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Selective ring-opening of methylcyclopentane on platinum-based bimetallic catalysts

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ABSTRACT

Several monometallic catalysts supported on alumina were tested in methylcyclopentane ring-opening under pressure. Among the monometallic catalysts tested (Ru, Re, Rh, Pt and Ir), iridium and rhodium catalysts were the most active but iridium was by far the most selective in ring-opening (RO) products (2-methylpentane, 3-methylpentane and *n*-hexane), the formation of C1–C5 products being negligible, as already reported in the literature. Thereafter, platinum-based bimetallic catalysts supported on alumina were prepared by redox surface reaction in order to favor the metal–metal interaction. The aim was to obtain bimetallic catalysts leading to selectivity towards RO products similar to that of the iridium catalyst. Two types of modifiers were studied, namely (i) inactive species such as copper and germanium and (ii) active promoters for hydrogenolysis reactions, such as ruthenium and rhodium. It was shown that with inactive metals, the parent platinum catalyst undergoes mainly a dilution of its active phase. 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. On the contrary, the addition of Rh allowed us to increase the activity of the platinum parent catalyst and to obtain bimetallic catalysts with selectivity towards RO products similar to that obtained with iridium in same conditions.

1. Introduction

To answer to the increasingly strict regulations for the protection of environment, it is necessary to produce cleaner and cleaner automobile fuels. In particular, aromatic compounds must be reduced and replaced by paraffins, substituted in the case of the gasoline, or linear in the case of diesel oil. The production of such fuels supposes the total hydrogenation of the aromatic compounds in naphthenic compounds, then the selective opening of the latter to paraffins while avoiding the secondary reactions in particular deep hydrogenolysis leading to light hydrocarbons. The ring-opening (RO) of methylcyclopentane (MCP) (monocyclic naphthene) has been widely used as a catalytic probe for the particle size, especially for platinum catalysts [1]. The RO reaction of MCP produces *n*-hexane (*n*-C6), 2-methylpentane (2MP) and 3-methylpentane (3MP). Nevertheless, this test reaction is usually performed at atmospheric pressure, and the distribution of products is discussed for conversions generally lower than 10%. In these conditions, Ir-based catalysts are reported to be the most active and selective ones among the studied metals for MCP hydrogenolysis i.e. the C1–C5 cracking products are in a very small quantity.

Among the studies concerning the monocyclic naphthene RO, few ones [2–7] report the catalytic behavior of monometallic catalysts under high pressure conditions, and only one is partly devoted to the MCP RO [2]. Moreover, the comparison of the catalytic performances of the catalysts is difficult since they are often evaluated in very different conditions. In this way, McVicker et al. [2] studied the selective ring-opening of one ring naphthenes to alkanes. The model molecules chosen were five- or six-membered-ring naphthenes. The hydrogenolysis of MCP was studied at 28.5 bar on Pt, Ni, Ru and Ir catalysts supported on silica or alumina in order to obtain the best selectivity in ring-opening products. Depending on the catalyst studied, the space velocity and the temperature were varied. The most active and selective catalyst was 0.9 wt.% Ir/Al_2O_3, which allowed reaching 52% conversion at 275 °C with 99% selectivity in ring-opening products, whereas at the same temperature, C1–C5 cracking products were favored in the presence of 1.5 wt.% Ru/SiO_2. Pt-based catalysts were less active in hydrogenolysis reactions than iridium and ruthenium, and consequently they were tested [2] at higher temperature (350 °C) and contact time. However, at this temperature, only 24% conversion was obtained but with an acceptable selectivity in ring-opening products, with only 0.3% of cracking products.

The use of bimetallic catalysts may result in important changes in the activity and selectivity of MCP RO [8–14]. Contrary to monometallic catalysts, to the best of our knowledge, no publication reports the study of MCP ring-opening at high pressure

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in the presence of bimetallic catalysts. Thus, the aim of the present study is to modify a Pt/Al_2O_3 catalyst by addition of another metal in order to obtain Pt-based bimetallic catalysts with selectivity comparable to those of Ir catalysts for MCP hydrogenolysis in the same conditions. For that purpose, platinum-based bimetallic catalysts supported on alumina will be evaluated in a wide range of temperature but at the same space velocity and pressure. Two types of modifiers will be studied, namely (i) inactive species such as copper and germanium and (ii) active promoters for hydrogenolysis reactions, such as ruthenium and rhodium. Monometallic catalysts will be also evaluated in the same conditions to serve as reference for bimetallic catalysts.

2. Experimental

2.1. Catalyst preparation

The support was a γ-alumina (AXENS) with a specific surface area (BET method) of 215 $m^2 g^{-1}$. The support was crushed and sieved, in order to retain particles with sizes between 0.25 and 0.40 mm, and calcined in flowing air at 450 °C for 4 h.

Monometallic catalysts were prepared by impregnation of the precursor salt (H_2PtCl_6, H_2IrCl_6, $RhCl_3$ or $RuCl_3$) in an acidic solution (HCl 0.1 M). The Re/Al_2O_3 catalyst was prepared by impregnation of $HReO_4$ in water. After evaporation of the solvent, the catalysts were activated by calcination at 300 °C (except for the Pt/Al_2O_3 catalyst prepared from H_2PtCl_6 that was calcined at 450 °C) under air for 4 h and reduced at 500 °C for 4 h.

Bimetallic Pt-X/Al_2O_3 catalysts were prepared by deposition of the X modifier by a surface redox reaction, namely either catalytic reduction or refilling method. A given amount of the parent platinum catalyst was placed in a reactor, outgassed with nitrogen and then reduced under hydrogen (60 mL min^{-1}) at 500 °C (heating rate 10 °C min^{-1}) for 1 h. Then, the catalyst was cooled down to room temperature under nitrogen (refilling method) or hydrogen (catalytic reduction), and a volume of water was added to moisten it.

For the catalytic reduction, a solution of hydrochloric acid (pH 1) containing a well-defined amount of the modifier salt ($CuCl_2$ or $GeCl_4$) was added and maintained in contact with the catalyst under hydrogen flow for 15 min.

For the refilling method, the suspension of catalyst was at first maintained under hydrogen flow in order to preadsorb hydrogen on the platinum surface and then placed under nitrogen flow for 15 min to remove dissolved or weakly adsorbed hydrogen. Afterwards the solution of hydrochloric acid (pH 1) containing the modifier salt ($RhCl_3$ or $RuCl_3$) was added and let under nitrogen flow in contact with the catalyst for 1 min. Then, hydrogen was introduced in the reactor during 14 min.

In both cases (catalytic reduction and the refilling method), the redox reaction between the Pt parent catalyst and the X modifier salt can be schematized as the following:

$$2\mathrm{Pt} + \mathrm{H_2} \rightarrow 2\mathrm{Pt\text{-}H} \qquad (1)$$

$$n\mathrm{Pt\text{-}H} + \mathrm{X}^{n+} \rightarrow \mathrm{Pt}_n\text{-}\mathrm{X} + n\mathrm{H}^+ \qquad (2)$$

Whatever the deposition method, the solution was filtered out after reaction and the catalyst was dried overnight under N_2 before to be reduced under hydrogen flow at 500 °C for 1 h (2 °C min^{-1} heating rate).

2.2. Catalysts characterization

The metal content was determined at the "Service central d'analyse" of the CNRS.

The metal dispersion was calculated from the H_2 chemisorption measurement, carried out in a pulse chromatographic system, using a stoichiometry H/Metal equal to one. It is known [15] that this may lead to erroneous relative metallic dispersions but we have checked that the values of the particle size estimated by the hydrogen chemisorption measurements are in accordance with those determined from the TEM pictures. For all the catalysts, the H_2 chemisorption measurement was carried out at room temperature. The metal particle size was calculated from the dispersion D (in %) using the classical hypothesis of cubic particles with one face in contact with the support (five faces exposed to the gases), and considering an equidistribution of the (1 0 0), (1 1 0) and (1 1 1) faces.

The model reaction of cyclohexane dehydrogenation was performed in order to study the effect of the X modifier deposit on the Pt metallic phase. This reaction was carried out in a continuous flow reactor at 270 °C under atmospheric pressure on 10 mg of catalyst. Injection of cyclohexane was made using a calibrated motor-driven syringe. The partial pressures were 97 and 3 kPa for hydrogen and cyclohexane, and the corresponding flow rates 6 L h^{-1} and 2 mL h^{-1}, respectively. The resulting space velocity was $V_{H_2} = 100\,cm^3\,min^{-1}$. Analysis of the reaction products was performed by gas chromatography with a flame ionization detector (Varian 3400X) on a HP-PLOT Al_2O_3 "KCl" column. The only detected product was benzene.

TEM measurements were carried out with a Philips CM120 electron microscope operating at 120 kV with a resolution of 0.35 nm.

2.3. Catalytic test

The catalysts were evaluated in methylcyclopentane hydrogenolysis under a total pressure of 28.5 bar in a temperature range from 200 to 475 °C. The experiments were carried out in a fixed-bed, continuous reactor. Typically, 255 mg of catalyst were mixed with 245 mg of α-Al_2O_3 and placed inside the reactor (a stainless steel tube of 1.3 cm inner diameter) and the reactant mixture with a molar ratio H_2/MCP = 7.5 was injected at a flow rate adjusted in order to obtain a weighted hourly space velocity (WHSV) of 12 h^{-1}. For Pt/Al_2O_3, an experiment was also performed at a WSHV of 6 h^{-1} in order to increase the conversion in the same range of temperature. For the same reason, the tests were performed at a WSHV of 6 h^{-1} for bimetallic catalysts with low activity in MCP conversion. In this case only, the WHSV is reported in the figure caption. These reaction conditions are similar to those chosen by McVicker et al. [2] for the study of the performances of Pt/Al_2O_3 catalysts. For ruthenium, nickel and iridium-based catalysts, these authors chose a WHSV equal to 30 h^{-1}. The methylcyclopentane flow was controlled using a calibrated motor-driven syringe. Effluent products were analyzed by an on-line chromatograph (Varian 3400) using a FID and equipped with a CP-Sil 5 capillary column. The conversion was varied by changing the reaction temperature: in a typical experiment, the reaction was started at the lower temperature, chosen as a function of the catalyst activity, in order to obtain a conversion lower than 10% and then the temperature was increased in steps of 25 °C up to a conversion of 80–90%. The duration of each step was 2 h and four measurements were performed at each temperature. Conversion, defined as the percentage of MCP converted, was determined as a function of temperature. The only reaction products were 2-methylpentane, 3-methylpentane, n-hexane, C1–C5 products and 2,3-dimethylbutane. Neither cyclohexane nor benzene was detected as reaction products. As the maximum yield in 2,3-dimethylbutane was 1%, this product was neglected and the selectivity of the catalysts for ring-opening (hydrogenolysis of only one endocyclic C–C bond) was estimated from the yield in C1–C5 products resulting from deep hydrogenolysis: the lowest the C1–C5 yield, the highest the RO products yield and then the highest the MCP ring-opening