onyestyák et al. [5] and McVicker et al. [6] have studied the ring opening of naphthenes alkyl substituted of C$_6$–C$_{10}$. They have demonstrated the catalytic selectivity of Ir for ring opening of cyclopentane. RO rates on Ir are reduced significantly as the degree of alkyl substitution increases, being directly proportional

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to the number of secondary C–C bonds. As opposed to Ir, Pt is more active to break substituted C–C bonds. However, this activity depends on the cis/trans ratio of methyl substituted cyclopentane and decreases with increasing concentration of trans isomers. For acid catalysts, as opposed to metal assisted RO, it is believed that the opening of naphthenic rings of C_6 and C_7 proceeds on Brønsted acid sites, being initiated by protolytic cracking and followed by chain reactions involving carbenium ions [7–9].

The mechanism of cracking and isomerization of alkanes on acid catalysts have been widely studied [10–14], and it may also apply to naphthenes with unsaturated C–C bonds. Results from experimental works and predictions of theoretical calculations allow inferring that either protolytic cracking, protolytic dehydrogenation, hydride transfer, skeletal isomerization, and the β-cleavage and alkylation of adsorbed ions [15,16] are involved. The ring opening of more complex molecules with two fused rings has been much less studied. Decalin ring opening reaction can proceed by acid or metal mechanisms as reported in detail by Resasco et al. [17]. Experimental results indicate that more active and suitable catalysts are those based on supported Ir. They lead to a lower occurrence of exocyclic chain breaks, although a favorable product distribution is achieved for rings of 5 carbon atoms and not for 6 atoms rings. One solution is to promote the ring contraction by using a support with medium acidity strength. There are catalysts that perform the conversion of cyclohexane to methylcyclopentane with high selectivity and low deactivation [18]. These catalysts could be coupled with a ring opening catalyst. Acid catalysts could however produce chain branching with the subsequent cetane loss. Some SRO patents propose the use of Ir catalysts added to medium acidity mesoporous support, being the acidity controlled by the addition of alkali ions [19]. Recently, it was reported the experimental use of SRO coupled to catalytic assisted sulfur traps (CAST), indicating that the performance of an SRO-CAST process is superior to traditional hydrocracking to upgrade the diesel fuel of refinery [20].

As it was mentioned before, several works on selective ring opening focus their attention on Pt–Ir supported catalysts prepared by common methods. In our case ring-opening Pt–Ir/Al$_2$O$_3$ catalysts were prepared by a non-classical catalytic reduction method. This preparation method has been reported to produce a strong interaction between the metals (Pt–Ir) [21–23]. A strong Pt–Ir interaction is known to enhance the reactions of hydrogenolysis [24]. Moreover the modifications of the acid function by Mg addition have not been reported previously in the open literature. The aim of this study was to evaluate the catalytic properties of Mg doped Pt–Ir/Al$_2$O$_3$ catalysts prepared by the catalytic reduction method during the selective ring opening of cyclonaphthenes. A special focus is put on the effect of the support acidity on the activity and selectivity.

The aim of this study was to evaluate the catalytic properties of Pt–Ir/Al$_2$O$_3$ catalysts prepared by the catalytic reduction method to produce the selective ring opening and to study the effect of support acidity.

2. Experimental

2.1. Catalysts preparation

Pt/Al$_2$O$_3$ catalyst. It was prepared using alumina supplied by Ketjen (CK-300, 200 m^2 g^{-1}, 0.55 cm^3 g^{-1}). The support was crushed and sieved in order to keep particles sizes between 0.25 and 0.40 mm and then they were calcined in flowing air at 650 °C for 4 h. The catalyst was prepared by a conventional impregnation method. Firstly an aqueous solution of HCl (0.2 mol L^{-1}) was added to the support and the system was left for 1 h without stirring at room temperature. Then an aqueous solution of H$_2$PtCl$_6$ was added. The

slurry was gently stirred for 1 h at room temperature. Then, it was dried by atmospheric evaporation 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 concentration of the impregnating solutions was adjusted in order to obtain 1.0 wt% Pt in the final catalyst. Then, the catalyst was calcined in a flowing air system at 300 °C for 4 h, and cooled down to room temperature under flowing nitrogen. Finally the catalysts were reduced under flowing hydrogen (60 cm^3 min^{-1}) at 500 °C for 4 h. A heating rate of 10 °C min^{-1} was employed for all heating steps.

Pt–Mg/Al$_2$O$_3$ catalyst. In order to modify the acidity, a solution of Mg(NO$_3$)$_2$·6H$_2$O was added to the Pt catalyst. The Pt/Al$_2$O$_3$ catalyst calcined at 300 °C for 4 h was impregned with Mg solution in order to obtain 1.0 wt% of Mg and was left for 1 h without stirring. Then, it was dried in a thermostated bath at 70 °C until a dry solid was obtained. The drying was completed in a stove at 120 °C. Finally, the Pt–Mg/Al$_2$O$_3$ catalyst was calcined (air, 60 cm^3 min^{-1}, 300 °C, 10 °C min^{-1}, 4 h) and reduced (H$_2$, 60 cm^3 min^{-1}, 500 °C, 10 °C min^{-1}, 4 h).

Preparation of Pt–Ir–Mg/Al$_2$O$_3$ and Pt–Ir/Al$_2$O$_3$ catalysts. They were prepared by catalytic reduction by making use of the catalytic action of Pt present in the parent catalyst (Pt) using a special all glass apparatus [25]. Monometallic (Pt) or bimetallic (Pt–Mg) parent catalysts were first reduced at 300 °C for 1 h in hydrogen (60 cm^3 min^{-1}) and then cooled down to room temperature under hydrogen flow. Then, a degassed H$_2$IrCl$_6$ solution with the appropriate concentration was poured in the reactor. After 1 h of contact with the catalyst under constant hydrogen flow (300 cm^3 min^{-1}), the solution was drained. Then, the catalyst was dried at 100 °C under hydrogen overnight. Finally, the catalyst was activated by reduction in hydrogen flow at 500 °C for 2 h. The content of Ir solution was varied in order to obtain 0.1, 0.3 and 0.6 wt% of Ir. The catalysts were named Pt–Ir(x) and Pt–Mg–Ir(x), where x is the nominal content of Ir.

2.2. Catalyst characterization

Measurement of the Pt, Ir and Mg contents. The composition of the metal function was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 2100 DV) after digestion in an acid solution and suitable dilution.

Temperature-programmed desorption of pyridine. This test was used for measuring the amount and strength distribution of the acid sites. Samples of 200 mg were impregnated with an excess of pyridine. Once the excess base had been removed, 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 500 °C. To measure the amount of desorbed pyridine, the reactor exhaust was directly connected to a flame ionization detector. The detector signal (in mV) was sampled at 1 Hz and recorded in a computer device. The total amount of adsorbed pyridine was determined by comparing the area under the obtained TPD traces with the area from calibrated pyridine pulses (1–2 μl) injected to the empty reactor.

Temperature-programmed reduction (TPR). These tests were performed in an Ohkura TP2002 equipment 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 and the corresponding TCD signal was recorded.

Transmission electron microscopy. Transmission electron micrographs (TEM) were obtained in a Jeol JEM 1200 EXII microscope. The supported catalysts were ground in an agate mortar and dispersed in ethanol. A diluted drop of each dispersion was placed on a 150 mesh copper grid coated with carbon. The micrographs