Journal of Catalysis 307 (2013) 305-315

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Continuous production of the renewable ρ -cymene from α -pinene

M. Golets ^{a,*}, S. Ajaikumar ^a, M. Mohln ^b, J. Wärnå ^c, S. Rakesh ^d, J.-P. Mikkola ^{a,c,*}

^a Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-90187 Umeå, Sweden ^b Microelectronics and Materials Physics Laboratories, EMPART Research Group of InfoTech Oulu, University of Oulu, P.O.BOX 4500, FI-90014 Oulu, Finland

^c Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo-Turku, Finland

^d Department of Chemistry, Podhigai College of Engineering and Technology, Tirupattur 635601, Tamilnadu, India

ARTICLE INFO

Article history: Received 30 April 2013 Revised 6 August 2013 Accepted 11 August 2013

Keywords: ρ-Cymene α-Pinene isomerization Heterogeneous catalyst Flow-through reactor

1. Introduction

The possibility of application for ρ -cymene as a solvent in dyes and varnishes, as an additive for flavors and fragrances, and as an industrial odorant and raw material for chemical synthesis demonstrates the high importance of this product for chemical industry [1]. Moreover, prospectively terephthalic acid could be produced from ρ -cymene via oxidation [2]. Alternatively, ρ -cymene can be converted to ρ -cresol, which is conventionally produced via alkylation of toluene with propylene followed by oxygen mediated hydroperoxide cleavage. The further treatment of ρ -cresol leads to 2,6-di-tert-butyl- ρ -cresol – a well-known antioxidant [1,3]. Further, ρ -cymene could be converted to isopropyl phenols that are major intermediates in resins synthesis [4]. Non-nitrated musks and polymers, such as synthetic fibers or antiseptics, are also produced from the aforementioned chemical [5].

Conventionally, ρ -cymene is produced via alkylation of toluene with propene or 2-propanol. Friedel – Crafts catalysts, for example, HCl, H₂SO₄, AlCl₃, or BF₃ are commonly applied. In the second step, the obtained mixture of ρ , o-, and m-isomers is separated. However, nowadays, due to both environmental and sustainability related reasons, the endeavor is that the share of petroleum-derived chemicals should continuously diminish and be replaced by

ABSTRACT

The aim of this work was to demonstrate the feasibility to produce ρ -cymene, an important commodity chemical, in a continuous, one-pot reaction system from abundant α -pinene, available e.g. as a by-product of pulping industry. The isomerization reactions of α -pinene over bimetallic heterogeneous catalysts, 3 and 5 wt% Pd–Zn (1:1, 1:4, 4:1, 1:0, and 0:1), supported on Al-SBA15 were studied. The principal reaction products were identified as ρ - and m-cymenes, limonene, camphene, and ρ -menthene, respectively. The highest concentration of ρ -cymene reached 77 wt% under the optimized reaction conditions: 300 °C and α -pinene feed of 0.03 mL/min. Two main reaction pathways toward ρ - and m-cymenes were described, and a mechanistic kinetic model, based on a plausible reaction network in line with Langmuir–Hinshelwood approach, was developed. The catalyst characterization revealed the reduction in Pd(II) sites, catalyst coking, and decline of surface area over the course of time. The catalyst recovery and reuse was addressed. © 2013 Elsevier Inc. All rights reserved.

natural, renewable feedstocks [6,7]. On the other hand, the application of liquid mineral acids and soluble Lewis acid catalysts is disadvantageous due to problems associated with corrosion, handling, and safety as well as due to the difficulties encountered upon separation and reutilization of the products and the catalysts [7]. Evidently, it would be elegant to design a process leading to ρ -cymene that utilizes renewable raw materials and, at the same time, is a simple one-pot process. In fact, α -pinene and related terpenes are easily available from the Nordic pulping industry and could alternatively be utilized for this purpose. Chemical pulping and biorefining results in e.g. tall oil and turpentine fractions that predominantly contain α -pinene, along with other terpenes. Today, these fractions are undervalued and to a large extent burned in the recovery boilers to supply energy.

Previously, straight dehydrogenation and dehydroisomerization of α -pinene to ρ -cymene were studied by several groups [1,6,8]. Also, in comparison with the α -isomer, β -pinene was observed to possess similar reactivity [1,9,10]. Limonene conversion over supported Pd catalysts [2,11–16], zeolites [16,17], and Lewis acids [18] to ρ -cymene has also been investigated. Buhl et al. reported promising results for a mixture of terpenes, including α -pinene, limonene, terpinolene, and cineoles aiming at ρ -cymene over a Pd/SiO₂ catalyst. An analogous study of 3-carene was reported by Krishnasamy [19].

The well-known mesoporous SBA-15 support is characterized by its high surface area, relatively large-sized pores and high stability. In an earlier study taking advantage of this versatile material, Du et al. described the dehydrogenation of dipentene





JOURNAL OF CATALYSIS

^{*} Corresponding authors. Address: Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-90187 Umeå, Sweden (M. Golets).

E-mail addresses: Mikhail.Golets@chem.umu.se (M. Golets), Jyri-Pekka.Mikkola@chem.umu.se (J.-P. Mikkola).

^{0021-9517/\$ -} see front matter @ 2013 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcat.2013.08.007

over Al/SBA-15 and Zn/SBA-15, leading to ρ -cymene as the main product. According to Du et al., the presence of Zn, in fact, minimized the formation of cracking products due to the lack of Brønsted acidity of the catalyst [20]. On the other hand, the presence of moderate Lewis acidity in Zn/SBA15 contributed to 87 wt% yield of ρ -cymene according to their results [20]. In a yet another study, Chinayon et al., observed upon hydrogenation of acetylene over Pd/ α -Al₂O₃ that a significant improvement of acetylene conversion and ethylene selectivity could be obtained when the Pd sites were modified with Zn. In particular, the authors claimed that less coking could be observed for Pd–Zn/ α -Al₂O₃ than for Pd/ α -Al₂O₃ [21].

In this study, we investigated the possibility to design a onestage continuous process for efficient conversion of α -pinene to ρ -cymene over Pd–Zn/Al-SBA15 catalysts with various ratios and loadings of Pd and Zn metals. The structure of the catalysts, characterization results, as well as the optimized reaction conditions was discussed. Still, a kinetic model was proposed that accounts for the described reaction mechanism.

2. Experimental

2.1. Materials

The hydrogen gas used was purchased from a commercial source (AGA AB) and had a purity of 99.999%. All the catalysts were in-house prepared and characterized at Technical Chemistry, Department of Chemistry, Umeå University. High purity (\geq 95 wt%) standards of camphene, limonene, ρ -cymene, ρ -menthene, α -pinene, and γ -terpinene were obtained from Sigma–Aldrich and used as received for calibration of the gas chromatograph (GC) to obtain quantitative and qualitative analysis of the reaction mixtures.

2.2. Apparatus and general reaction procedure

The reaction was carried out in a tailor-made flow-through reactor made of quartz glass and equipped with a heating jacket and a reflux condenser operated at atmospheric pressure and the equipped with control unit (CAL 9500P, CAL Controls) for accurate temperature control of the catalyst bed. The catalyst was loaded in the reactor tube (0.25 g in a typical experiment) along with the thermocouple. The catalytic bed was immobilized in the middle of the tube with the help of glass wool and glass balls. The tube was fitted inside of the heater and connected with a collection flask and a reflux condenser coupled to a collection flask. The reactant and gas inlet feed pipes were connected at the top of the glass tube for top-down flow, and the temperature was adjusted to the preset level. Prior to the each and every experimental run, the system was exposed for 2 h to hydrogen flow to facilitate catalyst activation and to obtain thermal steady state of the system. Thereafter, the reactant feed was initiated by continuously pumping α -pinene to the top of the upper section of the reactor tube acting as a vaporizer by means of an HPLC pump (high-precision liquid chromatography pump), and thus, the reaction was commenced. For the reliable investigation of the reaction kinetics, continuous sampling from the collection flask was performed. The optimal temperature and reactant flow were evaluated during the preliminary experiments (Section 3.1). In all cases, a constant hydrogen flow of 10 mL/min was applied.

2.3. Product analysis

The reaction products were analyzed by means of a gas chromatography (GC, Agilent Technologies, Model No. 7820A), equipped

with an HP-PONA capillary column (50 m, 0.2 mm I.D., 0.25 µL film thickness) and a Flame Ionization Detector (FID). Nitrogen was used as the carrier gas (1.0 mL/min). The temperature programming was as follows: the injection port and detector temperature were set to 250 °C, column temperature was adjusted to rise from 70 up to 230 °C, with a holding time of 0.5 min at the initial temperature, and a heating ramp of 10 °C/min was applied. The reactant and product retention times (min) were evaluated as follows: α -pinene (8.63), camphene (8.90), trans-pinane (9.50), ρ-menthene (9.72), m-cymene (10.45), ρ-cymene (10.68), limonene (10.75), and γ -terpinene (11.45) (Fig. 1). To evaluate the possible formation of dimers [22], a prolonged GC analysis method was tried (30 min) at an elevated temperature of 320 °C. However, no additional products were detected in the GC chromatograms upon extended run times. For a detailed product analysis and identification. GCMS analysis (Gas Chromatography coupled to Mass Spectrometry: Thermo Trace DSO) was applied (column VF-5MS. 30 m., 0.25 mm I.D., phase 0.25 µm). Constant nitrogen flow rate of 1.5 mL/min was utilized. The temperature of the injection and initial oven temperatures were 230 °C and 50 °C, respectively. The maximum temperature applied was 300 °C (ramping 20 °C/ min), after one (1) minute of hold time. A representative sample GC chromatogram with specified retention times is presented in Fig. 1.

The concentrations were expressed in terms of wt% in reference to the whole amount of the reacted α -pinene and other reactants in the product mixture. Prior to this, each and every standard species was calibrated in order to identify and quantify the reaction products. In addition, ρ -cymene was distinguished from m-cymene with the help of earlier observations [1]. The following formulas were used for the calculation of the conversion, product selectivities, and yields, respectively:

X (%)

= $\frac{\text{initial reactant}(s) \text{ GC peak area} - \text{final reactant}(s) \text{ GC peak area}}{\text{initial reactant}(s) \text{ GC peak area}} * 100$

(1)

$$S_{\rm Y} \ (\%) = \frac{\rm GC \ peak \ area \ of \ the \ product \ \ Y}{\Sigma \rm GC \ peak \ area \ of \ all \ products} * 100 \tag{2}$$

Yield (%) = X (%) *
$$\frac{S_Y}{100}$$
 (3)

The weight hourly space velocity (WHSV) was expressed in (g/h)/g and calculated by the following formula:

$$WHSV = \frac{mass of reactant/h}{mass of catalyst}$$
(4)

2.4. Catalyst preparation

The synthesis of SBA-15 material was carried out as described elsewhere [20]. At first, for the preparation of Al-SBA15 (Si:Al ratio of 25), 20 g of PEO–PPO–PEO triblock copolymer (P123, 99.0%, Sigma–Aldrich) was dissolved in 150 mL of deionized water and mixed with 600 mL of 2.0 M HCl. Consequently, the mixture was left under stirring for 3 h, at 40 °C. As the next step, tetraethyl orthosilicate (TEOS, 99.0%, Sigma–Aldrich) and AlCl₃ (98.0%, Sigma–Aldrich) were added in amounts of 42.5 and 1.93 g, respectively. The mixture was stirred for 24 h at the above-mentioned temperature. At the next stage, the solution was aged in an oven (90 °C, 24 h). The obtained support structure was filtered and washed thoroughly with deionized water and 250 mL of ethanol. At the final stage, the formed Al-SBA15 was dried at 90 °C overnight and calcined at 550 °C for 6 h.



Fig. 1. GC chromatogram of the isomerized reaction products with their specific retention times.

For the metal impregnation, PdCl₂ and ZnCl₂ (99.0% and 98.0%, respectively, Merck Millipore) were selected as precursors. The required amounts of PdCl₂ and ZnCl₂ were diluted in HCl (0.1 M in deionized water). The amount of Pd or Zn loaded on the support was 3 and 5 wt%, respectively. The ratios of 1:1, 1:4, 4:1, 1:0, and 0:1 were prepared on a mass basis.

The support was dispersed in deionized water after which the solution of precursors and Al-SBA15 was stirred for 5 h to reach a uniform dispersion (wet impregnation) and dried in an oven at 100 °C for overnight. Consequently, the catalytic materials were calcined in a tubular oven (400 °C, 3 h, 10 mL/min, synthetic air). To obtain the final active form of the catalysts, a reduction in a tubular oven was carried out (300 °C, 3 h, 50 mL/min, H₂). The in situ catalyst activation was performed each and every time prior to the actual reaction (300 °C, 2 h, 10 mL/min H₂).

2.5. Catalyst characterization methods

Samples of the catalyst taken before and after the reaction, carried out under the optimized conditions, were characterized by means of nitrogen physisorption measurements. The catalyst surface area, pore volume, and diameter were measured in accordance with the Brunauer–Emmett–Teller (BET) method in a Micromeritics Tristar 3000 analyzer. About 0.1 g of the catalyst was degassed at 200 °C for 1 h prior to the actual measurement. The obtained adsorption isotherms served for the calculation of the specific surface area, pore volume, and pore size distribution, respectively.

Additionally, X-ray Photoelectron Spectroscopy (XPS) technique was applied to examine the chemical state of different species on the catalyst. For the XPS measurements, a Kratos Axis Ultra Electron Spectrometer equipped with a delay line detector was used with the following parameters: monochromated AlK α source (150 W), hybrid lens system (magnetic lens), charge neutralizer, and analysis area of 0.3×0.7 mm². The C1s line of aliphatic carbon (set at 285.0 eV) served as the reference for binding energy (BE) value. The Kratos software was used for the processing of the spectra.

To evaluate the distribution of the active metal sites on the catalyst surface and to analyze the structures formed, Transmission Electron Microscopy (TEM) was performed. First, the samples were suspended in ethanol, and consequently, drop casted on the TEM grid. The TEM images were taken using an Energy Filtered Transmission Electron Microscopy (EFTEM, Leo 912 Omega) operating at an acceleration voltage of 120 kV. The X-ray diffraction (XRD) analysis revealed the structural features of the studied catalyst, and a PANalytical diffractometer using CuK α (λ = 0.154 nm) radiation was utilized. The X-ray diffraction patterns of Pd–Zn/Al-SBA15 were recorded in the 2 θ range of 0.5–10°. During the analysis, steps of 0.015° were set with count time of 15 s at each point.

Temperature-programmed desorption (TPD) of ammonia was carried out using Micromeritics Instrument, AutoChem 2910. The catalyst was dried at 110 °C overnight. Certain amount of catalyst (50 mg) was placed in quartz made U-shaped tube. The catalyst was first pretreated in a flow of helium (AGA AB, 99.999%) at 550 °C for 1 h, followed by saturation with anhydrous ammonia in a flow of 10% NH₃-90% He mixture at 120 °C (20 cm³/min). The flushing of physisorbed NH₃ was performed at 105 °C during 2 h, and temperature-programmed desorption was carried out from ambient temperature to 500 °C (10 °C/min).

The thermo-gravimetric analysis (TGA) was carried out to quantify the coke and residual organic compounds located in the catalytic bed. The SDT-Q-600 (TA Instruments) analyzer was utilized at 650 °C with the ramping of 10 °C/min and air flow rate of 100 mL/min.

3. Results and discussion

3.1. Optimization of the reaction conditions

The reaction conditions were optimized during the preliminary studies. The most promising catalyst, Pd–Zn/Al-SBA15 1:1 (5 wt%), was investigated at various temperatures (250, 275, 300, 325, 340, and 400 °C) and flow rates (0.02, 0.03, 0.06, and 0.09 mL/min). The optimization results are presented in Tables 1 and 2, respectively.

In accordance with earlier literature [1], dehydroisomerization of α -pinene could not be performed at low reaction temperatures, and mostly bicyclic products, such as camphene, were produced. Earlier studies by Buhl et al. and Akpolat et al. suggested that a temperature range around 300 °C should yield optimal results, although catalyst poisons in the form of cleavage products would form [5,23]. Wadaani et al. indicated that lower flow rates that increase the reactant retention time would have a positive influence on the ρ -cymene selectivity when excess of camphene and limonene was fed [6].

Also in our case, the temperature of 300 °C was close to the optimal one. For the sake of comparison, an experimental runs were carried out at 340 and 400 °C. Despite the complete conversion of

Table 1 ρ -Cymene yield (wt%) upon temperature optimization (flow rate of α -pinene 0.3 mL/min).

Time (h)	Temperature (°C)					
	250	275	300	325	340	400
0.5	54.1	74.4	77.1	73.6	58.4	50.0
1	52.8	73.0	75.6	71.2	56.9	42.4
2	51.9	68.0	74.1	71.8	55.9	40.7
3	50.6	67.8	69.2	70.7	55.1	39.8
4	49.7	64.9	67.1	68.4	54.8	39.2
5	49.2	66.6	66.9	66.5	54.2	38.1

Table 2

 $\rho\text{-Cymene}$ yield (wt%) upon the flow rate optimization (at 300 °C).

Time (h)	Flow rate (mL/min)					
	0.02 ^a	0.03 ^b	0.06 ^c	0.09 ^d		
0.5	66.7	77.1	73.4	76.4		
1	71.9	75.6	73.3	73.6		
2	71.4	74.1	73.4	71.1		
3	70.8	69.2	71.3	69.1		
4	70.6	67.1	69.7	66.9		
5	69.6	67.0	67.1	66.0		

^a WHSV = 4.128 (g/h)/g.

^b WHSV = 6.192 (g/h)/g.

^c WHSV = 12.384 (g/h)/g.

^d WHSV = 18.576 (g/h)/g.

substrate, yields of ρ -cymene were suppressed (Table 1). After 30 min on stream, at 400 °C, roughly 10 wt% of cracking by-products (retention times yielding from 12 to 14 min) were observed. In effect, 42 wt% of undesired by-products were formed, and 50 wt% of ρ -cymene and 8 wt% of other main reaction products (camphene, ρ -menthene, and limonene) were found. Also, in general, the lower the reaction temperature, the better the production economics. Low temperature operations gave rise to elevated camphene and ρ -menthene yields up to 20 wt% but, at the same time, significantly hampered the selectivity toward ρ -cymene.

When the flow rate was only 0.02 mL/min, numerous by-products were observed. On the contrary, the studied catalyst demonstrated a solid performance at increased flow rates (from 0.06 to 0.09 mL/min). However, ρ -cymene concentration profiles observed at the outlet of the reactor were fluctuating more. Thus, an intermediate feed rate of 0.03 mL/min chosen in the present study in order to obtain reliable kinetic data. Furthermore, for this flow rate, the highest concentration of ρ -cymene was obtained (Table 2). The weight hourly space velocity (WHSV) was calculated for the evaluated flow conditions (Table 2). In conclusion, the reaction temperature of 300 $^{\circ}$ C and feed rate of 0.03 mL/min were selected as the optimal parameters for the subsequent testing.

3.2. Long-time reaction behavior

In case of the bimetallic catalyst formulation (Pd-Zn/Al-SBA15), ρ-cymene was obtained as the main reaction product. Additionally, limonene, camphene, m-cymene, and p-menthene were formed in small amounts (Fig. 1). Other non-identified products were formed in concentrations lower than 1 wt% and were not considered here. The highest yield of ρ -cymene obtained was 77 wt%, whereas the conversion of α -pinene was complete (100 wt%) in all cases studied. The catalytic activity was slowly deteriorating in terms of the selectivity in a time frame of 10 h although p-cymene yield still remained at around 60–65 wt% at this time. The performance of all bimetallic catalysts observed for the first 5 h on stream is depicted in Figs. 2-4, respectively. Moreover, for the sake of comparison, monometallic catalysts impregnated with 5 wt% of Pd or Zn were evaluated as well (Fig. 5). All experiments were performed at 300 °C and 0.03 mL/min of α -pinene flow rate. A non-catalytic reaction under similar conditions resulted in zero (0%) conversion.

As can be seen, the yield of ρ -cymene was lower for 3 wt% of Pd–Zn catalyst in comparison with the one having 5 wt% loading (Fig. 2). However, a strong correlation was observed when looking at the 3 wt% Pd–Zn catalyst (Fig. 2), and all catalysts prepared with 1:4 and 4:1 ratios of Pd and Zn, respectively (Figs. 3 and 4). In all cases, the ρ -cymene concentration obtained was within 5 wt% interval. Hence, the metal loading had no significant influence on the catalytic activity. On the other hand, as was finally established, apparently, a Pd:Zn ratio of 1:1 and a metal loading of 5 wt% were optimal in terms of maximal ρ -cymene yield. The formation of by-products was also minimized upon selection of the aforementioned ratio and loading. Evidently, the metal loading had no substantial influence on the catalytic stability as depicted in Figs. 2–4, respectively.

The influence of inert nitrogen atmosphere was tested as well. Interestingly, upon use of the best (1:1) catalyst, after 30 min on stream under nitrogen atmosphere, 15 wt% of camphene and only 55 wt% of ρ -cymene were observed, indicating that the hydrogen atmosphere was beneficial and it evidently improved the catalytic performance by maintaining the metal in its active form for extended periods of time.

As illustrated by the XPS analysis (Section 3.3), palladium sites were present on the catalytic surface in both oxidized and reduced forms. Thus, we decided to evaluate which of the oxidation states was actually active and responsible for the dehydrogenation reaction. The unreduced (non-activated) catalyst (Pd–Zn/Al-SBA15 1:1,



Fig. 2. The evolution of reaction products, Pd–Zn/Al-SBA15 1:1 (5 wt% – left, 3 wt% – right) (300 °C, 0.03 mL/min). Symbols: (•) total cymene; (○) ρ-cymene; (■) limonene; (□) m-cymene; (Δ) ρ-menthene.

308



Fig. 3. The evolution of reaction products, Pd-Zn/Al-SBA15 1:4 (5 wt% - left, 3 wt% - right) (conditions and symbols - Fig. 2.).



Fig. 4. The evolution of reaction products, Pd-Zn/Al-SBA15 4:1 (5 wt% - left, 3 wt% - right) (conditions and symbols - Fig. 2.).



Fig. 5. The evolution of reaction products, Zn/Al-SBA15 5 wt% - left, Pd/Al-SBA15 5 wt% - right (conditions and symbols - Fig. 2, (+) - trans-pinane).

5 wt%) was immediately tested after the calcination under the standard conditions (Fig. 2). A catalyst reduction in the tubular oven (Section 2.4) at 400 °C and subsequent in situ activation was run for the sake of comparison. In principle, the excess of hydrogen is released during the dehydrogenation of the substrate. Thus, it was also interesting to evaluate the necessity of the continuous H₂ flow in the reactor. A test run over non-activated, non-reduced sample of Pd–Zn/Al-SBA15 1:1 (5 wt%) was performed under the standard conditions and in the absence of hydrogen (Table 3).

In fact, self-activation by the reactant feed was observed since run 3 demonstrated high initial selectivity toward ρ -cymene (75 wt%). However, the ρ -cymene selectivity dropped to 64 wt% already after 3 h on stream. In comparison with the pre-reduced sample, the initial selectivity toward ρ -cymene was slightly higher in case of reactant-activated sample. Nevertheless, low catalyst stability was demonstrated in all three cases in contrast to optimized conditions. Thus, a standard procedure including reduction at 300 °C followed by the in situ activation is recommended. In addition, the increased formation of camphene was favored upon presence of the pre-reduced Pd sites.

Upon use of monometallic Pd or Zn catalysts (Fig. 5), the ρ -cymene concentration was suppressed in comparison with bimetallic catalysts (Figs. 2–4). Approximately two times more (38 wt%) ρ -cymene was formed when pure Zn was used instead of pure Pd. Thus, apparently, Zn sites seem more prone to facilitate

310 Table 3

Isomerization products obtained with various samples of Pd–Zn/Al-SBA15 1:1, 5 wt% (complete conversion, optimized conditions).

	Time (h)	ρ-Cymene	Camphene	ρ-Menthene
Sample 1 ^a	0.5	72.1	7.6	4.4
	1	67.6	7.0	3.5
	2	63.0	9.5	5.7
	3	61.9	11.2	6.8
	4	61.7	11.6	7.0
	5	60.1	12.3	7.3
Sample 2 ^b	0.5	70.0	2.4	6.2
	1	67.6	3.8	6.9
	2	66.1	5.2	6.8
	3	61.9	6.8	6.0
	4	60.2	7.1	5.7
	5	59.8	7.6	5.5
Sample 3 ^c	0.5	75.2	1.1	2.5
	1	74.1	1.1	3.5
	2	66.1	4.0	6.2
	3	64.0	6.4	3.5
	4	60.8	6.6	3.4
	5	59.7	7.1	3.4

^a Sample 1: pre-reduced under 400 °C, standard H₂ flow (10 mL/min).

^b Sample 2: non-activated and non-reduced, standard H₂ flow (10 mL/min).

^c Sample 3: non-activated and non-reduced, no make-up gas.

dehydrogenation, as observed earlier [20]. The hydrogenation reaction was promoted by use of the pure Pd, and hydrogenation products, such as trans-pinane (35 wt%), were mostly formed.

Native Al-SBA15 was also tested in order to evaluate the direct influence of the support acidity on the reaction performance. Consequently, Si-SBA15 support was prepared in line with the analogous procedure as before (Section 2.4). The results are presented in Fig. 6. On the basis of the data, the suitability of Al-SBA15 was further supported. The substantial acidity caused by alumina incorporation in Al-SBA15 gave rise to favorable properties of final catalyst in terms of acid-catalyzed reactions, including those of isomerization and dehydrogenation. Previous studies have referred to the lack [24–25] and absence [26] of acidity for pure siliceous mesoporous materials. Evidently, in case of Al-SBA15, both Lewis and Brønsted acid sites were present, and such medium acidic centers are typically related to the amount of alumina incorporated [24–28]. Consequently, the Brønsted acid sites could provide protons for the α -pinene internal ring cracking. Presumably, the Brønsted acidity also contributed to the oligomerization of the olefinic compounds; this being the main reason for coking [20].

All in all, 10–38 various by-products in concentrations less than 1 wt% could be seen in the GC chromatogram. Nevertheless, upon more detailed analysis, even more by-products (up to 170),

depending on the catalyst used, could be seen in very minor amounts (<0.025 wt%). Indeed, side reactions such as cracking reactions of α -pinene occurred to some extent. Interestingly, upon high palladium loading (ex. 4:1 Pd–Zn), less by-products were observed. On the other hand, lower relative amounts of Pd (e.g., in the case of Pd–Zn 1:4 catalyst) enhanced ρ -cymene yields but, at the same time, also lead to increased amounts of undesired reaction products.

3.3. Catalyst characterization

The XPS spectra were recorded for the freshly prepared Pd–Zn/ Al-SBA15 1:1 (5 wt%). Spent catalyst analyzed after third cycle (Section 3.5) was analyzed for comparison. At the surface of fresh catalyst, Pd was present as Pd(II). Nevertheless, the reduction step was performed after the preparation. The high reactivity of the catalytic material under study presumably gave rise to spontaneous formation of palladium oxides due to the access of humidity and air. As claimed by Albers et al., such a transformation took place for Pd/SiO₂ upon the hydrogenation of acetylene to ethylene under moderate temperatures (<200 °C) [29]. Further, other studies [30] have indicated the surface adsorption of oxygen monolayer and bulk oxidation of supported palladium within the temperature range of -73 to 200 °C, respectively. Delidovich et al. observed palladium oxide formation upon storage of Pd/C catalyst at room temperature and also confirmed this by means of XPS analysis [31]. In fact, the binding energy (BE) of Pd 3d_{5/2} decreased from 336.0 to 335.6 eV upon catalyst exposure to the reaction conditions. A decrease in BE of Pd $3d_{5/2}$ line indicates that Pd was primarily present at reduced forms in the spent catalyst [32]. Moreover, no Pd-Zn alloy peak was detected upon XPS analysis [32]. In addition, up to 17 at% (or 3 wt%) of the catalytic surface was coked in the spent catalyst. The major bond types of coke were C-C and C-H bonds (approx. 14 at%). Minor amounts (3 at%) of C-O bonds were also detected. The BE of Zn 2p_{3/2} remained at the constant value of 1022.7 eV. In fact, the monometallic palladium catalyst displayed no changes in BE that also corresponded to the suggested oxidation state of Pd(II) sites. The XPS analysis of monometallic Pd/Al-SBA15 and Zn/Al-SBA15 catalysts (Fig. 5) demonstrated the BE values of 336.0 and 1022.7 eV for Pd and Zn lines, respectively. Thus, there was no evidence of direct chemical interaction between Pd and Zn ions. The individual XPS spectra for fresh and spent catalysts are shown in Figs. 7 and 8, respectively.

The TEM measurement demonstrated perfectly formed catalytic structure (Pd–Zn/Al-SBA15 1:1, 5 wt%) with an even dispersion of Pd and Zn metals. Moreover, the catalytic properties remained unaltered throughout the experiment. Unfortunately, the metal



Fig. 6. Comparison of the reaction performance for Al-SBA15 (bricks) and Si-SBA15 (triangles) (conditions – Fig. 2.). Symbols: \blacksquare , \blacktriangle – α -pinene conversion; \Box , Δ – ρ -cymene yield.



Fig. 7. XPS spectra for the fresh Pd–Zn/Al-SBA15 1:1 (5 wt%). The peak with binding energy 336.0 eV is referred to the Pd(II) sites.



Fig. 8. XPS spectra for the spent Pd–Zn/Al-SBA15 1:1 (5 wt%). Peaks with binding energies 336.0 and 335.6 eV are referred to the Pd(II) and Pd(0) sites, respectively.

particles were not visible in the fresh catalyst due to the fact that the Pd was present in oxidized form. The visible Pd sites, in case of the spent catalyst, could be explained by the reduction in the Pd(II). This was also confirmed by the XPS analysis. The high-resolution TEM images, taken at 200 nm scale, are presented in Fig. 9. As can be seen in TEM images, relatively large-sized, spherically shaped nanoparticles simultaneously accumulated on the external surface of the support and resided in the pore system.

The nitrogen physisorption measurements confirmed the decline in surface area of the catalyst after the reaction, while changes in the pore volumes were negligible. The original values could, however, to a large extent, be restored in reactivated catalysts (Table 4). Thus, the nitrogen physisorption supported the XPS observations in terms of coking as the primary cause of catalyst deactivation.

The small-angle XRD patterns of spent and recovered Pd–Zn/Al-SBA15 1:1 (5 wt%) catalysts taken from the recovery trials (Section 3.5) are presented in Fig. 10. Three specific peaks were observed in the low angle (2θ) range at 2θ around 1.0° , 1.6° , and 1.8° , respectively, indicating the formation of well-ordered hexagonal structure of SBA15 [33]. The d_{100} spacing ($n\lambda = 2d \sin \theta$) and unit cell parameter ($a_0 = 2d_{100}/\sqrt{3}$) were calculated for the catalytic material in analogy with our previous study (Table 4) [33]. The hexagonal structure of the support was not affected during the isomerization reaction. However, the peak intensities, unit cell parameter, and d_{100} spacing values are increased during the recovery of spent catalyst that might be the result of the coke removal and restoration of the original properties of fresh catalyst.

As evaluated by the NH_3 -TPD measurement, the total acidity of Al-SBA15 support remained constant after the metal impregnation (Table 4). The mentioned total acidity value of 830 µmol/g was in line with the literature [24]. On the contrary, zero acidity was dem-

Table 4

Acid and textural properties data for Pd–Zn/Al-SBA15 1:1 (5 wt%): NH₃-TPD total acidity; BET surface area, pore size and pore volume; XRD d_{100} spacing and unit cell parameter.

Catalyst	NH ₃ -TPD	BET-N ₂ adsorption		XRD		
	Total acidity (µmol/g)	S _{BET} (m ² / g)	Pore size (nm)	Pore volume (cm ³ /g)	d ₁₀₀ (nm)	Unit cell-a ₀ (nm)
Fresh Spent Recovered	831 ^a 1254 1013	868.7 417.1 782.9	7.5 9.7 5.5	1.5 1.0 1.1	- 9.0 9.9	- 10.4 11.4

^a Same as for the unloaded Al-SBA15.

onstrated by Si-SBA15 as described previously (Section 3.2). Interestingly, the number of Pd–Zn/Al-SBA15 1:1 (5 wt%) acid sites was increased to 1250 μ mol/g in the spent catalyst. The recovered catalyst demonstrated a total acidity of 1010 μ mol/g. Presumably, immobilization of acidic by-products took place in the catalytic bed and facilitated the growth in total acidity. According to Zhao et al., the olefin-containing products could polymerize on the acidic catalysts causing their deactivation [34]. As supposed, the initial acidity of the studied catalytic material was optimal in terms of ρ -cymene formation.

Water, coke, and residual organics were altogether detected in the spent catalyst during the TGA analysis in approximate amounts of 1.5, 3, and 5 wt%, respectively (Fig. 11). In general, the XPS observation concerning coking and that of TPD concerning residual organics localized in the catalyst framework were confirmed by TGA.

3.4. Reaction network

An overall reaction mechanism was proposed capable of describing the experimental observations and also supported by the literature (Fig. 12) [1,5,6,9,11,17]. At the first stage, α -pinene is involved in the fast acid-catalyzed isomerization to form limonene and p-menthadienic compounds. The conjugated endocyclic menthadienes are characterized by strong adsorptivity on the catalytic surface and high reactivity in terms of both dehydrogenation and oligomerization. Presumably, the mentioned species were subject to dehydrogenation before the actual desorption; thus, they could not be observed in the product mixture [1,11]. According to Roberge et al. [1], acid cracking of the cyclobutane ring in α pinene C-C bond between the carbon atoms 1 and 6 is most probable to occur. The second stage was considered the rate-limiting step, i.e. the hydrogenation/dehydrogenation reactions occurring on the metal sites to yield ρ -menthene and ρ -cymene, respectively [6,35]. Additionally, minor amounts of p-cymene could be obtained via the dehydrogenation of previously formed intermediate



Fig. 9. TEM images taken for the fresh (left) and spent (right) catalyst (200 nm).



Fig. 10. Low-angle X-ray diffraction pattern of the Pd–Zn/Al-SBA15 catalyst (recovered – top, spent – bottom).

 γ -terpinene [1,9]. The formation of γ -terpinene was detected in concentrations less than 0.1 wt%. The presence of m-cymene and ρ -menthene, respectively, confirms the plausibility of the proposed reaction network. Furthermore, the concentrations of ρ -menthene (Figs. 2–4, respectively) substantially exceeded that of γ -terpinene, so the route via the formation of limonene was rather preferable.

In the presence of camphene, also m-cymene was observed. Initially, camphene isomerized to various intermediate m-menthadienic structures in analogy with the main pathway [1,11]. The camphene, which we assume as the intermediate product, was identified by the GC analysis, along with reaction products at the concentration range of 2.5–5 wt%, during the first 3 h on stream. The previously mentioned assumption was supported by the substantial growth in the camphene concentration (up to 10 wt% after 10 h of reaction) and also evidently contributed to the catalyst deactivation.

To explain the synergic properties of Pd–Zn, the reaction network (Fig. 12) was studied in light of the experiment carried out

with the monometallic catalyst (Section 3.2 and Fig. 5). As depicted in Fig. 5, zinc sites were involved facilitating dehydrogenation of m- and ρ -menthadienes to m- and ρ -cymenes, respectively [20]. The Pd sites interacted with p-menthadienes providing hydrogenation function responsible for the p-menthene formation. The complementary dehydrogenation function is also referred to the palladium sites, as also claimed in the literature [12]. As described by Buhl et al., the decline in activity or accessibility of Pd sites stimulated the formation of menthadienes and decreased the pcymene selectivity [5]. In a reaction studied by Roberge et al., Pd was supported on high surface area carriers: zeolites, silica, γ -alumina, and carbon. As described by Roberge et al., in case of monometallic catalyst, the absence of Pd eliminated the dehydrogenation function, and isomerization reaction only toward camphenic, fenchenic, and p-menthadienic compounds was possible. In opposite, only hydrogenated and aromatic compounds were formed in case when the Pd containing catalysts were utilized [1]. Thus, the individual activities of Pd and Zn improved the performance of bimetallic catalysts; nevertheless, no Pd-Zn alloy structure was observed (Section 3.3).

3.5. Catalyst reuse

The catalyst reuse was studied for Pd–Zn/Al-SBA15 1:1 (5 wt%) after 10 h of reaction. The reactor tube, containing the reduced catalyst, was placed in the tubular oven and treated at 500 °C in air flow of 50 mL/min for 5 h to burn off the coke formed. The recovered catalyst was activated and tested under the optimized reaction conditions (Section 3.1) upon which three consecutive cycles were performed. Data describing the performance of the recycled catalyst are presented in Fig. 13.

The catalyst investigated demonstrated high stability. The initial conversion remained unchanged (100 wt%) even after the third regeneration cycle, although the selectivity toward ρ -cymene decreased upon prolonged reaction times (10 h) for recycled catalysts. Upon the third recycling, the conversion decreased slightly



Fig. 11. TGA profile for spent Pd–Zn/Al-SBA15 1:1 (5 wt%), catalyst weight loss. Estimated temperature intervals: 0–150 °C – water; 150–450 °C – organics; 450–620 °C – coke.



Fig. 12. The overall reaction network.



Fig. 13. Long-term catalyst stability test cycles (from left to the right). Reaction conditions: Fig. 2.

after 10 h on stream. At the same time, up to 15 wt% of camphene and 15 wt% of limonene were detected. The decline in the catalytic activity could be explained by the coking of the catalytic surface and the organic residues accumulation in the catalyst framework (Section 3.3) [29]. A thin, visible layer of coke was also formed on the reactor walls.

3.6. Kinetic modeling

The kinetic model was proposed in accordance with the produced experimental data. Reaction network was organized in line with Fig. 14, which represented main pathways of the actual reaction network (Fig. 12).

To model the catalytic packed-bed reactor, the ideal plug flow model was used:

$$\frac{d\dot{n}_i}{dz} = r_i m_{cat} \tag{5}$$

where r_i denote the component generation rates and m_{cat} is the catalyst mass (g) in the reactor.

For the modeling of the reaction kinetics, the software Modest[®] 6.1 was used [36]. The software solves the reactor model equations



Fig. 14. Description of the reaction network used in the kinetic modeling (symbols: A – α -pinene, B – ρ -cymene, C – m-cymene, D – ρ -menthene, E – limonene, F – camphene).

(system of ordinary differential equations) with the backward difference method and optimizes the parameter values using a hybrid method involving Simflex and Levenberg–Marquardt methods. The goal function in the optimization is the sum of square function:

$$SSQ = \sum (y_{exp} - y_{model})^2 w$$
(6)

The weight factor *w* was set to 1 for all experimental points. For the optimization of the experimental data, the components α pinene, ρ -cymene, ρ -menthene, and camphene were used. The experimental values for m-cymene and limonene were not used, but the concentrations of them were calculated by the model according to the reaction scheme.

The temperature dependency was expressed with the normalized Arrhenius equation as follows:

$$A_{i} = k_{i} * e^{-\frac{\omega_{i}}{R} \left(\frac{1.000}{temp} - \frac{1.000}{Tmean}\right)}$$
(7)

where Ea_j are the activation energies (J/mol); *R* is the gas constant (J/mol K).

The reaction rates were expressed by means the following set of equations:

$$r_1 = k_1 * \frac{c_A}{D * deact} \tag{8}$$

$$r_2 = k_2 * \frac{c_A}{D * deact} \tag{9}$$

$$r_3 = k_3 * \frac{c_F}{D * deact} \tag{10}$$

$$r_4 = k_4 * \frac{c_E}{D * deact} \tag{11}$$

$$r_5 = k_5 * \frac{c_E}{D * deact} \tag{12}$$

where r_i denote the reaction rates (mol/ m_{cat} min) toward the respective product; C_i are the concentrations (mol/dm³); and k_i is the reaction rate constant (min⁻¹) and the parameter *deact* accounts for catalyst deactivation.

The flow-through reactor model is expressed as follows (Fig. 14):

$$ds(1) = \frac{(-r_1 - r_2)}{f * m_{cat}} A$$
(13)

$$ds(2) = \frac{r_4}{f * m_{cat}} \mathbf{B}$$
(14)

$$ds(3) = \frac{r_3}{f * m_{cat}} C$$
(15)

$$ds(4) = \frac{r_5}{f * m_{cat}} \mathbf{D} \tag{16}$$

$$ds(5) = \frac{r_2 - r_4 - r_5}{f * m_{cat}} \mathbf{E}$$
(17)

$$ds(6) = \frac{r_1 - r_3}{f * m_{cat}} \mathbf{F}$$
(18)

where ds(i) denote the generation rates (mol/ m_{cat} min) for each and every component and f denotes the flow rate (mol/min).

The degree of explanation was very good – 99.6%, and the calculated errors of the estimated parameters are all on an acceptable level (Table 5).

Fig. 15 represents a parity plot including all data points showing how well the model fits the data. Fig. 16 shows the calculated concentration profiles as a function of the longitudinal coordinate of the catalyst bed, the experimentally obtained concentrations are also shown at the outlet of the reactor.

3.7. Continuous reactors for feasible operations

Generally, to obtain good ρ -cymene yields in liquid phase, high catalyst loading is required [5], and the isomerization reactions toward camphene and related products are preferred [1]. A previous study by Grau et al. demonstrated only minor formation of ρ -cymene in liquid phase, although supported Pd catalysts were applied [11]. Respectively, upon use of our catalysts in liquid phase gave worthless results. Several trials were conducted in the laboratory

Table 5	
The numerical values of parameters and their errors.	

Estimated	Estimated	Est. relative error of parameters	Std. error (%)	Std error (%)
kde	0.252E-01	0.388E-03	1.5	64.8
k1	0.686E+00	0.486E-01	7.1	14.1
k2	0.265E+01	0.583E-01	2.2	45.5
k3	0.142E+01	0.429E+00	30.1	3.3
k4	0.974E+01	0.481E+00	4.9	20.2
k5	0.389E+00	0.950E-01	24.4	4.1
Ea1	0.329E+05	0.192E+04	5.8	17.1
Ea2	0.402E+05	0.693E+03	1.7	58.0



Fig. 15. Simulation of catalytic packed-bed reactor with the concentration of reactant as function of residence time (for temperatures 275 and 300 °C). Symbols: (o) α -pinene, (+) ρ -cymene, (\Box) ρ -menthene.

scale high-pressure reactor (PARR) at 150–250 °C with 0.25 g of Pd–Zn/Al-SBA15 1:1 (5 wt%) on the pure α -pinene substrate. Although a hydrogen pressure of 10 bar was applied, the conversion did not exceeded 5 wt%, and no dehydrogenation products were detected.

On the contrary to a batch reactor, a continuous reactor configuration allows for the simplicity of modifications, solventless operations, and good process control in both laboratory and industrial scales [37,38]. On the other hand, the use of continuous process and active catalysts is crucial in terms of providing high reaction rate per unit volume of reactor. Moreover, low liquid-to-solid volume ratio is needed to suppress the homogeneous side reactions [38,39]. Therefore, continuous flow-through reactor is the only feasible choice for the investigated reaction in terms of both improved selectivity toward ρ -cymene and suitability for the kinetic studies [38]. In addition, the camphene route could be suppressed by adjusting the retention time by means of tuning of the catalytic bed length at the suitable WHSV. The evaluation of the aspects such as the influence of the reactor walls, heat recovery, mixing



Fig. 16. Concentration profiles inside catalyst bed.

314

as well as separation aspects should be considered for the potential scale-up operations of the present process [38].

4. Conclusions

The results of the current study are summarized as follows:

- The proposed process design is clearly advantageous due to the complete (100%) conversion of α-pinene and high yield of valuable ρ-cymene 77% (by weight). Moreover, limonene, camphene, m-cymene, and ρ-menthene were detected as by-products. The modeling results further supported the hypothesis of the predominant reaction pathways.
- The best catalyst, Pd–Zn/Al-SBA15 1:1 (5 wt%), demonstrated good stability at high flow rates and a reasonable recoverability with prolonged times on stream. According to the TEM and XRD analyses, perfect hexagonal structure of the SBA15 was observed and retained after the reaction. Despite that XPS analysis detected no chemical interaction or alloy structure between Pd and Zn sites, their synergy was uncovered due to individual dehydrogenation activities provided by both metals. In opposite, upon use of monometallic catalysts and non-catalytic trials poor results were obtained.
- Coke and residual organics accumulated on the catalyst framework after longer experimental trials, which was confirmed by the XPS, NH₃-TPD, and TGA analyses; catalyst coking could evidently contribute to the observed decline in catalytic performance. Still, the initial acidity and textural properties of the catalyst could be restored with the recovery procedure.
- The described catalytic reaction represents a plausible example of a one-step green conversion of renewable feedstocks into value-added chemicals. The proposed approach could render a cheaper and more environmentally friendly process than the catalytic dehydrogenation strategy presently used by the industry. In summary, further studies are targeted toward the potential application of Pd–Zn/Al-SBA15 catalysts for the value-added upgrading of the industrial turpentine.

Acknowledgments

Processum Biorefinery Initiative AB, Domsjö Aditya Birla AB, Metsä Board, Holmen Skog, Kempe Foundations, and the Bio4Energy program are gratefully acknowledged for the financial support. COST CM0903 (UbioChem) is also acknowledged. Dr. Andrey Shchukarev (Umeå University) and PhD. Stud. Eero Salminen (Åbo Akademi) are acknowledged for their assistance during catalyst characterization experiments. This work is also associated with the Academy of Finland Research Program Nr. 268937.

References

[1] D.M. Roberge, D. Buhl, J.P.M. Niederer, W.F. Hölderich, Appl. Catal. A: Gen. 215 (2001) 111–124.

- [2] P.R. Makgwane, PhD Thesis, Faculty of Science, Nelson Mandela Metropolitan University, November 2009.
- [3] H. Fiege, Ullmann's Encyclopedia of Industrial Chemistry, vol. A8, VCH, Weinheim, 1985, p. 25.
- [4] K.S.N. Reddy, B.S. Rao, V.P. Shiralkar, Appl. Catal. A: Gen. 121 (1995) 191–201.
- [5] D. Buhl, P.A. Weyrich, W.M.H. Sachtler, W.F. Holderich, Appl. Catal. A: Gen. 171 (1998) 1–11.
- [6] F.A. Wadaani, E.F. Kozhevnikova, I.V. Kozhevnikov, Appl. Catal. A: Gen. 363 (2009) 153–156.
- [7] N.N. Binitha, S. Sugunan, Catal. Commun. 8 (2007) 1793–1797.
- [8] A. Stanislaus, L.M. Yeddanapalli, Can. J. Chem. 50 (1972) 61-74.
- [9] B.G. Harvey, M.E. Wright, R.L. Quintana, Energy Fuels 24 (2010) 267-273.
- [10] C. Fernandes, C. Catrinescu, P. Castilho, P.A. Russo, M.R. Carrott, C. Breen, Appl. Catal. A: Gen. 318 (2007) 108–120.
- [11] R.J. Grau, P.D. Zgolicz, C. Gutierrez, H.A. Taher, J. Mol. Catal. A: Chem. 148 (1999) 203–214.
- [12] P.A. Weyrich, W.F. Holderich, Appl. Catal. A: Gen. 158 (1997) 145-162.
- [13] P.A. Weyrich, PhD Thesis, RWTH Aachen, Germany, 1995.
- [14] D. Buhl, D.M. Roberge, W.F. Hölderich, Appl. Catal. A: Gen. 188 (1999) 287– 299.
- [15] P. Lesage, J.P. Candy, C. Hirigoyen, F. Humblot, J.M. Basset, J. Mol. Catal. A: Chem. 112 (1996) 303–309.
- [16] M.A. Martın-Luengo, M. Yates, M.J. Martınez-Domingo, B. Casal, M. Iglesias, M. Esteban, E. Ruiz-Hitzky, Appl. Catal. B: Environ. 81 (2008) 218–224.
- [17] M.A. Martin-Luengo, M. Yates, E.S. Rojo, D. Huerta Arribas, D. Aguilar, E. Ruiz Hitzky, Appl. Catal. A: Gen. 387 (2010) 141–146.
- [18] C. Catrinescu, C. Fernandes, P. Castilho, C. Breen, Appl. Catal. A: Gen. 311 (1) (2006) 172–184.
- [19] V. Krishnasamy, Aust. J. Chem. 33 (1980) 1313-1321.
- [20] J. Du, H. Xu, J. Shen, J. Huang, W. Shen, D. Zhao, Appl. Catal. A: Gen. 296 (2005) 186–193.
- [21] S. Chinayon, O. Mekasuwandumrong, P. Praserthdam, J. Panpranot, Catal. Commun. 9 (2008) 2297–2302.
- [22] H.A. Meylemans, R.L. Quintana, B.G. Harvey, Fuel 97 (2012) 560-568.
- [23] O. Akpolat, G. Gunduzb, F. Ozkanc, N. Besun, Appl. Catal. A: Gen. 265 (2004)
- 11-22.
 [24] M. Gomez-Cazalilla, J.M. Merida-Robles, A. Gurbani, E. Rodriguez-Castellon, A. Jimenez-Lopez, J. Solid State Chem. 180 (2007) 1130–1140.
- [25] A.K. Medina-Mendoza, M.A. Cortés-Jácome, J.A. Toledo-Antonio, C. Angeles-Chávez, E. López-Salinas, Ignacio Cuauhtémoc-López, María C. Barrera, J. Escobar, J. Navarrete, I. Hernández, Appl. Catal. B: Environ. 106 (2011) 14–25.
- [26] Y. Li, W. Zhang, L. Zhang, Q. Yang, Z. Wei, Z. Feng, C. Li, J. Phys. Chem. B 108 (2004) 9739–9744.
- [27] A. Gedeon, A. Lassoued, J.L. Bonardet, J. Fraissard, Micropor. Mesopor. Mater. 44–45 (2001) 801–806.
- [28] G.V. Shanbhag, S.M. Kumbar, S.B. Halligudi, J. Mol. Catal. A: Chem. 284 (2008) 16–23
- [29] P. Albers, J. Pietsch, S.F. Parker, J. Mol. Catal. A: Chem. 173 (2001) 275–286.
- [30] Z. Li, G.B. Hoflund, J. Nat. Gas. Chem. 12 (2003) 153–160.
- [31] I.V. Delidovich, O.P. Taran, L.G. Matvienko, A.N. Simonov, I.L. Simakova, A.N.
- Bobrovskaya, V.N. Parmon, Catal. Lett. 140 (1–2) (2010) 14–21. [32] N. Takezawa, N. Iwasa, Catal. Today 36 (1997) 45–56.
- [33] S. Ajaikumar, M. Golets, W. Larsson, A. Shchukarev, K. Kordas, A.-R. Leino, J.-P. Mikkola, Micropor. Mesopor. Mater. 173 (2013) 99–111.
- [34] G. Zhao, J. Teng, Z. Xie, W. Jin, W. Yang, Q. Chen, Y. Tang, J. Catal. 248 (2007) 29–37.
- [35] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis, Wiley, New York, 1994.
- [36] H. Haario, Modest 6.0 A., User's Guide, ProfMath, Helsinki, 2001.
- [37] E. Jones, K. McClean, S. Housden, G. Gasparini, I. Archer, Chem. Eng. Res. Des. 90 (6) (2012) 726–731.
- [38] F.S. Mederos, J. Ancheyta, J. Chen, Appl. Catal. A: Gen. 355 (2009) 1-19.
- [39] Z. Kuzeljevic, PhD Thesis, School of Engineering and Applied Science, Department of Energy, Environmental and Chemical Engineering, Washington University, May 2010.