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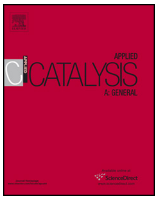

Influence of chlorine on the catalytic properties of supported rhodium, iridium and platinum in ring opening of naphthenes

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ABSTRACT

Pt, Ir and Rh were deposited on SiO_2 or Al_2O_3 using chlorinated precursors and various amounts of HCl in the impregnation medium. The Brønsted and Lewis acidities increased with the chlorine content of the alumina supported catalysts. The silica-supported catalysts only presented Lewis acid sites. The catalysts were evaluated in methylcyclopentane (MCP) and methylcyclohexane (MCH) ring-opening (RO) under pressure (2.85 and 3.95 MPa, respectively), from 200 to 425 °C. For MCP conversion, the acidity of the alumina support had no sensitive effect on the activity and selectivity to RO products, and few effects on the distribution of RO products. No isomerization or hydrocracking products were observed, confirming that these reactions occurred mainly on the metal function, which was not modified by the presence of chlorine. The nature of the support, SiO_2 or Al_2O_3, had a strong effect on both the activity (1.9 against 0.5 mol h^{-1} $g^{-1}{}_{metal}$ for Ir/Al_2O_3 and Ir/SiO_2, respectively at 225 °C) and selectivity to RO products (99.6% against 97.5% for Ir/Al_2O_3 and Ir/SiO_2, respectively, at 80% of MCP conversion) for Ir catalysts only. Interestingly, the Rh/SiO_2 exhibited a high selectivity for converting MCP to RO products, similar to Ir/Al_2O_3, *i.e.* 99.6% at 80% of conversion. Depending on the metal and the supports, three types of behavior were observed for MCH ring-opening: (i) a direct ring-opening on the metal function whatever the support for Ir, (ii) a first step of isomerization, and then a need of a sufficiently acidic support, for Pt and (iii) an intermediate behavior for Rh, which was able to either directly convert MCH in absence of acidic support or favor a bifunctional mechanism on chlorinated alumina.

1. Introduction

Selective ring-opening (SRO) of naphthenic molecules to alkanes is a potential solution for significantly improving cetane number of light-cycle oils or the octane number of gasoline after hydrogenation of aromatics [1–6]. This reaction consists in the selective hydrogenolysis of one endocyclic C—C bond. It is accompanied by a number of reactions such as isomerization, deep hydrogenolysis and cracking leading to a decrease in the number of carbon atoms in the molecules, dehydrogenation and aromatization. This reaction is generally carried out on noble metal catalysts supported on Al_2O_3, SiO_2, TiO_2, zeolites [4,5,7–15]. Among the noble metals active for this reaction, namely Pt, Pd, Ru, Rh and Ir, Ir monometallic catalysts have shown the best catalytic performances in terms of activity and selectivity to ring-opening products [2,4,16–18]. Recently, Pt—Rh bimetallic catalysts have demonstrated performances similar to Ir for methycyclopentane (MCP) and methylcyclohexane (MCH) ring-opening, considered as two model molecules for selective ring-opening [19–21].

On the one hand, MCP ring-opening can occur on metallic, acidic or bifunctional catalysts [1,3,22–29]. On acidic alumina [24], ring-opening reaction proceeds at high temperature (>350 °C) by a direct opening of MCP ring *via* carbonium ion intermediate. On metal-supported catalysts, MCP ring-opening may occur on pure metallic sites or at the metal-support interface [30,31]. It was shown that, on sulphur modified platinum-based mono and bimetallic catalysts supported on alumina [32], MCP conversion yields 2-methylpentane (2MP), 3-methylpentane (3MP) on metal sites while cyclohexane (CH), benzene (Bz) and *n*-hexane (nH) are formed on both the metal and the acidic sites. Galperin et al. [33] prepared Pt catalysts with the same metal active sites on supports with various acid-basic properties. All the catalysts on acidic supports favored the formation of cyclohexane and aromatics. Consequently, they concluded that an acidic support is detrimental to high selectivities in ring-opening products.

On the other hand, McVicker et al. [4] demonstrated that, whatever the metal, Pt, Ni, Ru, Ir, supported on silica or alumina, MCH ring-opening is more difficult than MCP ring-opening, due to the lower ring strain in six-membered compared to

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five-membered-ring naphthenes. Only Ir is able to directly open MCH, whereas on the other catalysts, a ring-contraction step using an acidic catalyst is necessary for obtaining afterwards a reasonable yield in ring-opening products. Thus, McVicker et al. clearly established that the acidity is important for selective ring-opening of six-membered-ring naphtenes. For this reason, except for Ir-based catalyst, the metal catalysts are frequently supported on acidic supports, such as zeolites, for MCH ring-opening [5,12].

In this context, the objective of the present work was to study the effect of the acidity of a γ-alumina support by varying the chlorine content and to evaluate the catalytic properties of Rh, Ir and Pt catalysts on these supports in MCP and MCH conversion, in order to find a moderate acidity compatible with high selectivity to RO products whatever the initial reactant. Silica supported catalysts were also evaluated for comparison.

2. Experimental

2.1. Catalysts preparation

A γ-alumina (Axens) and silica (Degussa) with a specific surface area (BET method) of 215 $m^2 g^{-1}$ and 175 $m^2 g^{-1}$, and a total pore volume of 0.51 $cm^3 g^{-1}$ and 0.47 $cm^3 g^{-1}$, respectively, were used as supports. They were crushed and sieved in order to retain particles with sizes between 0.25 and 0.40 mm, and then calcined in flowing air at 450 °C for 4 h before impregnation of the metal precursor.

The catalysts were prepared by impregnation of the support with solutions of H_2PtCl_6, H_2IrCl_6 or $RhCl_3$. The volume of the solutions was adjusted in order to obtain a final metal content of 0.6 wt.% on the support.

For the alumina support, three kinds of preparation conditions were used in order to vary the final chlorine content in the catalyst:

1. The solution of the metal precursor salt was directly put in contact with the support. In this case, the final chlorine content depends only on the chloride content of the precursor salt.
2. Hydrochloric acid was added to the precursor salt solution to adjust the chlorine content to 1 wt.% in the final catalyst. Then, the support was impregnated with this precursor salt solution.
3. The support was put in contact with hydrochloric acid, with a concentration of 0.2 mol L^{-1} in order to obtain a final pH of 1. Then, the solution of the precursor salt was added. In this catalyst series, the theoretical chlorine content is of 2.5 wt.%.

The mixture was stirred on a sand bath at 60 °C up to a complete evaporation of the solvent and then dried overnight at 120 °C. Finally, the catalysts were calcined in flowing air at 300 °C (Rh and Ir supported catalysts) or 450 °C (Pt catalysts) for 4 h and reduced in flowing hydrogen at 500 °C for 4 h.

The silica-supported catalysts were prepared according to the procedure (1).

2.2. Characterization

The metal and chlorine contents were determined by elemental analysis involving ICP-OES technique (inductively coupled plasma optical emission spectrometry, Perkin).

2.2.1. Hydrogen chemisorption

The H_2 chemisorption measurement was carried out in a pulse chromatographic system. After reduction under hydrogen at 500 °C and outgassing for 2 h in an argon stream at the same temperature, 500 mg of catalyst were cooled down to room temperature. Then, pulses of pure hydrogen were introduced onto the catalyst up to saturation. The amount of hydrogen in the effluent was continuously analyzed by a thermal conductivity detector. This allowed the determination of the total amount of hydrogen adsorbed on the catalyst Hc_1. In order to remove the hydrogen reversibly adsorbed, the catalyst was degassed under pure argon at RT for 30 min and then a second series of hydrogen pulses was introduced onto the catalyst. The hydrogen adsorbed during this second step is Hc_2. The amount of chemisorbed hydrogen Hc is given by $Hc = Hc_1 - Hc_2$. The results are expressed in the form of H/M values, related to the amount of hydrogen atoms chemisorbed per atom of metal. It is generally admitted that for Pt and Rh, there is one hydrogen atom chemisorbed per surface metal atom, and this was checked by TEM measurement in Ref. [20]. Thus, for the Pt and Rh catalysts, the H/M value is similar to the dispersion value. For Ir, the stoichiometry may change with the dispersion of the metal [14], and an increase in the H/M value is just an indication of an increase in the dispersion.

2.2.2. Characterization of the acid sites by FTIR of adsorbed pyridine

The Fourier Transformed Infra-Red (FTIR) spectroscopy was used to characterize the acid sites of the support by adsorption of a basic probe molecule, *i.e.* pyridine. 20–25 mg of catalyst were pressed into thin wafers with diameter of 16 mm and surface of 2 cm^2. After a pretreatment under ultra-high vacuum at 450 °C for 12 h, the sample was cooled to room temperature and then pyridine vapors were injected in the cell under a pressure of 2×10^2 Pa for 10 min. After evacuation under vacuum (6×10^{-4} Pa) for 1 h at 150 °C, spectra were recorded using a Nicolet Nexus spectrometer in order to determine the total number of acidic sites. In order to estimate the strength of these acidic sites, spectra were also recorded after evacuation at 250 and 350 °C for 1 h. Band intensities were corrected from slight differences in sample weight and band areas were calculated by fitting the spectral profile with a Gaussian–Lorentzian function using IR OMNIC software. The concentration of Lewis acid sites was calculated from the integrated area of the band at 1455 cm^{-1} using the value of the molar extinction coefficient of this band (1.28 cm μmol^{-1}) determined by Guisnet et al. [34], in the same conditions and in the same experimental device as those used in the present study. The total amount of Lewis acid sites was calculated from the spectrum obtained at 150 °C. The distribution of acid strength was evaluated by difference between the amount adsorbed at a given temperature and the amount not desorbed at higher temperature.

2.2.3. Characterization of the Brønsted acid sites by isomerization of 3,3-dimethyl-1-butene

The skeletal isomerization of 3,3-dimethyl-1-butene (33DMB1) was used as model reaction to characterize the Brønsted acid sites. Kemball et al. [35] demonstrated that the Lewis centers of alumina are not involved in this reaction and the 33DMB1 isomerization is likely to occur through a pure protonic mechanism on Brønsted acidic sites [36–38].

Catalyst samples (0.1 g) were calcined at 450 °C in flowing air (30 mL min^{-1}), in order to deactivate the metallic phase, and then purged under nitrogen. The catalytic reactions were carried out at 250 °C at atmospheric pressure with a reactant flow rate of 15.2 mmol h^{-1} and a reactant partial pressure of 20 kPa. Analysis of the reaction products was performed by gas chromatography with a flame ionization detector (AlphaMos PR2100) on a Rtx-1 (Restek) column (105 m × 0.53 mm × 3.00 μm). The detected products were 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene. The 33DMB1 disappearance rates were determined from the 33DMB1 conversion and normalized by the BET surface area.

2.3. Catalytic tests

The cyclohexane dehydrogenation, which occurs only on the metal function, was performed in order to study the effect of the