Selective ring opening of methylcyclopentane on bimetallic Pt-X catalysts supported on alumina

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Introduction

Cetane number improvement of diesel fuels is a difficult task that refiners will face in the near future. Key products quality requirements for diesel-range distillate include ultra-low-sulfur contents and reduced multiring aromatic concentrations. Some researchers have suggested that a selective ring opening (SRO) process is a potential solution for significantly improving cetane number [1-4]. The ring opening of methylcyclopentane (MCP) on supported metal catalysts has been extensively studied [4-7]. Among the studied metals, monometallic Ir catalysts are generally the most active and the most selective for the MCP hydrogenolysis (i.e. the C1-C5 products are in a very small quantity). The SRO reaction of MCP produces n-hexane (*n*-C6), 2-methylpentane (2MP) and 3-methylpentane (3MP) (Figure 1).

However, few studies are reported concerning the SRO of MCP under industrial conditions, especially under high-pressure. In the present work, industrial conditions are used in order to study the hydrogenolysis of MCP on Pt catalysts supported on alumina. The aim of the present study is to synthesize bimetallic Pt-X/Al_2O_3 catalysts in order to increase the selectivity of the platinum for ring opening.

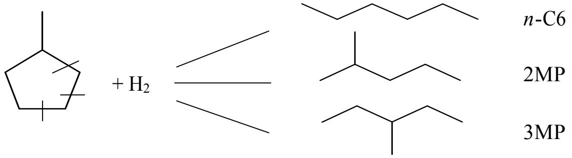

Figure 1. Ring opening of methylcyclopentane (MCP).

Materials and Methods

Monometallic 0.6wt% Pt/Al_2O_3 catalyst was prepared by impregnation of the support using an acidic aqueous solution of H_2PtCl_6 (the pH of this solution was adjusted to 1 with HCl). The catalyst was dried at 120°C for 12 h, after calcined in air at 450°C for 4 h and finally reduced in hydrogen at 500°C for 4 h (heating rates=10°C.min^{-1}). The Pt/Al_2O_3 sample was used as parent catalyst for the preparation of various Pt-X/Al_2O_3 bimetallic systems (X=Cu, Ge, Ru or Rh). Bimetallics were synthesized by surface redox reaction between hydrogen activated on the parent catalyst and the precursor salt of the X modifier. After the bimetallic samples were reduced under hydrogen flow at 500°C for 1 h (2°C.min^{-1} heating rate). Blank Pt catalyst was prepared following the same procedure but the modifier salt was replaced by a hydrochloric solution at the same pH (pH=1). The experimental conditions for the MCP hydrogenolysis were the followings: total pressure=28.5 bar, WHW=15^{-1}, H_2/MCP=5, temperature range=200-425°C.

Results and Discussion

As expected, in the experimental conditions used the Pt/Al_2O_3 monometallic catalyst is less active and selective than an Ir/Al_2O_3 system with the same metal loading and the same metal particle size (60% MCP is converted in the range 250-275°C on Ir/Al_2O_3 with 99% of selectivity for the RO reaction, whereas the same conversion is obtained at 350°C on Pt/Al_2O_3 with 96% of selectivity). The introduction of a modifier on the parent Pt/Al_2O_3 catalyst induces modifications of its catalytic properties, the obtained behaviors being a function of the nature of the modifier. With inactive metals as Ge or Cu, the parent catalyst undergoes mainly a dilution of its active phase without modification of the RO selectivity. An increase of the activity is observed for the Pt-Ru/Al_2O_3 systems compared to the parent one, but also an increase of the C1-C5 products. Among the studied samples, the Pt-Rh/Al_2O_3 catalysts are the most interesting, since the introduction of a given amount of Rh allows one to increase both the activity and the RO selectivity of the Pt system (Figure 2).

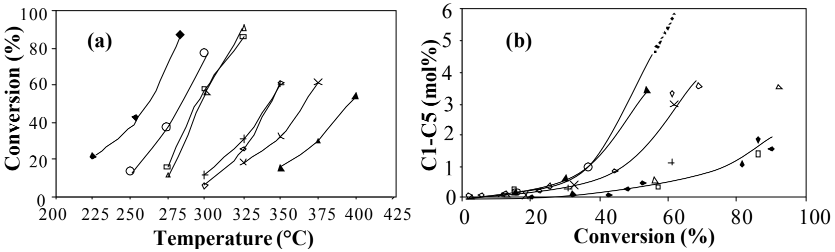

Figure 2. (a) MCP conversion as a function of the temperature and (b) mol% of C1-C5 products as a function of the conversion on 0.6wt% Pt/Al_2O_3 (◇), blank 0.6wt% Pt/Al_2O_3 (▲), 0.6wt% Ir/Al_2O_3 (♦), 0.3wt% Rh/Al_2O_3 (○) and Pt-xRh/Al_2O_3 catalysts (x=0.04wt% (x), 0.06wt% (+), 0.14wt% (□), 0.23wt% (△)).

Significance

The modification of a Pt/Al_2O_3 system by an appropriate metal modifier allows one to improve its activity and selectivity for the ring opening of MCP, inducing RO selectivity similar to that of Ir/Al_2O_3 catalysts, considered as the best systems until now.

References

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