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A preliminary study of the n-heptane conversion over supported platinum acid–base ZrPON catalysts

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The catalytic behaviour of zirconium phosphate oxynitrides ZrPON and Pt supported ZrPON catalysts in n-heptane conversion is examined. The results show that the distribution of the products depends on the reaction temperature. In addition, it has been established that the acid–base properties of ZrPON supports greatly influence the n-heptane reforming reactions since the increase of ZrPON basicity enhances both n-heptane conversion and aromatics selectivity.

Keywords: heptane aromatisation, Pt/ZrPON, acid–base catalysts, basicity

1. Introduction

Catalytic reforming is one of the most important refining processes. In the US, for example, the larger part of benzene, toluene and xylene used in the petrochemical industry is produced by linear hydrocarbon reforming. An important reaction in catalytic reforming is the dehydrocyclisation of paraffins to aromatics such as n-heptane conversion to toluene. The latter reaction is strongly endothermic, requiring high operating temperatures [1]. Such high temperatures favour the formation of polyolefinic coke precursors, entail an increase in the rates of the hydrocracking and hydrogenolysis side reactions, and increase the production of gases from methane to butane which are less valuable than the reformat and H_2 [2]. The selectivities for the different reactions depend on the nature of the catalyst involved in the reaction.

Conventional catalysts used in hydrocarbon-reforming processes are mainly composed of noble metal clusters supported on an acidic carrier such as Al_2O_3. These catalysts are reported to operate through a bifunctional mechanism in which the noble metal provides a dehydrogenation–hydrogenation site and the acidic support catalyses structural rearrangements of the hydrocarbon chains [3]. The selectivities of these catalysts for aromatisation of C_6 and C_7 hydrocarbons are quite poor since isomerisation and hydrogenolysis reactions are favoured [4].

Platinum particles supported on non-acidic zeolite L were also used in dehydrocyclisation reactions and they were found to exhibit a high activity and selectivity for n-hexane and n-heptane aromatisation [5–7]. The absence of acidity in the Pt/zeolite L and the correlation of the reaction rate with Pt loading suggest that the catalytic function of this catalyst depends only on the platinum particles [6].

Other neutral supports have also been tested. Pt/activated carbon or Pt/SiO_2 catalysts, for example, are reported to catalyze n-heptane reforming [8–10]. For all non-acidic supports, aromatisation reactions are suggested to proceed following a monofunctional mechanism over platinum particles.

Conversely, Davis et al. have observed that Pt deposited on hydrotalcite-derived magnesia Mg(Al)O, non-zeolitic and basic support, shows the same high activity and selectivity for n-hexane aromatisation as Pt/zeolite L catalysts [11,12]. These authors suggested that the basicity of the support is a key parameter for aromatisation reactions. More recently, bifunctional acid–base catalysts have been tested in C_6–C_8 n-paraffins reforming. Pronounced catalytic activities and high aromatics selectivities have been found for TiO_2–ZrO_2 catalysts [13,14]. These results were attributed to the presence of adjacent acid and base sites with moderate strength acting together to facilitate the aromatisation reaction [13].

A non-conventional family of acid–base catalysts, the oxynitrides, is now well described in the literature [15–21]. The adjustment of the nitrogen/oxygen ratio in oxynitride solids allows their acid–base properties to be tuned since growing nitrogen content induces an increase of the basicity and a reduction of the acidity. The careful control of synthesis parameters during the preparation of zirconium phosphate oxynitrides (ZrPON), for example, allows one to obtain new solids with soft surface, where weakly acid sites are juxtaposed to weakly basic sites [17,18]. In order to extend the catalytic performance of oxynitride solids, particularly in C–H bond activation, platinum has been deposited on their surface [22–24]. Pt supported on AlPON or AlGaPON oxynitrides have been successfully used in the dehydrogenation of isobutane [22,23].

The aim of the present study is a preliminary attempt to evaluate the catalytic properties of ZrPON oxynitrides

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used either as catalysts or as catalyst supports. The tested reaction is the dehydrocyclisation of n-heptane. As described previously, basic or acid–base solids are reported to be suitable catalysts for n-alkane aromatisation reactions. The influence of platinum supported on a ZrPON surface will be examined. Afterwards, the effect of the nitrogen content, which determines the acid–base properties of the ZrPON surface, on the catalytic activity and selectivity will be investigated. Finally, the stability of Pt/ZrPON catalysts at high temperature of reaction will be discussed.

2. Experimental

2.1. Preparation and characterisation of the catalysts

The ZrPON oxynitride supports were obtained by nitridation of an amorphous and high specific surface area precursor, as described previously [17]. Pt/ZrPON, containing initially 0, 11 and 19 wt% N, are prepared by the incipient wetness impregnation method with $(NH_3)_4Pt(NO_3)_2$ methanolic solution. The procedure used is as follows: 0.030 g of $(NH_3)_4Pt(NO_3)_2$ was dissolved in 10 ml of distilled water and 40 ml of methanol (HPLC grade) was added to the solution. 1 g of ZrPON powder was added and the mixture was kept at room temperature under mechanical stirring for 24 h. The mixture was then evaporated to dryness under vacuum and the resulting sample was dried in air at 120 °C overnight. The amount of platinum nitrate amine impregnated (0.030 g) is equivalent to 0.015 g platinum metal, which is equivalent to 1.5 wt% of the Pt/ZrPON catalyst. The impregnated sample was then reduced at 500 °C under pure H_2 flow for 3 h (heating rate of 1.5 °C/min up to 120 °C and of 2 °C/min up to 500 °C).

The amount of platinum after the impregnation procedure was determined by plasma emission spectroscopy (ICP-AES Philips PV8490 equipped with PV8250 spectrometer). The specific surface area of the samples was measured by the single-point BET method ($P/P_0 = 0.3$) in a Micromeritics Flowsorb 2000 apparatus. The metal dispersions were determined by H_2 chemisorption in a static volumetric apparatus Micromeritics ASAP 2000 analyser. H_2 uptake was used to determine the metal dispersion by assuming that the hydrogen/platinum stoichiometry is one.

2.2. Equipment and reaction procedure

The n-heptane reaction was carried out in a continuous-flow micro-reactor system at atmospheric pressure. 200 mg of catalyst was used in the experiments. The n-heptane was fed into the reactor by bubbling a flow of N_2/H_2 (99%/1%) through a saturator maintained at 30 °C. The $H_2/n\text{-}C_7H_{16}$ molar ratio was kept low, ranging from 0.1 to 0.2 depending on the experimental conditions. The effluents of the reactor were analysed by an on line gas chromatograph (Intersmat IGC120FL) equipped with an FID detector and squalane capillary column (Chrompack, length 100 m and diameter 0.25 mm). Helium was the carrier gas. Data were collected over a wide range of experimental conditions: temperature 300–550 °C; H_2 partial pressure $9.2\text{–}9.7 \times 10^{-3}$ atm; n-C_7 partial pressure $5.3\text{–}7.9 \times 10^{-2}$ atm; total gas flow 5–50 ml. Conversion is defined as the amount of n-heptane converted to other products. Selectivities are calculated as the amount of n-heptane converted into each product divided by the total amount of n-heptane converted.

3. Results

Some differences have been observed in the physico-chemical characterisation of ZrPON and Pt/ZrPON catalysts. The specific surface areas, for example, generally decrease by 10% after the impregnation–reduction procedure and are still ranging from 100 to 200 m^2/g. The nitrogen content is also slightly modified and a decrease of 10% must be taken into account. The amount of platinum supported on ZrPON solids after the impregnation procedure corresponds to 1.3 wt% and its dispersion, evaluated by H_2 chemisorption measurements, is weak whatever the nitrogen content (<10%).

The major conversion endothermic reactions of n-heptane over Pt/ZrPON solids include aromatisation to toluene and benzene, isomerisation to branched C_7 hydrocarbons and hydrogenolysis to form C_2–C_6 hydrocarbons (alkane and alkenes). Coke formation has been also observed.

3.1. Influence of the temperature and Pt particles

Figure 1 shows the dependence of n-heptane initial conversion on temperature for ZrPON 11.2 wt% N catalysts. The catalytic activity of ZrPON supports is deeply enhanced by the presence of platinum particles since ZrPON alone does not give rise to significant n-heptane conversion. Actually, the weak conversion observed at 550 °C corresponds to the thermal cracking of the n-heptane molecules. With the

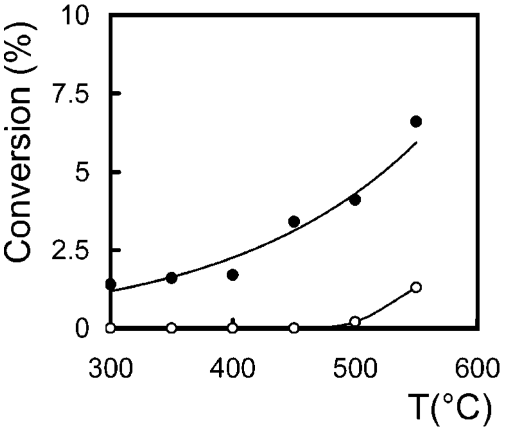

Figure 1. Influence of the temperature on n-heptane initial conversion over ZrPON (○) and Pt/ZrPON (●) catalysts. N content = 11 wt%, WHSV = 3 h^{-1} and $H_2/n\text{-}C_7$ ratio = 0.2.

Table 1
Influence of the nitrogen content on the catalytic activity of Pt/ZrPON in n-heptane conversion.[a]

N content (wt%)	n-C_7 conversion (%)	Selectivities (%)			
		Aromatisation	Dehydrogenation	Isomerisation	Hydrogenolysis
0	5	19	28	2	39
11.2	7	34	30	2	25
19.0	10	38	30	2	22

[a] $T = 550\,°C$, WHSV $= 3\ h^{-1}$ and H_2/n-C_7 ratio $= 0.2$.

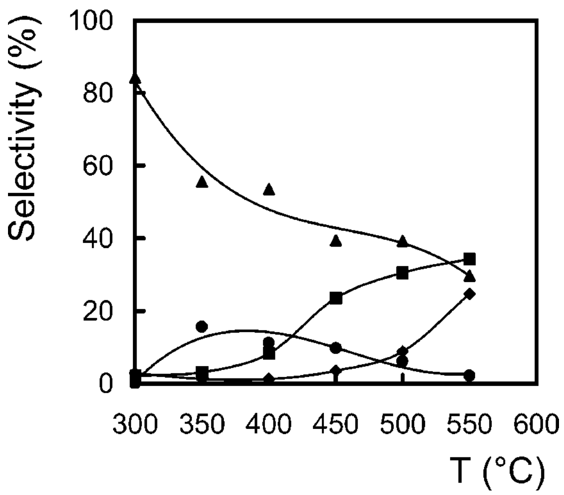

Figure 2. Influence of the temperature on selectivity for n-heptane reforming products over Pt/ZrPON catalyst: (■) aromatisation, (▲) dehydrogenation, (◆) hydrogenolysis and (●) isomerisation. N content = 11 wt%, WHSV $= 3\ h^{-1}$ and H_2/n-C_7 ratio $= 0.2$.

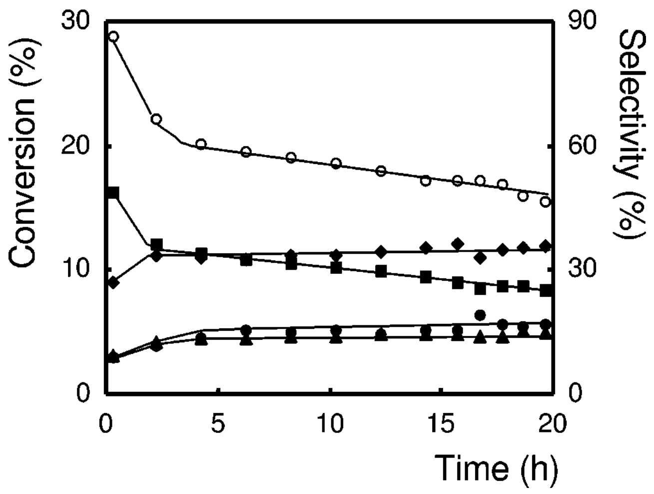

Figure 3. Deactivation of Pt/ZrPON during reaction of n-heptane. WHSV $= 0.5\ h^{-1}$ and H_2/n-C_7 ratio $= 0.1$. Influence of the time of heat treatment at 550 °C on conversion (○) and product selectivities: (■) aromatisation, (▲) dehydrogenation, (◆) hydrogenolysis and (●) isomerisation.

Pt/ZrPON catalyst an increase of the conversion with temperature up to 550 °C is observed. At this temperature, the three major reactions were dehydrogenation of n-heptane in heptene isomers, aromatisation in toluene and benzene and hydrogenolysis in C_1–C_5 hydrocarbons (figure 2). Isomerisation of n-C_7 is also observed but the selectivity for these products remains weak. At low temperature, dehydrogenation reactions are predominant. With increasing temperature, the selectivity for dehydrogenation decreases while cyclisation increases. 550 °C has to be reached for observing a significant contribution of hydrogenolysis.

3.2. Influence of the nitrogen content

The conversion and the selectivities of n-heptane reforming reactions depending on the nitrogen content are shown in table 1. Catalytic conversion depends directly on the nitrogen content of the support. As the nitrogen content increases, the dehydrocyclisation of n-heptane is enhanced while hydrogenolysis selectivity decreases. Selectivity for isomerisation and dehydrogenation remains unchanged whatever the N content. Note that the selectivity for aromatic products is mainly directed to toluene formation since benzene selectivity is very low (around 1%) for all the studied samples. Conversely, the selectivity for hydrogenolysis products is reduced by 45%, when nitrogen content increases from 0 to 19 wt%.

3.3. Influence of the time on stream

Figure 3 shows the evolution of n-heptane conversion and products distribution with time on stream. Catalyst deactivation is observed: after 20 h of reaction, the Pt/ZrPON activity falls to a level of about 40% of its initial activity with most of the change occurring in the first 4 h of reaction. Similar activity–time curves were obtained for the other catalysts of the series. The deactivation can be attributed to coke formation at the surface of the catalysts due to the high reaction temperature.

4. Discussion

Based on the results exposed by Fung and Wang about acid–base bifunctional TiO_2–ZrO_2 catalysts, the use of ZrPON as new acid–base solids could be considered in naphtha reforming reactions. However, the presence of platinum is essential in order to obtain catalytic n-heptane conversion with ZrPON catalysts. Indeed the very low activity observed for ZrPON 11.2 wt% N at 550 °C corresponds to the thermal cracking of n-heptane molecules which cannot be associated to any catalytic activity (figure 1). It is then assumed that, in addition to the acidic and basic sites present at the oxynitride surface, the dehydrogenation/hydrogenation function of platinum particles is also an important factor for n-heptane reforming even if the dispersion of the metal at the surface is very low ($<10\%$). The acid/base sites ratio is also an important parameter for the enhancement of the Pt/ZrPON activity. Table 1 shows that the increase in nitrogen content in the ZrPON support induces an increase in the catalytic activity. The product selectivities are also influenced by the oxygen for nitrogen substitution: aromatisation reactions are promoted by the growing nitrogen presence in ZrPON catalysts while hydrogenolyses are less favoured (table 1). In contrast, dehydrogenation and isomerisation side-reactions are not influenced. Concurrently, it has been previously reported that the adjustment of the N/O ratio in oxynitride solids allows their acid–base properties to be controlled [17,18]. More precisely, the increase in nitrogen content in ZrPON solids is directly correlated to the increase in both the number and the strength of their basic sites, while the initial acidity of the precursor decreases [17,18].

The conversion and selectivity modifications observed in table 1 can be then obviously attributed to the presence of basic centres at the ZrPON surface. Note that these changes cannot be connected to a modification of the impregnation process induced by nitrogen since dispersions on the three catalysts are very weak.

Different hypotheses have been proposed by Davis et al. [12] to explain the role of basic support during aromatisation reactions over Pt/Mg(Al)O systems. Firstly, metal–support interactions could modify the atomic and electronic structure of Pt clusters in such a way that aromatics production would be improved. Because the support magnesia is highly basic, another explanation could be that the metal-catalysed aromatisation reaction is favoured over unwanted isomerisation or hydrogenolysis side reactions known to occur on acid sites. In this case, the support magnesia would only act as an inert carrier for the Pt clusters. Finally, the aromatisation of n-hexane over Pt/Mg(Al)O could occur through a bifunctional mechanism, where the metal sites dehydrogenate n-hexane while the support basic sites catalyse cyclisation and aromatisation. At this stage, it is quite difficult to choose between these different hypotheses in order to explain the n-heptane transformation mechanism over Pt/ZrPON. Note that, in any case, the Pt dispersion is very weak and the basicity of the ZrPON support is the main parameter influencing the n-heptane conversion.

When Pt/ZrPON are used for a long time, some activity loss is observed (figure 3). Sintering of platinum particles due to severe operating conditions could be responsible for the catalytic activity loss. However, the dispersion of platinum atoms at the beginning of the reaction is very poor, and it is most unlikely that further decrease of platinum dispersion could influence the activity to a large extent. The deactivation of the ZrPON-supported platinum catalysts is then most probably due to carbon deposition on the metal particles during the reaction.

Actually, n-heptane reforming reactions are endothermic requiring a high-temperature process to reach acceptable levels of conversion, which favours the formation of coke. Despite unfavourable equilibrium conditions, the presence of hydrogen in the feed is thus required to permit the hydrogenation of the coke precursor limiting the deactivation rate. Some studies on dehydrogenation of isobutane in isobutene over Pt/AlGaPON have shown that the catalyst deactivation, which is correlated to the carbon deposition rate, decreases when hydrogen concentration increases in the feed [23]. However, at very high hydrogen pressure, the platinum surface is kept clear of carbon so that the reforming reaction rate is not yet limited by hydrogenation of adsorbed hydrocarbon. The hydrogen surface coverage rises, decreasing the number of reforming active sites [25].

It is thus assumed that the deactivation of Pt/ZrPON catalysts (25% over the first 20 min) could be limited by increasing the H_2/n-heptane ratio in the feed. Indeed, the very low partial pressure of hydrogen (9×10^{-3} atm) applied in these experiments probably does not allow hydrogenation of the carbon residues blocking the platinum dehydrogenation sites. Consequently, the reforming reaction rate is lowered.

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