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Conversion of decalin and 1-methylnaphthalene over AlSBA-15 supported Pt catalysts

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ABSTRACT

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Keywords: Decalin Ring opening 1-Methylnaphthalene Hydrogenation Platinum catalyst AlSBA-15 Platinum catalysts (1.5 wt.%) containing AlSBA-15 obtained with various aluminium precursors were tested for activity in 1-methylnaphthalene hydrogenation. Experiments were carried out in a continuous-flow system at atmospheric pressure (240–350 °C, W/F=0.8 g s/cm³). It was found that 1-methylnaphthalene conversion over Pt-loaded catalysts was not influenced by the aluminium precursor used in the preparation of the Pt/AlSBA-15 catalysts. However, the Pt catalyst prepared with AlSBA-15 obtained from aluminium sulphate provided a higher *cis*-methyldecalins/*trans*-methyldecalins ratio in the reaction products as compared to the catalysts obtained with aluminium mitrate or aluminium isopropoxide. Consideration was also given to the influence of platinum amount (0.5, 2.5 and 4.5 wt.%) on the catalytic performance of bifunctional Pt/AlSBA-15 catalysts (AlSBA-15 obtained with aluminium sulphate) in decalin hydroconversion. It was shown that impregnation of AlSBA-15 with H₂PtCl₆ increased Brønsted acidity. Investigations into decalin conversion were conducted in a continuous-flow system with a fixed-bed reactor (5 MPa, 300–380 °C, H₂:CH = 500 N m³/m³; WHSV = 2 h⁻¹). Incorporation of 0.5 wt.% Pt into AlSBA-15 yielded a catalyst with the highest dispersion of the platinum phase and the highest yield of ring opening products, amounting to 26.4 wt.% at 380 °C.

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1. Introduction

In view of obtaining greener and advanced diesel fuels, it is highly desirable to enhance the efficiency of aromatics hydrogenation, especially when an increased amount of oil fractions obtained by FCC is used for transportation fuel production. Hydrogenation of polynuclear aromatics (PAHs) (*e.g.*, naphthalene, anthracene, phenanthrene and their derivatives) and also, ring opening of cycloparaffin hydrocarbons formed offer the possibility of significantly reducing the content of aromatics and improving the cetane number beyond what can be obtained with aromatic saturation alone. The ideal process would be selective ring opening that reduces the number of ring structures while the carbon number of a product molecule is retained.

Taking into account the hydrocarbon content of the diesel oil fraction, it is conventional to use naphthalene or 1methylnaphthalene as a model compound for assessing the activity of hydrogenating catalysts [1–3]. When investigating the reaction of selective ring opening, use is made, *inter alia*, of decalin (a product of complete naphthalene hydrogenation), which acts as the model compound [4,5]. Lin et al. have demonstrated [6] that during hydrogenation of aromatics to decalin catalyst selectivity increases with the drop in reaction temperature and rise in hydrogen pressure. The rate of tetralin to decalin hydrogenation is slower than that of naphthalene to tetralin hydrogenation. In consequence, even under thermodynamically favourable conditions of decalin formation, tetralin is the main product of naphthalene hydrogenation, whereas decalin forms when naphthalene conversion approaches 100% [2]. Hydrogenation of tetralin fails to occur in the presence of naphthalene because of the competitive adsorption of the latter [7]. It has also been reported that *cis*decalin and *trans*-decalin have different reactivities in the ring opening reaction, and that *trans*-decalin is more stable in thermodynamic terms [8]. The mechanisms governing the hydrogenation of 1-methylnaphthalene over Pt/USY and the hydrogenation of naphthalene over Pt(Pd)/mordenite and Pt(Pd)/H-Y have been described by Arribas et al. [3] and Schmitz et al. [9].

Decalin conversion was investigated over monofunctional acidic zeolites, H-Beta, H-Y, and H-Mordenite [10–15] and bifunctional catalysts [5,14,16–19]. The mechanism of conversion over monofunctional acidic zeolites has been discussed by Du et al. [14]. Corma et al. [15] have examined the effect of zeolite pore topology of the catalyst on product distribution in decalin cracking. Their research involving zeolites with varying pore size distribution, *e.g.* ZSM-5, ITQ-2 (medium sized), USY, Beta (large sized) and UTD-1 (ultralarge sized), has led to the finding that larger pores (USY, Beta) allow faster diffusion of product molecules, thereby reducing the probability that secondary cracking and dealkylation may occur.



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In ring opening reactions over bifunctional catalysts, the activity and selectivity of the catalyst is influenced by the following factors: the type of the metal used, the size of metal particles, the acidity and pore size of the support, the distance between metal and acid sites, and the reaction conditions (temperature, hydrogen pressure) [14]. Decalin conversion over H-Beta, H-Y, H-Mordenite and La-X zeolites with noble metal contents (mainly Pt and Ir) as well as Ni and Mo has been the focus of several studies [5,16–18]. Kubička et al. examined the ring opening of decalin over protonform and platinum-modified zeolites (H-Beta, H-Y, H-mordenite). In their experiments the incorporation of a noble metal (2 wt.% Pt) into the H-Beta zeolite framework produced yields of ring opening products approaching 30 mol%, which were approximately 3 times as high as over proton-form zeolites [11,19].

In the past few years, much consideration has been given to the application of mesoporous materials, such as MCM-41 [20-22] and SBA-15 [23-25], as supports for hydrotreating catalysts. Results of decalin conversion over mesoporous MCM-41 loaded with Ru (2.5 and 5 wt.%) or Pt(Ir) (0.22-1.88 wt.%) have been reported by Murzin et al. [26] and by Mouli et al. [27], respectively. The low acidity of mesoporous siliceous materials is an obvious limitation to their use as supports for isomerization, hydrocracking, hydrodecyclization and hydrogenation catalysts. A common method of upgrading their acidity involves substitution of Al atoms for Si atoms. For the preparation of such supports use is made of a method where Al atoms are incorporated either during synthesis of the porous material [28,29] or during impregnation of the siliceous material with the aluminium precursor [30,31]. The effect of the aluminium precursor on the AlSBA-15 properties was examined by Li et al. [32]. The degree of Si substitution (coprecipitation method) increases in the following order: aluminium sulphate < aluminium nitrate < aluminium isopropoxide [33].

This work is focused on the contribution of aluminium sources to the catalytic properties of Pt/AlSBA-15 (1.5 wt.% of Pt) in 1-methylnaphthalene (1-MeN) conversion as well as to the *cis*methyldecalins/*trans*-methyldecalins ratio. Consideration is also given to the problem of how the Pt content (0.5–4.5 wt.% of Pt) of the Pt/AlSBA-15 catalyst influences conversion and selectivity to ring opening products in the transformation of decalin.

2. Experimental

2.1. Catalysts preparation

Mesoporous molecular sieves AlSBA-15 were synthesized by the method described for SiSBA-15 in [34]. Samples with Si/Al = 20 ratio were obtained *via* the direct hydrothermal method using aluminium sulphate (Al₂(SO₄)₃·18H₂O; Aldrich), aluminium nitrate (Al(NO₃)₃·6H₂O; Aldrich) and aluminium isopropoxide ([(CH₃)₂CHO]₃Al, Acros) as metal sources. These samples are denoted by AlSBA-15(S), AlSBA-15(N), and AlSBA-15(IP), respectively.

Pt/AlSBA-15 catalysts were prepared by impregnating the mixture of AlSBA-15 and 20 wt.% of boehmite (Pural KR-1, Sasol GmBH; S_{BET} = 304 m²/g, 0.54 mmol NH₃/g) with a solution of hexachloroplatinic acid (POCh). After Pt impregnation the samples were dried at 20 °C (24 h), 50 °C (30 min), 70 °C (30 min) and 100 °C (12 h), and then calcined at 150 °C (1 h), 250 °C (1 h), and 350 °C (3 h). The extrudates from the powder catalysts were obtained using 3% nitric(V) acid. All extrudates were made subject to drying (110 °C, 12 h) and calcination (450 °C, 3 h). According to the Al precursor applied, the catalysts (1.5 wt.% Pt) were denoted by Pt/AlSBA-15(S), Pt/AlSBA-15(N) and Pt/AlSBA-15(IP). The experiment which aimed at determining the effect of the amount of platinum on the activity and selectivity of the catalysts in decalin hydroconversion was conducted in the presence of catalysts with a 0.5 wt.%, 2.5 wt.% and 4.5 wt.% Pt content, supported on the AISBA-15(S) material; the catalysts were denoted by 0.5Pt/AISBA-15(S), 2.5Pt/AISBA-15(S) and 4.5Pt/AISBA-15(S), respectively.

2.2. Catalysts characterization

Texture: Nitrogen adsorption and desorption isotherms were measured at 77 K with the Autosorb-1C Quantachrom sorption analyser. Specific surface area was calculated using the BET model. The BJH method was applied for determining the pore diameter.

XRD and MAS NMR: The powder X-ray diffraction patterns of the AlSBA-15 materials were collected on a Siemens D5005 diffractometer using CuK α (λ = 0.154 nm) radiation. ²⁹Si MAS NMR and ²⁷Al MAS NMR spectra were recorded with an AC200 Bruker spectrometer.

Acidity: Acidity was determined by adsorption of pyridine (Py-IR) at 170 °C. Prior to acidity measurement, the samples were activated at 450 °C for 30 min (10^{-5} mbar). IR spectra were recorded with a Tensor 27 Bruker spectrometer. The A_{350}/A_{170} ratio where A_{170} is the intensity of the Py ion band upon evacuation at 170 °C and A_{350} is the intensity of the same band upon desorption at 350 °C was taken as a measure of the acid strength. Acidity was also evaluated by chemisorption of ammonia (NH₃-TPD) at 180 °C in through-flow system equipped with katharometer. The sample was pretreated in the stream of argon at 550 °C for 2 h and then cooled to 180 °C. After desorption of physically adsorbed ammonia, the sample was heated up to 550 °C at a rate of 10° /min.

Chemical analysis and dispersion: Pt content was determined by XRF (Canberra Packard, 1510). Pt dispersion was measured by oxygen titration. The catalysts were made subject to reduction in hydrogen at 500 °C for 5 h, followed by introduction of 0.05 ml pulses of oxygen at RT. Dispersion of Pt over the AlSBA-15 surface was calculated according to Bergeret et al. [35].

TOF-SIMS: The time-of-flight secondary ion mass spectrometry (TOF-SIMS) investigations were performed using an ION-TOF instrument (TOF-SIMS IV) equipped with a 25 kV pulsed ⁶⁹Ga⁺ primary ion gun in the static mode.

2.3. Catalytic experiments

The influence of the aluminium precursor in AISBA-15 synthesis on the catalytic performance of bifunctional Pt/AISBA-15 (1.5 wt.% of Pt) catalysts for the hydrogenation of 1-methylnaphthalene (1-MeN) was examined using a continuous fixed-bed atmospheric pressure reactor (240–350 °C, W/F = 0.8 g s/cm³).

The effect of platinum content of Pt/AlSBA-15(S) catalysts on the ring opening of decalin was investigated in a continuous-flow system with a fixed-bed reactor under the following conditions: p = 5 MPa, H₂:CH = 500 N m³/m³ and WHSV = 2 h⁻¹. Decalin (10 vol.% in *n*-heptane) was supplied by means of an HPLC Gilson 307 pump (model 5SC). Activity tests were performed using 0.25 g of powder catalyst (grain size of 0.4–0.63 mm) diluted with SiC up to 2 cm³. Before activity tests the samples were reduced with H₂ at 300 °C for 1 h and 450 °C for 30 min (30 cm³ min⁻¹, 5 MPa). The activities of the catalysts were measured at reaction temperature of 300, 340 and 380 °C.

Liquid samples (accumulated for 1 h) were weighed and analysed by GC–FID equipped with an RTX-1 capillary column (100% dimethylpolysiloxane, 60 m, 0.53 mm, 1.0 μ m). Since decalin conversion yields numerous products, they were identified by means of the GC–MS method. The GC–MS analysis was carried out in an HP6890 instrument. The same column and separation conditions as for the GC–FID analysis were used.



Fig. 1. XRD patterns of calcined materials (a) AlSBA-15(S), (b) AlSBA-15(N) and (c) AlSBA-15(IP).

According to the literature data [12,27] all the reaction products were grouped as follows:

- (1) Cracking products (CP, compounds containing less than 10 carbons): mainly derivatives of cyclopropene, cyclopentane, cyclopentene, cyclohexane and cyclohexene.
- (2) Ring contraction products (RC, compounds containing 10 carbons): C₆ rings fused to C₅ or/and C₃ rings, and two C₅ rings.
- (3) Ring opening products (RO, compounds containing 10 carbons): mainly derivatives of cyclohexane, cyclohexene, cyclopentane or benzene, and OCD – open chain decenes.
- (4) Dehydrogenation products (DP): tetralin, naphthalene and indane derivatives.

3. Results and discussion

3.1. Aluminium precursor used for the preparation of AlSBA-15 based supports for Pt catalysts and its influence on 1-MeN hydroconversion

3.1.1. Influence of aluminium precursor on physicochemical properties of AISBA-15

The powder XRD patterns of AlSBA-15 samples obtained with various aluminium sources (Fig. 1) demonstrate a high degree of structural ordering. The low angle XRD patterns display three well resolved peaks in the 2θ range of $0.8-1.8^{\circ}$: an intense peak (100), as well as low-intensity (110) and (200) reflections, which are associated with p6 mm hexagonal symmetry. This characteristic XRD patterns of the AlSBA-15 hexagonal phase also matches well with relevant XRD patterns reported in the literature [36]. The shape of the XRD spectrum of the AlSBA-15 samples is almost the

same as that of the siliceous SBA-15 sample (not shown), indicating that the hexagonally ordered two-dimensional structure is retained even after incorporation of huge Al quantities into the wall structure of AlSBA-15 (Si/Al = 20). The same effect has been reported by Shanbhag [37] and Vinu [38].

The nitrogen adsorption–desorption isotherms are shown in Fig. 2. As can be seen from these plots, the AlSBA-15 samples exhibit isotherms of type IV (IUPAC) typical of mesoporous materials. They also display an H1-type broad hysteresis loop, which is typical of large-pore mesoporous solids. All isotherms show a sharp condensation step at relative pressures within the range of 0.6-0.8. When use is made of Al(NO₃)₃·6H₂O (AlSBA-15(N) sample), the capillary condensation step is shifted to higher relative pressures. The p/p_0 position of the inflection point for AlSBA-15(N) is correlated with the presence of macropores. When aluminium precursors are added, respective counterions such as NO₃⁻, C₃H₇O₃⁻, and SO₄²⁻ neutralize the micellar charge. Stronger charge neutralization would help the formation of more rigid micelles and hence better hexagonal structure [33]. Lower charge neutralization takes place when Al(NO₃)₃·6H₂O is used as the alumina precursor.

The mesoporous materials obtained display a similar porous structure (Table 1). BET specific surface areas vary from 798 to $875 \text{ m}^2/\text{g}$. Pore volume and mean pore diameter are within the range of 1.1-1.4 cm³/g and 9.5-10.5 nm, respectively. The length of the hexagonal unit cell a_0 is calculated in terms of the formula $a_0 = 2 \cdot d_{100} / 3^{1/2}$. It is interesting to note that the unit cell parameter of AlSBA-15(S) decreases after aluminium incorporation as compared with the unit cell of SiSBA-15 (not shown). For samples obtained from aluminium nitrate and aluminium isopropoxide, a rise is observed in the a_0 parameter. The increase in the unit cell parameter suggests the presence of metal in the SBA-15 walls [36]. This indicates that the incorporation of Al atoms into the SBA-15 silica framework is more successful for AISBA-15(N) and AISBA-15(IP) than for AISBA-15(S). These observations are in agreement with the results of the ²⁷Al MAS NMR measurements (Fig. 3), which revealed the highest contribution of non-framework aluminium atoms in AlSBA-15 prepared with aluminium sulphate (AlSBA-15(S)). Wide angle XRD patterns make it clear that the AISBA-15(N) and AISBA-15(IP) samples do not contain any other phase (Fig. 1).

The condensation ratio of the mesoporous matrix was determined by the ²⁹Si MAS NMR method [39]. The ²⁹Si MAS NMR spectra (Fig. 3) of AlSBA-15 samples show three peaks around the shifts of -91, -100 and -110 ppm. They are assigned to silicon groups in the following structures: geminal silanol species (OSi)₂-Si(OH)₂ (Q_2), isolated silanol species (OSi)₃-SiOH (Q_3) and the most polymerized Si-(OSi)₄ (Q_4) units, respectively [37,40].

In the case of metal containing materials, the presence of $(OSi)_2$ —Si— $(O-X)_2$ and $(OSi)_3$ —Si—(O-X) units can be expected, where X may stand not only for a hydrogen but also a metal atom (Al in this study) [41,42]. Signals δ_{29Si} from aluminium containing groups are overlapped with peaks from geminal Q_2 and single Q_3 silanol groups, respectively. Some authors [37,43,44] observed a shoulder at about –107 ppm ascribed to Si(3Si,1Al) species. The analysed spectra (Fig. 3) exhibit no additional signal that might indicate the presence of Si(3Si,1Al) units. The absence of this peak may be attributed to the low degree of Al substitution for Si atoms

Table 1 Textural properties of AISBA-15 determined by powder XRD and $N_{\rm 2}$ sorption.

Sample	$S_{\rm BET}(m^2/g)$	$V_{\rm p}({\rm cm^3/g})$	APD (nm)	$d_{\rm p}({\rm nm})$	$a_0 (nm)$	$w_{\rm t}({\rm nm})$
AlSBA-15(S)	875	1.3	5.8	9.5	10.6	1.1
AlSBA-15(N)	800	1.4	7.2	10.5	11.5	1.0
AlSBA-15(IP)	798	1.1	5.6	10.4	11.8	1.4

Note: V_p , pore volume; APD, average pore diameter; d_p , pore diameter; a_0 , unit cell parameter; w_t , wall thickness.



Fig. 2. N₂ adsorption-desorption isotherms (left) and pore size distribution calculated using the BJH method (right) of mesoporous materials (a) AlSBA-15(S), (b) AlSBA-15(N) and (c) AlSBA-15(IP).

(but such statement would be inconsistent with the results of XRD, N₂ sorption and ²⁷Al MAS NMR examinations) or to the fact that these chemical shifts of low intensity would hardly be observable due to the overlap with the strong signal of the SiOH groups occurring at -100 ppm. Table 2 shows the relative amounts of the silicon groups, determined by the deconvolution of ²⁹Si MAS NMR spectra. There are no significant differences in the ²⁹Si MAS NMR spectra of the investigated AISBA-15 materials. The comparatively low portion of Q_4 units (which form during calcination via condensation of nonconnected internal silanol groups, *i.e.* Q_2 and Q_3) is nearly constant for all substituted samples. The frameworks of all the AlSBA-15 samples exhibit a high contribution of isolated silanol groups. The low framework connectivity could have been caused by the high degree of isomorphous substitution. According to Kosslick et al. [45], the steric hindrances caused by the different radii of the substituted atom and by the minimum intertetrahedral bond angles of the Si-O-Si and the Si-O-Me bridges should make condensation within the framework more difficult, when the degree of substitution is increased.

Fig. 3 shows solid state ²⁷Al MAS NMR spectra of AlSBA-15. Each spectrum exhibits a strong and sharp signal at about 50 ppm, as well as a weak and broad one at about 0 ppm, regardless of the Al precursor. The signal at 50 ppm was assigned to tetrahedrally coordinated aluminium atoms located in framework positions

 $(T_d-Al(IV))$ [39,46]. The $T_d-Al(IV)$ species can be regarded as Brønsted acid sites [21]. The signal at 0 ppm was ascribed to distorted or octahedrally coordinated $(O_h-Al(VI))$ aluminium atoms at extra-framework positions or in a separate phase [47,48]. Kosslick et al. [49] report that non-framework aluminium species $(O_h-Al(VI))$ are formed by dealumination of mesoporous aluminosilicate during calcination at 550 °C. However, the formation of octahedrally coordinated aluminium atoms at some stage in synthesis cannot be excluded.

The results show that for all samples Al was incorporated into the molecular sieve framework predominantly by isomorphic substitution of Si (T_d-Al(IV)). The signals from T_d-Al(IV) for samples obtained with aluminium nitrate and aluminium isopropoxide display high intensities. But the chemical shifts of 0 ppm with respect to $Al(H_2O)_6^{3+}$ suggest that some of the aluminium species were incorporated with an octahedral coordination. The ²⁷Al MAS NMR spectrum displays a signal at about 0 ppm generated by octahedrally coordinated aluminium atoms, which is significantly higher for the AlSBA-15(S) material than for AlSBA-15(N) and AlSBA-15(IS). However, most of the aluminium atoms remain in a tetrahedral oxygen coordination at framework positions. The foregoing results suggest that the contribution of T_d-Al(IV) and O_h-Al(VI) in the mesoporous materials can be controlled using different aluminium precursors.

 Table 2

 Connectivities of the framework of AISBA-15 determined by the deconvolution of ²⁹Si MAS NMR spectra.

Sample	Q2		Q3		Q4	Q ₄	
	δ (ppm)	% of area	δ (ppm)	% of area	δ (ppm)	% of area	
AlSBA-15(S)	-91.5	15.5	-99.9	59.4	-111.0	25.1	0.33
AlSBA-15(N)	-91.5	23.3	-100.2	50.4	-109.6	26.3	0.35
AlSBA-15(IP)	-91.5	17.2	-99.9	59.5	-110.5	23.4	0.31



Fig. 3. ²⁹Si MAS NMR (left) and ²⁷Al MAS NMR spectra (right) of the mesoporous materials (a) AlSBA-15(S), (b) AlSBA-15(N) and (c) AlSBA-15(IP).

3.1.2. Influence of aluminium precursor on 1-MeN hydroconversion over Pt/AISBA-15

The results of 1-MeN hydrogenation over AlSBA-15 supported platinum catalysts (1.5 wt.% of Pt), at atmospheric pressure and temperatures ranging from 240 to 350 °C, are shown in Table 3. Measured data make it clear that the aluminium precursor does not significantly affect the conversion of 1-MeN. For all the catalysts examined, the reaction temperature of 240 °C provides 1-MeN conversion of about 80%. Conversion passes through the minimum with all the Pt catalysts tested (at 280 °C). The increase in reaction temperature from 280 °C to 320 and 350 °C slightly increases 1-MeN conversion.

 Table 3

 Influence of the aluminium precursor in Pt/AISBA-15 catalysts on 1-MeN conversion.

$T_{\rm R}$ (°C)	Pt/AlSBA-15(S)	Pt/AlSBA-15(N)	Pt/AISBA-15(IP)						
Conversion (%)									
240	78.2	79.9	79.0						
280	63.4	65.6	62.5						
320	68.1	69.4	67.6						
350	69.6	69.4	67.8						
MeTs vield	(wt.%)								
240	62.4	71.5	61.1						
280	60.6	64.5	59.7						
320	66.3	68.6	66.2						
350	67.9	68.4	65.7						
MeDs yield	(wt.%)								
240	15.8	8.4	17.9						
280	2.8	1.1	2.8						
320	1.8	0.8	1.4						
350	1.7	1.0	2.1						
cis-MeDs/tr	cis-MeDs/trans-MeDs								
240	0.4	0.2	0.3						

The enhancement of the hydrogenation activity of the Pt/AISBA-15 catalysts in the range temperature of 280-350°C can be attributed to the Brønsted acid sites which contribute in hydrogenation at relatively high temperatures. Aboul-Gheit et al. investigated H-ZSM-5 and Pt/H-ZSM-5 in hydrogenation of cyclohexene [50]. They have found that Pt sites are primarily responsible for cyclohexene hydrogenation reactions at low reaction temperatures (50-150 °C), whereas the Brønsted acid sites in the H-ZSM-5 zeolite are responsible for hydrogenation at relatively higher temperatures than hydrogenation on the metallic sites. Lin and Vannice [51–53] proved that the increase in benzene hydrogenation activity of Pd and Pt supported on acidic supports compared to catalysts on non-acidic supports is caused by the presence of extra hydrogenation sites in the metal-acid interfacial region, which participate in the hydrogenation of aromatic. These sites are the generally Brønsted acid sites located close to the metal sites where the spillover hydrogen could react with the adsorbed aromatic compound.

In our work, it was shown that incorporation of platinum (1.5 wt.%) into AlSBA-15(S) material may bring an approximately six-fold increase in Lewis acid site concentration and five-fold increase in Brønsted acid site concentration as compared with AlSBA-15(S) (Table 4). The interaction of pyridine with Pt crystallites accounts for the increase of Lewis acidity, given that the metal crystallites are known to be acceptors of electron pairs, *i.e.* to act as Lewis acids [54]. The explanation for the increase in the Brønsted acidity is more complicated. The chemical composition of the surface of the Pt catalysts under this study determined by TOF-SIMS method has revealed that the surface of all catalysts is covered by chlorine species resulted from incomplete decomposition of H₂PtCl₆ or HCl (HCl was incorporated during AlSBA-15 synthesis). The ratio of Cl⁻/total ion is comparable for all Pt catalysts tested and it amounts to 0.04. The negative secondary ions mass spectrum of Pt/AlSBA-15(S) as an example is presented in

Table 4
Acidity results (Py-IR) of AISBA-15(S) and AISBA-15(S) supported Pt catalyst.

Catalyst	italyst APyH ⁺ (μmol/g)					APyL (µmol/g)				
	170 °C	250°C	350 °C	A ₃₅₀ /A ₁₇₀	170°C	250°C	350 °C	A ₃₅₀ /A ₁₇₀		
AISBA-15(S)	20	20	13	0.67	25	25	22	0.88		
Pt/AlSBA-15(S)	98	72	26	0.27	154	151	129	0.84		

Fig. 4. According to the literature data the incorporation of Cl⁻ ions into various supports, either as part of the Pt precursor (incomplete decomposition of H₂PtCl₆) or after noble metal impregnation (chlorination) may cause Brønsted acid sites to appear [55–58]. Corma et al. [55] observed that halogenation (in his work fluorination) of γ -Al₂O₃ created Brønsted acid sites able to interact with pyridine molecules. Recently Aboul-Gheit et al. [56] who investigated the effect of hydrochlorination on the properties of Re/H-ZSM-5 catalysts, observed that after hydrochlorination with 3% HCl, followed by drying, calcination and reduction, about 50% of Cl-ions remained in the catalyst. Karhu et al. [57] reported that in the Pt/Al₂O₃ and Pt/SiO₂Al₂O₃ (3 wt.% Al₂O₃) catalysts chlorine residues (incomplete decomposition of H₂PtCl₆) remained in the vicinity of platinum particles after reduction at 400 °C. They also demonstrated that Pt catalyst supported on pure silica showed no chlorine residue upon reduction. According to these authors, chlorine remaining on the catalyst surface contributed significantly to the performance of the catalysts in gas-phase ortho-xylene hydrogenation. The presence of chlorine in SiMCM-41 and NbMCM-41 supported Pt catalysts as a result of impregnation with of H₂PtCl₆ has been confirmed by Sobczak [58].

Activity results of our catalyst show that the main products of 1-MeN hydroconversion are methyltetralins (MeTs) and methyldecalins (MeDs) (Table 3). Within the range of 240–350 °C, the rise in temperature primarily leads to the formation of incomplete hydrogenation products, *i.e.* MeTs. The temperature of 240 °C brought about the highest yield of completely saturated hydrogenation products, *i.e.* MeDs, irrespective of the Al precursor. Considering the increasing yield of MeDs, the catalysts can be ordered as follows: Pt/AlSBA-15(N) (8.4 wt.%) < Pt/AlSBA-15(S) (15.8 wt.%) < Pt/AlSBA-15(IP) (17.9 wt.%). The results indicate that the aluminium source influences not only the yield of MeDs, but also the ratio of *cis*-MeDs/*trans*-MeDs. It was found that Pt/AlSBA-15(S) provides a higher *cis*-MeDs/*trans*-MeDs ratio in the reaction products as compared with Pt/AlSBA-15(N) and Pt/AlSBA-15(IP). According to literature data [27], *cis*-decalin is more reactive in the hydrodecyclization reaction than *trans*-decalin.

3.2. Influence of platinum amount in Pt/AlSBA-15 catalysts on decalin ring opening

In this study, consideration was also given to the problem of how metal (0.5, 2.5 and 4.5 wt.% of Pt) content in the Pt catalysts influences conversion and selectivity to ring opening products during transformation of decalin. AlSBA-15 synthesized with $Al_2(SO_4)_3$.18H₂O was selected as a support for catalysts because of the relatively high yield of MeDs (at 240 °C) and the highest *cis*-MeDs/*trans*-MeDs ratio obtained in 1-MeN conversion over 1.5/Pt/AlSBA-15(S).

Table 5 shows the metal content of the catalysts (Pt atoms, n_{Pt} ; accessible Pt atoms, $n_{Pt,A}$) and summarizes the results of H₂—O₂ titration (metallic surface, S_{Pt} ; metallic dispersion, D; average diameter of Pt crystallites, d) as well as catalyst acidity (number of total



Fig. 4. Negative TOF-SIMS spectrum of Pt/AISBA-15(S) catalyst.

Table 5
Characterization of metal function and acidity of platinum catalysts.

Catalyst	$S_{\rm BET}~(m^2/g)$	Pt (wt.%)	$n_{\rm Pt} (10^{-19}{ m g}^{-1})$	D (%)	D(nm)	$S_{Pt} (m^2 g_{cat}^{-1})$	$n_{\rm Pt_A} (10^{-19}{\rm g}^{-1})$	$n_{\rm NH_3-TPD} (10^{-19} { m g}^{-1})$	$n_{\rm B}(10^{-19}{ m g}^{-1})$	$n_{\rm L} (10^{-19}{ m g}^{-1})$
0.5Pt/AlSBA15(S)	556	0.50	0.11	100.0	1.1	249.1	0.14	16.9	3.6	5.2
2.5Pt/AlSBA-15(S)	511	2.50	7.72	36.2	3.1	90.2	2.79	21.7	10.7	21.6
4.5Pt/AlSBA-15(S)	491	4.50	13.9	24.2	4.6	60.4	3.37	25.3	6.3	11.0

Note: n_{Pt} , platinum atoms; D, Pt dispersion; d, average diameter of Pt crystallites; S_{Pt} , surface of the metal; $n_{Pt,A}$, accessible platinum atoms, n_{NH_3-TPD} , number of total acid sites determined from NH₃-TPD method; n_B and n_L number of Brønsted and Lewis acid sites determined from Py-IR method.

acid sites determined from NH₃-TPD method, $n_{\text{NH}_3\text{-TPD}}$; number of Brønsted and Lewis acid sites determined by the Py-IR method, n_{B} and n_{L}). As can be seen from these data, 0.5Pt/AISBA-15(S) is characterized by extremely high dispersion. Considering the decreasing metallic surface of Pt, the catalysts can be ordered as follows: 0.5Pt/AISBA-15(S)>2.5Pt/AISBA-15(S)>4.5Pt/AISBA-15(S).

The IR spectra of pyridine adsorbed are presented in Fig. 5 for all the samples examined. Lewis acid sites (PyL) have formed on the surface of all samples as can be seen from the absorption bands around 1620 and 1454 cm⁻¹ [59]. The bands at the frequency of 1638 and 1545 cm⁻¹ represent Brønsted acid sites (*PyH*⁺) [60]. The absorption band at 1490 cm⁻¹ corresponds to the vibrations of pyridine chemisorbed either on Lewis or Brønsted acid sites $(PyL + PyH^+)$ [61]. The three absorption bands at approximately 1445, 1578 and $1603 \,\mathrm{cm}^{-1}$ are ascribed to hydrogen-bonded pyridine [62], physisorbed pyridine and pyridine coordinated through its aromatic π -electrons to 1607 cm⁻¹ [63], respectively. Results indicate that for all investigated catalysts the amount of pyridine molecules associated with protons (PvH^+) is lower than that associated with coordinatively unsaturated sites (PyL). Py-IR measurements have furthermore revealed that there is no correlation indicating that the platinum enrichment of AlSBA-15(S) supported catalysts leads to an increase in their acidity. As can be seen from Table 5, the total amount of acid sites in the 2.5Pt/AlSBA-15(S) catalyst is higher as compared to the 0.5Pt/AlSBA-15(S) and 4.5Pt/AlSBA-15(S) catalysts. Acidity determined by the NH₃-TPD method (Table 5)



Fig. 5. FT(IR spectra of pyridine adsorbed at 170 $^\circ$ C on (a) AlSBA-15(S), (b) 0.5Pt/AlSBA-15(S), (c) 2.5Pt/AlSBA-15(S) and 4.5Pt/AlSBA-15(S).

demonstrates that the total acid sites number of 4.5Pt/AlSBA-15(S) is by 8.4 and $3.6 \times 10^{19} \text{g}^{-1}$ higher than the total acid sites numbers of 0.5Pt/AlSBA-15(S) and 2.5Pt/AlSBA-15(S), respectively. This discrepancy between NH₃-TPD and Py-IR measurements can be ascribed to the impact of platinum particle size on the diffusion of probe molecules (pyridine or ammonia) into the pores of the catalysts. The relatively large particle size of Pt species in high Pt loaded catalysts *i.e.* 4.5Pt/AlSBA-15 sample might limit pyridine adsorption on the acid sites.

²⁷Al MAS NMR analysis of the platinum catalysts was carried out to determine the ordering of the Al atoms in the framework of AlSBA-15(S) after impregnation with hexachloroplatinic acid, and the results are shown in Fig. 6. A Pt-free sample i.e. AISBA-15(S)(Fig. 3a, right) was compared with both 0.5Pt/AlSBA-15(S) and 4.5Pt/AlSBA-15(S). It is clearly observed that the peak assigned to tetrahedrally coordinated aluminium atoms located in framework positions (Td-Al(IV)) is significantly lower for the 0.5Pt/AlSBA-15(S) material than for AlSBA-15(S) and completely disappeared in 4.5Pt/AISBA-15(S) sample. Additionally, in the case of 4.5Pt/AISBA-15(S) a signal at -5.7 ppm is observed, which corresponds to the extra-framework aluminium [45]. It indicates that incorporation of Pt over the AlSBA-15(S) surface using hexachloroplatinic acid leads to partly or completely dealumination. The determination of the aluminium content in the catalysts shows that the Si/Al ratio slightly increases (in comparison with AlSBA-15(S)) and it is about 21. It indicates that aluminium remains in the material as an extraframework species.

Catalytic activities and product distribution over Pt catalysts for decalin hydroconversion are summarized in Table 6. The results show that conversion increases with a rise in temperature, which



Fig. 6. ^{27}Al MAS NMR spectra of the platinum catalysts (a) 0.5Pt/AlSBA-15(S) and (b) 4.5Pt/AlSBA-15(S).

Table 6

The products yield on Pt/AlSBA-15 catalysts (decalin hydroconversion).

Catalyst	0.5Pt/AlS	.5Pt/AlSBA-15(S)			2.5Pt/AISBA-15(S)			4.5Pt/AISBA-15(S)		
Reaction temperature, °C	300	340	380	300	340	380	300	340	380	
$\sum CP$	1.5	7.7	14.6	3.7	4.2	9.6	1.5	2.4	7.1	
∑RC	3.4	13.1	19.7	2.1	10.2	18.3	1.6	9.1	12.8	
∑ RO	3.1	12.1	26.4	1.2	6.2	18.6	1.5	5.6	14.2	
Cyclohexane derivatives ^a	n.d.	2.2	7.2	n.d.	0.8	4.0	0.7	0.7	2.8	
Cyclohexene derivatives ^b	3.1	6.1	10.3	0.6	3.5	7.0	0.7	2.9	5.2	
Cyclohexane derivatives ^c	n.d.	2.1	3.8	n.d.	0.5	2.9	n.d.	0.3	1.7	
Cyclopentane derivatives	n.d.	1.7	3.2	n.d.	1.0	2.5	n.d.	0.9	2.2	
Benzene derivatives	n.d.	n.d.	1.6	n.d.	0.4	2.0	n.d.	0.6	2.1	
OCDs	n.d.	0.1	0.4	n.d.	0.1	0.2	n.d.	n.d.	0.2	
$\sum DP$	n.d.	2.7	8.5	n.d.	1.4	11.7	n.d.	3.8	17.4	
Č balance, wt.%	0.5	2.7	3.9	0.2	1.0	3.6	0.3	0.8	2.4	
Conversion, wt.%	8.5	38.3	73.1	7.2	23.0	61.8	4.9	21.7	53.9	

^a Absence of the double bond.

^b Double bond in the ring structure.

^c Double bond in the alkyl substituent.

holds true for all the Pt catalysts tested. The increase in Pt content from 0.5 to 4.5 wt.% fails to improve decalin conversion. At any of the test temperatures, the highest conversion was reached over the 0.5 wt.% Pt catalyst. Incorporation of 2.5 and 4.5 wt.% of Pt into AlSBA-15(S) produces catalysts with a lower activity than that of 0.5Pt/AlSBA-15(S).

According to the classical mechanism [10,17], the hydroconversion of decalin over bifunctional catalyst occurs through two parallel reactions: ring contraction of decalin on Brønsted acid sites yielding skeletal isomers with five-membered naphthenic rings (RC, i.e. ring contraction products, mainly spiro[4.5]decane, bicyclononanes and bicyclooctanes) (step 1 in Fig. 7) followed by hydrogenolysis of those isomers on metal sites to C₁₀ one-ring naphthenes (RO, i.e. ring opening products, mainly cyclohexane derivatives) (step 2) as well as direct hydrogenolysis on metal sites vielding RO which is less favoured in the case of six-membered naphthenic rings (step 3). Conversion of decalin includes also a second ring opening step leading from C₁₀ one-ring naphthenes to open chain decane isomers (OCD) (step 4), cracking of RO (CP, *i.e.* cracking products containing less than 10 carbons) (step 5) and dehydrogenation of decalin (DP, i.e. dehydrogenation products, mainly tetralin, naphthalene, and 1-methylindane) (step 6). Fig. 7. does not include reactions which lead to heavy products and carbonaceous deposits.

Concerning the effect of Pt content on the activity of AlSBA-15(S) supported catalysts it was found that even though 2.5 wt.% and 4.5 wt.% Pt catalysts displayed a higher acidity, the their activities were lower than over 0.5Pt/AlSBA-15(S), which at 380 °C provided the highest yield of both ring contraction (19.7 wt.%) and ring opening (26.4 wt.%) products. As Brønsted acid sites are crucial in ring contraction followed by ring opening on metal sites, we expected the lower activity of 0.5Pt/AlSBA-14(S) catalyst as compared to the



Fig. 7. Scheme of principle reactions during decalin hydroconversion.

activity of high Pt-loaded catalysts. Recently, Rabl et al. [17] have demonstrated that Pt metal sites posses activity for ring contraction (isomerization) of decalin. Hence, we can postulate that over 0.5Pt/AISBA-15(S) with extremely high Pt dispersion the amount of the metal sites involved in ring contraction of decalin is higher than over 2.5 wt.% and 4.5 wt.% Pt-loaded catalysts.

It is worth noticing that over 0.5Pt/AISBA-15(S) the yield of dehydrogenation products such as tetralin and naphthalene is the lowest.

4. Conclusions

The objective of this work was to study 1-methylnaphtalene and decalin conversion over bifunctional Pt/AlSBA-15 catalysts.

- 1. The type of the aluminium precursor used for the preparation of the AISBA-15 support does not significantly affect the activity of Pt catalysts for 1-methylnaphthalene conversion.
- 2. The enhancement of the hydrogenation activity of the Pt/AISBA-15 catalysts in the range of 280–350 °C can be attributed to Brønsted acid sites (additionally generated by the presence of chlorine ions) which contribute in hydrogenation at relatively high temperatures.
- 3. The Pt catalyst supported on AlSBA-15 precipitated with aluminium sulphate provides a higher *cis*-methyldecalins/*trans*-methyldecalin ratio than Pt catalysts supported on AlSBA-15 precipitated with aluminium nitrate or aluminium isopropoxide.
- 4. The decrease in Pt content from 4.5 wt.% to 0.5 increases decalin conversion over Pt/AISBA-15 catalysts. The yield of ring opening products is greatly enhanced over the catalyst with low (0.5 wt.%) amount of Pt and amounted to 12.1 and 26.4 wt.% at 340 °C and 380 °C, respectively. Extremely high Pt dispersion in catalyst containing 0.5 wt.% of Pt enables to increase isomerization function of catalyst (an increase in ring contraction products) and hence its activity in the ring opening reaction.

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