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Selectivity of platinum–zirconia catalysts in *n*-paraffins hydroisomerisation process

Jerzy Walendziewski[*], Barbara Pniak, Bożena Malinowska

Institute of Chemistry and Technology of Petroleum and Coal, Wrocław University of Technology, ul. Gdańska 7/9, 50-310 Wrocław, Poland

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Abstract

Tungstated and sulphated zirconium hydroxides produced by MEL Chemicals were used as a raw material for preparation of *n*-paraffins hydroisomerisation catalysts. The preparation involved forming of zirconium hydroxides with peptised aluminium hydroxide, thermal treatment and impregnation of the obtained supports with platinum hexachloric acid solution. The obtained catalysts, 0.5 wt.% Pt/(SO_4/ZrO_2 + Al_2O_3) and 0.5 wt.% Pt/(WO_3/ZrO_2 + Al_2O_3) were tested in a continuous flow process of *n*-cetane hydroisomerisation. It was occurred, that the applied doped zirconium oxides are mesoporous materials of relatively low pore volume in comparison with other known support materials, mesopores consists ca 80% of the total pore volume and 65% of the specific surface area. Addition of the alumina binder in the support forming stage increased pore volume and specific surface area of the obtained supports, mainly in the range of the mesopores diameter size. We have stated that the sulphated zirconia–alumina based platinum catalyst is highly active, low temperature hydrocracking catalyst; it gives total conversion (hydrocracking) of the feed at temperature process below 200 °C. In our opinion the sulphated zirconia is not the suitable support component for the preparation of catalysts for hydroisomerisation of long chain hydrocarbons. The second of the prepared catalysts, the tungstated zirconia based one, is far more promising; it is less active but more selective in the *n*-paraffins hydroisomerisation process. Selection of the proper process parameters, hydrogen pressure and LHSV of the feed, makes it possible to attain 50–60% conversion with almost 90% hydroisomerisation selectivity. Products of hydrocracking (C_5–C_{13} hydrocarbons) obtained at low conversion level (e.g. 28%) are mainly linear isomers (70%), but the increase in the conversion level up to 60–70% causes that products of hydrocracking were mainly branched isomers (≈80%).

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Keywords: Zirconia; Platinum; Tungsten; Alumina; Hydroisomerisation activity; Selectivity

1. Introduction

Hydroisomerisation processes of *n*-paraffins containing fractions are as a rule carried out over the bi-functional catalysts. The typical examples of the isomerisation catalysts are the platinum–zeolite Y or mordenite based catalysts. The role of metallic active sites is dehydrogenation of paraffinic hydrocarbons to olefins and hydrogenation of *iso*-olefins to *iso*-paraffins, while the main role of the second catalyst function, acid sites, is skeletal isomerisation of olefins via carbenium ions. Due to the limited activity and the required commercial productivity rate this type of catalysts has to be exploited at the relatively high temperature range. Yet from the point of view of the increased yields of *iso*-alkanes and the thermodynamics limitations, the low temperature hydroisomerisation processes are more preferred. As the result of the difficulties in achieving high isomerisation activity the catalysts for hydroisomerisation and selective hydrocracking of gasoline, diesel fuels and lubrication oils are intensely studied [1–4]. The main goal of these studies is the search for the high selectivity isomerisation catalyst for upgrading of the low quality lubricants, jet and diesel oils instead of the Pt, Pd, Ni promoted molecular sieves, zeolite and silica–alumina bi-functional catalysts. One of the possible options are zirconia based catalysts. Literature data on the low temperature reaction of *n*-butane isomerisation (150 °C or lower) over sulphated zirconia indicates that it is possible to lower considerably temperature of the commercial hydroisomerisation processes of petroleum fractions [5,6]. High isomerisation activity and stability of the zirconia based catalysts were also confirmed in pentane and light naphtha conversion processes [7]. The same results indicated however, that the hydroisomerisation of higher hydrocarbons (*n*-hexadecane) over the sulphated zirconia catalysts is accompanied by cracking, the extent of which is increasing with the temperature and reaction time [3]. According to Larsen and Petkovic,

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[*] Corresponding author. Tel./fax: +48-71-320-3551.
E-mail address: walendziewski@nw.pwr.wroc.pl (J. Walendziewski).

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pre-reduction of platinum dispersed on the tungstated zirconia catalyst ($Pt/ZrO_2/WO_3$) improves isomerisation selectivity of short chain hydrocarbons [8]. Last Zhang et al. studies on *n*-hexadecane isomerisation confirmed observation that the ($Pt/WO_3/ZrO_2$) catalyst is suitable for use as hydroisomerisation catalyst and at the same time indicated that platinum on sulphated zirconia ($Pt/SO_4/ZrO_2$) is good hydrocracking catalyst of low isomerisation selectivity [9].

The essential problem in the case of application of the zirconia based catalysts is their relatively small specific surface area, difficulties in obtaining the shaped form of the catalyst grain and mechanical strength, the very important properties in commercial applications. We have not found in literature the adequate information about shaping of the zirconia based supports and hydroisomerisation activity of the obtained catalysts. Therefore, in the catalyst preparation stage we have applied the zirconia supports formed by using alumina hydroxide as the binder (50/50 wt. ratio). The sulphated and tungstated zirconium hydroxide samples applied in the catalyst preparation were delivered by MEL Company (England). The prepared, $Pt/WO_3/ZrO_2 + Al_2O_3$ and $Pt/SO_4/ZrO_2 + Al_2O_3$ catalysts were tested in the hydroisomerisation process of *n*-cetane fraction (mixture of C_{14}–C_{20} normal hydrocarbons).

2. Experimental

2.1. Preparation of catalysts

2.1.1. Materials

- Tungstated, sulphated and no doped zirconium hydroxides were obtained from MEL Company, England:
  - MELCat XZO 880/01: no doped zirconium oxide (ZrO_2);
  - MELCat XZO 1248/01: 15–25% sulphate zirconium oxide (SO_4/ZrO_2);
  - MELCat XZO 1250/01: 15–20% H_2WO_4 (WO_3/ZrO_2).

  Porous structure (pore size distribution) for all calcined (550 °C, 4 h) zirconium hydroxides (oxide form) is presented in Table 1.
- Laboratory prepared aluminium hydroxide was used as the support binder (after calcination at 500 °C: specific surface area—283 m^2/g, bulk density—533 kg/m^3 and impurities—sodium 0.006 wt.%).
- Hexachloric platinum acid was applied in the catalyst preparation step for platinum supporting by dry impregnation method.

2.1.2. Preparation of the zirconia based supports and catalysts

The delivered by MEL Chemicals company zirconium hydroxides consisted of powder and it was necessary to form them in order to obtain the grain of supports and catalysts. Forming of the zirconia hydroxide samples was carried out by using the aluminium hydroxide peptised with 2 wt.% nitric acid at 60 °C for ca 5 h. The peptised aluminium hydroxide was mixed with the equivalent weight of the zirconium hydroxide, formed in the cylinder shape, dried overnight at ambient temperature, 24 h at 110 °C and then calcined in the temperature range 150–550 °C (4 h at 550 °C). The weight of the alumina binder and zirconia samples used in the forming stage allowed to obtain 50 wt.% content of ZrO_2 in the final support. After final calcination (4 h at 550 °C) the obtained catalyst supports were crushed and 0.3–0.6 mm sieve grains were selected for catalyst preparation.

Preparation of platinum catalysts was carried out by dry impregnation of the supports with H_2PtCl_6 solution. Concentration and volume of the platinum acid solution made it possible to attain 0.5 wt.% content of platinum in the catalysts. The final catalysts contained—$Pt/WO_3/ZrO_2 + Al_2O_3$ and $Pt/SO_4/ZrO_2 + Al_2O_3$ platinum: 0.5 wt.%; $Pt/WO_3/ZrO_2 + Al_2O_3$ tungsten: 3.92 wt.% and sulphate ions: 0.91 wt.%; $Pt/SO_4/ZrO_2 + Al_2O_3$ tungsten: 0.22 wt.% and sulphate ions: 6.40 wt.%.

Table 1
Porous structure and specific surface area of the calcined zirconia hydroxides doped with sulphate ions or tungsten oxide (calcination temperature, 550 °C; time, 4 h)

Sample	Pore volume (cm^3/g)				Specific surface area (m^2/g)			
	<2 nm	2–10 nm	10–50 nm	<50 nm	<2 nm	2–10 nm	10–50 nm	<50 nm
SO_4–ZrO_2	0.030	0.092	0.027	0.149	81	134.5	5.5	221
WO_3–ZrO_2	0.026	0.085	0.044	0.155	70	120.6	5.7	196.3
Support-1[a]	0.035	0.148	0.061	0.244	91	199.3	12	302.3
Catalyst-1[b]	0.032	0.149	0.059	0.240	88	188.2	13.7	290
Support-2[c]	0.035	0.166	0.042	0.243	97	183.4	12	292
Catalyst-2[d]	0.035	0.162	0.046	0.243	97	180.7	13.1	291

[a] $SO_4/ZrO_2 + Al_2O_3$.
[b] 0.5% Pt/($SO_4/ZrO_2 + Al_2O_3$).
[c] $WO_3/ZrO_2 + Al_2O_3$.
[d] 0.5% Pt/($WO_3/ZrO_2 + Al_2O_3$).

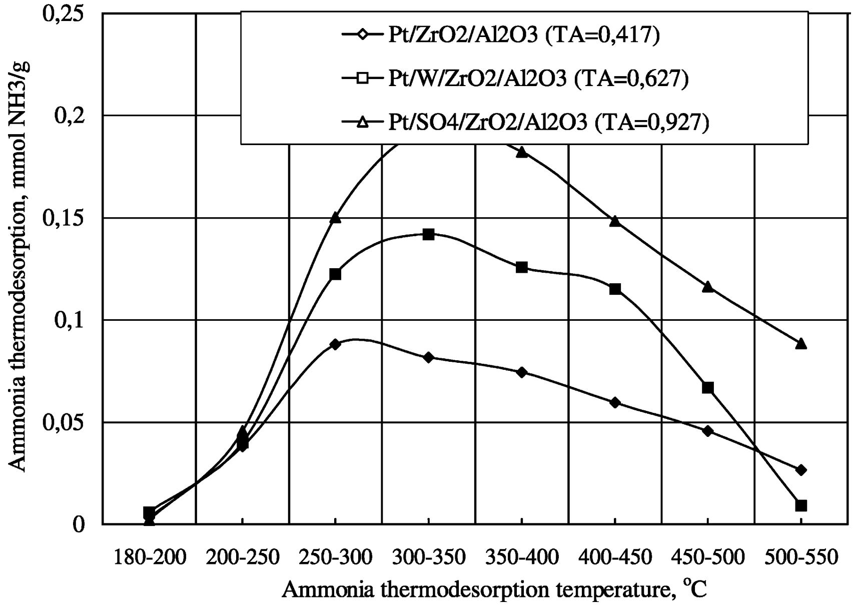

Fig. 1. Acidity site strength distribution determined by ammonia thermodesorption method for the prepared catalysts (TA—total acidity, mmol NH_3/g).

2.2. Determination of physicochemical properties

- *Pore size distribution* in the pore radius range 1.5–100 nm was obtained from benzene adsorption–desorption isotherms (Mc Bain–Backr balance) (Table 1).
- *Total pore volume* was calculated from volume of water adsorbed by a sample of supports or catalysts.
- *Surface acidity* was measured by temperature programmed desorption (TPD) of ammonia in the range of temperature 180–550 °C. Samples of support or catalyst in glass micro-reactor were calcined in argon stream at 550 °C, saturated with ammonia at 50 °C and stabilised at 180 °C. Total acidity and acidity sites strength distribution were determined by TPD of ammonia in the range of temperature 200–550 °C. Quantity of desorbed ammonia (in mmol/g) at the determined temperature ranges, e.g. 200–250 °C was accepted as acidity of catalyst or support and surface area measured at chromatographical chart for the given temperature range multiplied by calibration coefficient was accepted as partial acidity. It was assumed that the higher ammonia thermodesorption temperature the higher acid site strength (Fig. 1). The acidity of the catalysts was also determined by titration method with using of *n*-butylamine in benzene solution as a base, HCl solution as a titrant and methyl orange as an indicator.
- *XRD analysis* of the prepared zirconia based catalysts was carried out by using Siemens D5005 apparatus, Co Kα radiation, voltage 35 kV, current strength 25 mA. In order to compare our XRD results to the literature data obtained with Cu Kα radiation [4,12], we have applied Virtual Crystallographic Calculator V2 for recalculation of the 2Θ values (Table 2).
- *Loss of attrition* was measured by tumbling of 10 g support (catalyst) in a drum at 60 rpm for 5 min. Attrited fines of size less than 1 mm that felt through the screen were collected and weighted.
- *The crushing strength* was obtained by determination of force necessary to crush cylinders along the radial direction.

Table 2
The results of XRD studies of the prepared zirconia based catalysts

Pattern sample PtWZrO$_2$ MEL [4]		Lab. pattern sample PtWZrO$_2$ [4]		Pt/W/ZrO$_2$ + Al$_2$O$_3$ MEL (1248)			Pt/SO$_4$/ZrO$_2$ + Al$_2$O$_3$ MEL (1250)		
2Θ	Intensity (%)	2Θ	Intensity (%)	2Θ	*d*	Intensity (%)	2Θ	*d*	Intensity (%)
x	x	x	x	21.41	4.15	6.42	21.40	4.15	6.66
x	x	x	x	24.82	3.57	7.34	25.1	3.55	5.55
27.7	7.0	27.7 (M)	85.3	x	x	x	x	x	x
30.6	100	30.6 (T)	100	30.83	2.95	100	30.83	2.95	100
x	x	31.5 (M)	73.3	x	x	x	x	x	x
35.4	18.6	35.4 (T)	33.3	35.29	2.64	22.94	35.12	2.55	20.0
51.0	37.2	51.0 (T)	60	50.60	1.80	35.32	50.53	1.81	37.78
60.9	26.7	60.9 (T)	40	60.2	1.54	23.85	60.13	1.54	22.22

2.3. Determination of catalysts activity

Cetane fraction, mixture of normal C_{10}–C_{21} hydrocarbons, mainly C_{14}–C_{19}, of density 774.6 g/dm^3 was used as a feed for the test hydroisomerisation process. Chemical composition of the feed was as follows:

Hydrocarbons	Content (wt.%)
$<C_{10}$	0.08
C_{10}	0.16
C_{11}	0.21
C_{12}	0.4
C_{13}	1.88
C_{14}	8.89
C_{15}	21.39
C_{16}	26.29
C_{17}	20.85
C_{18}	12.04
C_{19}	5.16
C_{20}	1.82
C_{21}	0.62
$>C_{21}$	0.21

The main components of the cetane fraction were C_{13}–C_{20} hydrocarbons. Melting point of the cetane feed is below 0 °C, sulphur content 2.3 ppm.

Hydrogen—electrolytic purity.

Determination of activity of the prepared catalysts in the hydroisomerisation process of cetane fraction. Studies of the catalysts activity were carried out in a pressure continuous flow micro-reactor unit (OL 115/09). The reactor unit consisted of: reactor ($\phi = 8$ mm, length $= 160$ mm, up to 4 cm^3 catalyst volume), feeding system (cetane fraction and hydrogen), temperature controlling and registration system, cooling and liquid–gas separation system.

Experiments were carried out under the following conditions:

Temperature range (°C)	150–360
Total pressure (MPa)	1–3
LHSV (h^{-1})	2.7, 5.3
Catalyst volume (cm^3)	3
Hydrogen to feed mole ratio	4.25–17
Catalyst grain size (mm)	0.3–0.6

The experiments were carried out at the presence of non-reduced as well as reduced catalysts (hydrogen stream, 9 dm^3 per hour, for 4 h at 500 °C and at atmospheric pressure).

Activity test series of each catalyst lasted 100–120 h. During the first 20–25 h of the activity tests we have observed loss of catalysts activity and therefore activity determinations were initialised after 30 h of the run, when catalyst activity was more or less stable. The results presented in this paper were obtained then between 30 and 80 h (first run) and 80–120 h (the second, repeated run). In the course of catalyst activity measurements, 2 h for stabilisation of process parameters and 3 h for receiving of each product samples were assigned. As a result of the relatively high boiling feed and process parameters, i.e. the process temperature and total process pressure it is the three-phase process (solid catalyst, gaseous hydrogen and liquid hydrocarbon feed).

Results of activity and selectivity determination are given in Tables 3–6 and Fig. 2.

Chromatographic analysis of the feed and reaction products:

- Composition of gas products from the activity tests were analysed using capillary column (60 m, SE-30 liquid phase, FID detector).
- Compositions of liquid products from the activity tests were analysed using capillary column (HP-5, 15m, 5% biphenyl–95.5% dimethylsiloxane copolymer) FID detector, HP 4890 D apparatus, and programmed temperature 30–200 °C.

Yields of isomerisation product ($\sum C_{14}$–C_{21} isomers) and *yields of cracking products* ($\sum C_1$–C_{13}) in reaction mixtures were calculated on the base of chromatograms.

3. Results and discussion

3.1. Physicochemical properties

The zirconia hydroxides samples submitted by MEL Chemicals are white, porous powders, which have to be transformed into the catalyst supports. Preliminary calcination of the hydroxides gave the zirconia supports in a powder form with porous structure presented in Table 1. In comparison with the porosity of the typical catalyst supports such as alumina or silica (0.4–0.7 cm^3/g) they are micro- and mesoporous materials of rather small porosity ($\approx$0.15 cm^3/g). However due to the considerable content of micropores (diameter $<$ 2 nm) and small content of mesopores (diameter 2–50 nm) the obtained zirconium oxides possessed quite high specific surface area, ca 200 m^2/g. It is worth adding that the small pores, micro- and mesopores with diameter up to 5 nm create almost the whole specific surface area.

Although we have made some trials in order to obtain formed zirconia supports (by extrusion method), we have not achieved any significant results. The mechanical strength and attrition resistance of the obtained extrudates were low, insufficient for the technical and commercial applications. Therefore, in the presented studies we have applied a forming method of the zirconium hydroxide precursors with the alumina binder according to the description presented in Section 2. The obtained mixed zirconia–alumina supports were characterised by the attrition resistance (99.4 wt.%) and crushing strength (0.9 kG/extruder) which nearly approached the suitable properties determined for pure commercial alumina supports. Porous structure of the mixed

Table 3
Influence of temperature on cetane conversion and hydroisomerisation selectivity[a]

	Reaction temperature (°C)								
	161	167	175	179	192	195	200	211	219
Conversion 1 (%)	4.1	8.7	56.8	93.7	99.4	99.5	99.6	–	–
Iso-selectivity 1 (%)	72.5	71.7	7.5	0	0	0	0	–	–
Conversion 2 (%)				0.6	29.3	37.5	83.4	93.0	99.7
Iso-selectivity 2 (%)				90.3	17.7	11.6	0	0	0
Conversion 3 (%)				8.9	35.3	44.7	86.5	99.1	99.9
Iso-selectivity 3 (%)				36.7	11.4	4.8	0.4	0	0

[a] Catalyst 1: 0.5% Pt/(SO_4/$ZrO_2 + Al_2O_3$). Series 1: 1.0 MPa; LHSV ≅ 2.7 h^{-1}; H_2/HC mole ratio ≅ 8.5; without hydrogen reduction. Series 2: 1.0 MPa; LHSV = 2.7 h^{-1}; H_2/HC mole ratio ≅ 8.5, with hydrogen reduction. Series 3: 1.0 MPa; LHSV = 2.7 h^{-1}; H_2/HC mole ratio ≅ 17, with hydrogen reduction.

Table 4
Influence of temperature on cetane conversion and hydroisomerisation selectivity[a]

	Reaction temperature (°C)							
	263	281	292	299	306	319	340	360
Conversion 0 (%)		–	–	–	1.7	2.3	3.8	4.9
Iso-selectivity 0 (%)	–	–	–	–	98.6	97.5	96.6	96.1
Conversion 1 (%)	6.4	39.4	54.7	79.5	83.9	90.2	–	–
Iso-selectivity 1 (%)	94.1	88.6	79.4	48.7	39.8	31.0	–	–
Conversion 2 (%)	4.3	16.7	28.1	40.3	51.4	68.46	90.4	92.2
Iso-selectivity 2 (%)	87.0	84.2	88.5	86.2	84.7	74.2	49.6	45.8
Conversion 3 (%)	2.8	6.4	11.8	23.3	38.1	44.1	53.2	53.9
Iso-selectivity 3 (%)	84.0	81.3	86.3	83.4	79.8	75.9	68.4	66.3
Conversion 4 (%)	2.9	7.1	12.7	23.3	38.4	43.1	52.0	54.2
Iso-selectivity 4 (%)	82.0	80.8	85.5	83.2	77.9	76.0	69.6	65.8

[a] Catalyst 2: 0.5% Pt/(WO_3/$ZrO_2 + Al_2O_3$); without hydrogen reduction. Series 0: 1.0 MPa; LHSV = 2.7 h^{-1}; H_2/HC mole ratio ≅ 8.5 for Pt/Cl/Al_2O_3, catalyst. Series 1: 1.0 MPa; LHSV = 2.7 h^{-1}; H_2/HC mole ratio ≅ 8.5. Series 2: 3.0 MPa; LHSV = 2.7 h^{-1}; H_2/HC mole ratio ≅ 8.5. Series 3: 3.0 MPa; LHSV = 5.3 h^{-1}; H_2/HC mole ratio ≅ 8.5. Series 4: 3.0 MPa; LHSV = 5.3 h^{-1}; H_2/HC mole ratio ≅ 4.25.

Table 5
Influence of process temperature on light hydrocarbons (C_5–C_{13}) composition[a]

	$\succ C_5$	i-C_5	n-C_5	i-C_6	n-C_6	i-C_7	n-C_7	i_p-C_8	i_m-C_8	n-C_8 (feed = 0.01)	i_p-C_9	i_m-C_9	n-C_9 (feed = 0.07)
292 °C	0.34	0.13	0.07	0.13	0.01	0.09	0.09		0.10	0.10		0.10	0.21
300 °C	0.09	0.11	0.06	0.15	0.09		0.21	0.10	0.04	0.22	0.11	0.06	0.25
319 °C	1.13	1.42	0.71	1.93	0.95	2.60	1.03	0.56	2.63	1.02	0.92	2.67	1.00
		i_p-C_{10}	i_m-C_{10}	n-C_{10} (feed = 0.16)	i_p-C_{11}	i_m-C_{11}	n-C_{11} (feed = 0.21)	i_p-C_{12}	i_m-C_{12}	n-C_{12} (feed = 0.40)	i_p-C_{13}	i_m-C_{13} (feed = 0.07)	n-C_{13} (feed = 1.81)
292 °C		0.11	0.25	0.25	0.09	0.27	0.27	0.07	0.31	0.40	0.24	0.78	1.51
300 °C		0.04	0.29	0.27	0.04	0.27	0.39	0.09	0.23	0.45	0.15	0.22	0.52
319 °C		1.75	2.28	0.92	1.60	2.57	0.94	1.68	1.92	0.84	1.66	3.12	1.43

[a] Catalyst 2: 0.5% Pt/(WO_3/$ZrO_2 + Al_2O_3$), without hydrogen reduction; 3.0 MPa; LHSV = 5.3 h^{-3}; H_2/HC mole ratio = 4.25. i_m, i_p: mono- and poly-branched hydrocarbons, respectively.

Table 6
Influence of process temperature on branched hydrocarbons content in the C_5–C_{13} and C_{14}–C_{21} hydrocarbons product fractions, catalyst 2: 0.5% Pt/(WO_3/$ZrO_2 + Al_2O_3$), without hydrogen reduction; 3.0 MPa; LHSV = 5.3 h^{-1}; H_2/HC mole ratio—4.25

Process temperature (°C)	Hydrocarbons content (%)					
	i-C_5–C_{13}	$i + n$-C_5–C_{13}	i-C_5–C_{13}/$i + n$-C_5–C_{13} ratio (%)	i-C_{14}–C_{21}	$i + n$-C_{14}–C_{21}	i-C_{14}–C_{21}/$i + n$-C_{14}–C_{21} ratio (%)
292	1.69	5.66	29.8	28.55	93.34	30.58
306	3.26	6.22	52.35	49.27	93.78	52.53
319	30.46	39.30	76.33	50.95	60.69	83.94

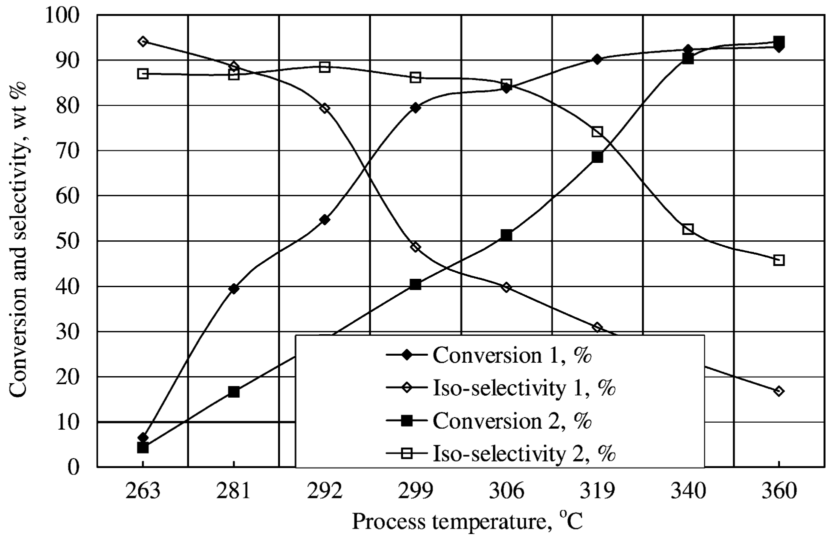

Fig. 2. Influence of process parameters on selectivity of cetane isomerisation process over 0.5% Pt/(WO_3/ZrO_2+Al_2O_3). Series 1: 1.0 MPa; LHSV = 2.7 h^{-1}; H_2/HC mole ratio ≅ 8.5; Series 2: 3.0 MPa; LHSV = 5.3 h^{-1}; H_2/HC mole ratio ≅ 4.25.

zirconia–alumina supports is also presented in Table 1. The mixing, peptisation, forming and thermal treatment operations of two porous powders of quite different porosity gave quite new material of the moderate porosity (ca 0.25 cm^3/g) and the surface area value (ca 300 m^2/g) specific for alumina supports. The relatively low porosity and moderate high specific surface area is characteristic for rather narrow pore supports. Besides Table 1 depicts pore structure and specific surface area distribution for platinum catalysts obtained with the use of the prepared zirconia supports. The data in Table 1, similar for supports and catalysts inform us that active metal deposited on the zirconia supports by dry impregnation method have no influence on the pore structure and the surface area distribution of the final isomerisation catalysts. The same observation is presented by Zhang et al. [9] for higher content of platinum, palladium and nickel deposited on tungstated zirconia supports without any binder. Furthermore it is worth noticing that zirconia supports prepared by Zhang et al. presented appreciable lower specific surface area (62–75 m^2/g) in comparison with non-formed zirconia supports (ca 200 m^2/g) obtained by calcination of zirconium hydroxide submitted by MEL Chemicals. Norman et al. inform about similar values of specific surface area, ca 160 m^2/g [10] while Fărcasiu et al. applied the zirconia supports of the surface area above 100 m^2/g [11]. According to the results of their studies, there is straight linear dependence of specific surface area of the zirconia containing supports on the applied calcination temperature, from ca 160 to less than 10 m^2/g when calcination temperature is increased from 500 to 950 °C. Furthermore, according to Norman et al. [10] the rate of the specific surface area loss during calcination is a function of the method of sulphate ions introduction into the zirconia precursor and the total content of sulphate ions. Therefore, adduced above the relatively low surface area values of zirconia supports studied by Zhang et al. [9] were presumably a result of different method of sulphates doping and higher calcination temperature of the supports (630 °C) in comparison to calcination of the supports in our studies (550 °C).

It is generally accepted that the sulphated zirconia oxides are strong solid acids, even super acids with $H_0 \geq -12$ or even -16 for some calcination temperatures [6]. Although all supports prepared in this studies contained 50 wt.% aluminas they presented quite different total acidity values and the acid sites strength distributions (Fig. 1). In this figure for comparison purpose the results of acidity determination for Pt/$ZrO_2 + Al_2O_3$ catalyst were also attached. One can see that its acidity was the lowest one and was comparable or even lower than the obtained one for the typical commercial alumina based supports and catalysts (0.45–0.65 mmol NH_3/g). In comparison with the other catalysts, very high acidity, over 0.92 mmol NH_3/g, especially in the strongest acid sites region (the highest ammonia thermodesorption temperature) presented sulphated zirconia containing support and catalyst. On the other hand, the acidity of the Pt/W/Al_2O_3 + ZrO_2 catalyst attained intermediate value (over 0.62 mmol NH_3/g). The obtained results clearly indicate not only the highest acidity but also considerably high content of the strongest acid sites of the sulphate ions containing zirconia based catalyst. Additional acidity measurements with the use of *n*-butylamine confirmed above-mentioned results of "ammonia acidity" determination. We have found that in this case the acidity values were a little lower, 0.38; 0.60 and 0.77 mmol of *n*-butylamine per gram of Pt/Zr_2, Pt/W/Al_2O_3 + ZrO_2 and Pt/SO_4/Al_2O_3 + ZrO_2 catalyst, respectively. The sequence of acidities values obtained with the use of the both methods acidity determinations for the studied catalysts was the same. It is necessary to add that the all prepared catalysts contained the highest quantity of medium strength acid sites.

Results of XRD studies of the prepared platinum–zirconia catalysts are presented in Table 2. The XRD patterns obtained for our catalysts are strictly the same as presented by Zhang et al. for $PtWZrO_2$ catalyst. We have found not only the same quantity of peaks and similar 2Θ values but also more or less similar ratios of peak intensities, characteristic for tetragonal form of zirconia. Both series catalysts were prepared with using zirconia oxides produced by MEL Chemicals, calcined at 700 °C (Zhang) and 550 °C (our studies). The increase in calcination temperature resulted in the increase in tetragonal phase content (higher peaks intensity). Very similar XRD patterns for zirconia oxides prepared using zirconyl nitrate as a precursor and calcination temperature in the range 610–700 °C were obtained by Fărcasiu and Li [12]. They also contain mainly tetragonal phase of zirconia. Quite different XRD patterns were determined by Zhang for tungstated zirconia catalysts prepared with using of zirconium chloride as a support precursor (Table 2). They evidenced comparable content of tetragonal and monoclinic phase in this catalyst. It means that content of both crystallographic forms depends mainly on the applied support precursor. XRD patterns obtained for both catalyst samples in our studies (with sulphated and tungstated zirconia) were almost identical and we did not find there any peaks of tungsten oxide. Presumably tungsten oxide in our $Pt/W/ZrO_2 + Al_2O_3$ catalyst was well dispersed and WO_3 clusters too small to be detected by XRD method. High content of tetragonal phase of zirconium oxide, well dispersed tungsten oxide and relatively large specific surface area of this catalysts indicate possibility of high hydroisomerisation activity of the catalyst.

3.2. *Hydroisomerisation activity of the zirconia catalysts*

The results of the activity studies of the prepared catalyst are given in Tables 3–6 and Fig. 2. Generally, the results of the presented studies are similar to those obtained by Zhang et al. [9] despite of the fact that we have applied zirconia based catalysts shaped with alumina, quite different raw material and activity test parameters. We have found that even in the presence of 50 wt.% of alumina binder the prepared $Pt/(SO_4/ZrO_2 + Al_2O_3)$ catalyst first of all presents very high activity in hydrocracking process. In the process temperature lower than 200 °C, we have stated very high extent of feed hydrocracking (Table 3). Relatively high isomerisation selectivity (≈71%) was determined only for very low conversion level of the feed, below 10%. Higher activity of Zhang's, 0.5 wt.% $Pt/ZrO_2/SO_4$ catalyst [9], 76.7% conversion at 150 °C, can be explained by the lack of alumina binder in his catalyst. Zhang studies indicated also some isomerisation selectivity (19.8%) at 76.7% *n*-hexadecane conversion. The extremely high hydrocracking activity of sulphated zirconia based catalyst in low temperature can be explained not only by high total acidity but first of all by considerably high content of the strongest acid sites (see Fig. 1), result of the high content of sulphate ions in this catalyst (6.4 wt.%). The data presented in Table 2 clearly indicate that preliminary hydrogen reduction of the catalyst diminishes hydrocracking activity and the total feed conversion was attained in process temperature higher by ca 30 °C (compare Series 1 and 2). In both cases the hydroisomerisation selectivity of the process was negligible. The increase in hydrogen to feed ratio (from 8.5 to 17 mole/mole) resulted in the further decrease in isomerisation selectivity but small increase in the feed conversion was stated (Table 2, Series 2 and 3). The detrimental influence of hydrogen reduction of $Pt/ZrO_2/SO_4 + Al_2O_3$ catalyst can be explained by partial reduction of sulphate ions in catalysts with evolving hydrogen sulphide. We have also stated the existence of this phenomenon in our earlier studies in the case of Pt/Al_2O_3 and Ni/Al_2O_3 catalysts prepared with using sulphate ions containing alumina supports.

From hydroisomerisation selectivity point of view considerably better results were obtained for tungstated zirconia based catalyst, i.e. $Pt/(WO_3/ZrO_2 + Al_2O_3)$. This type of hydroisomerisation catalyst presented lower activity and perceptible feed conversion was observed in the quite different (higher) temperature range, i.e. from 240 to 360 °C (Table 4, Fig. 2). According to Zhang et al. [9] the same catalyst type yet without alumina binder enabled 85.9% conversion of *n*-hexadecane with 83.2% selectivity. Application of the alumina formed catalyst in our studies has given a little worse result. At moderate raw material feeding ($2.7\,h^{-1}$), low hydrogen pressure (1 MPa) and 55% conversion, ∼80% isomerisation selectivity level of the process was stated. At higher conversion, above 90%, only 31% isomerisation selectivity could be attained (Series 1). A little lower efficiency of our catalyst in comparison to the described in literature ones [4,9] can be result of the relatively low tungsten content (ca 4 wt.% W).

The next series of experiments has revealed a significant influence of hydrogen pressure on activity and selectivity of $Pt/(ZrO_2/WO_3 + Al_2O_3)$ catalyst. Data presented in Table 4, Series 2 and 3, indicate that in comparison with the low hydrogen pressure process (1 MPa), the heightened hydrogen pressure (3 MPa) and the same LHSV give distinctly lower feed conversion, differences in conversion from 2 up to 39%, when process temperature attained 299 °C. Hydroisomerisation selectivity at ca 50% conversion for high and low hydrogen pressure attained almost similar values, 80 and 85%. Very quick lowering of selectivity was observed with the increase in process temperature and feed conversion in low pressure process. However, one can notice that at the heightened conversion level, 90–92% at 340–360 °C, the higher hydroisomerisation selectivity was stated for high pressure process (45.8–49.6%) in comparison with the low pressure process (below 31%, by approximation).

The almost twofold increase in LHSV of the feed (from 2.7 to $5.3\,h^{-1}$) at the same hydrogen flow (Series 3) resulted in lowering of the feed conversion, at the high LHSV ($5.3\,h^{-1}$). It was not possible to attain conversion level higher than 54% (Table 4, Series 3). Due to the different feed velocities comparable conversion levels i.e. 51–54% were obtained at the same hydrogen pressure and quite different process temperatures—310 and 360 °C and LHSV, Series 2 in comparison to Series 3, respectively. It is necessary to notice that parameters of Series 2 of our experiments ($2.7\,h^{-1}$ and 3 MPa) make it possible to attain the highest process selectivity. At the relatively high total conversion (51.4%) hydroisomerisation selectivity was almost 84.7%. The high process temperature in Series 2 applied for high LHSV is the reason of the low hydroisomerisation selectivity (ca 66%). It is evident that the influence of hydrogen to feed ratio for conversion and selectivity is rather negligible (compare results of Series 3 and 4).

The activity studies results lead to the conclusion that the preferable process parameters are the heightened hydrogen pressure (3 MPa), moderate LHSV (ca $3\,h^{-1}$) and moderate feed conversion (≈50%). The application of these process parameters enables ca 85% hydroisomerisation selectivity (Fig. 2). From hydroisomerisation selectivity point of view, it is also possible also that lowering of LHSV and process temperature can give better results. The additional advantage of the increased hydrogen pressure should be higher catalysts life stability. This phenomenon, observed in refinery hydrogen processes such as hydrorefining or hydroisomerisation ones is caused by lowering of the rate of carbonaceous matters deposition at the catalyst surface area. Yet due to the relatively short time duration of activity tests (max. 120 h) and only two catalyst samples used in activity studies it was not possible to confirm this finding in our studies. The spent sulphate ions containing catalyst ejected from micro-reactor contained a considerably higher weight of coke (1.15%) in comparison to the spent tungsten oxide containing one (0.78%). It is the result of the high acidity of the former catalyst.

Pt/alumina especially chloride ions doped catalysts are moderately effective in hydroisomerisation process. Therefore, one can suppose that 50% of alumina binder in $Pt/(WO_3/ZrO_2 + Al_2O_3)$ catalyst doped with chloride ions can present some isomerisation activity. However results of Series 0 in our experiments (Table 4) show low feed conversion at the applied process parameters, ca 350 °C. Similar results were also obtained in our laboratory [14] and by Ali et al. [15] in the case of hydroisomerisation of pentane and hexane hydrocarbons.

Table 5 characterises composition of light products of hydrocracking reactions from individual hydrocarbons content point of view. The applied feed for the test contained only small quantity of linear n-C_8–C_{13} hydrocarbons, e.g. 1.8% in the case of n-C_{13}. In a result of the hydroisomerisation process some part of the feed was hydrocracked. It is interesting to notice that mono-branched hydrocarbons are the main products of hydrocracking, especially in the case of lower boiling hydrocarbons e.g. i_m-HC content/i_p-HC content for C_8 hydrocarbons attained value 4.7 while only 1.15 for C_{12} and 1.88 for C_{13}. The increase in the process temperature favours first of all yielding of mono-branched products of hydrocracking, in the next step poly-branched hydrocarbons and after all—linear hydrocarbons (e.g. C_{12} and C_{13} hydrocarbons).

These observations are strongly confirmed by selected data given in Table 6. It gives information about total content of branched and linear hydrocarbons in light (C_5–C_{13}) and heavy products (C_{14}–C_{21}). It is visible that the increase in process temperature in the range of 292–319 °C causes almost threefold increase in relative branched isomers content in hydrocracking product of the process (i.e. from 29.8 to 76.3%). Similar increase can be observed in the case of C_{14}–C_{21} hydrocarbons composition yet in this case the reason of the strong increase of branched isomers content in the product is mainly hydroisomerisation, in a less degree hydrocracking process. Actually, the increase in the process temperature resulted both in isomerisation and hydrocracking of n-paraffins (e.g. at 319 °C isomerisation selectivity attained 74.16%, Table 3) and at this process temperature and 68.6% conversion content of branched isomers in C_{14}–C_{21} amounted almost 84% (Table 6).

Tungstated zirconia based catalysts are more active in n-paraffins conversion than SAPO-11 containing ones. For instance, in our studies we have stated that in the case of SAPO-11 based catalysts the highest isomerisation selectivity was 79% at temperature of 384 °C and 79.2% conversion, while in the case of tungstated zirconia based catalyst the highest isomerisation selectivity was 88.5% at 292 °C and conversion level 28% as well as 84.7% at 306 °C and conversion 51.37% [13]. It means that conversion and selectivity for these both catalysts are quite different dependent on temperature.

4. Conclusions

1. Tungstated and sulphated zirconium oxides produced by MEL Chemicals are mesoporous materials of relatively low pore volume in comparison with other known support materials, mesopores consist ca 80% of the total pore volume and 65% of the specific surface area.
2. Formed supports (and catalysts) with alumina as a binder present satisfied mechanical strength and attrition resistance.
3. Sulphated zirconia based platinum catalyst even with the addition of 50 wt.% of binder is a very good low temperature hydrocracking catalyst (total feed conversion at temperature below 200 °C). It should not be applied in hydroisomerisation process of n-paraffins.
4. In comparison with the above-mentioned catalyst, the tungstated zirconia based one is less active in hydro-conversion reactions (reaction temperature range 250–320 °C) but far more selective in hydroisomerisation reactions. The highest iso-selectivity 88.5% was

determined for 28.1% conversion level at 292 °C. As a rule the higher total conversion the lower isomerisation selectivity.

5. At the low total conversion level, the main products of isomerisation are mono-branched hydrocarbons but at the higher process temperature the share of poly-branched isomers significantly increases.
6. Hydrocracking of the cetane fraction over Pt-tungstated zirconia + alumina catalyst at low conversion level (28%) gives mainly linear isomers (70%). The increase in conversion level up to 68% causes increase in isomerisation extent and decrease in linear isomers content in C_5–C_{13} fraction from 70 to 23.7%.

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