Pt/SAPO-5 and Pt/SAPO-11 as Catalysts for the Hydroisomerization and Hydrocracking of *n*-Octane

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n-Octane hydroisomerization and hydrocracking on SAPO-5 and SAPO-11 catalysts containing 0.5 wt.% Pt have been investigated in a flow reactor over a wide range of temperatures (573–708 K) and pressures (atmospheric, 3 and 5 bar). These studies have shown that hydroisomerization is a function of the total conversion. The primary products obtained with *n*-octane were the monobranched isomers. Multibranched feed isomers and cracked products were formed in subsequent reactions. In all cases, hydrogen pressure had a strong influence on the activity and time-on-stream deactivation. Hydroisomerization can be considered to be the primary reaction, with hydrocracking occurring to a significant extent only at higher conversions (>40% for Pt/SAPO-5 and >65% for Pt/SAPO-11). The selectivity patterns found in these molecular-sieve catalysts are interpreted in terms of a series of reaction pathways incorporating both confinement effects and shape selectivity factors.

If an *n*-alkane is converted on a bifunctional catalyst in the presence of hydrogen, two principal reactions take place: isomerization to isoalkanes and hydrocracking to products with lower carbon atom numbers than the feed. In the past two decades, extensive studies with model alkanes and largepore zeolite catalysts such as Pt/CaY and Pt/USY, led to a detailed understanding of the reaction mechanism in the absence of shape selectivity.¹⁻⁶ A simplified reaction network is that in which hydroisomerization and hydrocracking occur in series: in a first step, the n-alkane is isomerized to a set of its isomers with single branches. In a consecutive step, these isomers are again isomerized, whereby dibranched isoalkanes are produced. If a further isomerization occurs, however, the tribranched species produced undergo a very rapid hydrocracking referred to as type A β -scission. In addition to this main pathway of hydrocracking via tribranched species, there is some contribution to hydrocracking reactions starting from dibranched species (referred to as type **B** β -scission).

The actual mechanism is much more complex. It is generally accepted that the reactions proceed via alkenes (formed from the feed by dehydrogenation at the metal sites) and alkylcarbonium ions (formed by protonation of the alkenes at the Brønsted acid sites). Also, competitive sorption/ desorption seems to play an important role.' A somewhat more realistic reaction network indicates that both skeletal isomerization and carbon-carbon bond cleavage occur at the level of alkylcarbonium ions. The main pathway from a longchain *n*-alkane to the hydrocracked products goes along the dibranched and tribranched alkylcarbonium ions, provided that the pores of the catalyst are sufficiently large, but goes along monobranched and dibranched ones in catalysts with medium-sized pore diameter. In the present context, it is important that isomerization and hydrocracking of an nalkane are stepwise reactions. As a consequence, monobranched isoalkanes are exclusively formed on most bifunctional catalysts at low conversions. It is obvious that the bulkiness of an isomer increases with its degree of branching; when the pore system of the catalyst is spacious enough (e.g. as in zeolites Y, Beta and ZSM-20) all possible isomers are formed. However, when there are spatial constraints, the bulkier isomers are lacking in the product.

A large number of molecular sieves based on aluminophosphates have been synthesized and identified in recent years.^{8,9} An ideal AIPO consists of tetrahedra of oxygen surrounding equal amounts of aluminium and phosphorus

atoms in a neutral framework. Imbalance of aluminium and phosphorus via replacement by silicon leads to silicoaluminophosphate (SAPO) molecular sieves with ionexchange capacity¹⁰ of interest here. SAPOs have pore structures similar to conventional zeolites, but are usually associated with a milder acidity, owing to the presence of phosphorus.¹¹ The unique combination of pore shape variability and somewhat adjustable acidity suggests the potential of SAPO-n sieves in many catalytic applications. Evidence for selectivity in some hydrocarbon reactions using silicoaluminophosphate molecular sieves as solid acid catalysts has also recently been reported.12-17 For example, in propene oligomerization, n-hexane dehydrocyclization and xylene isomerization, both enhanced selectivities and decreased deactivation rates have been observed for the medium pore-size range silicoaluminophosphate (SAPO) and metalloaluminophosphate (MeAPO) molecular sieves. This was attributed to a combination of mild acidity and shape selectivity. However, little has been reported about the catalytic properties of bifunctional Pt/SAPO. The main objective of the present work is to examine the effect of surface acidity and shape selectivity with both Pt/SAPO-5 and Pt/SAPO-11 using n-octane hydroconversion as a test reaction.

Experimental

Catalyst Preparation

SAPO-5 and SAPO-11 samples were hydrothermally synthesized using a procedure based on those given by Union Carbide.¹⁸ The templates were chosen to be tri-n-propylamine (SAPO-5) and di-n-propylamine (SAPO-11); Al, Si and P sources were aluminium triisopropylate from Merck or pseudoboehmite from Vista, fumed silica (Aerosil 200) from Serva and 85 wt.% H₃PO₄ from Merck, respectively. Synthesis was performed by stirring the solution mixture vigorously and then pouring the mixture into a PTFE-coated stainlesssteel autoclave. Heating at 473 K (SAPO-5) and 423 K (SAPO-11) was maintained for 24 h and 165 h, respectively. The samples were filtered, washed and dried at 393 K. They were then calcined by heating at 873 K (150 K h^{-1}), in static conditions for 7 h. The chemical compositions of the crystalline samples were determined by an atomic absorption method after digestion in a pressure pump and the results, given in terms of oxide contents, were $(Si_{0.07}Al_{0.45}P_{0.48})O_2$ for SAPO-5 and (Si_{0.01}Al_{0.45}P_{0.54})O₂ for SAPO-11.

Metal loading was carried out by wet impregnation with $Cl_2(NH_3)_4Pt$ (Aldrich, 98% purity); a known amount of SAPO-5 or SAPO-11 was added to a concentrated aqueous salt solution containing the amount of metal necessary to obtain the desired weight loading (0.5 wt.%). After impregnation for 24 h, the materials were dried in air at room temperature, for at least 48 h, then at 393 K overnight and finally calcined in flowing O₂ (60 ml min⁻¹) at 673 K for 2 h and reduced in flowing H₂ (100 ml min⁻¹) at 648 K for 3 h. Metal dispersions were estimated by H₂ pulse chemisorption at room temperature on a Micromeritics TPD/TPR 2900 apparatus. Table 1 gives, for Pt/SAPO-5 and Pt/SAPO-11 catalysts, the metallic area, S_{Pt}, and metal dispersion, D.

Details of SAPO-5 and SAPO-11 characterization have been reported elsewhere.¹⁹ The surface area, S_{BET} , pore volume, V_p , and average pore radius, r_p , are collected in Table 1.

Surface Acidity Measurements

Previous surface acidity (sum of Brønsted and Lewis sites) measurements^{19–21} (Table 2) in a dynamic mode by means of the gas-phase adsorption of pyridine (py) and 2,6-dimethyl-pyridine (DMPY) using a pulse-chromatographic technique, indicated that SAPO-5 exhibits the highest density of acid centres, which ought to make this catalyst the most active for cumene dealkylation.¹⁹ 0.5 wt.% Pt deposition does not change the acidity function of the SAPOs.

Diffuse reflectance infrared (DRIFT) spectra of adsorbed probe molecules (py and DMPY) have been recorded on a BOMEN MB-100 instrument equipped with a diffuse reflectance attachment (Spectra-Tech, Collector) that has a controlled environment chamber (Spectra-Tech P/N 0030-100). The spectra (256 scans) were recorded in absorbance mode with a resolution of 8 cm⁻¹ and a gain factor of one.

Measurements were carried out on pure SAPO catalysts previously dried at 400 K for 24 h under vacuum. For most diffuse reflectance experiments the catalysts were used in powder form of *ca.* 200 mesh size. Afterwards, the catalyst was placed in the controlled environment chamber cell and then heated at 573 K (1 h) in dehydrated and deoxygenated nitrogen (10 ml min⁻¹). Higher nitrogen flushing rates or vacuum treatment did not modify the DRIFT spectra.

Afterwards, the DRIFT spectrum of the sample (i.e. the reference) was recorded under a flowing inert stream of nitrogen. The cell was sequentially cooled to 473 K and then to 373 K under nitrogen and the respective reference spectra were obtained. The adsorption of the probe molecule,

 Table 1
 Physicochemical characteristics of SAPO and Pt/SAPO catalysts

catalyst	$\frac{S_{\text{BET}}}{/m^2 g^{-1}}$	$\int_{cm^{3}g^{-1}}^{V}$	r _p /nm	$/m^2 g^{-1}$	D (%)
SAPO-5	214	0.18	1.7	_	_
SAPO-11	123	0.49	7.9		
Pt/SAPO-5	182	0.62	8.1	187	76
Pt/SAPO-11	103	0.54	20.6	113	46

Table 2 Surface acidity properties of SAPO and Pt/SAPO catalysts

	py/µmol g ⁻¹		DMPY/µmol g ⁻¹	
catalyst	573 K	673 K	573 K	
SAPO-5	160	141	102	
SAPO-11	72	67	24	
Pt/SAPO-5	149	130	89	
Pt/SAPO-11	68	60	16	

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nitrogen-flushed from a saturator kept at a constant temperature of 298 K, was then carried out and was followed by subsequent heatings as described below.

The probe molecule was allowed to be adsorbed at 373 K for 2 h. This procedure allows for the complete saturation of the catalyst surface as a large excess of the probe molecule is admitted in the DRIFT cell. The adsorption step was followed by flushing for 3 h with nitrogen to remove any unreacted physically adsorbed reagent. The characteristic spectrum of the various forms of base retained on the catalyst was recorded. Subsequent flushings were performed at 473 and 573 K, and the corresponding spectra (including reference spectra) were recorded at those temperatures

Catalytic Activity Measurements

n-Octane was purchased from Aldrich (>99 mol% purity). The experiments were carried out in a flow reactor system incorporating a 1/4 in† id tubular reactor and with a normal catalyst charge of 120 mg. Liquid hydrocarbon feed was pumped into a feed-system vaporizer via a syringe pump (Harvard Model 4400), mixed with a hydrogen flow (25 ml min⁻¹) at 443 K and fed to the reactor. The reactor effluent was sampled and analysed using a high-resolution gas chromatograph (HRGC), equipped with a 100 m long and 0.25 mm id fused-silica capillary column Petrocol DH, with a flame ionization detector. The products were characterized by gas chromatography-mass spectrometry (GC-MS) (VG Autospec).

The reaction was carried out over a wide range of operating conditions: temperature, 573-708 K, liquid *n*-octane flow rates, 0.6-3.6 ml h⁻¹; total pressure, atmospheric, 3 and 5 bar. The catalyst was pretreated at 673 K for 1 h in flowing hydrogen (25 ml min⁻¹).

Results and Discussion

Surface Acidity

Gas-chromatographic pulse techniques can provide acidity information at catalytic reaction temperatures. However, they are unable to distinguish Brønsted and Lewis centres unless specific basic probes are used. It is known that (DMPY) is selectively adsorbed on Brønsted acid sites, but not on Lewis acid centres, because of the steric hindrance of two methyl groups, whereas sterically unhindered py is adsorbed on both Brønsted and Lewis acid sites.^{22,23}

Fig. 1A and B show DRIFT spectra of py adsorption at 373 K followed by desorption at 373, 473 and 573 K, with



Fig. 1 DRIFT spectra of pyridine adsorbed on A, SAPO-5 and B, SAPO-11 at (a) 373, (b) 473 and (c) 573 K

 $\dagger 1 \text{ in} = 25.4 \text{ mm}.$

SAPO-5 and SAPO-11 catalysts, respectively. The procedure gives rise to pyridinium cations, produced by the reaction of py with surface Brønsted acid sites (band at *ca.* 1540 cm⁻¹) and to species coordinated to Lewis acid sites (band at 1448 cm⁻¹). The band at 1490 cm⁻¹ can be attributed to py chemisorption on both Brønsted and Lewis sites.²³⁻²⁵ The desorption of py at increasing temperatures results in the removal of both Brønsted- and Lewis-bound py. However, the latter decreases significantly faster than the former. At 573 K, Brønsted-bound py remained evident on both catalysts, especially on SAPO-5.

The development of Brønsted acidity in these catalysts is also shown by DMPY adsorption through the presence of the band at 1636 cm⁻¹ (Fig. 2A and B),• attributed to the vibration of 2,6-dimethylpyridinium ions.^{22,26} On both catalysts, the band at 1636 cm⁻¹ remains even at 573 K, showing the presence of a great number of Brønsted acid centres with high strength. Furthermore, since the area of the adsorption peak is proportional to the amount of DMPY adsorbed on active Brønsted acid centres, the change in the peak area with temperature reflects the strength of those centres, indicating that SAPO-5 is the solid with the higher acid strength.

n-Octane Hydroconversion

If the hydroconversion of *n*-octane is taken as a probe reaction, the main steps in the catalytic process are cracking on strong acid sites and dehydrogenation on metallic sites. In addition, the *n*-octene generated by dehydrogenation undergoes isomerization to isooctenes on acid sites. These isooctenes undergo either hydrogenation to isoalkanes on metallic sites or cracking on acid sites. If adjacent pairs of acid-base sites are present, *n*-octene undergoes an aromatization reaction to give ethylbenzene and xylenes.

Effect of Reaction Temperature

1636

Α

0.1

The typical dependences of *n*-octane transformation on conversion into octane isomers, both with Pt/SAPO-5 and with Pt/SAPO-11, are collected in Fig. 3. The catalyst has a marked effect on the distribution of the isomerization and cracking products; however, the same products are formed on all catalysts. They can be classified into three families: (a) Methylheptanes (2-MC₇, 3-MC₇ and 4-MC₇): monobranched isomers. (b) Dimethylhexanes (2,2-DMC₆, 2,3-DMC₆, 2,4-DMC₆, 2,5-DMC₆, 3,3-DMC₆ and 3,4-DMC₆): dibranched isomers. (c) Light alkanes C_1-C_7 : cracked products, mainly butane fractions, with propane and pentane in equimolar amounts.

The amount of aromatic products was negligible, especially at lower-temperature reactions. Pt/SAPO-5 produced larger

В

0.1

636



Fig. 2 DRIFT spectra 2,6-dimethylpyridine adsorbed on A, SAPO-5 and B, SAPO-11 at (a) 373, (b) 473 and (c) 573 K



Fig. 3 Isomerization conversion of *n*-octane on (\Box) Pt/SAPO-5 and (\triangle) Pt/SAPO-11 catalysts as a function of the total conversion of *n*-octane. Conditions: pressure, 5 bar; H₂ flow, 25 ml min⁻¹; *n*-octane flow, 0.6–3.6 ml h⁻¹; 120 mg of catalyst; temperature, 573–708 K.

amounts of both p- and m-xylene, products expected from the cyclization of C₈-isoalkanes. However, the dominant aromatics from the conversion of *n*-octane with Pt/SAPO-11 are ethylbenzene and *o*-xylene, formed by direct cyclization of *n*-octane.

Isomerization is the major reaction with Pt/SAPO-11 catalyst in all temperature ranges, but as the severity of the reaction conditions increases, it passes through a maximum, owing to the consumption of isomerized products in consecutive hydrocracking reactions.¹ The maximum conversion into n-octane isomers amounted to 41 wt.% with this catalyst. Isomerization is the major reaction with Pt/SAPO-5 only at low reaction temperatures (isomerization selectivity of the nalkane is close to 100% at low conversion levels), the maximum conversion being into n-octane isomers of 32 wt.%; at higher temperatures, cracking is the main reaction and isomerization drops very rapidly. These facts eliminate the possibility of direct cracking of n-octane. Fig. 3 shows that, with all catalysts, the ratio of isomerized to cracked noctane decreases when conversion increases. This suggests that n-octane is transformed successively into isomers and into cracking products, the isomerization leading to monobranched, then to multibranched isomers. Thus, isomers are the only primary products.

The yield and distribution of octane isomers need to be considered, since the industrial application of this reaction is aimed at the improvement of research octane numbers (RONs) in gasoline. Fig. 4 shows the molar distribution of octane isomers with temperature, obtained for Pt/SAPO-5 and Pt/SAPO-11, according to their branching grades and monobranched distributions. As a general result, all possible n-octane isomers (mono- and di-branched) are produced with Pt/SAPO-5. On increasing the severity of the reaction conditions, the content of dibranched isomers increases, but in all cases the monobranched ones are predominant. Isomer products obtained with Pt/SAPO-11 were monobranched ones (small amounts of dibranched ones appear only at high conversions), indicating diffusional limitations in the one dimensional porous framework of SAPO-11 (medium pore size). The distribution of isomerized products as a function of the degree of conversion can be explained in terms of a carbocation mechanism, by the relative reactivity of these



Fig. 4 Molar distribution of octane isomers vs. temperature with (a) Pt/SAPO-5 and (c) Pt/SAPO-11, according to their branching grade; •, monobranched; \Box , dibranched. Monobranched distribution [(b) and (d), respectively] •, 2-MC7; \Box , 3-MC7; \diamondsuit , 4-MC7. Conditions: pressure, 5 bar; 120 mg of catalyst; H₂ flow, 25 ml min⁻¹; *n*-octane flow, 1.8 ml h⁻¹.

isomers for further isomerization and, more importantly, for hydrocracking. Fig. 5 shows the temperature dependence of the cracked products distribution for both catalysts. In all cases, butane fractions in one part, and propane and pentanes (in equimolar proportions) in the other, are the main cracking products obtained. Methane and ethane are formed with the Pt/SAPO-11 catalyst: a superimposed hydrogenolysis on the metal crystallites is a possible cause for this. The branched isomers of the cracked products represent a more important fraction in Pt/SAPO-5 than in Pt/SAPO-11 and their concentrations are slightly dependent on the conversion to butane and pentane.

Effect of Hydrogen Partial Pressure

The influence of hydrogen pressure was investigated at 648 K, between atmospheric pressure and 5 bar. Fig. 6 shows global *n*-octane conversion and isomer selectivity with Pt/SAPO-5 and Pt/SAPO-11 as a function of reaction time. At atmospheric pressure the deactivation as a function of time-



Fig. 5 Molar distribution of cracked products vs. temperature with (a) Pt/SAPO-5 and (b) Pt/SAPO-11; \bullet , C₁; \Box , C₂; \diamond , C₃; Δ , C₄; ∇ , C₅; \bigcirc , C₆; +, C₇. Conditions: pressure, 5 bar; 120 mg of catalyst; H₂ flow, 25 ml min⁻¹; *n*-octane flow, 1.8 ml h⁻¹.

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Fig. 6 Influence of hydrogen pressure on global conversion and isomer selectivities with (a) Pt/SAPO-5 and (b) Pt/SAPO-11 catalysts. (----) conversion and (.....) selectivity; \Box , atmospheric pressure; \diamond , 3 and \bullet , 5 bar. Conditions: 120 mg of catalyst; H₂ flow, 25 ml min⁻¹, *n*-octane flow, 1.8 ml h⁻¹; temperature, 648 K.

on-stream is important, especially with Pt/SAPO-5 catalyst. This deactivation is caused by the formation of coke deposits. On increasing the H_2 pressure, the catalyst stability is greater. One of the characteristics of flow reactions is the large reactive quantities in contact with the catalyst. This causes the catalyst deactivation process to have a greater weight.

Experimental results show that the different structures of the two kinds of catalysts we have synthesized impose different reactivities on *n*-octane hydroconversion. Pt/SAPO-5 acts as an excellent *n*-octane hydroisomerization catalyst at lower temperatures (lower conversions) but at higher temperatures is ineffective, while Pt/SAPO-11 behaves as an excellent isomerization catalyst over the whole temperature range tested, including temperatures above 673 K. However, both catalysts produce nearly the same products but in different proportions depending on their structure and reaction temperature (conversion).

The distribution of Pt/SAPO-5 products is very similar to that observed for the ultrastable Y zeolite containing 0.5% Pt catalyst^{2,3} because they are molecular sieves with similar pore diameters. It is accepted that *n*-alkane hydroconversion catalysed by bifunctional metal/acid catalysts occurs along a series of steps where cracking is preceded by linear chain isomerization. The product distribution depends on the number of acid centres available to the alkene during its diffusion between two hydrogenation centres and, consequently, on the ratio of acid centres to metallic centres.

It is generally accepted that the branching of alkene intermediates occurs through protonated cyclopropane intermediates.²⁷⁻²⁹ This is the case for the isomerization of n-octane into 2-, 3- and 4-methylheptanes and for that of methylheptanes into dimethylhexanes. Monobranched isomers predominate, especially with the Pt/SAPO-11 catalyst. The distributions indicate several differences and similarities of the catalysts: (1) The distribution of monomethyl isomers is independent of the temperature and partial pressures of the reactants, depending only on global n-octane conversion. (2) The composition of that fraction varies only slightly with global conversion (temperature) and approaches its equilibrium distribution only with Pt/SAPO-5. We conclude that on Pt/SAPO-5, the rate of interconversion of the monobranched alkanes is higher than the rate of formation or conversion into multibranched structures.

The distribution of the dibranched isomers, formed in consecutive reactions from the monobranched octanes, has different characteristic features depending on the catalyst we are studying. (1) Dimethylhexanes with a methyl group in the 2position are predominant with both catalysts, except 2,2dimethylhexane in Pt/SAPO-11 which appears only in a very small amount because it has the largest molecular diameter. (2) The relative amounts of dimethylhexanes hardly change

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with operating conditions, but do not reach equilibrium values. The preferential cracking of some of the isomers with respect to others is a possible explanation for this. An alternative one is that the differences between catalyst pore diameters permits formation of bulky isomer products in Pt/SAPO-5 but not in Pt/SAPO-11.

However, this does not mean that cracking products may be the only result of a direct β -scission of linear C₈ (type D, requires at least one primary carbenium ion); a hydrogenolysis process also takes place on Pt crystallites, especially with Pt/SAPO-11. This can be explained by suggesting that some of the alkene intermediates find enough active acid centres to undergo successively isomerization and cracking during their migration between two platinum sites. This can be related to a slower migration of the alkene intermediates in the narrowest pore network of Pt/SAPO-11. This structural parameter is very significant as it is well known that molecular circulation may have a significant effect on reaction kinetics as well as on product distribution in a great number of reactions.³⁰ In our case, the constraints exerted by the SAPO-11 pore structure on the diffusion of the intermediate alkenes would ensure a longer contact time (than in the case of SAPO-5) between the alkene and the acid sites. Moreover, the configurational limitations could also explain the low rate of formation of dibranched products: the dibranched alkenes formed by isomerization of monobranched alkenes would not migrate and would be transformed on-site into cracking products.

The size of the pores, as well as the size and the shape of the space available near the acid centres, can thus determine to a large extent the selectivity of *n*-octane transformation in bifunctional Pt/SAPO catalysts. The differences in selectivity between Pt/SAPO-5 and Pt/SAPO-11 samples can be explained by the slow migration of alkene intermediates in the SAPO-11 channels and by steric constraints.

The diffusional behaviour will also be related to configurational influences. Qualitative prediction of the diffusion of molecules in medium-pore zeolites can be made by comparing the critical molecular diameter of the sorbates with the zeolite pore diameter.³¹ This is defined as the smallest cylinder which can enclose the molecule in its most favourable equilibrium configuration. The critical molecular diameters are 0.49 nm for n-octane, 0.56 nm for monobranched and dibranched isomers averaged over different isomers and 0.70 nm for dibranched isomers averaged over the same isooctanes. Comparison of these with the elliptical channels of SAPO-11 (0.39 nm \times 0.64 nm) indicates clearly that the lowest diffusional restriction is for the *n*-alkane. Further, in comparison with the other C₈ hydrocarbons, for the dibranched isomers there is stronger diffusional retardation because of their larger molecular diameter and their lower flexibility. This causes them to appear only in trace amounts at high conversions. The presence of steric restrictions due to the SAPO-11 structure leads to a general suppression of highly branched intermediates in cracked products.

Conclusions

In summary, the reaction schemes for n-octane transformation on Pt/SAPO-5 and Pt/SAPO-11 catalysts are not the same as a result of their different structures. The composition of the branched isomerization and cracking products obtained on these bifunctional catalysts provides a wealth of information on the intracrystalline pore architecture. Hydrogen pressure strongly influences the reaction: a strong decrease in conversion with time-on-stream is observed at atmospheric pressure owing to the formation of coke deposits.

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