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p-Cymene production from orange peel oil using some metal catalyst in supercritical alcohols

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ABSTRACT

In this study, orange peel oil which had been produced by cold press technique was processed. The catalytic reaction of limonene composed of 90–95% of the orange peel oil carried out in different supercritical alcohols, and it was obtained the compound *p*-cymene mainly. The experiments processed in a packed bed reactor using Pt/Al_2O3, Ni/Al_2O_3 and Pd/Al_2O_3 catalysts in over supercritical conditions of ethanol and 2-propanol. Experiments of reaction time, temperature and pressure scanning were carried out in the ranges of 10–50 s, 245–340 °C and 6.5–12.5 MPa, respectively. It was observed that Ni/Al_2O_3 was ineffective to the conversion of limonene. However, when Pd/Al_2O_3 and Pt/Al_2O_3 catalysts were used, *p*-cymene was produced mainly. Especially, when Pd/Al_2O_3 catalyst was used, it was detected that limonene converted completely and obtained *p*-cymene in yield of 80%. Furthermore, *p*-cymene selectivity of Pd/Al_2O_3 was much better compared with Pt/Al_2O_3.

1. Introduction

The world orange production has passed over 64.9 million tons, however, 19 million tons of those could be processed in 2009/2010 season [1]. When orange fruits are processed in the juice production, 50–70% of their weight is thrown out as waste consisting of peel, membrane, vesicles, seeds, etc. The waste is generally used as dairy cattle feed or compost [1,2]. Nevertheless it causes a significant pollution with phenolic compounds and huge landscape occupation whilst holding. Actually, orange peel has a noticeable economic value. One of the most valuable orange peel products is its essential oil. Raw orange peel has 1.45 ± 0.16 mL essential oil per kg according to Association of Official Agricultural Chemists (AOAC). Essential oil which produced from orange peel is a low-cost and abundant material and includes many components are used in synthesis of some food, cleaning, cosmetic, drug, etc. chemicals [2,3]. Indeed, orange peel essential oil may include upwards of 200 components depending on sort and maturity of the orange, kind of extraction and separation processes [4]. Though approximately 90–95% of the essential oil are terpenes. However, compounds which create essential oil's special character are mainly oxygenated derivatives of terpenes. Besides these, there can be also nitrogenous or sulfuric compounds in the oil. On the other hand, terpenes generally decompose under the sway of heat, light and/or air [5].

More valuable products can be synthesized in consequence of terpene transformations through hydrogenation, oxidation, isomerization/rearrangement, hydration, hydroformylation, condensation, cyclization, ring contraction, etc. Especially, more favorable and high-price compounds like *p*-cymene can be manufactured with catalytic transformations of compounds like limonene which is in the orange peel essential oil in the ratio of about 90%. It was proposed that limonene tends to turn into monocyclic terpenes like terpinenes and terpinolenes. It is dissociated into menthenes and cymenes as final products. The dissociation needs space volume because of bimolecular reaction, so it is limited by process progressing on microporous heterogeneous catalysts [6].

p-Cymene can be added in inks, adhesives, varnishes, pigments, perfumes, pharmaceuticals, allaying foul industrial smells, producing cresol and some products that are normally obtained from petroleum-based compounds. *p*-Cymene is conventionally produced via Friedel-Crafts alkylation of toluene with propene or 2-propanol. In default of toluene, benzene can be used with methyl and isopropyl halides. This operation is processed in company with acid catalysts like HCl containing $AlCl_3$, HF, BF_3 or H_2SO_4. Because of chemicals are used, current production of *p*-cymene is highly polluting, unhealthy and destructive. Using of zeolite supported catalysts can overcome the acidic problem, however by-products like *n*-propyltoluen, m- or o-cymene are formed substantially in that time. Instead of this process, *p*-cymene production can be occurred by the way of transformations of compounds that

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Table 1
Chemical composition of the raw orange peel oil.

Compounds	Content, %
α-Pinene	0.66
β-Phellandrene	0.41
δ-3-Carene	0.22
β-Myrcene	1.79
dl-Limonene	96.56
Sabinene	0.36

generated via isomerization or hydrogenation as well as limonene dehydrogenation directly [7].

Nickel or palladium supported by carbon or alumina, platinum supported by carbon, chromium oxide with/without copper or zinc oxide, Fuller's earth, copper-nickel, activated alumina, heteropolyacid $H_5PMo_{10}V_2O_{40}$ are some catalysts that are used on dehydrogenation of terpenes [8]. Brönsted acid sites are not functional in the matter of *p*-cymene production because of its low selectivity. On the other hand, Pd or CaO have high conversion rate and selectivity in the acceptable reaction conditions. Onto CaO catalyst, it was claimed that only limonene dehydrogenation to *p*-cymene took place and its conversion rate was up to 98% and selectivity was about 100%. When it comes to base catalysts, Mg/Al hydrotalcides are neither active nor selective [7]. With effects of carbocation mechanism on the acid sites, *p*-cymene selectivity is quite low in the end of multiple reactions. Thus dominant trend is using catalysts which are not acidic [9,10].

p-Cymene production from limonene can be carried out via isomerization and hydrogen transfer on acid sites, hydrogenation/dehydrogenation on metallic sites or transformation on both acidic and metallic sites [6]. It was suggested that *p*-cymene selectivity of limonene transformations onto acidic catalysts can be increased via using an alkali element like Na^+ [11,12]. Besides, existences of α-olefins as H_2 acceptors in the reaction media improve the *p*-cymene selectivity of silica supported Pd catalysts [13].

It had been seen that hydrogenation/dehydrogenation catalysts were active and selective in the *p*-cymene production processes from limonene. *p*-Cymene selectivity has been enhanced up to 97% under favour of Cr_2O_3, CuO, ZnO, ZrO_2, MgO, La_2O_3, ThO_2, and C supported Pd doped with Se catalysts [14,15]. Titanium oxide catalyst overperformed than silica and alumina supported catalysts in the matter of product yield and *p*-cymene selectivity [7]. It was claimed that *p*-cymene also was synthesized in the ratio of 19.5% as a result of H_2 disproportionation mechanism while polymerization of limonene with catalytic effect of silicophosphoric acid [16].

Industrial dipentene vapor that includes 36.9% limonene was fed into a packed bed reactor with H_2 under atmospheric pressure at 200°C. On HZSM-5 catalyst with Brönsted acid sites, only limonene cracking reaction was occurred but on Al/SBA-15 catalyst with Lewis-Brönsted acid sites, it was produced that *p*-cymene as the dehydrogenation product and toluene as the cracking product. Zn/SBA-15 has Lewis acid sites and is more stable and more selective for *p*-cymene. It was found that dipentene conversion rate has been up to 98.2% and selectivity of *p*-cymene has been up to 88.3% [17]. In the study of [18], dipentene transformation was performed with Cu/Ni formate. While essential oil that had obtained from turpentine was boiling, addition of the catalyst was about 2% by weight of the oil. In the end of 8 h, product that was gained from condenser contained 2 units (p-, o- and m- isomers of) cymene and 1 unit menthane of every 3 units.

According to [9,10], *p*-cymene selectivity was smaller than selectivities of m- and o-cymene when hydroisomerization proceeded on through Pd-on-ZSM-5 but in case of same reaction was fulfilled on zeolite Y, the selectivities were similar. Despite this, supporting with Ce improved the *p*-cymene selectivity up to 60.1%. It was also established that Ce addition to zeolite supported Pd catalyst not only prevents to transalkylation reactions and catalyst poisoning but also improves the *p*-cymene selectivity during dehydrogenation. Pd parts of catalyst can give rise to isomerization reaction by the way of hydrogenation/dehydrogenation mechanism. Pt and Pd catalysts were investigated by Bogel-Łukasic et al. [19–21] for limonene hydrogenation. As reported by those studies, Pt has a higher activity than Pd but also it is more unstable because its metal part shows a tendency to poisoning and being washed away. It was studied that alkanes can be generated via hydrodeoxigenation of lipids or stearic acid with released H_2 following the limonene dehydrogenation into *p*-cymene in [22,23] on the purpose of bio-jet fuel production. Pd/HZSM-5 and Ni/HZSM-5 structures have higher conversion ratios for limonene and stearic acid. However it was suggested that the more H_2 addition to the atmosphere, the less *p*-cymene selectivity because of hydrogenation dominance.

Supercritical fluid technology is an eligible and effective technology for chemical transformation of essential oils' compounds, specially. Its some benefits are lasting a short time, finishing with high efficiency, expediting transport phenomena, reducing catalyst poisoning and not affecting quality of the essential oil adversely through the agency of its own characteristic properties [24–26].

In a heterogeneous catalysis, the interaction between reactant(s) and the active surface of catalyst is normally limited by concentration (s) of the reactant(s) around the catalyst. Furthermore, resistance against mass-transfer for transport is strong at interphase boundaries of materials in the adsorption-desorption processes. When a supercritical fluid is used as the reaction media, single-phase mixture around the catalyst removes these problems. Using of supercritical fluids accelerates the catalytic processes and intensifies the reactivities via enrichments of solubility and diffusivity [27]. Also, supercritical alcohols are in the most interesting supercritical fluids. The critical points of ethanol (240.7°C and 6.137 MPa) and 2-propanol (235.1°C and 4.762 MPa) are relatively mild conditions for organic reactions [24]. Besides, ethanol can be produced from orange peel with fermentation process [3].

In this work, chemical transformation of orange peel essential oil

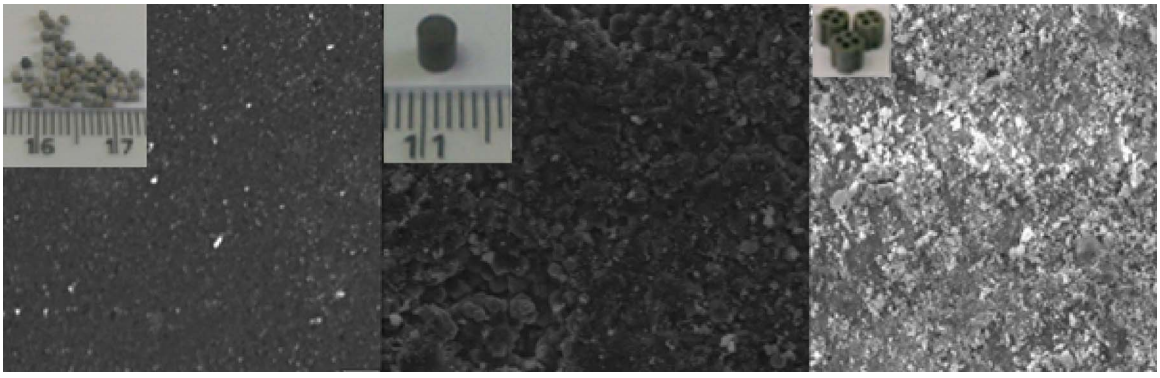

Fig. 1. SEM images of Pt/Al_2O_3, Pd/Al_2O_3 and Ni/Al_2O_3 catalysts, respectively.

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