Catalytic behavior and reaction routes of MEK oxidation over Pd/ZSM-5 and Pd–Ce/ZSM-5 catalysts

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HIGHLIGHTS

- ▶ The MEK oxidation processes were systematically studied by thermal desorption/GC–MS technique.
- ▶ PdCe(9.6 wt%)/ZSM-5 can offer more lattice oxygen and therefore possesses higher activity.
- ▶ Catalyst acidic changes the reaction routes and byproducts distribution.
- ▶ The oxidation products over Pd–Ce bimetallic catalysts are closely related to the surface CH_3^* species.

GRAPHICAL ABSTRACT

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ABSTRACT

Catalytic oxidation is a widely used pollution control technology for removing volatile organic compounds. Pd–Ce/ZSM-5 catalysts with different Ce contents were prepared by a co-impregnation method, and their catalytic performance was investigated for the oxidation of methyl ethyl ketone (MEK). The by-products of the reaction were monitored using gas chromatography and collected in thermal desorption tubes, which were further analyzed by gas chromatography/mass spectrometry. The PdCe_{9.6}/ZSM-5 catalyst displayed the highest catalytic efficiency, as a consequence of a higher amount of strong acid sites and a superior PdO–Pd redox cycle in the presence of a CeO₂ additive. The introduction of CeO₂ enriched the by-product species. The formation mechanisms and oxidation routes of typical by-products, such as methyl acetate, 1-penten-3-one and 3-buten-2-one, 3-methyl, during MEK oxidation over Pd–Ce/ZSM-5 catalysts was also analyzed. CH_3^* species that formed on the catalyst were identified as reaction intermediates. Trace amounts of acetic acid and methyl vinyl ketone were also detected and were further oxidized to methyl acetate, 1-penten-3-one and 3-buten-2-one, 3-methyl.

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1. Introduction

The presence of volatile organic compounds (VOCs) in the atmosphere results in various environmental problems including photochemical smog, ozone depletion, and ground-level ozone generation. VOCs emitted from industrial activities can be controlled by various techniques, such as thermal incineration,

catalytic oxidation, adsorption, and biofiltration [1–4]. Among these, catalytic oxidation is considered to be one of the most effective and energy-saving techniques due to its potential to completely convert pollutants into carbon dioxide (CO₂) and water at low reaction temperatures.

Methyl ethyl ketone (MEK) is a commonly used solvent in several chemical industries, but emissions of MEK to the atmosphere can lead to human health concerns and wider environmental problems. Therefore, as a hazardous material, emissions of MEK into the atmosphere must be controlled. In recent years, several studies have focused on the elimination of MEK [5–11]. Some studies have identified that the partial oxidation products of MEK, such as diacetyl (DAC) and acetic acid, are generally more toxic than

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MEK [7–10]. Therefore, the reaction processes and catalytic reaction mechanisms must be clearly understood to avoid and control the formation of by-products.

Noble metals (such as Pt, Pd) [12] and metal oxides [5,13] are both catalysts for VOC oxidation. Generally, the catalytic performance of noble metal-based catalysts is higher than metal oxides. Previous studies have reported that noble metal catalysts loaded on zeolite display excellent catalytic activities in the oxidation of aromatic and chlorinated VOCs. He et al. [14] showed that the acidity of zeolites has an important role in enhancing the catalysis of VOC oxidation. Compared with Beta, MOR, and FAU zeolites, ZSM-5 displays a greater catalytic activity and is more stable [15]. Noble metal catalysts are generally accepted to be more active than metal oxide catalysts but the latter are cheaper, more thermally stable, and have a greater resistance to poisoning. Recently interest has arisen in the use of cerium (Ce) and several studies using Ce oxide (CeO_2) as an additive on a palladium (Pd)-supported catalyst have been reported [12,15–19].

The use of bimetallic metal/ZSM-5 catalysts in the MEK oxidation process has seldom been reported. In particular, the effect of CeO_2 on the reaction selectivity and pathways should be further explored. The purpose of this study was to explore the oxidation route and mechanisms of MEK conversion over the Pd–Ce/ZSM-5 (PCZ) catalysts, including the formation of various by-products and their concentrations during MEK oxidation.

The following abbreviations are used throughout the text, and are summarized as follows: methyl ethyl ketone, MEK; diacetyl, DAC; methyl vinyl ketone, MVK; acetaldehyde, ACH; methyl acetate, MA; acetone, DK; acetic acid, AcOH; Pd/ZSM-5, PZ; Ce/ZSM-5, CZ; Pd–Ce/ZSM-5, PCZ.

2. Materials and methods

2.1. Material preparation

ZSM-5 zeolite (Si/Al = 25; Tianjin Chemical Plant, Tianjin, China) was impregnated into aqueous solutions of $\text{Ce}(\text{NO}_3)_2$ (9.6 wt%) and $\text{Pd}(\text{NO}_3)_2$ (0.5 wt%) to obtain the CZ and PZ catalysts, respectively. The Pd–Ce bimetallic catalysts were prepared by a similar co-impregnation method in solutions of $\text{Pd}(\text{NO}_3)_2$ (0.5 wt%) and $\text{Ce}(\text{NO}_3)_2$ (1.6 wt%, 3.2 wt%, 6.4 wt%, 9.6 wt%). All samples were dried at 80 °C for 24 h, and calcined at 500 °C for 4 h. The resulting catalysts were referred to as CZ, PZ, $\text{PC}_{1.6}\text{Z}$, $\text{PC}_{3.2}\text{Z}$, $\text{PC}_{6.4}\text{Z}$, and $\text{PC}_{9.6}\text{Z}$, respectively.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a powder diffraction system (X'Pert PRO; PANalytical, Almelo, The Netherlands) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) in the 2θ range of 10–80° (scanning rate of 4°/min). N_2 adsorption/desorption isotherms of the catalysts were collected at 77 K on a gas sorption analyzer NOVA 1200 (Quantachrome Corp., Boynton Beach, FL, USA). All samples were degassed under vacuum at 300 °C for 3 h before measurement. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of about 0.99. The specific surface area (S_{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method. The elemental composition of each sample was analyzed by X-ray fluorescence (XRF) (XRF-1800 spectrometer; Shimadzu, Kyoto, Japan) using an Rh tube as excitation source.

X-ray photoelectron spectroscopy (XPS) (AXIS-Ultra instrument; Kratos Analytical, Hadano, Japan) was undertaken using monochromatic Al $\text{K}\alpha$ radiation. To compensate for surface charge effects, binding energies were calibrated using the C1s hydrocarbon

peak at 284.80 eV. The curve fitting was performed with CasaXPS software.

The temperature programmed reduction of H_2 (H_2 -TPR) was performed on a chemisorb analyzer (Chemisorb 2720; Micromeritics, Norcross, GA, USA). TPR profiles were obtained by passing a 5% H_2/He flow (50 mL/min) through the catalysts (approximately 50 mg), which had been previously dried in a helium flow (50 mL/min) at 300 °C for 1 h.

The temperature programmed desorption of NH_3 (NH_3 -TPD) was also performed on the Chemisorb 2720 analyzer. Prior to each TPD test, the sample (50 mg) was pretreated in a helium flow (50 mL/min) at 300 °C for 1 h. Then the samples were adsorbed with NH_3/He (2%/98%, v/v) to saturate with NH_3 . The catalyst was flushed with He (50 mL/min) at room temperature to remove the physisorbed NH_3 . The desorption profile of NH_3 -TPD was then recorded from 25 °C to 800 °C at a heating rate of 10 °C/min.

2.3. Catalytic activity evaluation

All evaluation experiments were performed in a continuous flow fixed-bed reactor, consisting of a steel tube (6 mm, i.d.) at atmospheric pressure. In each test, 0.3 g of the catalyst (40–60 mesh) was placed into the tube reactor. A gas containing VOCs was generated by bubbling air through the VOC saturator, which was further diluted with another airstream before reaching the reaction bed. The total flow rate was kept at 300 mL/min, i.e., a gas hourly space velocity (GHSV) of 28,000 h^{-1} with an MEK concentration of 1000 ppm. The reaction temperature (R_T) was first raised to 130 °C as the feed stream passed over the reactor bed and was then stabilized for 30 min. The reaction bed temperature was increased to the following setting and maintained for 20 min for online detection before the next experimental procedure.

Online analysis was performed by gas chromatography (GC; model 6820; Agilent, Santa Clara, CA, USA) and GC–mass chromatography (MS; Agilent 6890) simultaneously. A gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was employed for the quantitative analysis, and GC–MS was used for the qualitative analysis. The by-products were collected on a Tenax TA tube for 10 min at each temperature point and then desorbed by a thermal desorber (Unity 2 series; Markes International Ltd., Llantrisant, UK) before passing into the GC–MS device.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD and BET analysis

The XRD patterns of PZ, CZ, $\text{PC}_{1.6}\text{Z}$, $\text{PC}_{3.2}\text{Z}$, $\text{PC}_{6.4}\text{Z}$, and $\text{PC}_{9.6}\text{Z}$ catalysts are presented in Fig. 1. All catalysts exhibited profiles ascribable to HZSM-5 [14]. Slight differences were observed for Ce-containing samples. The CeO_2 fluorite structure (JCPDS file No. 43-1002) was observed in the CZ, $\text{PC}_{3.2}\text{Z}$, $\text{PC}_{6.4}\text{Z}$, and $\text{PC}_{9.6}\text{Z}$ samples, and the corresponding diffraction peak became stronger and broader as the amount of CeO_2 increased. No diffraction peaks ascribable to Pd metal and oxides were observed. The Pd loading had a negligible effect on the original porous structure of the support [14].

The specific surface area (S_{BET}) and total pore volume (D_v) of the prepared samples are summarized in Table 1. PZ possesses a relatively high S_{BET} (330.1 m^2/g) and D_v (0.17 cm^3/g), which was smaller than $\text{PC}_{9.6}\text{Z}$ (391.7 m^2/g and 0.24 cm^3/g , respectively), but slightly larger than CZ (287.6 m^2/g and 0.16 cm^3/g , respectively). In the Ce-containing samples, both the S_{BET} and D_v increased as the amount of CeO_2 additive increased.

Fig. 1. XRD profiles of catalysts: PZ, CZ, PC_{1,6}Z, PC_{3,2}Z, PC_{6,4}Z, PC_{9,6}Z.

Table 1

Physicochemical properties of the synthesized catalysts.

Catalyst	S_{BET}^a (m ² /g)	D_v^b (cm ³ /g)
PZ	330.1	0.17
CZ	287.6	0.16
PC _{1,6} Z	293.1	0.13
PC _{3,2} Z	309.0	0.18
PC _{6,4} Z	326.4	0.19
PC _{9,6} Z	391.7	0.24

^a BET specific surface area.

^b Total pore volume estimated at $P/P_0 = 0.99$.

3.1.2. NH₃ temperature-programmed desorption

A NH₃ temperature-programmed desorption was used to evaluate the acid strength and acid site number. The results are displayed in Fig. 2. The temperature was above 100 °C, eliminating the physisorption of NH₃ [20]. For pure CeO₂, only one weak desorption peak was observed at about 150 °C [21], indicating that few weak acid sites were present. Three types of NH₃ desorption peaks were observed for all catalysts investigated, corresponding to three types of acid sites. The desorption temperature and

Fig. 2. NH₃-TPD profiles of (a) PZ, (b) CZ, (c) PC_{3,2}Z and (d) PC_{9,6}Z.

Table 2

Acidity of PZ, CZ, PC_{3,2}Z and PC_{9,6}Z catalysts.

Catalyst	Desorption temperature (°C)			Acidity ^a (mmol NH ₃ /g-cat)			
	I	II	III	I	II	III	I + II + III
PZ	113	193	428	0.26	0.21	1.06	1.53
CZ	125	196	415	0.21	0.29	0.65	1.15
PC _{3,2} Z	111	194	381	0.26	0.29	1.08	1.63
PC _{9,6} Z	105	175	362	0.26	0.30	1.15	1.71

^a Amounts of NH₃ desorbed at different temperatures.

quantitative molar number of acid sites are listed in Table 2. The peaks in the range of 100–200 °C correspond to the weak acid sites [21]. The high desorption temperature peak (HT peak) in the range of 300–500 °C was attributable to ammonia desorption from the strong acid sites, which plays an important role in the catalytic reaction. From Table 2, the acidity of samples reduced as follows: PC_{9,6}Z (1.15 mmol NH₃/g-cat) > PC_{3,2}Z (1.08 mmol NH₃/g-cat) > PZ (1.05 mmol NH₃/g-cat) > CZ (0.65 mmol NH₃/g-cat). In addition, a sharp peak at 411 °C was observed over the PC_{3,2}Z catalyst. This peak was present at 400 °C for PC_{9,6}Z, which was attributable to a new interface structure between Pd species and CeO₂ [22]. No peak was observed for the PZ and CZ catalysts.

3.2. Hydrogen temperature-programmed reduction

H₂-TPR profiles for the PZ, CZ, PC_{1,6}Z, PC_{3,2}Z, PC_{6,4}Z, and PC_{9,6}Z catalysts are displayed in Fig. 3. A negative peak at 60 °C was observed for the PZ and PC_{1,6}Z catalysts owing to the desorption of weakly adsorbed hydrogen and the decomposition of PdH_x [23]. Padmasri et al. [24] found that PdCl₂ or PdO could be easily reduced to metallic Pd in a hydrogen atmosphere at ambient temperature, allowing the formation of PdH_x. A peak located at about 80 °C for the PC_{6,4}Z and PC_{9,6}Z catalysts was ascribed to the formation of PdO or PdO_x. The amount of PdO formed increased with an increase in CeO₂ content. This implies that more PdO was deposited on the CeO₂ than on the ZSM-5. The TPR signal of PC_{9,6}Z located at 80 °C was weaker than that of PC_{6,4}Z, indicating that the amount of CeO₂ loaded was beneficial for reduction. The peaks in the range of 350–450 °C were ascribed to the reduction of surface oxygen species, while the peaks above 600 °C were considered to represent the reduction of bulk Ce [20]. The two peaks shifted to a lower temperature and become

Fig. 3. H₂-TPR profiles of (a) CZ, (b) PZ, (c) PC_{1,6}Z, (d) PC_{3,2}Z and (e) PC_{9,6}Z.

narrower with increasing CeO₂ content, which was ascribed to an interaction between PdO and CeO₂. Luo et al. [25,26] reported that surface hydrogen atoms on Pt, Pd, Cu, and Ni can enhance the rate of reduction of CuO, NiO, and Co₃O₄, while CeO₂ can promote the rapid reoxidation of the reduced Pd on a PCZ catalyst. CeO₂ is assumed to effectively reduce the reversion between PdO decomposition and Pd oxidation, resulting in better mobility and availability of lattice oxygen, which is enhanced by the incorporation of Ce and the strong synergistic interaction between Pd and CeO₂.

3.3. XPS measurement

An XPS technique was used to determine the surface element composition and chemical states of various catalysts such as PZ, CZ, and PC_{9,6}Z. The high-resolution XPS spectra of Ce3d, Pd3d, and O1s core levels are shown in Fig. 4, and the surface compositions are detailed in Table 3. For the PCZ catalysts, the percentage of atomic Pd increases from 0.13% to 0.31%, while the percentage of atomic oxygen decreases, indicating the formation of more oxygen vacancies on the surface of PCZ catalysts [27].

The Pd3d XPS spectra of the PZ and PC_{9,6}Z catalysts are presented in Fig. 4b. The XPS curves could be fitted with two doublets, which were assigned to Pd3d_{5/2} and Pd3d_{3/2}. The XPS results imply that PdO is the main species formed in the Pd-containing catalysts. In addition, highly ionic Pd²⁺ (Pd3d_{5/2,3/2} = 337.8, 343.1 eV) existed in the catalysts due to residual Pd(NO₃)₂ from the synthesis process [28]. A similar result was reported previously [29], indicating that well-dispersed and ion deficient coordinated PdO was in intimate contact with the CeO₂ support, and subsequently promoted oxygen transfer from CeO₂ to Pd active sites.

The XPS spectra of O1s core electron levels for the PZ, CZ, and PC_{9,6}Z catalysts are shown in Fig. 4c. The corresponding binding energies (BEs) of O1s core levels and the quantitative values are summarized in Table 3. The O1s spectra can be arranged into two main regions: the lattice oxygen at the low BE component O_I(O²⁻), and the high BE component O_{II} assigned to other surface oxygen species (chemisorbed oxygen O₂⁻ and O⁻) [30]. The PZ catalyst contained only the O_{II}-type oxygen. A higher percentage of O_{II} was present in PC_{9,6}Z than CZ. O_{II} species have a strong oxidizing capability and high mobility, which can enhance oxygen transfer and the redox cycle by transforming the lattice oxygen with abundant oxygen vacancies. In addition, oxygen vacancies can reportedly act as active sites for oxygen adsorption or activation [29]. This suggests that the PC_{9,6}Z catalyst possesses more oxygen vacancies, which promotes catalytic activity.

The Ce3d core-level spectra shown in Fig. 4a indicate the presence of both Ce³⁺ and Ce⁴⁺. The curves are fitted into eight peaks corresponding to the two spin-orbit components (U and V) to distinguish Ce³⁺ and Ce⁴⁺ [29]. The six features (u, u'', u''', v, v', and v''') refer to the spectrum of Ce⁴⁺, while the other two features (u' and v') refer to the spectra of Ce³⁺. A estimation of the relative amounts of Ce⁴⁺ and Ce³⁺ was made based on the fitted peak areas of the respective XPS Ce3d peaks, and the results are presented in Table 3. A higher amount of Ce⁴⁺ was present in PC_{9,6}Z than that in CZ. These results suggest that more O_{II} is present on the surface of the PC_{9,6}Z catalyst, indicating a stronger oxidizing ability [29]. Therefore, the O_{II} species on the surface was speculated to accelerate the transformation of some Ce³⁺ to Ce⁴⁺.

3.4. MEK oxidation

3.4.1. Catalytic behavior

The catalytic behavior of the PZ, CZ, PC_{1,6}Z, PC_{3,2}Z, PC_{6,4}Z, and PC_{9,6}Z catalysts during MEK oxidation is presented in Fig. 5. Based on the T₉₀ values, the order of activity of the catalysts is as follows: PC_{9,6}Z > PC_{6,4}Z > PC_{3,2}Z > PZ > PC_{1,6}Z > CZ. The PC_{9,6}Z catalyst

Fig. 4. XPS results of PZ, CZ, PC_{9,6}Z catalysts: (a) Ce3d, (b) Pd3d and (c) O1s.

exhibits the best catalytic performance among these samples, but PC_{1,6}Z exhibits a lower catalytic activity compared with other PCZ catalysts due to the weaker interactions revealed by the H₂-TPR results. Catalytic activity is strongly dependent on the nature of the support material. The PCZ catalysts were more active than the PZ catalyst. Several reasons for this are elaborated below. One of the main factors is likely to be the acidity. Pd loaded on an acidic support is reportedly more effective in catalyzing an oxidation reaction than when it is loaded on neutral or basic supports because the electrophilic character of acidic supports results in an electron deficiency in Pd atoms [31,32]. In addition, it was also determined that the PCZ catalyst with more acid sites (especially the strong acid

Table 3
Chemical and surface compositions of various catalysts.

Catalyst	Pd ^a (wt%)	Surface atoms percentage ^b (%)			Relative abundance of Ce ³⁺ and Ce ⁴⁺ ^b (%)		Relative abundance of O _I and O _{II} ^b (%)	
		Pd	Ce	O	Ce ³⁺	Ce ⁴⁺	O _I	O _{II}
PZ	0.31	0.13	–	59.36	–	–	–	100
CZ	–	–	6.63	53.97	18.53	81.47	16.37	83.63
PC _{9,6} Z	0.47	0.31	6.65	54.91	14.91	85.09	15.16	84.84

^a Pd content by XRF analysis.

^b Surface compositions by XPS analysis.

sites) has a higher catalytic activity. The redox property of Ce can be considered as another important factor. CeO₂ has a cubic fluorite structure and a relatively high density of oxygen vacancies exists in the CeO₂ lattice. This is in a good agreement with the H₂-TPR and XPS results. During the active phase of VOC oxidation over a Pd-supported catalyst, Pd²⁺ has been proposed to catalyze the hydrocarbon oxidation, and Pd⁰ to promote the catalytic activity by maintaining a Pd²⁺–Pd⁰ cycle during dissociation of VOCs, thus accelerating the reaction rate [33–35]. In addition, the catalytic oxidation of VOCs usually involves the participation of surface lattice oxygen species via the Mars-van Krevelen model [36]. This effect operates when the catalyst is reduced by VOCs and is then recovered by oxidation. The available oxygen originates from either chemisorbed oxygen or lattice oxygen. Hence, the Ce³⁺/Ce⁴⁺ redox cycle can supply adequate lattice oxygen for the reaction. The detection of ACH as a by-product would confirm the operation of this mechanism, since ACH, which can be observed over a long period during the catalytic oxidation, is the first oxidation intermediary of alcohols. Compared with the PZ catalyst, more ACH was formed at low temperatures on the Pd–Ce bimetallic catalysts and rapidly transformed to CO₂ (the conversion temperature of ACH to CO₂ is lower) at high temperatures. Therefore, CeO₂ could provide a convenient pathway for the oxygen atoms to approach or dissociate from the Pd active species, which leads to an increase in catalytic activity.

3.4.2. The distribution of the by-products of MEK oxidation

For efficient VOC catalytic oxidation, not only is an understanding of the catalytic activity important, but the reaction process is also crucial and needs to be investigated [7–11]. In the present work, when PZ was used as a catalyst for MEK oxidation, the by-products were mainly ACH, DK, and DAC, as well as trace

amounts of AcOH and propionic acid. However, the incorporation of CeO₂ affects the acidic sites and the resulting by-products [37]. When CeO₂ were incorporated into the catalyst system, MVK and MA were the main by-products, and trace amounts of 1-penten-3-one and 3-buten-2-one, 3-methyl were observed. These results are completely different from previous reports [5–10], in which MA, 1-penten-3-one and 3-buten-2-one, 3-methyl have never been observed arising from the MEK oxidation process. Fig. 6 exhibits the yields (moles of MEK converted into by-product/moles of initial MEK) of the main reaction products obtained on the PZ, CZ, PC_{1,6}Z, PC_{3,2}Z, PC_{6,4}Z, and PC_{9,6}Z catalysts. By increasing the amount of CeO₂ on the PCZ catalysts, the amount of by-products generated increased, which suggests that the presence of the Ce species is the main factor leading to the partial oxidation of MEK. Fig. 6 shows that the amount of ACH generated from all these catalysts was similar (below 7.0E–3) in the working range of 120–300 °C. DK and DAC are formed at 130 °C and are transformed into CO₂ at temperatures lower than 280 °C. In the working range of 230–260 °C, MEK is transformed to MA and MVK over catalysts containing Ce. The MS signal resulting from thermal desorption/GC–MS and the relative molar ratio attained by GC are clearly presented in Table 4. A trace amount of AcOH was detected by GC/MS. The AcOH signature disappears at 230 °C over PC_{9,6}Z, which is higher than that over PZ and CZ. Propionic acid appeared at a higher temperature (260 °C) over a PZ catalyst, whereas it formed at 167 °C over the CZ and PC_{9,6}Z catalysts. 1-Penten-3-one and 3-buten-2-one, 3-methyl collected by thermal desorption tubes produced a more intensive MS signal over CZ than that over PC_{9,6}Z. As a result of by-product formation, the CO₂ yield was low over all catalysts at temperatures below 200 °C. At higher reaction temperatures, all of the by-products were transformed into CO₂ and H₂O.

3.4.3. MEK oxidation routes

McCullagh et al. [8] reported that enol was involved as an intermediate during MEK oxidation over some catalysts under specific reaction conditions and particularly under a high oxygen partial pressure. The study proposed four reaction pathways of MEK oxidation. In the present work, the main reaction by-products obtained over the PZ, CZ, and PC_{9,6}Z catalysts were recorded from online GC. Trace amounts of by-products can also be measured by gathering the reaction gases into a thermal desorption tube followed by GC/MS analysis. MEK oxidation over PCZ may proceed through different reaction mechanisms, based on the experimental results.

In particular, ACH is the primary C₂ scission product of MEK. The diol (butane-2,3-diol) as an intermediate is oxidatively cleaved to form two ACHs. In addition, AcOH is also formed, originating from the direct scission of the enol [8]. The former is the major step among the two pathways mentioned above.

The formation of MA is related to the Ce species incorporated in the catalyst (Fig. 6). MA is hypothesized to be formed via AcOH

Fig. 5. Catalytic behaviors of PZ, CZ, PC_{1,6}Z, PC_{3,2}Z, PC_{6,4}Z, PC_{9,6}Z catalysts for MEK decomposition.

Fig. 6. Yields of MEK oxidation products as a function of reaction temperature over PZ, PC_{1.6}Z, PC_{3.2}Z, PC_{6.4}Z, PC_{9.6}Z, CZ catalysts: CO₂, AOH: CH₃CHO, DK: CH₃COCH₃, DAC: CH₃COCOCH₃, MVK: CH₂=CHCOCH₃, MA: CH₃COOCH₃.

reacting with a methyl group or formaldehyde in the temperature range of 230–250 °C. However, no direct evidence of formaldehyde formation during the reaction process exists. Compared to PZ and CZ, the PCZ catalysts possess more strong acid sites. Therefore, one may logically conclude that abundant CH₃* species are more likely to be formed over the PCZ catalyst.

DAC and MVK appear to be formed via the same intermediate (3-hydroxybutan-2-one) by the dehydrogenation and dehydration process, respectively [7]. The selectivity for DAC formation in MEK oxidation has been observed over vanadium phosphorous catalysts, which is considered to be a consequence of attacking *n*-butane

Table 4
Oxidation products of MEK oxidation over PZ, CZ and PC₃₆Z catalysts.

Catalyst	Temp. (°C)	Oxidation products (moles of the product/moles of the MEK fed)										CO ₂ yield (%)
		CH ₃ CHO	CH ₃ COCH ₃	CH ₃ COCOCH ₃	CH ₃ COOH	C ₂ H ₅ COOH	CH ₃ COOCH ₃	CH ₃ COCH=CH ₂	CH ₃ COC(CH ₃)=CH ₂	C ₂ H ₅ COCH=CH ₂		
PZ	127	1.27E-03	1.63E-04	8.16E-05	✓	-	-	-	-	-	7.83	
	167	1.25E-03	5.14E-04	1.96E-04	✓	-	-	-	-	-	14.05	
	198	2.57E-03	1.62E-03	4.98E-04	✓	-	-	-	-	-	79.6	
	224	4.26E-03	2.21E-03	6.12E-04	✓	-	-	-	-	-	90.86	
	264	4.56E-03	3.09E-03	0	✓	✓	-	-	-	-	96.44	
	278	4.39E-03	2.07E-03	0	✓	✓	-	-	-	-	96.74	
301	6.48E-03	0	0	-	-	-	-	-	-	97.03		
CZ	127	5.56E-04	9.60E-04	4.24E-04	✓	-	0	0	-	-	3.98	
	167	6.37E-04	3.92E-03	5.15E-04	✓	✓	0	0	✓	✓	17.68	
	198	7.38E-04	1.38E-02	9.70E-04	✓	-	0	0	✓	✓	49.28	
	208	8.49E-04	1.98E-02	1.58E-03	✓	-	0	0	✓	✓	62.33	
	228	2.30E-03	3.91E-02	2.52E-03	✓	-	8.60E-04	1.60E-02	✓	✓	82.01	
	254	5.87E-03	8.81E-02	8.91E-03	✓	-	9.50E-03	2.12E-01	✓	✓	92.61	
280	4.44E-03	0	0	-	-	0	0	-	-	96.06		
PC ₉ 6Z	127	9.80E-04	2.17E-03	3.11E-04	✓	-	0	0	-	-	6.85	
	167	1.64E-04	9.19E-03	7.65E-04	✓	✓	0	0	-	-	36.71	
	220	5.43E-03	2.98E-02	8.98E-03	✓	✓	9.45E-03	0	✓	✓	91.54	
	230	1.26E-02	0	7.55E-03	✓	✓	8.69E-02	4.26E-01	✓	✓	95.78	
	254	1.57E-02	0	0	-	-	0	0	-	-	96.38	
	270	8.46E-03	0	0	-	-	0	0	-	-	98.2	

Note. -; no MS signal.

selectively at the methylene carbons [38]. In our present work, the dehydrogenation of the intermediate that occurred over the PZ catalyst is the only pathway in the parallel reactions. This result is consistent with Ai's [7] conclusion that MVK may be not an intermediate for the formation of DAC from MEK. A similar process has been previously reported for the catalytic combustion of 2-propanol over Au-Al₂O₃ [39]. The study suggested that gold favored dehydrogenation as a result of dehydroxilation of surface. However, less DAC than MVK was formed over Ce-containing catalysts. The introduction of CeO₂ to the PZ catalysts likely changed the acidic properties, which promoted the transformation of 3-hydroxybutan-2-one (intermediate) into MVK by dehydration.

Moreover, MVK is considered to be an intermediate in the formation of 1-penten-3-one and 3-buten-2-one, 3-methyl. As mentioned previously, the surface CH₃* species substituted two different α-C positions of MVK, forming 1-penten-3-one and 3-buten-2-one, 3-methyl. From the MS signal (not shown here), the abundance of the latter was twice higher than the former, which suggests a stable molecular structure.

The presence of propionic acid and DK confirms that the C=C bond scission possibly occurs not only in the C₂ position, but also in C₁ or C₃. The scission products of CH₂=C(OH)CH₂CH₃ (intermediate) are propionic acid and DK [40]. More DK appeared over the PCZ and CZ catalysts than over PZ, as shown in Table 4. One may reasonably conclude that the mobility of oxygen species from Ce-containing catalysts suggests the diol oxidation route is favored.

Ketones possess a weak base on the carbonyl group. The reaction has been confirmed and is closely connected to the strength of the acid on the support material [9]. Basic oxides and acidic oxides with various acid base properties have been shown to generate different reaction processes [8]. In this study, CeO₂ as a neutral oxide altered the strong acidity of ZSM-5. One may hypothesize that more cracking and scission reactions take place on the stronger acid sites over the PCZ catalysts, and deeper oxidation occurs over the monometallic PZ or CZ catalysts. The secondary by-products that are formed (MA, 1-penten-3-one, and 3-buten-2-one, 3-methyl) are related to the stronger acid sites. Low activity leads to an abundance of by-products through a long reaction period. Thus, the CZ catalyst with the lowest catalytic performance produced the maximum levels of by-products. In addition, a higher oxidation capability over the PCZ catalyst, with a higher CeO₂ content, was linked to a stronger potential for scission. As a result, the C=C bond can be easily broken, generating more complex side products.

4. Conclusions

In summary, a series of ZSM-5-based Pd catalysts, with or without Ce additives, were prepared by an impregnation method. The catalytic processes of MEK oxidation over the PZ, CZ, PC_{1.6}Z, PC_{3.2}Z, PC_{6.4}Z, and PC_{9.6}Z catalysts were studied by GC and thermal desorption/GC–MS techniques. The PC_{9.6}Z catalyst was determined to possess the best catalytic activity. The addition of CeO₂ significantly enhanced the strong acid sites of Pd-containing catalysts and increased the reoxidation of active phase Pd, thus reducing the reversion process of the PdO–Pd cycle. The catalytic MEK oxidation process could be explained by the Mars–van Krevelen mechanism.

Monometallic PZ catalysts were the most selective catalysts for the complete oxidation of MEK. The oxidation products of MEK on the Pd–Ce (different Ce contents)/ZSM-5 catalysts in excess oxygen included ACH, AcOH, DK, DAC, propionic acid, MVK, MA, 1-penten-3-one, 3-buten-2-one, 3-methyl, CO₂, and H₂O. The different oxidation pathways can be attributed to the following: first, Ce-containing catalysts promoted the dehydration of intermediate (3-hydroxybutan-2-one) to form MVK and second, second-order products such as MA, 1-penten-3-one, and 3-buten-2-one, 3-methyl were formed over PCZ catalysts. CeO₂ is not only the promoter of the catalytic reaction, but also contributes to the formation of more strong acid sites that produce more by-products.

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