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Hydrocracking of phenanthrene over bifunctional Pt catalysts

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Abstract

Hydrocracking of phenanthrene was studied in a fixed bed continuous flow reactor under 60 bar total pressure using a bifunctional catalyst constituted of Pt deposited on silica–alumina. GC–MS analysis was utilised in order to identify the numerous products formed during phenanthrene hydrocracking. Following a kinetic study, a reaction pathway was proposed based on a multi-step mechanism: hydrogenation of aromatic rings, isomerisation and cracking of naphtenic rings, and rearrangements. Reaction temperature showed a great effect in terms of selectivity and catalysts comparison was therefore done at a temperature of 300°C. Three bifunctional catalysts: platinum supported on silica–alumina, on H-Y zeolite and on H-β zeolite were compared in terms of activity and selectivity. A close examination of product distribution indicated that the major contributing factor was the pore structure of the support. Zeolite structures favoured overcracking because of the numerous collisions with acid sites that perhydrophenanthrene could undergo during its diffusion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrocracking; Bifunctional catalyst; Zeolite; Silica–alumina; Phenanthrene

1. Introduction

Hydrocracking is a catalytic petroleum refining process that is commonly applied to upgrade the heavier fractions obtained from the distillation of crude oils. Hydrocracking plays a key role in petroleum refining since it is also used to upgrade some of the products obtained from other processes, such as coker gas oil, deasphalted oil and fluid catalytic cracking (FCC) cycle oils. It is a process of considerable flexibility in that it allows the conversion of a wide range of feedstocks to a variety of products. These products obtained are commonly of high quality. Nowadays the European demand for good quality middle distillates (kerosene, gasoil) is high and one important goal for the refining is to selectively transform feedstocks into middle distillates. To understand how this transformation occurs and to design better hydrocracking catalysts, studies on model compounds have been investigated. Numerous studies have been devoted to paraffin hydrocracking ($n\mathrm{C}_6$–$n\mathrm{C}_{10}$) and this point is now well understood [1,2]. However, these molecules do not fully represent heavy petroleum fraction. Detailed studies on hydrocracking of larger molecules with more than 10 carbon atoms are sparse in literature [3,4]. In the present study, the hydrocracking of phenanthrene ($x = 11.1$ Å, $y = 7.5$ Å and $z = 3.4$ Å in the three directions of space, determined with Cerius II software) was studied over a platinum on silica–alumina catalyst. Preliminary experiments have shown that the first step of its transformation is a total hydrogenation reaction which leads to perhydrophenanthrene. This naphtenic compound (14 carbon atoms) is a bulky molecule too ($x = 11.4$ Å, $y = 6.9$ Å and $z = 5.1$ Å). Then we compared three kinds of hydrocracking catalysts. These catalysts are bifunctional with a hydrogenating function (NiMo sulphide for real feedstocks, Pt in our study) and an acid one: amorphous silica–alumina, H-Y zeolite and H-β zeolite. Our aim is to compare these

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hydrocracking catalysts in terms of activity and selectivity, thanks to our model reaction, and to correlate the catalytic performances with solid properties.

2. Experimental

2.1. Model reaction

Phenanthrene used in the present study was obtained commercially and used without further purification. Hydrocracking reactions were performed in a fixed bed continuous flow reactor equipped with liquid and gas collectors. In order to be pumped, phenanthrene was dissolved in cyclohexane in the concentration of 4 wt.%. Experiments were performed under 60 bar total pressure (H_2 partial pressure of 51 bar) and with a molar ratio H_2/hydrocarbon of 6. Reactions were carried out at 300 and 330°C. Under these conditions, all catalysts are stable and the transformation of solvent is limited to isomerisation in methylcylopentane [5]. The conversion of phenanthrene was varied by modifying the contact time t_c between catalyst and hydrocarbon (t_c = feed flow/catalyst volume). Both liquid and gas products were analysed quantitatively by a gas chromatograph (Hewlett Packard 5890) equipped with a 50 m length PONA column. The column temperature was controlled at 40°C for 10 min and then heated to 280°C at a heating rate of 2°C/min. Identification of the products formed during phenanthrene hydrocracking was performed by GC–MS analysis.

2.2. Catalysts

Platinum was deposited on supports by cationic exchange with NH_4NO_3 as competitor and $Pt(NH_3)_4Cl_2$ as platinum precursor. The three studied solids acid were: silica–alumina (30–70 wt.%), H-Y zeolite (Si/Al = 17) and H-β zeolite (Si/Al = 10). Final catalysts were used under extrudate form. The composition of these catalysts is summarised in Table 1. Pt content in each catalyst was determined using X-ray fluorescence analysis. The metal dispersions were measured by H_2 chemisorption and H_2–O_2 titration. Because of their strong acidity compared to amorphous silica–alumina, H-Y and H-β zeolites were diluted with inert alumina whereas silica–alumina was used pure. Before experiments, catalysts were calcined in a stream of air at 420°C for 4 h, and then reduced under H_2 flow at 450°C for 2 h. As a reference which does not possess bifunctionality, an Al_2O_3 supported Pt (0.5 wt.%) catalyst was prepared.

3. Results

3.1. Hydrogenation reaction

A preliminary study using the monofunctional catalyst Pt/Al_2O_3 showed the hydrogenation of phenanthrene to be fast and to achieve completion. In a large range of contact times ($0.1 < t_c(h) < 2$), 100% of phenanthrene is converted into perhydrophenanthrene. No partially hydrogenated phenanthrene species such as dihydro-, tetrahydro- and octahydrophenanthrene were observed. Under these conditions, platinum can be seen to be a very strong hydrogenating agent. This preliminary experiment indicates that in studies with Pt-bifunctional catalysts, we have to consider perhydrophenanthrene molecules as the reactant. Consequently, conversion has been calculated from the disappearance of the six conformational isomers of perhydrophenanthrene [6]. Furthermore, no cracking products were observed with this monofunctional catalyst, allowing us to affirm that in the reaction temperature range, thermal cracking does not occur. Finally, with this good hydrogenating function in relatively large quantities, we are in the regime of a good metal/acid balance as described by Alvarez et al. [7].

Table 1
Characteristics of the studied bifunctional catalysts

Catalysts	Pt (wt.%)	Pt dispersion (%)	Solid acid content in extrudate (wt.%)	Pore opening (Å)
Pt/H-Y	0.10	56	2.5	7.4
Pt/H-β	0.10	70	0.5	6.4 × 7.6
Pt/SiO_2–Al_2O_3	0.60	56	100	80

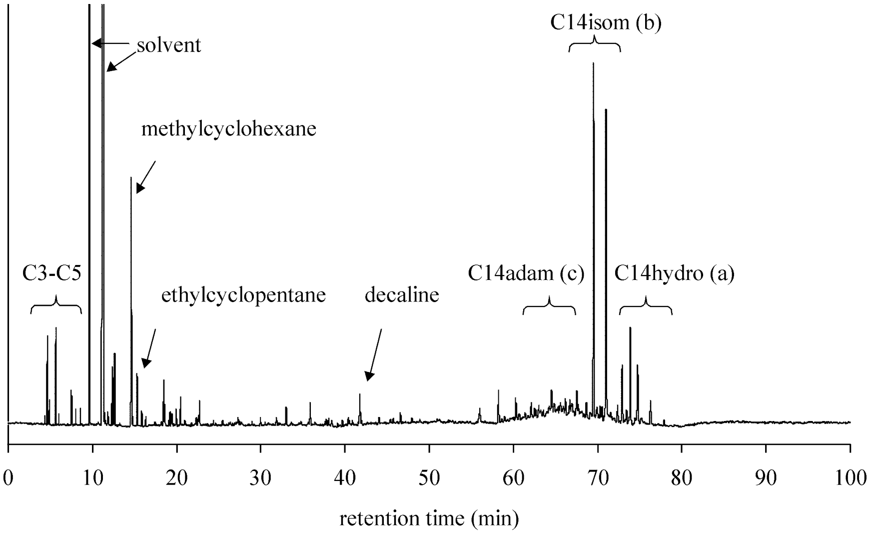

Fig. 1. Chromatogram of liquid products of phenanthrene hydrocracking.

In this situation, the quantity of the hydrogenation component is large enough for the reaction to depend only on the acidic component of the support. This point has been checked in a previous work by studying catalysts with different quantities of platinum.

3.2. Hydrocracking reaction

The model reaction has been first studied with the silica–alumina-based catalyst. Hydrocracking of phenanthrene on Pt/SiO_2–Al_2O_3 leads to more than one hundred products detected by gas chromatography analysis (Fig. 1). Ensuing GC–MS analysis allows the classification of these products into three main families. The first one is constituted by molecules resulting from total hydrogenation of phenanthrene, that means the perhydrophenanthrene molecules (Fig. 2(a)). This group is called C14hydro and is considered as the reactant group. The second family contains molecules having always 14 carbon atoms but presenting a mass spectrum showing the presence of one or two methylcyclopentyl saturated ring (Fig. 2(b)). We call these compounds the C14isom group. Finally, the last family is constituted by molecules having less than 14 carbon atoms and resulting from a primary (methylcyclohexane for example) or a secondary (propane or butane) cracking of species with 14 carbon atoms: $C14^-$. Another family of products: the alkyladamantane (C14adam) have been identified in liquid products (Fig. 2(c)). The formation of these molecules during hydrocracking reactions, which has not previously been discovered, is probably due to a series of carbocationic rearrangements. According to Schneider and Warren [8], perhydroaromatics having three rings and 12 or more carbon atoms, in the presence of an aluminium halide catalyst, undergo rearrangements to form various types of derivatives. The main products are hydrocarbons of the thermodynamically favoured adamantane structure. However, because of their low concentrations, this parallel reaction will not be further considered and the C14adam group will be included in the C14isom group.The investigation at 300°C of the evolution of products yields for the silica–alumina-based catalyst with contact time is represented in Fig. 3. This leads to the proposition of the apparent reaction pathway described in Fig. 4. Isomerisation products are primary products whereas cracked products appear to be secondary products. Cracked products are essentially seven carbon atom products such as methylcyclohexane, dimethylcyclopentane or ethylcyclopentane. It seems that the central ring is more favourably cracked. No cracked products with 10 carbon atoms were observed, which differs from the study of Haynes [9]. In this work,

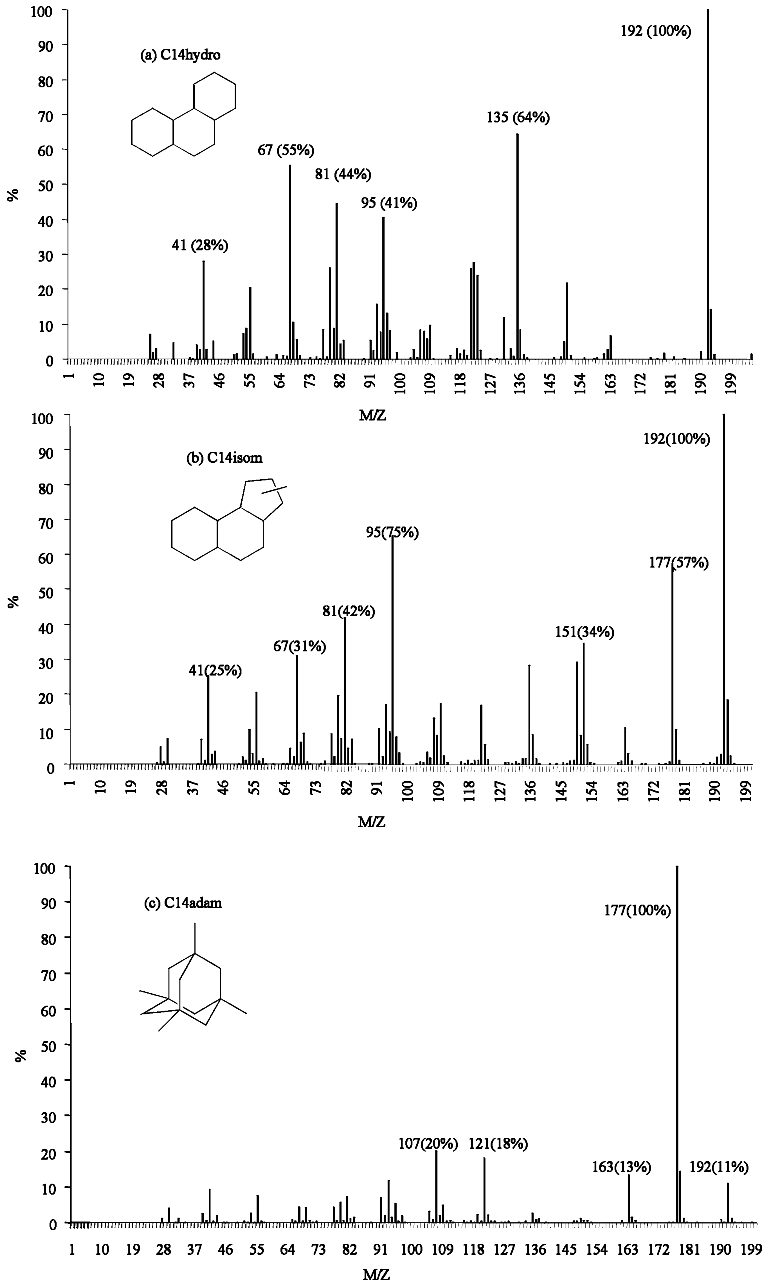

Fig. 2. Mass spectra of C14hydro (a), C14isom (b), and C14adam (c).

hydrogenation of phenanthrene was not achieved, so perhydrophenanthrene molecules were replaced by partially hydrogenated phenanthrene. The cracking of these molecules occurs in a different manner.

3.3. *Effect of temperature on the reaction*

Fig. 5 shows the yield in C14isom products versus conversion for the silica–alumina-based catalyst

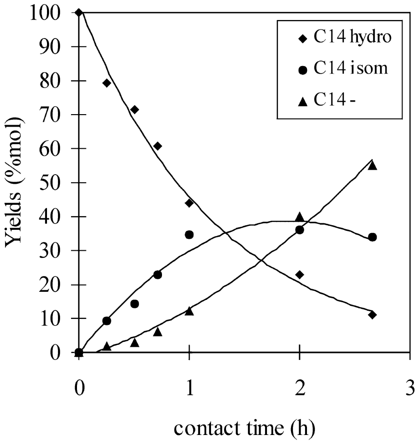

Fig. 3. Reaction products yield as a function of contact time ($T = 300°C$, $P_T = 60$ bars).

for two studied temperatures: 300 and 330°C. It can be clearly seen that an increase in temperature has a strong effect on yields. At 330°C, cracking reactions are favoured to the detriment of isomerisation reactions. For example, at a conversion level of 75%, C14isom yield is 48% at 300°C and 36% at 330°C. These results indicate that comparison of catalytic performances between different solids acid needs to be performed at the same temperature. If reaction temperatures are different, this temperature effect could hide solid properties effect. An apparent activation energy was calculated and a value of 30 kcal/mol was found, which is in agreement with literature values for hydroconversion of naphtenic feeds over Pt/solid acid-based catalysts [10].

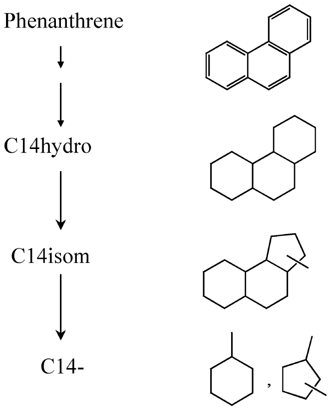

Fig. 4. Proposed reaction pathway for phenanthrene hydrocracking.

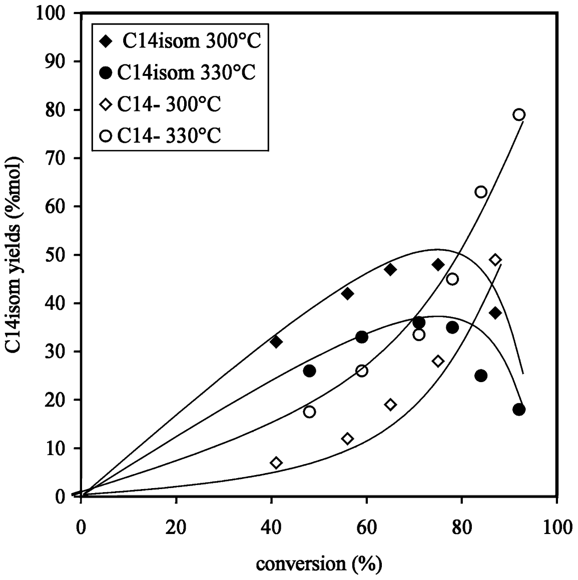

Fig. 5. C14isom yields as a function of phenanthrene conversion for the two studied temperatures and for the silica–alumina-based catalyst.

3.4. Effect of pore opening

The model reaction has been first studied for the silica–alumina-based catalyst in Section 3.2. Before comparing the three supports, it has been verified that products of reaction and reaction pathway were the same for the three catalysts. Figures similar to Fig. 3 have been established for the two other catalysts.In terms of activity, the order observed for hydrocracking of phenanthrene, illustrated in Table 2 is: H-β >

Table 2
Conversion and activity of catalysts at 300°C and for a contact time of 0.25 h

Catalysts	Conversion (%)	Activity (mol/h g)
Pt/0.5% H-β–99.5% Al_2O_3	31	200
Pt/2.5% H-Y–97.5% Al_2O_3	76	100
Pt/SiO_2–Al_2O_3	26	1

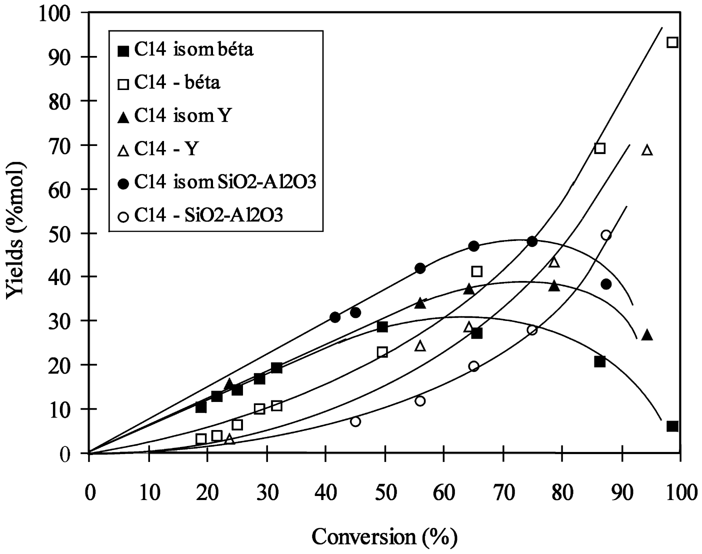

Fig. 6. Conversion dependence of phenanthrene hydrocracking products yields for H-β-based catalyst, H-Y-based catalyst and amorphous silica–alumina-based catalyst at 300°C.

H-Y $\gg$ SiO_2–Al_2O_3. In this work, the calculated activity is the number of moles of perhydrophenanthrene converted per hour and per gram of solid acid, i.e. to say that we have taken into account the zeolite content of the catalysts. In the case of silica–alumina catalyst, the support is totally constituted by silica–alumina and consequently no dilution factor is considered. We demonstrate here clearly that H-Y zeolite and H-β zeolite (i.e. large pore zeolite) based catalysts are effective in processing bulky molecules having dimensions of the same order as phenanthrene.

In order to compare these catalysts in terms of selectivity, the variation of yields of two families of products C14isom and $C14^-$ with respect to reactant conversion was studied. Results for this can be seen in Fig. 6 for Pt/H-β, Pt/H-Y and Pt/SiO_2–Al_2O_3 catalysts. At 300°C, the classification obtained for C14isom selectivity is: $Pt/SiO_2–Al_2O_3\,(48.0\%) > Pt/H\text{-}Y\,(38.0\%) > Pt/H\text{-}\beta\,(28.5\%)$ (in brackets is indicated the maximum yield in C14isom). For example, at 70% conversion, C14isom yields are 25, 35, and 45 mol%, respectively, for H-β, H-Y and silica–alumina-based catalysts. H-β zeolite can be seen to be the most favourable structure for producing cracked products. Higher the catalyst activity, lower its C14isom selectivity. The silica–alumina-based catalyst is the least active but exhibits the highest selectivity for isomerised products. In our point of view, the differences in catalytic performances between crystalline and amorphous aluminosilicates are mainly due to a "structure effect". In his calculations of "collisions number", Fraissard [11] has shown that zeolite structures allow a larger number of collision between active sites and reagents than amorphous solids. He used this point to explain why zeolites are so much more active than amorphous silica–alumina. We propose that we can use this consideration to explain also why zeolites are less selective for intermediate products like C14isom than silica–alumina. Indeed, if the number of collisions between acid sites and perhydrophenanthrene is higher in the case of the zeolites, it follows that these species will have a larger residence time in zeolitic structure compared to silica–alumina. Consequently, after an isomerisation on an acid site and desorption in an olefinic form, readsorption and cracking on a neighbouring acid site is probable. This consideration is also useful to explain differences between H-β zeolite and H-Y zeolite since H-β is a little more closed structure (without supercages) than H-Y.

4. Conclusion

Study of hydrocracking of phenanthrene has been studied at 300 and 330°C at a total pressure of 60 bar using an amorphous catalyst: $Pt/SiO_2–Al_2O_3$. After GC–MS analysis, the numerous products have been identified and a reaction pathway has been proposed. Hydrocracking of phenanthrene under the conditions employed, typical of the hydrocracking process, proceeds via a multi-step mechanism involving hydrogenation, isomerisation and cracking reactions. In order to compare the different catalysts in terms of activity and selectivity, the products have been classified into three product families: (1) the six isomers of perhydrophenanthrene, considered as reactant molecules, (2) the isomers of perhydrophenanthrene with one or two methyl cyclopentyl saturated rings (C14isom) which are primary products and (3) the products resulting from the cracking of C14isom and possessing less carbon atoms than the reactant ($C14^-$) which are secondary products. Adamantane derivatives (C14adam), resulting of multiple carbocationic rearrangements, have also been identified. For the silica–alumina-based catalyst, a temperature effect study has been performed. It can be seen from this that comparisons between catalytic performances of different supports had to be made at the same temperature. Then, we have compared three hydrocracking catalysts on different supports: two zeolites: H-Y and H-β and a silica–alumina. These catalysts have been classed in term of activity and C14isom selectivity at 300°C. The observed activity decreases in the order: $Pt/H\text{-}\beta > Pt/H\text{-}Y > Pt/SiO_2–Al_2O_3$ whereas the selectivity decrease in the order: $Pt/SiO_2–Al_2O_3 > Pt/H\text{-}Y > Pt/H\text{-}\beta$. An explanation has been proposed in terms of the number of collisions with active sites that large molecules undergo in zeolitic structures. This favours overcracking. On the other hand, silica–alumina, which possesses large mesopores, allows greater diffusion of these compounds. This support is less active but more selective in intermediate products. However, other parameters such as nature, force and number of acid sites need to be taken into account to have a greater understanding of the phenomenon. They are going to be studied in the continuation of this work.

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