



Impact of Parent Zirconia Crystallinity/Amorphylicity on the n-heptane Isomerization over Pt/WO₃-ZrO₂ Catalysts

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Authors' contributions

This work was carried out in collaboration between all authors. Author ZS designed and supervised the study, authors DK and PS carried out main part of experimental work and wrote the first draft of the manuscript, author OB contributed substantially, namely by providing materials and their primary surface area and porosity characteristics, authors JMH and RC contributed importantly by performing specific spectroscopic and kinetic analysis techniques. All authors read and approved the final manuscript.

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ABSTRACT

A series of WO₃-ZrO₂ catalysts containing 18% of WO₃ were prepared from Zr(OH)₄ pre-calcined at temperatures between 25 to 700°C, before W-introduction by impregnation. Thus, in accordance with that, the resulting parent Zr(OH)₄ support possessed different degree of crystallinity and proportion of monoclinic to tetrahedral (M/T) phases which directly influenced the same M/T ratio in the final Pt/WO₃-ZrO₂ catalyst. The resulting catalysts varied in nuclearity and reducibility of formed WO_x species, as revealed by UV-Vis spectroscopy and TPR-H₂. Despite widely different

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surface area of the final catalysts, ranged from 140 to 47 m²/g, related to the proportion of M/T phases, ranged from 10%/90% to 90%/10%; the activity of the corresponding Pt/WO₃-ZrO₂ for isomerization of C₇ was found to be directly proportional only to the total surface area of the resulting catalysts without specific effect of the crystal modifications of the support. In accordance with that a correlation was observed between the isomerization activity in n-C₇ conversion, ranged from 65 to 31%, and the population of formed poly-nuclear WO_x species, ranged from 41 to 33%, directly controlled exclusively by the surface area of the support.

Keywords: Zirconia; amorphicity; crystallinity; phases; isomerization; heptanes; iso-heptanes; Pt/WO₃-ZrO₂.

1. INTRODUCTION

Zirconia represents a promising and intensively studied material, namely of its electronic structure and acidic properties [1-6]. Its application is broad indeed and ranges from high-temperature ceramics to sensor technology. Among other uses its important application lies in many branches of catalysis. Since Hino and Arata [7,8] recognized WO₃-ZrO₂ as a strong acidic material which isomerizes n-paraffins, a large amount of research work has been devoted to analysis of the material. The complexity of catalyst preparation process has been studied and reported in number of studies [9-16]. The preparation steps usually include: 1. preparation of parent zirconium hydroxide (step I), usually by precipitation, which is followed with impregnation of the solid by tungsten and/or other metallic precursors (step II), calcined at high temperatures typically 700°C and then with final impregnation by Pt (step III). Alternatively, the WO₃-ZrO₂ materials could be also prepared by co-precipitation technique [9]. Mostly, the best results are obtained by using amorphous hydrous zirconia material for tungsten impregnation [10,11]. The preparation procedure of the WO₃-ZrO₂ was also reported in numerous patents [12-17]. As a rule they recommend the preparation to proceed from zirconia hydroxide as prepared, i.e. without calcination and/or increased temperature steps preceding the catalyst impregnation. Lebarbier et al. [18], compared the activity of Pt/WO₃-ZrO₂ catalysts prepared by impregnation of Zr(OH)₄ calcined at 120°C and 500°C and obtained highly active catalysts for n-hexane isomerization prepared by impregnation of zirconium hydroxide pretreated at low temperature, whereas the catalysts obtained by impregnation of zirconia treated at 500°C were less active. The authors suggest that the effect could be due to difference in the ratio of tetragonal/monoclinic forms in the support. Recently, Jermy et al. [19] studied extensively the effects of the various preparative variables on

the activity and selectivity of the Pt/WO₃-ZrO₂ catalysts in the heptane isomerization, including: (1) "pre-drying" temperature of amorphous parent zirconium hydroxide, (2) the way of tungsten impregnation, i.e. incipient wetness vs. wet impregnation method, (3) the pH of the solution during impregnation using the solution of ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀) used as tungsten precursor, (4) the resulting WO₃ loading, (5) temperature of catalyst calcination after tungsten impregnation, (6) the atmosphere used during calcination, and (7) variation in the Pt source, i.e. use of hexachloroplatinic acid (H₂PtCl₆) and/or tetraammine platinum(II) chloride (Pt(NH₃)₄Cl₂). The authors studied catalysts from parent pretreated in the range of 100-400°C, and concluded that zirconium hydroxide should be impregnated with tungsten precursor in the form of amorphous material: impregnation of the support calcined at 400°C resulted in catalyst with high proportion of ZrO₂ in the form of monoclinic phase and with lower catalytic activity. According to the authors, the optimal temperature for pretreatment of the zirconium hydroxide before impregnation by tungsten is in the range of temperatures of 100-300°C.

It could be summarized that the published results contain still some contradiction in approaches: on one hand the importance of initial amorphous state and/or crystal phase composition in subsequent stages of preparation is believed as crucially important [7-10], on the other hand there are results stressing the irrelevance of the initial state of impregnated material and no effect on final catalyst, in some reports [10,11]. In all cases, the main parameter directing the catalyst activity could be seen in WO_x-coverage, i.e. degree of WO_x-formal monolayer coverage, instead of solely surface area and/or crystal phase composition [20,21].

The aim for the present article is to elucidate the role of the zirconia hydroxide

pretreatment/calcination temperatures between RT and 700°C for the activity of final Pt/WO₃-ZrO₂ catalyst in isomerization reaction of C₇ linear paraffin, and to analyze in detail the changes in the structural properties of the zirconia support accompanying such variations in the conditions of the preparation on the resulting isomerization activity. Under such conditions, the whole temperature region would provide for continuous transformation of the zirconium oxo-hydroxide between mostly amorphous up to highly crystalline materials with various level of monoclinic↔tetragonal phase transformation. To reach this goal the analysis of XRD and presence of different WO_x species by using UV-Vis spectroscopy is done, temperature programmed reduction, and analysis of the material acidity.

For comparison of the individual catalysts the temperature of 250°C was used as generally optimal for iso-heptane production, as at lower temperatures the conversion is further decreasing over all catalysts, and at higher temperatures the parallel reactions like cracking begin to take place (or even dominate).

2. MATERIAL AND METHODS

2.1 WO₃-ZrO₂ Preparation

The chemical composition of the used amorphous zirconium hydroxide Zr(OH)₄ (Eurosupport Czechia, Ltd., Ref. No.AV-SM-4) is given in the Table 1. The surface area of the amorphous material was >300 m²/g, measured by N₂ adsorption isotherm BET. The initial amorphous material was calcined for 3 h at temperatures between 100-700°C (“pre-calcination temperature”) and a degree of crystallinity of the prepared samples were characterized by XRD. The calcined products were further impregnated by appropriate amount of (NH₄)₆H₂W₁₂O₄₀ solution (concentration ca. 10 wt.%) to attain 18 wt.% of WO₃ in the resulting materials, and after drying the impregnated samples were finally calcined for 3 h at 700°C. The prepared samples were characterized by NH₃-TPD, H₂-TPR and UV-Vis. The individual samples are denoted in further text by temperature of pre-calcination and WO₃ content,

e.g. 100-18-WO₃-ZrO₂ represents a WO₃-ZrO₂ sample containing 18 wt.% of WO₃ and prepared by impregnation of ZrO_x(OH)_y pretreated/calcined at 100°C.

2.2 WO₃-ZrO₂ Material Characterizations

2.2.1 XRD diffractograms

Were recorded on Bruker D8 instrument (Bruker AXS, USA). The presence of zirconia monoclinic and tetragonal phases in samples was evaluated from 28.2°, 31.5° and 30.3° reflections, respectively [22]. The degree of crystallinity was estimated from the peak area of the mentioned reflections, related to its area in samples treated at 700°C, i.e. for samples where the was expected to be near unity). The BET specific surface area was determined from N₂ isotherms measured at 77K (at liquid N₂ temperature) on ASAP 2010 apparatus (Micromeritics, U.S.A.).

2.2.2 TPD-NH₃ analysis

The acidity of these solids was monitored by temperature-programmed desorption of ammonia (NH₃-TPD) using the AMI-200 apparatus (Altamira Instruments, Inc., USA), equipped by TCD detector. Samples (typically 100 mg) were pretreated at 250°C in a stream of hydrogen/argon mixture (10.01 vol.% of H₂) for 1 h (the analogous to conditions of catalyst reducing activation prior to catalytic test, as specified below), followed by the ammonia adsorption from a stream of 3.95 vol.% ammonia/helium mixture at 100°C for 40 min. The ammonia desorption then was carried out in a stream of a pure 5.0 helium at the temperature range 100-700°C using temperature rump of 20°C.min⁻¹.

2.2.3 TPR-H₂ analysis

The reducibility was monitored by temperature-programmed reduction by hydrogen (H₂-TPR), which was carried out on the same apparatus as for TPD-NH₃, i.e. AMI-200 (Altamira Instruments, Inc., U.S.A.). The samples (typically 100 mg) were pretreated in a stream of synthetic air at 450°C for 3 h and then cooled down to the laboratory temperature.

Table 1. Chemical elemental composition of the above specified parent Zr(OH)₄ material (Eurosupport Czechia, Ltd., Ref. No.AV-SM-4)

Component	ZrO ₂	HfO ₂	SiO ₂	Na ₂ O	CeO ₂	TiO ₂	CaO	Rest
wt. %	97.32	2.17	0.21	0.10	0.07	0.05	0.04	0.04

The H₂-TPR was then done in a mixture of hydrogen (10.01 vol.%) in argon at a flow rate of 30 cm³.min⁻¹ and with a temperature increase of 10°C.min⁻¹. The TCD served as a detector of H₂ consumption. The quantitative analysis was enabled using peak areas by calibration by H₂ pulse technique.

2.2.4 UV-Vis measurements

Diffuse-Reflectance UV-Vis spectra of the WO₃-ZrO₂ solids were recorded using a Perkin-Elmer Lambda 950 spectrometer, equipped with a diffuse-reflectance attachment with a Spectralon coated integrating sphere. Owing to the high absorption of the all measured samples (Schuster–Kubelka–Munk (SKM) function > 3), which would not allow quantitative analysis of the spectra, the samples were diluted with BaSO₄ (ratio of sample/BaSO₄ 5:1). Diffuse-reflectance spectra were recorded in a differential mode using a mixture of BaSO₄/ZrO₂ (ratio 5:1) in quartz cuvettes of 0.5 cm thickness as a reference. This procedure compensated adequately the absorption band of ZrO₂ at 43 500 cm⁻¹ and provided analysis of the tungstate species. All UV-Vis spectra were recorded in the range of 2500-200 nm at a speed of 240 nm.min⁻¹. The scanning step was 1 nm and slit width 5 nm. The ordinate units were finally expressed as wavenumbers (cm⁻¹). The absorption intensity was expressed as the Schuster–Kubelka–Munk function: $F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$, where R_{∞} is the diffuse reflectance from a semi-infinite layer and $F(R_{\infty})$ is then proportional to the absorption coefficient. Data processing was carried out using Microcal Origin 7.5 (Microcal Software, Inc., USA).

2.2.5 Catalysts preparation for isomerization test

The catalysts containing 1wt. % Pt were prepared by impregnation of the WO₃-ZrO₂ materials using proper amount of H₂PtCl₆ solution. (10.6 mg of H₂PtCl₆ dissolved in 0.5 ml of H₂O and used for impregnation of per 0.5 g of WO₃-ZrO₂ solid). The materials were then grained (0.25-0.50 mm), dried at 105°C/overnight and then exposed the activation before isomerization, as specified below in description of catalytic test.

2.2.6 Catalytic tests

The catalytic activity in heptane isomerization was established using a glass flow through-flow reactor, typically with 0.50 g of the catalyst in a

form of granules (0.25-0.50 mm fraction), placed on a porous glass bed. The activation conditions consisted of two steps: at first a catalyst was oxidized in a stream of oxygen (Messer Technogas, CZ) at 475°C for 3 h, purged by a nitrogen (Messer Technogas, CZ), then cooled down to 250°C, and reduced 1 h at 250°C in a H₂/N₂ stream (80 mol.% H₂ and 20 mol.% N₂). After this the n-heptane isomerization was tested in a feed containing 1 mol.% n-Heptane in H₂/N₂ (79 mol%, 20 mol% N₂), at a flow rate of 66 cm³.min⁻¹, which corresponded to WSHV 0.35 h⁻¹. n-Heptane (C₇H₁₆, Sigma-Aldrich CZ, Cat.No.51745 - puriss. p.a., ≥ 99.5 % - GC) was fed using a conventional saturator kept at the desired temperature. The composition of the outlet stream, i.e. content of n-heptane, isoheptanes (individual) and low molecular weight products (mostly methan, ethan, propane, butane = C₁-C₄; aromatics were not detected in the products) was analyzed by an on-line connected Finnigan 9001 gas chromatograph, equipped with a 50 m × 0.32 mm × 5 μm Al₂O₃/KCl capillary column and a TCD detector. The retention times and calibration for individual species were obtained using pure individual compounds (Sigma-Aldrich, CZ - GC). Steady-state conditions were achieved within 0.5-3.0 h of the reaction time-on-stream. All the parameters of the used catalysts testing methods are in detail given in the Ref. [23].

3. RESULTS

The zirconium hydroxide treated at temperatures below 400°C was amorphous according to the XRD results (Fig. 1), while calcination in the temperature range between 400 and 700°C induced formation of monoclinic and tetragonal phases. By increasing the temperature of calcination above 400°C the crystallinity of the ZrO₂ material increases with formation of both tetragonal and monoclinic phases and after calcination at 700°C the monoclinic phase dominates. The evolution of the individual ZrO₂ phases, obtained by evaluation of diffractograms, is shown in the Fig. 2. In parallel with the increasing calcination temperature and transformation from the amorphous to partially crystalline material, the surface area of the ZrO₂ material decreases, from 316 to 54 m²/g. The addition of W would participate in preserving the higher surface area of the pre-calcined support, as surface area over 18% WO₃ containing samples ranges from 140 to 47 m²/g. Thus, for ZrO₂ material pre-calcined at temperatures of 400°C or above, the addition of W would not

further induce any stabilization of the $\text{WO}_3\text{-ZrO}_2$ surface during final calcination at 700°C . It follows that rough correlation between the surface area of the pre-calcined ZrO_2 material and the final surface area of the $\text{WO}_3\text{-ZrO}_2$.

During the final calcination the complete crystallinity is reached over all samples, nevertheless the monoclinic/tetrahedral ratio depends (strongly) on the pre-calcination temperature.

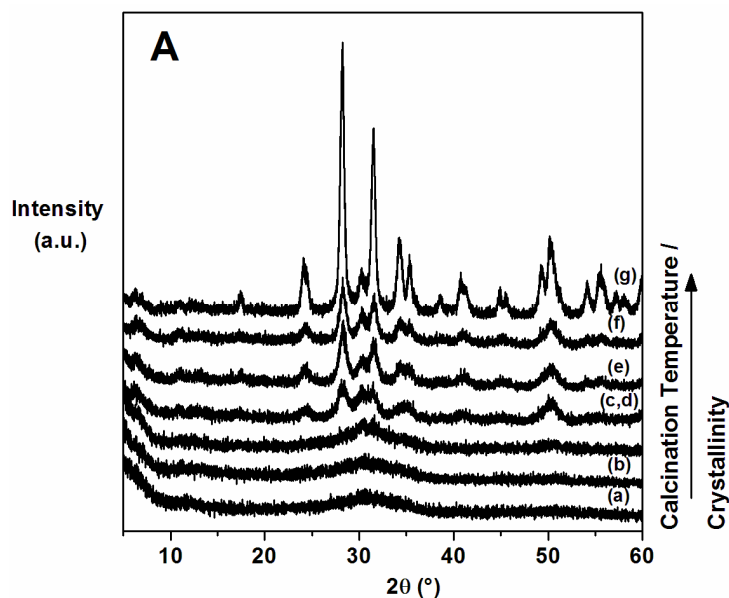


Fig. 1. (A) The evolution of crystallinity in ZrO_2 support during pre-calcination of parent $\text{Zr}(\text{OH})_4$ material as reflected in diffractograms. The temperature range of pre-calcination $25\text{-}700^\circ\text{C}$: (a) 25°C , (b) 200°C , (c) 300°C , (d) 400°C , (e) 500°C , (f) 600°C , (g) 700°C

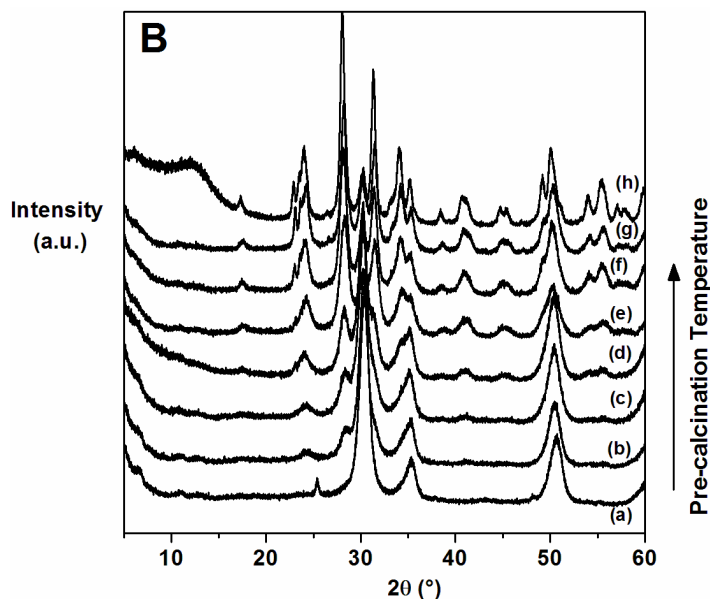


Fig. 1. (B) The evolution of crystallinity in resulting $\text{WO}_3\text{-ZrO}_2$ materials, prepared by W-impregnation on $\text{ZrO}(\text{OH})_2$ supports pre-calcined at temperatures specified above (Fig. 1A): (a) 25°C , (b) 100°C , (c) 200°C , (d) 300°C , (e) 400°C , (f) 500°C , (g) 600°C , (h) 700°C . (After W-introduction all the resulting materials were calcined at $700^\circ/3\text{h}$)

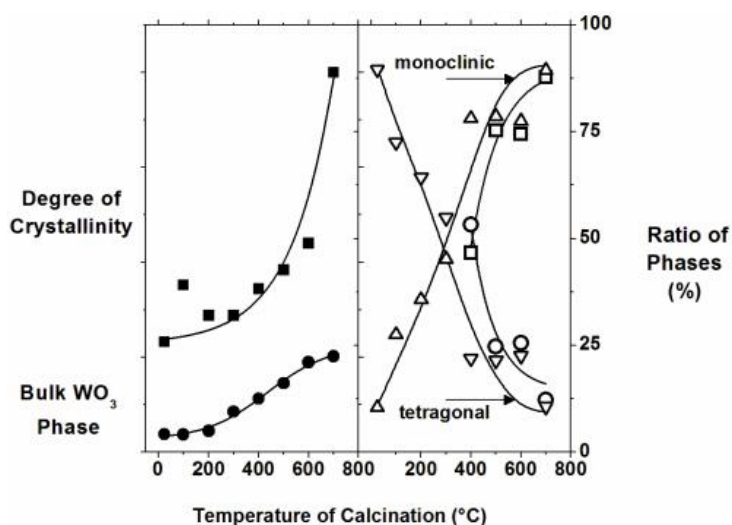


Fig. 2. The evolution of crystallinity (—■—) and tetragonal (—□—) and monoclinic (—○—) phases in parent $Zr(OH)_4$; and tetragonal (—▽—) and monoclinic (—△—) phases in resulting WO_3-ZrO_2 materials; finally relative ratio of WO_3 phase (—●—); all in dependence on temperature of pre-calcination

The UV-Vis spectra of the WO_3-ZrO_2 samples calcined at $700^\circ C$ are shown in the Fig. 3. In accordance with previous results [23] the complex spectra could be decomposed into four characteristic spectral bands, reflecting the four types of WO_x species, differing in nuclearity and identified by a maxima of absorption at $39\,000$, $35\,000$, $30\,000$ and $27\,000\text{ cm}^{-1}$, intensity of which were evaluated. From the changes in the relative intensities of the characteristic individual bands of WO_x species it follows that their formation and population are strongly influenced by pre-calcination of the support. The mononuclear $W-O-Zr$ species ($39\,000\text{ cm}^{-1}$) and two-dimensional poly-tungstate like WO_x species ($35\,000\text{ cm}^{-1}$) are formed when slightly pre-calcined support is used ($25-400^\circ C$ pre-calcination). They are started to transform into a larger defined WO_x , tri-dimensional clusters ($30\,000\text{ cm}^{-1}$) and to bulk-like WO_3 the absorption maximum of which is observed at $27\,000\text{ cm}^{-1}$. The procedure of evaluation of the populations of the individual WO_x species of samples prepared using pre-calcined at different temperatures consisted in separation into individual spectral bands and was according to [23]. This is exemplified by decomposed spectrum of sample pre-calcined at $200^\circ C$ given in the Fig. 4. Significantly, the band $35\,000\text{ cm}^{-1}$, reflecting the population of poly-nuclear WO_x species, which were in previous studies identified as reaction active species is gradually decreasing with increasing of the pre-calcination temperature,

and at the same time is accompanied by increase in the population of two types of bulk-like species, reflected in bands $30\,000 - 32\,000\text{ cm}^{-1}$ and $27,000\text{ cm}^{-1}$. The population of the individual WO_x species in dependence on temperature of pre-calcination was thus evaluated. All the technical details of WO_x species spectral characterization as well as their identification as active sites for isomerization are reported elsewhere [23].

In the all curves of the NH_3 -TPD of pre-calcined parent ZrO_2 samples and those of WO_3-ZrO_2 samples prepared from pre-calcined material, containing 18 wt.% WO_3 and finally calcined at $700^\circ C / 3h$, the 3 distinct bands of NH_3 -desorption were identified, in accordance with previous results [23]: desorption with maximum at cca $250^\circ C$ representing weak acidity, that at cca $400^\circ C$ representing medium acidity, and at $>550^\circ C$ representing strong acid sites. Obviously, the total acidity as well as the specific acidity expressed as the number of acid sites per square nm of the surface decreases with increasing the temperature of pre-calcination of the parent material. The all parameters obtained from UV-Vis and TPD, i.e. population of individual WO_x species and concentrations of the acid sites are discussed in Discussion Part.

The TPR curves of H_2 -TPR of 18wt.%- WO_3-ZrO_2 samples prepared using $Zr(OH)_4$ parents pre-calcined at different temperatures indicate the

change of the total H₂ consumption in dependence on temperature of pre-calcination. This indicates a complete reduction of the present WO₃ for sample prepared by impregnation of the ZrO_x pre-calcined at 100°C, while only ~70% in sample prepared by

impregnation of the ZrO_x pre-calcined at 700°C. The complex TPR profiles were decomposed into five individual reduction bands with maxima, at 450, 650, 750, 715, at about 850°C. The band at 650°C increases, while those at 850°C a 750°C decrease, with temperature of pre-calcination.

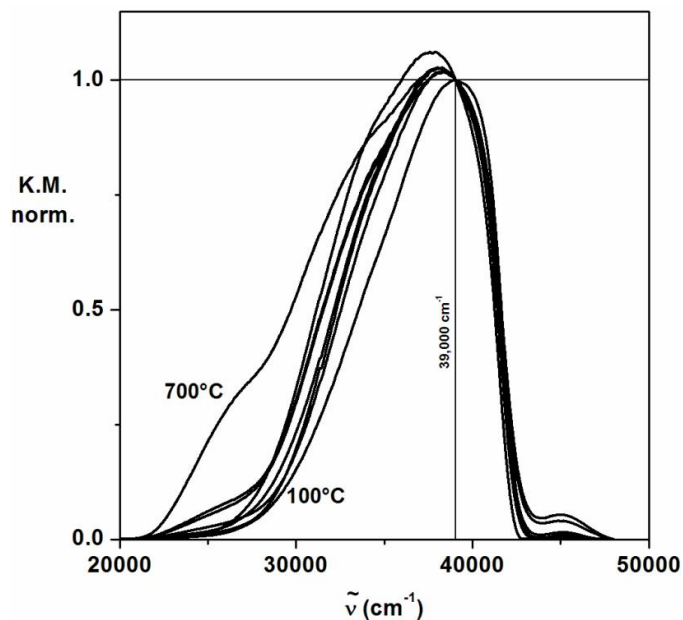


Fig. 3. The UV-Vis spectra of WO₃-ZrO₂ (18 wt.% WO₃) prepared using Zr(OH)₄ pre-calcined at various temperatures between 100-700°C, impregnated with tungsten and finally calcined at 700°C / 3h. The spectra are normalized at band 39 000 cm⁻¹

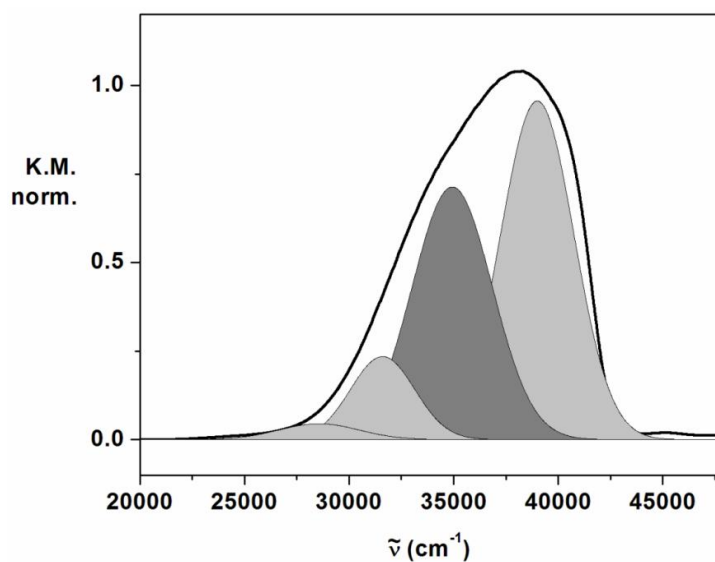


Fig. 4. The UV-Vis spectrum of WO₃-ZrO₂ (18 wt.% WO₃) obtained from parent Zr(OH)₄ pre-treated at 200°C, given as an example of decomposition spectra into individual bands

3.1 Catalytic Testing

The isomerization activity was studied in conversion of n-heptane to iso-heptanes over the samples prepared from pre-calcined parents at temperatures between 25°C and 700°C. The representative chromatogram is exemplified in the Fig. 5, where typical GC output obtained with 200°C pre-calcined WO₃-ZrO₂ sample, is shown. Formation of reaction products is summarized in Table 2, where the yield of iso-heptanes as well as undesired C₁-C₄ products, obtained at 250°C, are presented. Obviously, the yield of the iso-heptane at 250°C per gram of the used catalyst

decreases over samples prepared using ZrO_x support calcined at temperature above 300°C. Nevertheless the production of iso-C₇ varied in the range 4.5-7.5 mol.sec⁻¹.g⁻¹, if calculated per surface area of the final catalysts (see Discussion Part).

4. DISCUSSION

The principal question targeted by this article is the role of the initial state of the Zr(OH)_x/ZrO₂ used in the step of impregnation by WO₃ precursor for the properties of the final Pt/WO₃-ZrO₂ catalyst for paraffin isomerization.

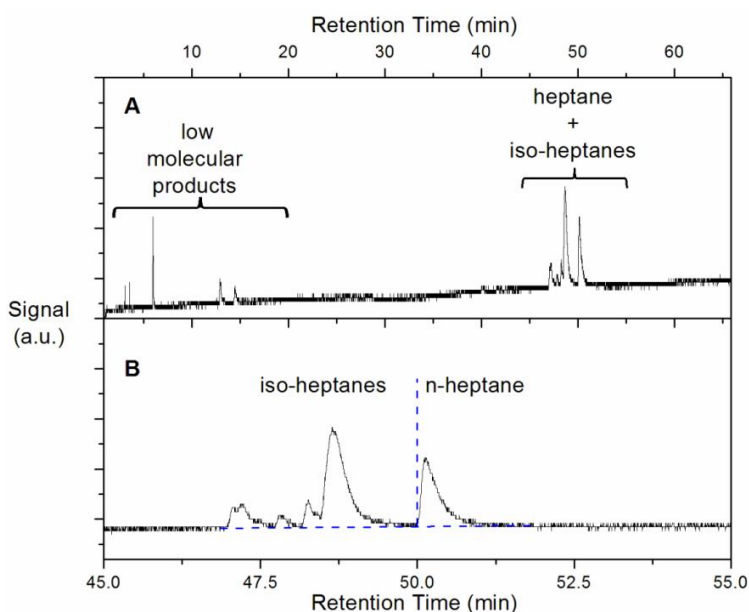


Fig. 5. The example of typical GC output, obtained with 200°C pre-calcined WO₃-ZrO₂ catalyst at 250°C reaction temperature. (A) The whole chromatogram 0-65 min; (B) It's detail in range 45-55 min of retention time

Table 2. The isomerization of n-heptane: Tabulated values of the yield of iso-C₇ at reaction T = 250°C and of the yield of low-molecular products (sum of C₁-C₄) as a function of parent ZrO₂ pre-calcination temperature

Pre-calcination temperature (°C)	Conversion of n-C ₇ (%)	Yield of iso-C ₇ (%)	Yield of low-molecular products (C ₁ -C ₄) (%)
25	81.9	64.9	17.0
100	70.7	57.9	12.8
200	69.3	55.9	13.4
300	71.1	58.6	12.5
500	59.2	50.9	8.3
600	61.1	52.1	9.0
700	39.4	31.0	8.4

For that goal $\text{ZrO}(\text{OH})_x/\text{ZrO}_2$ was prepared by standard precipitation consisting of reaction between zirconium oxo-chloride solution and concentrated ammonia. For the following step of impregnation by ammonium meta-tungstate the materials widely differing in the temperature of pretreatment were used, starting with wet material as isolated from the prepared suspension without any temperature treatment, up to materials isolated and pre-calcined to 700°C . By such approach, the impregnation was realized in extremes between highly amorphous material, still representing the $\text{ZrO}(\text{OH})_x$, up to well defined crystallized ZrO_2 . The dried or partially pre-calcined materials represented a sequence of materials with progressing transformation from nearly amorphous $\text{Zr}(\text{OH})_x/\text{ZrO}_2$ mixtures up to variously developed crystalline material with defined monoclinic-to-tetragonal phases ratio. As shown by the XRD results, the material precalcined up to 300°C display hardly any crystallinity and that is developed only at higher pre-calcination temperatures, above that point, and as typical, the material calcined at 700°C display high crystallinity accompanied by nearly full transformation into monoclinic phase. These transformations are regularly accompanied by changes of the specific surface area, decreasing down below $50 \text{ m}^2/\text{g}$ for the material after calcination at the highest temperature.

Accordingly, by using the same amount of WO_3 precursor and targeting the same value of 18 wt.% of WO_3 at the final material, the conditions during the impregnation step are widely different, and the formal WO_x/ZrO_x coverage in the impregnation step depends on the pre-calcination temperature. It represent roughly values of 8.2 W.nm^{-2} (for the 700°C) to 2.7 W.nm^{-2} (at 105°C), even if the surface area of the wet $\text{Zr}(\text{OH})_4$ isolated from the precipitated suspension could not be realistically evaluated. The same systematic variability concerns also the amorphicity/crystallinity ratio of the impregnated material as well as the morphological nature of these materials.

This wide variability in the sequence of the prepared impregnated supports then directly influence the following high temperature step and the produced materials systematic differ in all structural parameters.

There exists a nearly liner correlation between the surface areas of the materials before and after high temperature calcination (as said in

previous). In accordance with that the resulting formal WO_x coverage of the resulting ZrO_2 support varies between 2.7 and 8.2 W.nm^{-2} . These results also point into interconnectivity of the amorphicity of support before WO_3 introduction, and the decrease in concentration of acid sites and decrease in population of poly-nuclear WO_x species.

A well expressed systematic correlation exists also between the monoclinic/tetragonal (M/T) ratio of the resulting material and the state of the precursor ZrO_2 before impregnation. That is not surprising for the impregnated materials with already developed crystalline structure but it is very strongly expressed also for materials pre-treated at relatively moderated temperature which would not induce formation of a noticeable crystalline phases. Namely the existence of an expressed decrease of the (M/T) ratio ~ 0.12 between samples prepared from wet $\text{Zr}(\text{OH})_4$ samples and using material dried after isolation at 105°C is symptomatic for the important role of early interaction of the WO_3 precursor with the support. Actually, the prepared sequence of WO_x/ZrO_2 materials thus represents potential catalysts with WO_3 supported on nearly clean tetragonal and/or clean monoclinic modifications based materials, with a series of structures representing variation in the ratio of these two modifications.

For better illustration of the results the Table 3 summarizes the characteristics representing activity, i.e. the yield and isomerization rate together with level of crystallinity, concentration of WO_x expressed as coverage (according to [24]) and population of poly-nuclear WO_x species.

For practical purposes there clearly exists a correlation between the degree of crystallinity of initial $\text{Zr}(\text{OH})_4/\text{ZrO}_2$ support before WO_3 -introduction and the performance of the of final $\text{Pt}/\text{WO}_3\text{-ZrO}_2$ catalyst in *n*-C₇ isomerization (see Fig. 6).

Nevertheless, the changes in the degree of crystallinity of the initial $\text{Zr}(\text{OH})_4/\text{ZrO}_2$ support is transformed during the following steps of preparation into change in the surface density. As could be deduced by correlating the final surface area of the ZrO_2 support, the surface areas of the pure t and m phases would approach values of cca $160 \text{ m}^2/\text{g}$ and about $40 \text{ m}^2/\text{g}$, respectively.

Table 3. Summarization of activity characteristics, yield and reaction rate expressed per gram of catalyst and per surface area (i.e. per nm²) together with W coverage and population, surface density of polynuclear WO_x species, and (M/T) phase ratio

Pre-calcination T (°C)	Initial material - Crystallinity	Rate (mol* • sec ⁻¹ • gram ⁻¹) * 10 ⁷	Rate (mol* • surface nm ⁻²)	Coverage	Poly-nuclear WO _x (%)	M/T ratio
25	0.00	6.37	4.55	2.74	36.7	0.12
100	0.1-0.2**	5.69	5.47	3.69	40.8	0.38
200	0.1-0.2**	5.49	3.81	2.66	37.7	0.56
300	0.1-0.2**	5.76	4.80	3.19	37.0	0.82
400	0.20	3.00	2.56	3.28	36.3	3.57
500	0.27	5.00	6.10	4.68	34.2	3.67
600	0.37	5.12	7.64	5.72	33.3	3.44

* of iso-heptanes formed

** uncertainty is high due to broad diffractogram

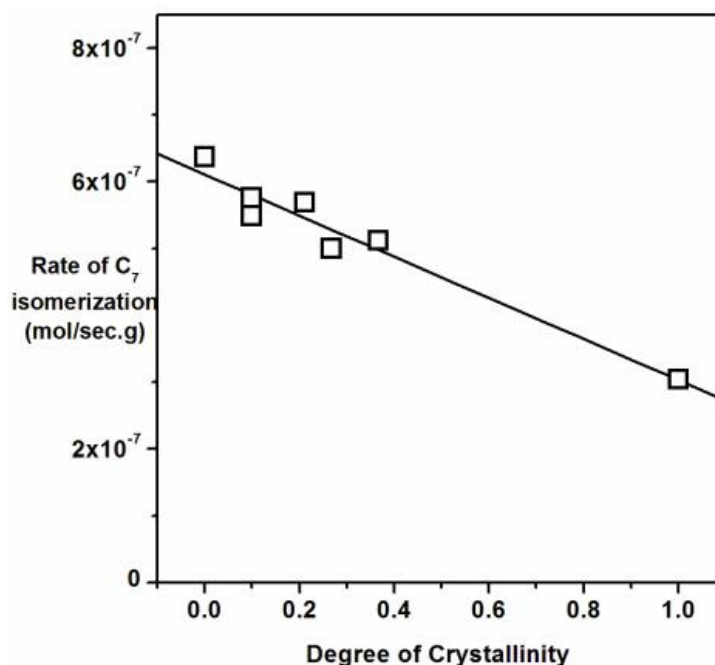


Fig. 6. Dependence of activity of final Pt/WO₃-ZrO₂ (18 wt.% WO₃) catalyst expressed as reaction rate per gram as a function of degree of crystallinity of initial Zr(OH)₄/ZrO₂ support before WO₃-introduction

Thus, the intermediate structures represent a formal combination of these two modifications, and their surface area would roughly represent a linear combination of both components in the established ratio. By keeping the final concentration of the WO₃ constant would provide for variation in the WO₃/ZrO₂ coverage, which will be manifested in the structural variation of the surface WO₃ species: That could be illustrated by changes in the population of the individual WO_x species and their distribution between mono-nuclear, poly-nuclear and bulk-like WO_x species

as revealed in the UV-VIS analysis (described above).

In accordance with these results, the primary correlation between increasing WO_x/ZrO₂ surface density will show the primary population of mono-nuclear species, followed by population of poly-nuclear ones and finally population of bulk-like WO_x species at higher coverage. The primary preparation parameter inducing these variations was thus here the temperature of pretreatment, inducing modification of the properties of the final

WO₃/ZrO_x impregnated material, i.e. the surface is during the following high temperature calcination step transformed, reflecting the very different state of the initial support before WO_x-impregnation and calcination. The final catalysts with basically different monoclinic-to-tetragonal proportion were thus obtained and also they are reflected in variation in the final surface area.

It has been thus confirmed that the initial state of the support before introducing WO₃ component is decisive factor determining the resultant properties the final WO₃/ZrO₂ material, and use of variation of the pre-calcination temperature could modify, in a controlled way, the surface area, the nominal coverage as well as the M/T ratio of the produced material.

That provides the principal conclusion, i.e. that the despite wide variation of the primary impregnated material, the proportion of the individual WO_x species follow the well-established trends in primary population of mono-nuclear species, followed by poly-nuclear ones at mediate coverage and finally in formation of bulk-like WO_x species at the highest coverage.

Using such approach, potential catalysts for isomerization of the highly reactive C₇ paraffins were prepared. The prepared sequence of materials display systematically changed structural parameters, some of them interconnected, e.g. the surface area, coverage, and M/T ratio, but still represent materials prepared from the same starting precipitated Zr(OH)₄ material and with the same nominal concentration of WO₃ (18%). The choice of the conditions for the evaluation of the catalytic activity of the prepared materials was directed by use of the optimal temperature region of reaction temperatures, which is between 225 - 275°C, so that of 250°C was chosen as generally optimal for iso-heptane production, as at lower temperatures the conversion is further decreasing over all catalysts, and at higher temperatures the parallel reactions like cracking begin to take place (or even dominate).

The conversion over all the individual materials was between 82 – 40%, and constantly decreases with increasing temperature of pre-calcination of the initial Zr(OH)₄, (in accordance with the decreasing surface area of the catalysts), and the corresponding yield of iso-C₇ analogously between 65 – 30%. The 65% of iso-C₇ was obtained with the sample prepared from completely amorphous zirconium hydroxide

(25°C), while it decreased to 30% if the zirconia support was used in a completely crystallized form, i.e. pre-calcined at 600 – 700°C.

Thus, the values of the yield of desirable iso-C₇ as well the undesirable lower C₁ to C₄ products were used to represent the catalytic performance and the role of the preparation history of the individual samples. Not surprisingly, there exist a direct correlation between the yield of iso-C₇ products per gram of the catalysts and the total surface area of the prepared materials. On the other hand, when the catalyst performances are expressed as amount of iso-C₇ produced per surface area of the material, the picture is reversed (see Fig. 7), and the production of iso-C₇ systematically increases with the WO₃ coverage not depending on the total surface area and ZrO₂ modification.

The conclusions which could be directly deduced from these observations could be summarized as follows:

- i) Despite changes in the ratio of the M/T modification of ZrO₂ the specific activity of the catalysts for C₇ isomerization is primarily controlled by the WO_x coverage over the ZrO₂ support and show a maximum at about WO_x/ZrO₂ of about 6 W.nm⁻², i.e. in the region generally above the formal monolayer, observed for these catalysts;
- ii) Thus, there seems to be no appreciable role of the crystal modification of the ZrO₂ as such, as the performance of the catalysts in the studied sequence follows the usual profile with changing WO_x/ZrO₂ surface coverage without disruption by the accompanying change of the relative proportion of both ZrO₂ modifications;
- iii) Accordingly, the effect of the changes at the M/T ratio is thus indirect as it controlled the final surface area of the final WO₃/ZrO₂ material;
- iv) The advantage of using the amorphous type of parent zirconia support for WO₃ impregnation is thus evident, but as shown by the results the reason behind that is by providing conditions for preventing transformation of the Zr(OH)₄ precursor into modification with lower surface area, while these results do not provide any argument for actual role of the ZrO₂ modification in formation of the WO₃ surface structure with higher activity.

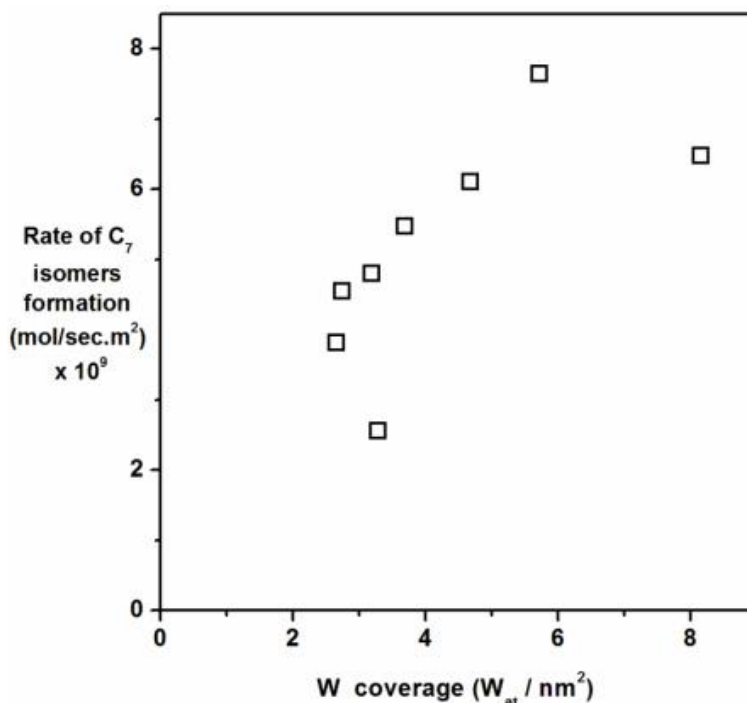


Fig. 7. Dependence of activity of final Pt/WO₃-ZrO₂ (18 wt.% WO₃) catalyst expressed as reaction rate (per sec) of isomers per surface area of catalyst (m²) as a function of W-coverage

All that point into the crucial role of the WO₃/ZrO₂ coverage reached in the material, while keeping high surface area is of the final catalyst is important of the performance of the catalyst in practical realization.

In accordance with the previous discussion, following the process of the catalyst development and changes in the surface, and proportion of the morphologic phases leading the manifestation of these structural changes into surface density of WO₃ species, the straightforward correlation exist between the specific activity (reaction rate per g) and population of the poly-nuclear WO_x species, not depending on total surface density. Thus, the important W-coverage [25,26] parameter could be seen as not only the one directing parameter [27,28] but as a parameter guiding the population of active poly-nuclear WO_x species among the other WO_x species, which thus finally play a decisive role in resulting catalyst activity.

Moreover, a good correlation could be find between the low-molecular products production, i.e. cracking reactions, (cracking rate per g) and population of bulk-like WO_x species (as reflected in the UV-Vis band 27 000 cm⁻¹), which is in agreement with general conception [29-32] that

such bulk-like species are responsible for undesired by-product activity of prepared catalysts. All the correlations found are in line with previously achieved understanding of the isomerization process occurring on Pt/WO₃-ZrO₂ catalysts and might be also of high importance for potential practical-industrial application [33,34].

5. CONCLUSION

Despite well expressed differences in the Monoclinic to Tetragonal (M/T) ratio in parent Zr(OH)₄/ZrO₂ support, influencing the transformation into final Pt-WO_x/ZrO₂ catalysts with similar variability in the M/T phases ratio, the specific activity of the catalysts for C₇ isomerization is shown to be primarily controlled by coverage of the ZrO₂ support by the WO_x species, while no appreciable effect of the M/T phases in the initial ZrO₂ as well as in the final WO₃-ZrO₂ was found for the catalyst performance in C₇ isomerization. Accordingly, the performance of the catalysts in the studied sequence ranging between two extremes, i.e. containing either almost clear Tetragonal or Monoclinic phase in ZrO₂, follows the usual profile with dominating effect of the WO_x/ZrO₂

surface coverage, without co-influence by the accompanying change of the relative proportion of both ZrO_2 phases. The effect of the changes at the M/T ratio has been found to be indirect and primarily to be controlled by the surface area of the final WO_3/ZrO_2 material.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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