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# Influence of the metallic content on Pt-Ir/$Nb_2O_5$ catalysts for decalin selective ring opening

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## ABSTRACT

Ring opening of naphthenic rings on Pt-Ir catalysts supported on $Nb_2O_5$ was studied in this work. The catalysts were prepared by impregnation. In the case of the bimetallic catalyst, the total metallic load was kept constant while varying the individual quantity of impregnated Ir and Pt. The samples were characterized by transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, $N_2$ sorption, $NH_3$ TPD and model reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis). The decalin ring opening capacity of the catalysts was evaluated. Monometallic Ir and Pt catalysts as well as bimetallic catalysts were active towards cyclohexane dehydrogenation and cyclopentane hydrogenolysis. Regarding the bimetallic catalysts, an increase on the Pt content promoted the cyclohexane dehydrogenation while hindering the hydrogenolytic activity. In the selective ring opening of decalin, the bimetallic catalysts presented activities comparable to the monometallic catalysts. Nonetheless, Ir(0.3%)/$Nb_2O_5$ catalyst presented the highest selectivity towards ring opening products with the lowest selectivity towards dehydrogenated products.

## 1. Introduction

Light Cycle Oil (LCO), a low value by product of the Fluid Catalytic Cracking (FCC) process, has been proposed as a potential source of diesel. However, diesel has to comply with certain quality requirements regarding cetane index, aromatic content, sulfur content, etc. to be used in motors due to numerous environmental regulations [1,2]. Although LCO contains hydrocarbons on the diesel range, its aromatic content (particulate material forming compounds) is very high and it is necessary to transform them into other hydrocarbons. It has been reported that LCO contains from 0.2 to 2 wt% of sulfur and between 48 and 69% of polyaromatics, yielding a cetane index (CI) between 22 and 25. The European norms in January 2009 demand an upper limit of 10 ppm of S and 11% of polyaromatics with a minimum cetane index of 51 [3]. The elimination of S and N compounds can be carried out by hydrotreatment technologies [4–6] which can also be useful to hydrogenate aromatics. However, a CI increase by conversion of polyaromatics to naphtenics is not enough since the CI of naphthenic compounds is pretty low [7,8]. The ring opening of at least one of the naphthenic rings is necessary to achieve an adequate CI. Selective ring opening occurs when the molecular weight remains almost constant since only internal C—C bonds on the naphthenic rings are broken, whereas a non-selective breaking of the external C—C bonds will lead to a variety of products with a lower overall molecular weight. This is clearly a difficult task, since endocyclic cracking of naphthenes is less thermodynamically favored than acyclic and exocyclic cracking reactions due to entropy considerations [9].

Calemma et al. [10] point out that three principal families of solid catalysts are usually distinguished for the cleavage of C—C bonds: (i) monofunctional acidic catalysts, (ii) bifunctional catalysts containing both Brønsted acid and metal sites and (iii) monofunctional metal catalysts. Onyestyák et al. [11] and McVicker et al. [12] have thoroughly studied the opening of alkyl-substituted mononaphtene rings in the $C_6$–$C_{10}$ range and have proven the good selectivity of Ir catalysts towards the aperture of five membered rings. The ring opening (RO) rate over Ir decreases significantly as the alkylsubsti-

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tution degree increases and is directly proportional to the number of secondary carbons. Contrary to Ir, Pt is found to be more active towards the breaking of C—C bonds on substituted carbons. However, the RO rate on Pt is sensitive to the cis/trans configuration on methyl-substituted cyclopentanes and diminishes proportionally to the concentration of the trans isomer. Cardoso et al. [13] found evidence of a bifunctional mechanism in the hydroconversion of decalin over Pt/Beta zeolite catalysts, since the selectivity depends on the metal/acid function balance.

In acid catalysts, contrary to metal-assisted ring opening reactions, it is thought that $C_6$–$C_7$ naphthenic RO occurs over the Brønsted acid sites and is initiated by protolytic cracking, followed by chained reactions involving the carbenium ion formed [14,15]. Kubicka et al. [16,17] found that acidity has an important role on the selectivity of bicyclic naphthenic ring opening.

Current experiences show that the more active and convenient catalysts are those based on supported Ir, since they have a very low contribution towards the rupture of exocyclic chains. Nonetheless, the most convenient product distribution occurs over five-membered rings instead of six-membered rings. Two recent studies thoroughly examined the reaction paths for the hydroconversion of decalin on non-acidic supports such as $\gamma$-$Al_2O_3$ [18] and $SiO_2$ [10]. Depending on the Ir content (between 0.5 and 2.6%), the decalin conversion starts between 250 and 350 °C with no skeletal isomerization. In perspective, silica-supported Pt catalysts require temperatures around 350–400 °C producing larger quantities of dehydrogenated products [18]. Furthermore, Vicerich et al. [19] studied the SRO of decalin at 325 °C and found that monometallic Pt and Ir catalysts supported on $SiO_2$ produces only dehydrogenated products. Recently, the experimental use of SRO coupled with Catalytic Assisted Sulfur Traps (CAST), has shown that the operation of a SRO-CAST process is superior to the traditional hydrocracking process to upgrade refinery cuts [20]. As a disadvantage, hydrogenolysis is extremely sensitive to sulfur poisoning. Hence, SRO reactions require a complete removal of S, including desulphurization of beta-dibenzothiophenes.

Open literature shows that acidic monofunctional catalysts suffer from coke deposition deactivation during decalin ring opening caused by the formation of significant quantities of hydrocarbons with more than 10 carbon atoms at high conversions while the formation of RO products is low, around 10% [21].

In this work, ring opening was studied on metallic catalysts of noble metals (Pt, Ir) deposited on $Nb_2O_5$. The objective was to produce active catalysts, stable and selective towards SRO of cycloalkanes with one or various rings. Model molecules used were decalin, cyclohexane and cyclopentane.

## 2. Experimental

### 2.1. Preparation of bimetallic Ir-Pt catalysts supported on $Nb_2O_5$

The niobium oxide used as support was obtained by calcination of hydrated niobium pentoxide (niobic acid HY-340, supplied by CBMM, Brazil) at 450 °C. The catalysts were prepared by impregnation of the support ($Nb_2O_5$) with metal precursor solutions ($H_2IrCl_6$ and $H_2PtCl_6$). The total metallic load was 1 wt% and the catalysts were prepared with a molar ratio Ir/Pt of 0.5, 1 and 2. First, $1.5\,cm^3\,g^{-1}$ of a solution of $HNO_3$ (2 M) was added to the support in order to favor the homogenous distribution of metals inside the support particles. The solution was left 1 h to rest. Then, the adequate amount of hexachloroiridic and/or hexachloroplatinic acid was added in order to reach a 1 wt% metal load and the desired Ir/Pt ratio. The system was left to rest for 1 h again to allow for a uniform distribution of the metals. In order to evaporate the solvent (water), the solid was put on a water bath at 70 °C under mild stirring until a dry powder was obtained. Later, it was further dried in a stove at 120 °C for 12 h. Finally, the samples were calcined at 450 °C, for 3 h and reduced with hydrogen at 500 °C, for 4 h.

### 2.2. Preparation of monometallic Ir and Pt catalysts supported on $Nb_2O_5$

The same procedure described for the bimetallic catalysts was used. Monometallic catalysts with 0.3, 0.5 and 0.7 wt% of Pt or Ir were prepared.

### 2.3. Evaluation of the Pt and Ir content

The composition of the metal phase was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Perkin Elmer, Optima 2100 DV) after digestion in an acid solution and dilution.

### 2.4. Specific surface area

Nitrogen adsorption isotherms (−196 °C) were recorded on an automatic Micromeritics ASAP-2020 apparatus. Prior to the adsorption experiments, the samples were outgassed at 140 °C, for 2 h. BET areas were computed from the adsorption isotherms ($0.05 < P/P0 < 0.27$). A value of $0.164\,nm^2$ was assumed for the cross section of the adsorbed $N_2$ molecule at −196 °C.

### 2.5. X-ray diffraction (XRD)

The analysis were performed at room temperature using a Shimadzu XRD-7000 diffractometer with monochromated CuK $\alpha$ radiation ($\lambda = 1.54$ Å) operated at 40 kV and 30 mA. Diffractograms were recorded in the $2\theta$ range from 10 to 80° at a resolution of 0.05° with a scanning speed of $2^\circ\,min^{-1}$, using a nickel filter. Samples were analyzed in powder form.

### 2.6. Transmission electron microscopy (TEM)

Micrographs were obtained in a Jeol JEM 1200 EXII microscope. Each supported catalysts was ground in an Agatha mortar and dispersed in ethanol. Diluted drops of these dispersions were placed on a 150 mesh copper grid with carbon. The micrographs were obtained in both bright and dark fields.

The dispersion was estimated as the ratio between the theoretical minimum particle diameter and the apparent particle diameter measured by TEM, according to the method of Kubika [22].

### 2.7. X-Ray photoelectron spectroscopy (XPS)

Before the XPS analyses were performed, the solids were treated in situ with a $H_2$:Ar mixture at 400 °C and then degassed to a residual pressure of $5.9 \times 10^{-7}$ Pa. For each sample the analyzed regions of the spectrum were those containing the signals due to the Pt $4f_{7/2}$ and $4f_{5/2}$, Ir $4f_{7/2}$ and $4f_{5/2}$ and Nb $3d_{5/2}$ and $3d_{3/2}$ core levels. The binding energy of carbon (C1s = 284.8 eV) was used for the calibration of XPS data. Spectrum peak areas were calculated by integration. Peaks were fitted to a 70/30 sum of Gaussian and Lorentzian functions and the background was considered to be of the Shirley type. More technical details can be found in a previous report [23].

### 2.8. Temperature programmed desorption of $NH_3$

A Micromeritics TPD/TPR 2900 model fitted with a TCD detector was used for the acidity measurements by $NH_3$-TPD. Samples were reduced for an hour at 300 °C ($50\,cm^3\,min^{-1}$ of $H_2$). After reduction,

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