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# CRACKING OF 2-DODECANONE OVER CERIUM (IV) OXIDE CATALYST

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# CRACKING OF 2-DODECANONE OVER CERIUM (IV) OXIDE CATALYST

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## Abstract

The cracking of 2-dodecanone has been studied over high surface area (HSA) cerium (IV) oxide (ceria), as compared to other catalysts including the commercial ceria, HZSM-5, alumina, and silica. The coprecipitation method assisted by CTAB surfactant was chosen for preparation of the nanocrystalline HSA ceria. According to powder X-ray diffraction, the fluorite structure of HSA ceria was successfully obtained with a small crystallite size of 8 nm. In agreement with this result, $N_2$ adsorption/desorption shows a relatively high surface area of 158 $m^2/g$. Raman spectroscopy confirms the cubic fluorite structure of HSA ceria (a peak at 460 $cm^{-1}$) and suggests the presence of oxygen vacancy sites (a broad peak at 600 $cm^{-1}$).

The cracking of different catalysts were tested with 2-dodecanone and dodecane. It was found that the catalytic activity for the conversion of 2-dodecanone is decreased in the order of: HZSM-5 (Si/Al=180) > $CeO_2$ (HSA) > Alumina, Silica and $CeO_2$ (com). HZSM-5 converted 2-dodecanone to propylene, and C4 and C5 hydrocarbons, via a series of reactions including aldol condensation, dehydration and cracking on the acid sites. On the other hand, the major products observed over HSA $CeO_2$ are C21 ketone, C24 ketone and C24 dihydrofuran. Dodecane was chosen as a model hydrocarbon compound to study the catalytic cracking activity. It was found that HZSM-5 is the only active catalyst for the cracking of hydrocarbon. The conversion of 2-dodecanone over $CeO_2$ (HSA) is increased to 78% when the contact time was increased to 800 g·h/mol. The major products over $CeO_2$ (HSA) were made via coupling, followed by decomposition, cyclization, disproportionation and cracking over redox active sites.

**Keywords:** 2-dodecanone, ceria, dodecane, redox sites

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# CONTENTS

# CONTENTS (CONTINUED)

# LIST OF TABLES

# LIST OF SCHEMES

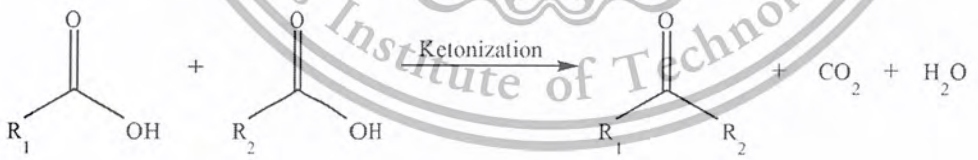
# LIST OF FIGURES

# CHAPTER 1

# INTRODUCTION

## 1.1 Motivation

In recent years, the deoxygenation of fatty acids into diesel fuel has received great attention. For example, Chalinee and coworkers [1] have reported the deoxygenation of palmitic acid ($C_{16}$ acid) over catalysts based on cerium oxide (also called ceria). The main products of such reaction include $C_{31}$ ketone, $C_{17}$ ketone, and the $C_{10}$-$C_{14}$ hydrocarbons from the cracking of the ketone. Interestingly, the yields of the ketone and hydrocarbons are somewhat equivalent. So, it was suggested that the reaction consists of two steps. Firstly, the ketone is produced from the ketonization of fatty acid **(Eq.1.1)** as is widely accepted over ceria-based catalysts. Nano-scaled ceria with abundant oxygen vacancies are capable of enhancing the catalytic activity in ketonization[2]. Ketonization plays a crucial role in many biomass conversion processes, as it can remove the highly reactive carboxylic functional groups while increasing the size of the carbon chain [3]. After that, the cracking of ketone into smaller hydrocarbons has been proposed. The details of this step, however, is not widely understood. For example, questions remain regarding the nature of the active sites responsible for the cracking, whether they are acid sites redox-active sites.



**(Eq.1.1)**

In this research, the cracking of ketone over cerium (IV) oxide ($CeO_2$) catalyst into smaller hydrocarbons will be studied. In order to identify the nature of the active sites, several catalysts will be investigated, including alumina, silica, HZSM-5 zeolite, and $CeO_2$. Alumina ($Al_2O_3$) and HZSM-5 zeolite are well known as acid catalyst capable of cracking hydrocarbons into smaller ones, including subsequent aromatization. On the other hand, the use of catalytically inert silica ($SiO_2$) will allow the estimation on the effect of the thermal cracking.

The performances of these catalysts will be compared to that of the redox-active $CeO_2$ catalysts (commercial product with low surface, and also a high surface area one synthesized by a surfactant-assisted method). Two model compounds will be studied including 2-dodecanone $CH_3(C=O)(CH_2)_9CH_3$ and dodecane $C_{12}H_{38}$. The former is analogous to the $C_{17}$ ketone produced in the earlier work [1], while the latter represents the hydrocarbon products from the cracking of ketone.

## 1.2 Objectives

1.2.1 To obtain small hydrocarbons from the decomposition of 2-dodecanone over $CeO_2$ based catalysts.

1.2.2 To understand the cracking behavior of 2-dodecanone and dodecane over ceria and HZSM-5 catalysts.

## 1.3 Scope of the study

The scopes of this thesis are as follows:

1.3.1 Preparation of $CeO_2$ catalysts by the surfactant assisted method.

1.3.2 Characterization of $CeO_2$ catalysts and the commercial one by X-ray diffraction (XRD), Raman spectroscopy, surface area and porosity analysis by $N_2$ adsorption/desorption and thermogravimetric analysis.

1.3.3 Investigation of the cracking of 2-dodecanone and dodecane by $CeO_2$, $Al_2O_3$, HZSM-5, and $SiO_2$ in a fixed-bed continuous flow reactor.

1.3.4 Qualitative and quantitative analysis of liquid products by gas chromatography.

## 1.4 Expected results

It is expected that this research will identify the nature of active sites in $CeO_2$ which are responsible for the cracking of ketone into smaller hydrocarbons.

# CHAPTER 2

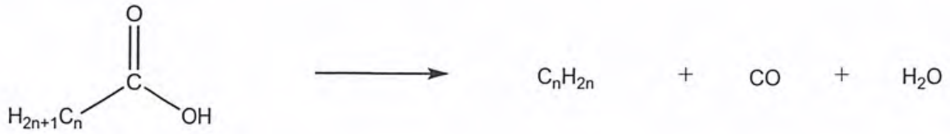
# THEORY AND LITERATURE REVIEWS

## 2.1 Production of diesel fuel via different approaches

Diesel fuel has become essential in everyday life and for economics, largely due to their use as liquid transportation fuels. Traditionally, diesel fuel is produced from petroleum. This resource, however, is being used up. Recently, the utilization of biomass as feedstock for the production of diesel fuel is becoming attractive. One might consider that plants remove carbon dioxide from the atmosphere as it grows through photosynthesis. So, biofuels are carbon neutral when certain conditions are met. First generation biofuels are made from vegetable oil or animal fats via transesterification of triglycerides with methanol, giving fatty acid methyl esters (FAMEs). While FAMEs have several advantages [4,5], these biodiesels are still derived from edible feedstock, are not fully compatible with standard diesel engines, and are relatively unstable due to the high oxygen content.

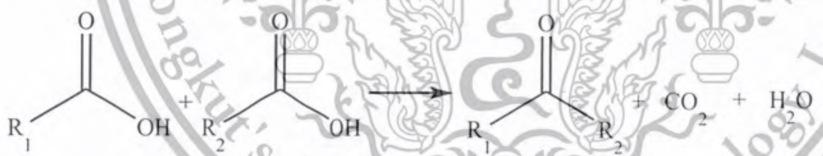
An alternative method to remove oxygen atoms from biomass-derived oils is known collectively as deoxygenation. Among them, the decarboxylation (decarbonylation) can convert carboxylic acids, particularly fatty acids, into the respective hydrocarbons with the production of $CO_2$ (CO). Ideally, there could be no loss of carbon atoms from the starting acids (except as $CO_2$/CO). So, these reactions are efficient in producing diesel fuel. The chemistry developed to transform carboxylic acids is also a ways towards upgrading bio-oil [6]. Decarboxylation reaction is shown in **Eq. 2.1** and decarbonylation is shown in **Eq. 2.2**. These two reactions are typically performed with noble metal such as Pt, Pd on supports such as carbon, silica, etc [7,8,9]. The use of relatively expensive metal catalysts is uneconomical. Therefore, alternative processes where inexpensive catalysts can be used are being sought.

Eq. 2.1



Eq. 2.2

Another method to remove oxygen atoms from carboxylic acids is via ketonization. Ketonization (or ketonic decarboxylation) is a reaction in which two molecules of a carboxylic acid convert into a symmetric ketone, carbon dioxide, and water as shown in Eq 2.3. This reaction is promoted either by heterogeneous base catalysts, or by catalysts with oxygen vacancy sites. The route through ß-keto acid has been proposed for carboxylic acids with ∞-hydrogen. Such ∞-hydrogen abstraction of adsorbed carboxylate results in the carboxylate anion, which then reacts with neighboring carboxylate or acyl to produce ß-keto acid. The ketone is formed by decarboxylation of this ß-keto acid intermediate [10,11]. The ketone can be further hydrogenated to alcohols that can be refined into renewable diesel [6,12].



Eq. 2.3

Ketonization is typically catalyzed by inorganic oxides such as $CeO_2$, $TiO_2$, $Al_2O_3$, and $ZrO_2$ at moderate temperatures (573–773 K) and atmospheric pressure. Ketonization could find application for catalytic upgrading of bio-oils for several reasons. First, carboxylic acids can be removed and transformed into larger ketone with increasing number of carbon atoms. Second, this transformation takes place without using hydrogen. Third, ketonization can be also applied to other compounds such as esters which typically present in bio-oils. Finally, this reaction tolerates a moderate amounts of water which is typically present in bio-oils [13].

Alternatively, it is suggested that [1] the ketone might be further cracked giving hydrocarbons as the product. One of such example is the methyl ketone with

17 carbon atoms obtained from the ketonization of palmitic acid followed by subsequent cracking. It is important to stress that the carbon atoms of cracked hydrocarbons must lie in appropriate range for use as diesel fuel. For example, methane ($C_1$) and ethane ($C_2$) are gaseous at ambient temperature and cannot be readily liquefied by pressure alone. Propane ($C_3$) and butane ($C_4$) can be liquefied under pressure. On the contrary, hydrocarbons larger than pentane ($C_5$) is a clear liquid at room temperature. The $C_6 - C_{10}$ alkanes, alkenes and isomeric cycloalkanes are the top components of gasoline, naptha, jet fuel and specialized industrial solvent mixtures [14]. In addition to cracking, ketones can also undergo coupling via aldol condensation, forming higher branched ketones [15]. The chemistry of cracking and coupling will be briefly described below.

## 2.2 Cracking [16]

Cracking can occur either thermally or catalytically. Both types involve the breaking of C-C bonds in relatively large molecule, thereby forming smaller molecules as the reaction products. Cracking is an important reaction converting low-demand fractions into higher demand fractions. For example, useful hydrocarbons not naturally present in crude oil are produced including alkenes (widely used as petrochemicals), cycloalkanes and branched alkanes (widely used in motor fuels) and aromatic hydrocarbons (used as petrochemicals and as motor fuels). Three main reaction steps include initiation, propagation, and termination:

Initiation: A single molecule breaks apart at the C-C bond into two free radicals.

$$CH_3CH_3 \longrightarrow 2\ CH_3^{\bullet} \qquad \text{Eq. 2.4}$$

Propagation: A free radical abstracts a hydrogen atom from another molecule. So, the second molecule is turned into a free radical. Then, a (new) free radical breaks apart into an alkene and another free radical.

$$CH_3^{\bullet} + CH_3CH_3 \longrightarrow CH_4 + CH_3CH_2^{\bullet} \qquad \text{Eq. 2.5}$$

$$CH_3CH_2^{\bullet} \longrightarrow CH_2{=}CH_2 + H^{\bullet} \qquad \text{Eq. 2.6}$$

A radical can also reacts with an alkene to form a larger free radical, which ultimately forms the aromatic products:

$$CH_3CH_2^{\bullet} + CH_2{=}CH_2 \longrightarrow CH_3CH_2CH_2CH_2^{\bullet} \qquad \text{Eq. 2.7}$$

Termination: In this reaction two free radicals react with each other and produce products that are not free radicals. Termination can be either recombination (two radicals combine to form one larger molecule) or disproportionation (one radical transfers a hydrogen atom to the other, giving an alkene and an alkane).

$$CH_3^{\bullet} + CH_3CH_2^{\bullet} \longrightarrow CH_3CH_2CH_3 \qquad \text{Eq. 2.8}$$

$$CH_3CH_2^{\bullet} + CH_3CH_2^{\bullet} \longrightarrow CH_2{=}CH_2 + CH_3CH_3 \qquad \text{Eq. 2.9}$$

Thermal cracking is a process in which hydrocarbons such as crude oil are heated at high temperature. The molecular bonds are broken and the molecular weight of the substance being cracked is reduced. Fractions which have a low boiling point, such as gasoline, will be released first. Thermal cracking is also known as pyrolysis, as it involves the controlled decomposition of a chemical compound under heat and pressure.

Catalytic cracking is superior to thermal cracking for two major reasons. The first is that catalytic cracking gives more control over the products. The catalytic cracking of large hydrocarbons at the middle of the molecules can be controlled, thereby minimizing the yield of light hydrocarbons and maximizing the yield of gasoline. Also, the gasoline produced in catalytic cracking is has high quality (i.e., high octane number). This is because catalytic cracking allows the skeletal isomerization, dealkylation, and dehydrogenation reactions to take place. In catalytic cracking, a catalyst is an essential component in facilitating the conversion of the heavier molecules into lighter products. The catalysts used in refinery cracking units are typically solid materials, some of which will be described in the next section.

## 2.3 Coupling

Coupling is a chemical reaction where the C-C bond is formed between two starting molecules, resulting in a relatively larger molecule. Coupling reactions have been useful especially in pharmaceutical industry and in the synthesis of conjugated organic materials. "Aldol condensation" is one of the most important coupling reaction in which ketones (or carbonyl containing species) can be transformed into larger molecules. Especially, the aldol condensation of ketones is widely used in organic synthesis for preparing chemicals containing a double bond conjugated with a carbonyl group.

By properly choosing the operating conditions, the C-C bond formation proceeds by a condensation between a molecule possessing a carbonyl group and another molecule containing an activated methylenic group. After subsequent dehydration, the product is an ∞, ß-unsaturated carbonyl compound. The aldol condensation of ketone initially results in a ß-hydroxy ketone. The formation of various products is possible, for example, via the self- and cross-condensations between the ß-hydroxy ketone itself or with another ketone. The aldol condensation of ketone is typically base-catalyzed, giving rise to the ∞, ß-unsaturated carbonyl compounds. However, this reaction can also occur through acid catalysis, where hydrocarbons are mainly obtained.

This project will compare the pathway in cracking of 2-dodecanone with dodecane. 2-Dodecanone is a long chain aliphatic methyl ketone with the chemical formula $C_{12}H_{24}O$ (**Figure 2.1**). It is a model compound for the methyl ketone with 17 carbon atoms obtained from the ketonization of palmitic acid in the previous work [14]. On the other hand, dodecane is a liquid alkane hydrocarbon with the chemical formula $C_{12}H_{26}$ (**Figure 2.2**).

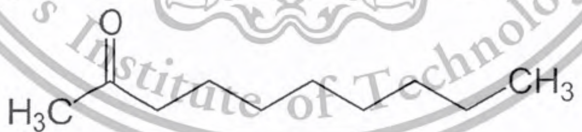


**Figure 2.1** The structure of 2-dodecanone

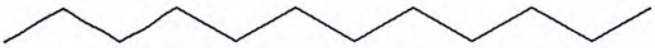


**Figure 2.2** The structure of dodecane

## 2.4 Acid Catalysts

Many industrial processes are catalyzed by "solid acids" such as zeolites, alumina, and various other metal oxides [17]. The mechanism of acid-catalyzed reactions is explained using the Brønsted–Lowry concept. There is an initial transfer of protons from an acidic catalyst to the reactant. Alternatively in terms of the Lewis theory, the reaction requires the sharing of an electron pair accepted by an acid catalyst [18]. Some of acid catalysts are as follows.

### 2.4.1 ZSM-5 Zeolite

ZSM-5 is an aluminosilicate zeolite belonging to the pentasil family of zeolites. Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ ($0<n<27$). This zeolite has a medium pore (~6 Å) with three-dimensional channels defined by 10-membered rings. The ZSM-5 structure is shown in **Figure 2.3**. It is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions [19,20]. There are a number of compensating cations depending on the Si/Al ratio, which ranges from 12 to infinity. When an $Al^{3+}$ cation replaces a $Si^{4+}$ cation, an additional positive charge is required to preserve charge-neutrality. With proton ($H^+$) as the cation, the material is therefore acidic. Thus, the acidity is proportional to the Al content. The very regular 3-D structure and the high acidity allows the utilization of ZSM-5 as a catalyst in various acid-catalyzed reactions such as hydrocarbon isomerization and the alkylation of hydrocarbons.

**Figure 2.3** The ZSM-5 structure [21]

### 2.4.2 δ-Alumina [22,23]

Aluminum oxides or alumina ($Al_2O_3$) are low cost materials extensively used in numerous industrial applications including catalyst supports, electronic-device fabrication, etc. Its catalytic activity is associated with the acidic properties of the surface. Typical reactions known to be catalyzed by alumina include hydrocarbon cracking and alcohol dehydration. It is generally believed that the active sites on alumina consists of electron pair donors (Lewis bases) and electron pair acceptors (Lewis acids). Lewis acid sites are formed during the dehydration process by the combination of two surface hydroxyl groups [24,25]. Alumina is mainly prepared by calcination of aluminum hydroxides precursor. When these precursors are heated, they undergo compositional and structural changes until all of the material is converted into ∞-alumina. Several "transitions" of alumina from one phase to another are known as shown in **Figure 2.4**. δ-Alumina used in this work can be obtained when boehmite is heated 800-900 °C.

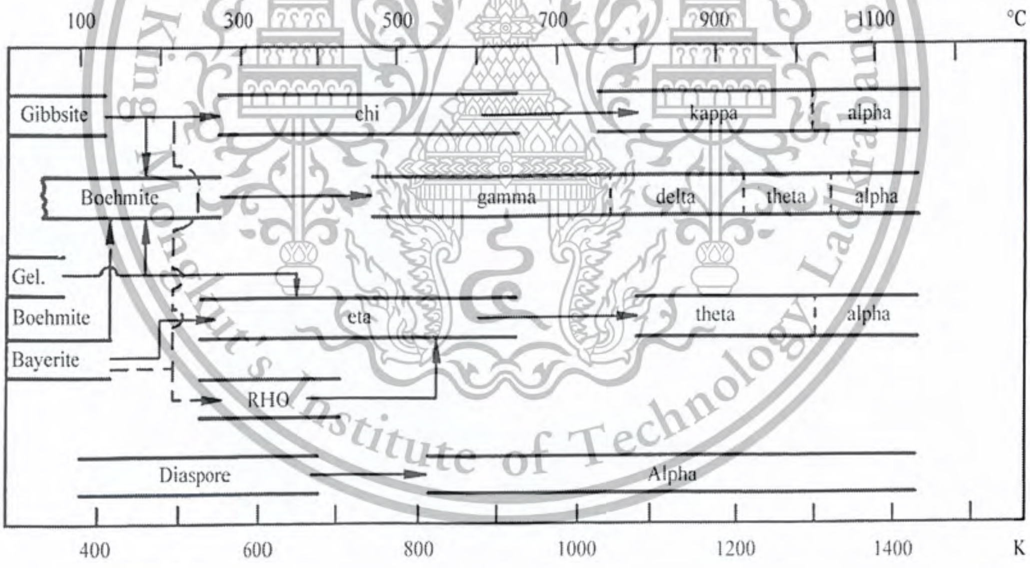


**Figure 2.4** Thermal transformation sequence of the aluminum hydroxides [26]

### 2.4.3 Silica [27]

Silica ($SiO_2$) is an amorphous solid. In comparison with surface of most metal oxides, silica surface is nearly inert. The most reactive groups are the silanol groups (-OH) that terminate the primary particles; these are just weakly acidic. The bulk may also be terminated entirely by silanol groups, which can be removed by dehydroxylation. So, using $SiO_2$ as a catalyst will allow the differentiation between thermal cracking and catalytic cracking.

## 2.5 Ceria

Cerium (IV) oxide (ceria) is a pale yellow-white powder with the chemical formula $CeO_2$ [28]. Cerium (IV) oxide has fluorite structure, with a face-centered cubic unit cell. In each unit cell, each cerium ion is surrounded by eight equivalent oxygen anions, and each anion is tetrahedrally coordinated by four cerium cations ($Ce^{4+}$) (**Figure 2.5**). As all oxygen atoms are in a plane with one another, a rapid diffusion of oxygen (assuming the presence of oxygen vacancies) around the crystals is permitted. The excellent redox properties of ceria is well known, owing to the very fast reduction of $Ce^{4+}$ to $Ce^{3+}$ associated with the formation of oxygen vacancies at the surface and in the solids. Because of its excellent redox property, it might be possible that ceria cracks hydrocarbons via the redox mechanism. So, the product distribution of the hydrocarbons obtained with different cracking catalysts with known chemical behavior must be compared.

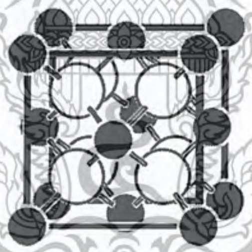


**Figure 2.5** The fluorite structure of ceria: black is $Ce^{4+}$, white is $O^{2-}$ [29]

Ceria is widely used as a catalyst in several applications such as the treatment of automobile exhaust, petroleum cracking and organic chemicals synthesis. The catalytic activity of cerium oxide is dependent upon its structural properties, especially the oxygen vacancy defects [30]. $CeO_2$ is usually prepared from hydroxide precursors, precipitated by the addition of a precipitant to an aqueous solution of cerium cations. Surfactant assisted precipitation route enables the synthesis of high surface area ceria [31].

## 2.6 Literature reviews

Recent work in our group [14] has shown that palmitic acid can be transformed into linear alpha olefins over ceria-based catalysts. In that work, two molecules of palmitic acid were coupled to $C_{31}$ ketone via ketonization, leaving carbon dioxide and water as byproducts. This ketone subsequently undergoes cracking to $C_{17}$ ketone (which is a methyl ketone) and hydrocarbons. However, the details of the cracking is not well understood. Therefore, this project will comparatively study the cracking of ketone and hydrocarbons into smaller hydrocarbons over ceria, including other catalysts of different chemical nature.

F. Billaud et al [32] studied the catalytic cracking of octanoic acid over activated alumina in a fixed bed reactor. It has been reported that at 450°C, two molecules of octanoic acid were ketonized into 8-pentadecanone (symmetrical ketone). The latter was then converted into 2-nonanone (methyl ketone) and $C_6$, $C_9$, $C_{15}$ olefins. Moreover, $C_{15}$ compounds can undergo additional cracking into smaller hydrocarbons at 500°C.

Zuogang Guo et al [33] studied the catalytic cracking of ketone components in biomass pyrolysis oil. The catalytic testing was carried out on a fix-bed reactor, using HZSM-5 as a catalyst. The volume hour space velocity (VHSV) was 3 $h^{-1}$ and the reaction temperature was 400°C. Model compounds tested as ketone components in bio-oil are acetophenone, acetone, butanone and 1-hydroxy-2-propanone. These authors reported the high conversion of ketone components, together with the high selectivity of aromatic hydrocarbons and unsaturated alicyclic hydrocarbons. Similarly, Wang et al [34] has reported the co-cracking behavior of hydroxypropanone (as the model compound of bio-oil ketones) with ethanol for bio-gasoline production, over HZSM-5 catalyst The conversion of hydroxypropanone with added ethanol reached 100%. The selectivity of the oil phase reached 31.9% under 400°C and 2 MPa. Moreover, the oil phase had a hydrocarbon content of 100% and mainly contained $C_7$ to $C_{10}$ hydrocarbons. The addition of ethanol as a co-reactant might assist the cracking of hydroxypropanone by providing important intermediates such as light olefins and methylated benzenes.

Thien An Le et al [35] studied the hydrodeoxygenation of 2-furyl methyl ketone (FMK) or 1-(2-furanyl)-ethanone over CoP/$\gamma$-$Al_2O_3$ catalyst into methylcyclopentane in the liquid phase and methane in the gas phase. The highest conversion of FMK and relatively high methylcyclopentane selectivity were achieved over the catalyst with 10 wt.% Co loading prepared at the calcination temperature of

500 °C. This catalyst has the highest acidity value, adequate surface area and pore size. This process was performed in a fixed-bed reactor at 400 °C.

Ya Wang et al [36] studied the cracking of several kinds of hydrocarbons, including highly branched iso-dodecane (mainly 2,2,4,6,6-pentamethylheptane, PMH) and n-dodecane. The cracking of reactants having different iso/n-dodecane ratios was conducted over HZSM-5 zeolite under supercritical conditions (673 K, 4.0 MPa). It was found that the conversion of n-dodecane in the mixture has decreased with the increase of PMH content. PMH can either play an active role by decreasing the partial pressure, or the negative role by resisting the diffusion. Recently, the selective catalytic cracking of n-hexane to propylene over MCM-22 catalysts dealuminated by nitric acid has been reported by Yong Wang et al [37]. With dealuminated MCM-22 (Si/Al = 34), a high n-hexane conversion (90%) and relatively high propylene selectivity (41%), comparable to H-ZSM-5 and H-Beta catalysts, can be obtained.

D. Randery et al [38] studied the condensation of two carboxylic acids to produce non-symmetric ketones over cerium oxide-based catalysts. It has been reported that the optimum temperature for methylcyclopropylketone (MCPK) production from acetic and cyclopropanecarboxylic acids (CCA) is 690–730 K, while for methylnonylketone (MNK) production from acetic and decanoic acids is 670–680 K. The deactivation was after 12 h at WHSV~4. The optimal $CeO_2$ loading on supports is equivalent to a monolayer one. However, the maximum yield appeared almost independent of the support. The addition of acidic or basic oxides to $CeO_2$ increased the formation of isomerization and aldol condensation products. Higher reaction temperatures also increased the formation of aldol condensation products.

Edward L. et al [39] studied the self-coupling of 2-hexanone over $Pd/CeZrO_x$ and $CeZrO_x$ catalysts at temperatures of 573-673 K, and pressures of 5–26 bar. It has been reported that the primary product of aldol condensation/hydrogenation from 2-hexanone is C12 ketone (7-methyl-5-undecanone). The ketone then underwent further reactions forming C9 and C18 ketones as secondary products, including light alkanes (C1–C7). The 0.25 wt% Pd loading is optimal for both the activity and selectivity for the production of C12 species. The selectivity of C9 species increased in the absence of Pd due to the decomposition of C18 condensation products. Lower metal loadings resulted in the enhanced selectivity to C12 products. While the catalytic performance was not substantially influenced, there was quite a measureable effect on the formation of secondary products.

# CHAPTER 3

# EXPERIMENTAL DETAILS

## 3.1 Chemicals

| Chemical | Grade/purity | Manufacturer |
|---|---|---|
| 1. Cerium(III) chloride heptahydrate | 99% | Acros |
| 2. Cerium(IV) oxide | 99% | *Riedel-de Haën* |
| 3.Hexadecyltrimethylammonium bromide | 99% | Sigma |
| 4. Dodecane | 99% | Acros |
| 5. 2-Dodecanone | 95% | Acros |
| 6. HZSM-5 (Si/Al = 180) | N/A | Zeochem |
| 7. Silicon dioxide | 99% | Carlo Erba |
| 8. Aluminium hydroxide | N/A | Panreac |
| 9. Ammonia | 30% solution in water | Carlo Erba |
| 10. Acetone | 99.97% | Zen point |
| 11. Air zero | 99.99% | Praxair |
| 12. Hydrogen gas | 99.99% | Praxair |
| 13. Nitrogen gas | 99.99% | Praxair |

## 3.2 Apparatuses

1. Catalytic testing rig
2. Mass flow controller (Brooks instrument Inc)
3. Tube furnace (VCTF4, Vecstar)
4. Syringe pump (KDS-100, KD scientific)
5. Glass syringe (25mL)
6. Quartz bead (600-850 micron)
7. Quartz wool
8. Vials
9. Heating tape
10. Oven (Memmert)
11. Furnace (VECSTAR)
12. Magnetic stirrer (IKA, RCT basic)
13. Magnetic bar

14. Laboratory glassware
15. Laboratory plasticware
16. Protector laboratory hood (Science technology)
17. Sieve (U.S.A standard sieve, AASHO N-92)
18. Gas chromatography (Hewlett Packard, HP 6890 series GC system, Scientific Instrumental Service Centre, KMITL)
19. X-ray powder diffractometer (Rigaku, DMAX 2200/Ultima+, Faculty of Science, Chulalongkorn University)
20. Thermogravimetric analyzer (Perkin-Elmer, Scientific Instrument Service Centre, KMITL)
21. Raman spectrometer (Thermoscientific, DXR Smart Raman, College of Nanotechnology, KMITL)
22. SEM (ZEISS, EVO/MA10, College of data storage innovation, KMITL)
23. Gas adsorption analysis unit (Autosorb-1C, Quantachorme, Faculty of Science, KMITL)

## 3.3 Preparation of catalysts

### 3.3.1 High surface area ceria

The high surface area $CeO_2$ catalyst was prepared by the surfactant assisted method [40]. Briefly, 370 mL of an aqueous solution of 0.1 M cetyltrimethylammonium bromide (CTAB) was added into a beaker containing 295 mL of 0.1 M cerium chloride ($CeCl_3{\cdot}7H_2O$). The mole ratio of cerium (III) cations to that of CTAB ([Ce]/[CTAB]) was kept constant at 0.8. The mixture was stirred and then aqueous ammonia was slowly added dropwise into the mixture until the pH was 11.5. The mixture was continually stirred for 3 h at room temperature, then sealed and placed in the thermostatic bath maintained at 90°C for 3 days. After that, the mixture was cooled down to room temperature naturally. The resulting yellow precipitate was filtered and washed repeatedly with hot DI water (twice) and acetone (twice) to remove the free surfactant. It was dried overnight in an oven at 110°C, and then calcined in air at 450°C for 2.5 h.

### 3.3.2 Commercial ceria

The commercial ceria catalyst was form *Riedel-de Haën*, 99%. It was calcined in air at 450°C at the heating rate of 2°C/min for 2.5 h prior to use.

### 3.3.3 HZSM-5 Catalyst

The HZSM-5 (Si/Al ratio 180) catalyst was form Zeochem. It was calcined in air at 550°C at the heating rate of 2°C/min for 6 h prior to use.

### 3.3.4 Silica Catalyst

The silica catalyst was prepared by calcination of precursor silicon dioxide form Carlo Erba at 550°C at the heating rate of 2°C/min for 6 h prior to use.

### 3.3.5 Alumina Catalyst

The Delta alumina catalyst was prepared by calcination of precursor aluminium hydroxide (Carlo Erba, 99%) at 250°C for 5 h (heating rate of 5°C/min), followed by another heating at 550°C for 5 h (heating rate 5°C/min).

## 3.4 Characterization of catalysts

### 3.4.1 X-Ray powder diffraction

The structure of catalyst was determined by X-ray diffractometer (XRD). The sample was prepared by packing the catalyst into the sample holder. Cu-$K_\alpha$ radiation was used for analysis at 40 kV and 30 mA. The sample was scanned over the 2$\theta$ ranged from 5 to 80 degrees.

### 3.4.2 Gas adsorption analysis

Surface area of the catalyst can be determined by a gas adsorption analyzer (Autosorb-1C, Quantachorme). Approximately 0.02-0.04 g of the sample was loaded into the cell, which is attached to the outgassing station equipped with a heating mantle. The temperature was raised to 350ºC under vacuum so as to drive off the adsorbed gas from the surface. After that, nitrogen gas was introduced to the sample cell. The $N_2$ adsorption at 77 K on the surface of the materials can be measured at the partial pressure ($P/P_0$) from 0.05 to 0.30. The adsorption isotherm and the corresponding surface area was analyzed using the Brunauer-Emmett-Teller (BET) method.

### 3.4.3 Raman spectroscopy

The sample to be investigated was manually pressed into a pellet. Raman spectra were collected using a DXR Smart Raman (Thermoscientific) at College of Nanotechnology, KMITL, from 50-4000 $cm^{-1}$. The laser employed has the wavelength of 532 nm, and the laser power was 5 mW. A total of 15 spectra were collected per one sample, with the exposure time of 2 s each.

### 3.4.4 Thermogravimetric analysis

The amount of coke deposited on a catalyst can be determined employing thermogravimetric analysis (TGA). Approximately 10 mg of the sample was weighed into the platinum pan. The temperature scanned is from 30 to 900°C at the heating rate at 10°C/min, under the purge of 20 mL/min of nitrogen atmosphere.

### 3.4.5 Scanning electron microscopy (SEM)

The catalyst surface morphology was determined by SEM technique. The sample was manually dispersed on an SEM stub and then coated with a gold thin film. After that, the sample was placed in a chamber which was evacuated from ambient pressure to below $10^{-4}$ Torr. Then, the sample holder was adjusted, tilted and moved in the X, Y and Z directions. As a consequence, sample surface was viewed from almost any perspective.

## 3.5 Catalytic activity testing

The catalytic activity of materials was investigated at atmospheric pressure in a continuous fixed-bed reactor made of a quartz tube (outside diameter 8 mm) as shown schematically in **Figure 3.1**. The catalyst bed was packed into the middle of the reactor. The reactor was positioned at the center of a vertical tube furnace. The gas flow rate was controlled by a mass flow controller and checked by a bubble flow meter. Before the catalytic testing, catalysts (silica, alumina and HZSM-5 zeolite) were activated at 550°C (heating rate of 2°C /min) under air zero (30 mL/min) for 2 hours. The activation of cerium (IV) oxide catalysts (high surface area and commercial one) was done similarly, but also includes the reduction under the stream of hydrogen gas (30 mL/min) for 2 hours. In some runs, reduction of $CeO_2$ catalysts prior to the reaction was omitted, so as to test the effect of the presence of oxygen vacancy on catalytic activity. Then, for all catalysts either with or without reduction, $N_2$ gas was flowed (60 mL/min) to the catalyst bed to eliminate the remaining air zero in the line, and to cool the reactor to the reaction temperature (400°C). After that, 2-dodecanone (or dodecane) was fed into the reactor at a flow rate of 0.6 mL/h by a syringe pump at contact time 50 g.h/mol. The reaction was operated for a total time on stream (TOS) of 360 min. The products were analyzed by online gas chromatography.

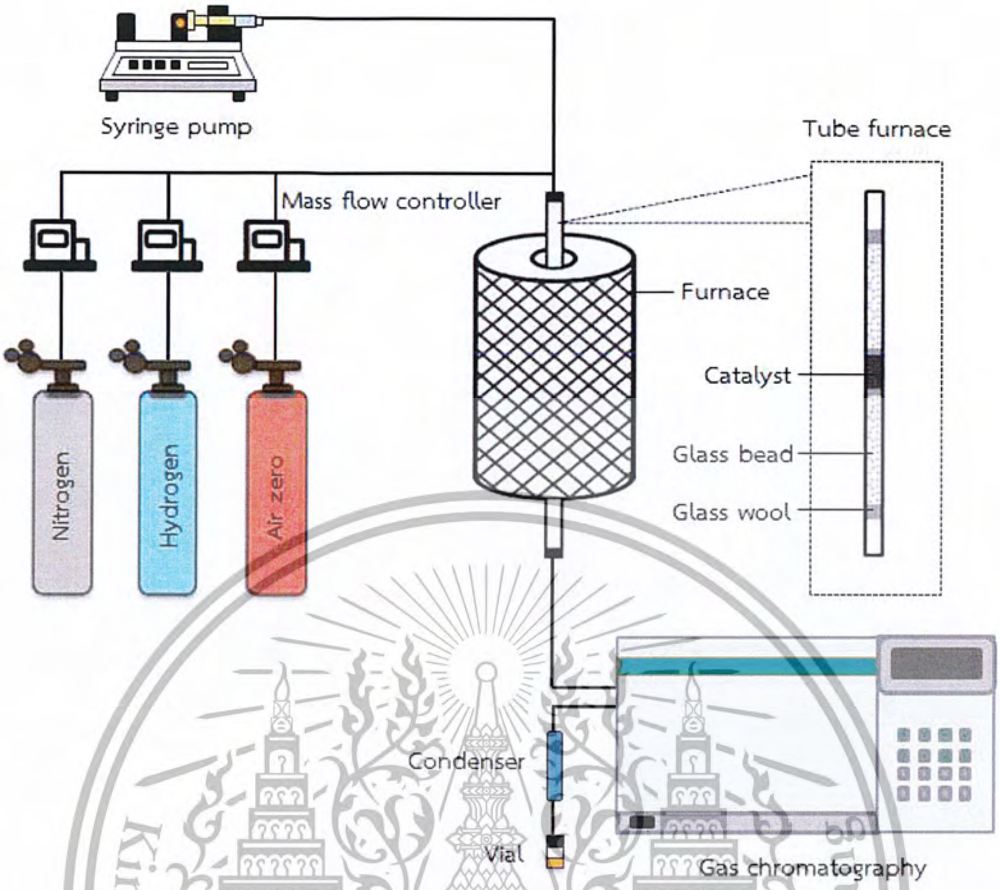


**Figure 3.1** Schematic diagram of catalytic testing rig

### 3.6 Analysis of products

The liquid products were analyzed by an onlined gas chromatograph (GC) (HP 6890 series) equipped with a DB-1 capillary column (length, 30m; internal diameter, 0.32 mm; film thickness, 5.00 μm) and a flame ionization detector (FID) with split ratio 80/1. The column temperature was set initially at 40°C (5 min), followed by a ramp at 15°C/min to 280°C before another hold at this temperature for 24 minutes. The temperatures of the injection port and FID were kept constant at 275°C during analysis. Identification of substances was performed by comparing the retention time with known standards, and also with help of a mass spectrometer coupled with a gas chromatograph (GC/MS).

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Characterization of catalysts

### 4.1.1 Powder X-ray diffraction

The high surface area (HSA) $CeO_2$ catalyst prepared by the surfactant-assisted method was obtained as the yellow powder after calcination at 450°C for 2.5 h. The PXRD pattern of this sample shown in **Figure 4.1b** exhibits several peaks corresponding to the (111), (200), (220), (311), (222), (400), (331) and (420) reflections of a cubic fluorite structure $CeO_2$ [41]. The peak positions agree well with those of the commercial (low surface area) sample shown for comparison in **Figure 4.1a**. The broadness of the peaks in the synthesized sample suggests its relatively small crystallite size compared to the commercial one.

The crystallite size of ceria-based catalysts were estimated by applying Scherrer equation on the first peak found in the PXRD pattern. The FWHM of high surface area (HSA) $CeO_2$ and commercial one are 1.130 and 0.205 degrees, corresponding respectively to the crystallite size of 8 nm and 44 nm.

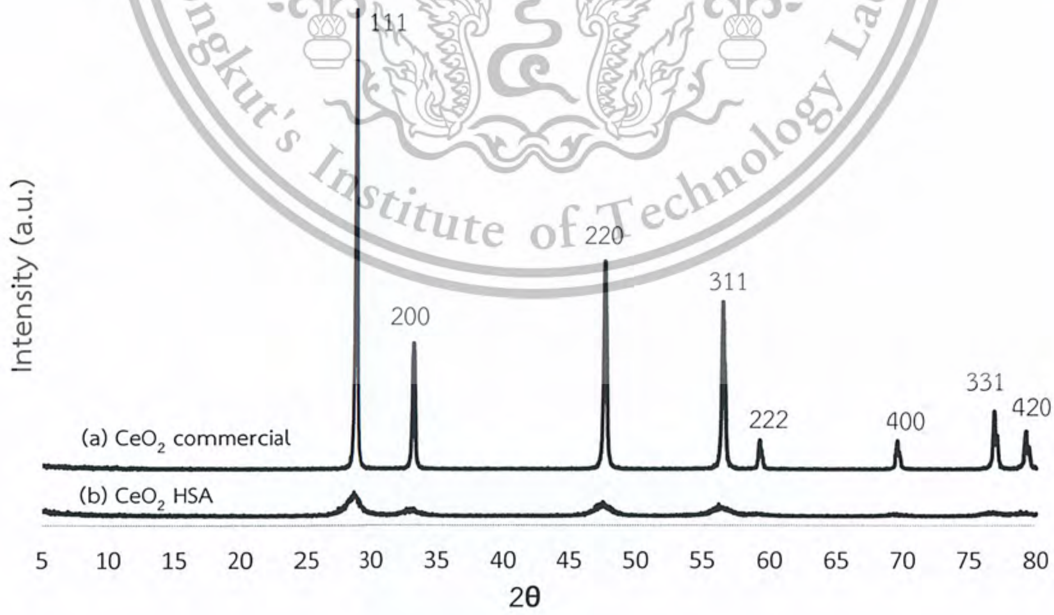


**Figure 4.1** PXRD patterns of $CeO_2$ after calcined at 450°C for 2.5 h: (a) commercial, (b) high surface area

### 4.1.2 Raman spectroscopy

Raman spectra of the catalysts are shown in **Figure 4.2**. The spectrum of HSA ceria after calcination was dominated by a strong band at 460 $cm^{-1}$ assigned to the $F_{2g}$ Raman vibration mode of the fluorite $CeO_2$ [42]. In addition, another broad band at 600 $cm^{-1}$ due to $O^{2-}$ vacancy sites [43] can be detected. This band due to the vacancy sites is absent in the commercial sample. So, one can deduce that a larger concentration of oxygen vacancy sites exist in HSA $CeO_2$ sample.

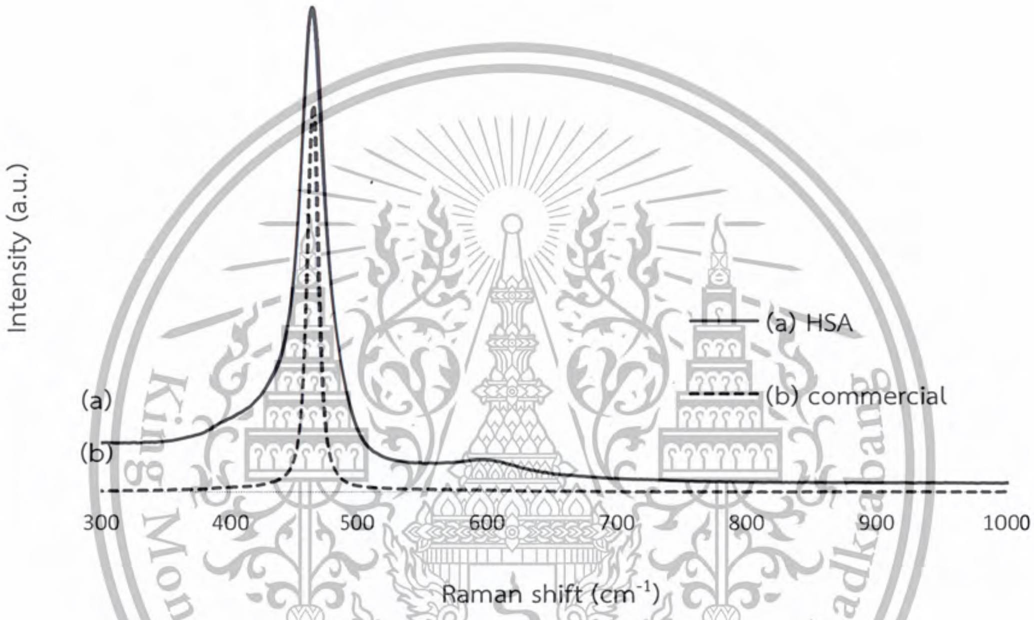


Figure 4.2 Raman spectra of $CeO_2$ after calcined at 450 °C for 2.5 h:
(a) commercial, (b) high surface area

### 4.1.3 Scanning electron microscopy (SEM)

**Figure 4.3** shows the particle morphology of the ceria catalysts prepared via a surfactant-assisted method and the commercial one. The SEM image of commercial ceria in **Figure 4.3a** and **4.3c** indicates the presence of large particles with the size in the range of ~1-2 μm. On the other hand, the high surface area $CeO_2$ sample exists as agglomerated powder having much smaller particle size as shown in **Figure 4.3b** and **4.3d**.

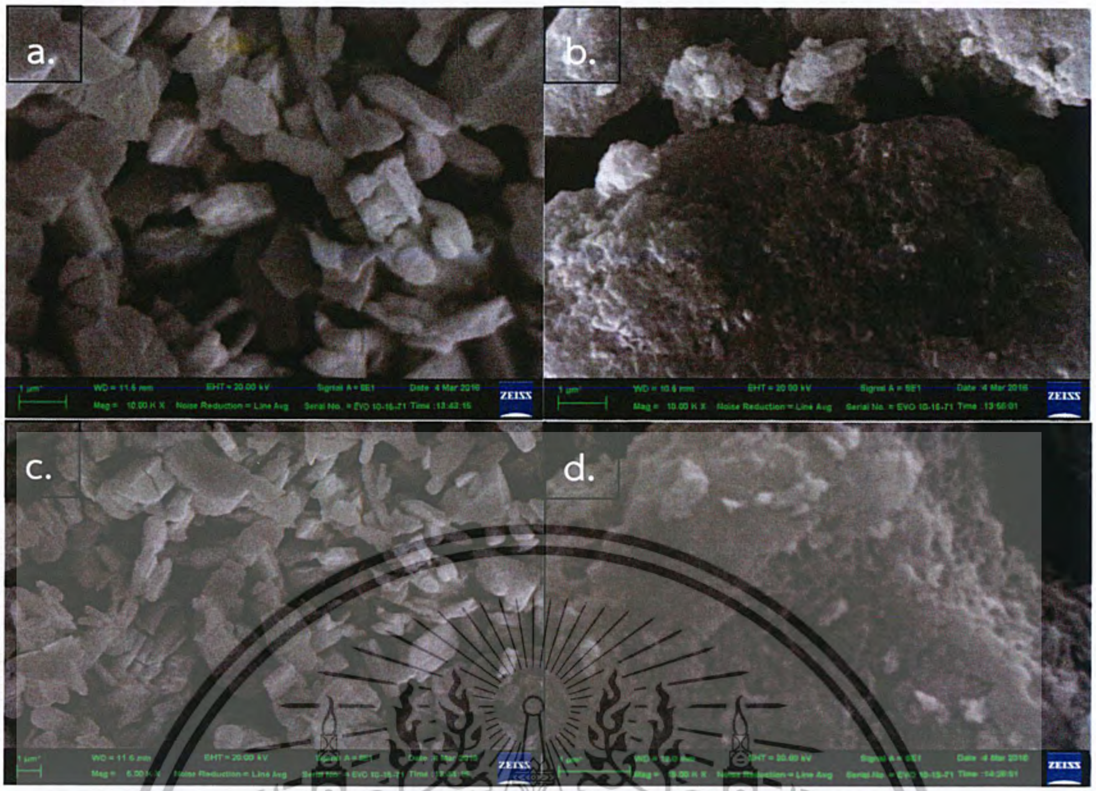


**Figure 4.3** SEM images of (a) $CeO_2$ commercial: 1 μm x 10.00 K
(b) $CeO_2$ high surface area: 1 μm x 10.00 K
(c) $CeO_2$ commercial: 1 μm x 5.00 K
(b) $CeO_2$ high surface area: 1 μm x 15.00 K

### 4.1.4 The specific surface areas

The specific surface areas for each catalyst are presented in **Table 4.1**

**Table 4.1** Surface areas of the catalysts

| Catalyst | $S_{BET}$ ($m^2/g$) | Pore volume ($cm^3/g$) | Pore diameter (°A) |
|---|---|---|---|
| $CeO_2$ (commercial) | 8 | 0.03 | 169.30 |
| $CeO_2$ (HSA) | 158 | 0.32 | 80.89 |
| HZSM-5 | 415 | 0.26 | 24.63 |
| $Al_2O_3$ | 277 | 0.32 | 56.02 |
| $SiO_2$ | 242 | 0.75 | 124.80 |

The surface areas of catalysts are in the range 8-415 $m^2/g$. The higher specific surface area of $CeO_2$ (HSA) that prepared by the surfactant-assisted method compared to that of $CeO_2$ (commercial) is as expected, considering the smaller particle size from SEM image and lower crystallinity from XRD measurement.

## 4.2 The catalytic activity of 2-dodecanone

The activities of $CeO_2$ (high surface area), $CeO_2$ (commercial), HZSM-5 (Si/Al =180), alumina and silica for the conversion of 2-dodecanone. The result is shown in **Figure 4.4**

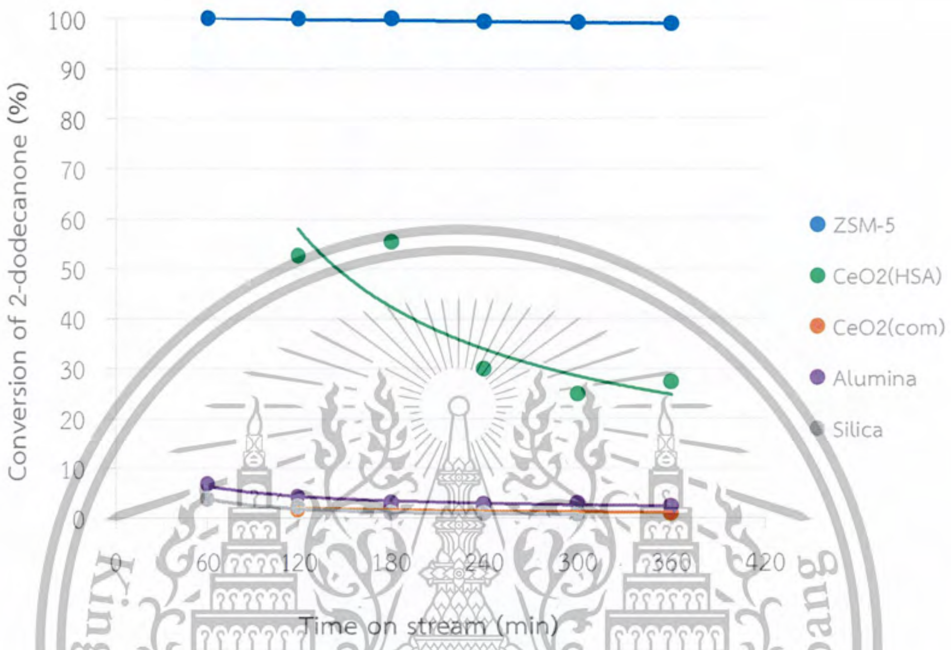


**Figure 4.4** The catalytic activity of 2-dodecanone over various catalysts

*(Reaction conditions: reaction temperature 400°C, contact time 50 g·h/mol under $N_2$ atmosphere, data collected every 60 mins and up to 6 h)*

It can be seen that the catalytic activity is decreased in the following order: HZSM-5 > $CeO_2$ (HSA) > Alumina, Silica, $CeO_2$ (com). For HZSM-5 with Si/Al ratio of 180, 2-dodecanone conversion was nearly 100% while $CeO_2$ (HSA) gives 39% conversion. However, other catalysts include $CeO_2$ (com), alumina and silica are inactive for cracking 2-dodecanone, as compared with HZSM-5 and $CeO_2$ (HSA) at the identical contact time 50 g·h/mol. The product distribution over each catalyst is shown in **Table 4.2**.

**Table 4.2** Product distribution from the reaction of 2-dodecanone over various catalysts

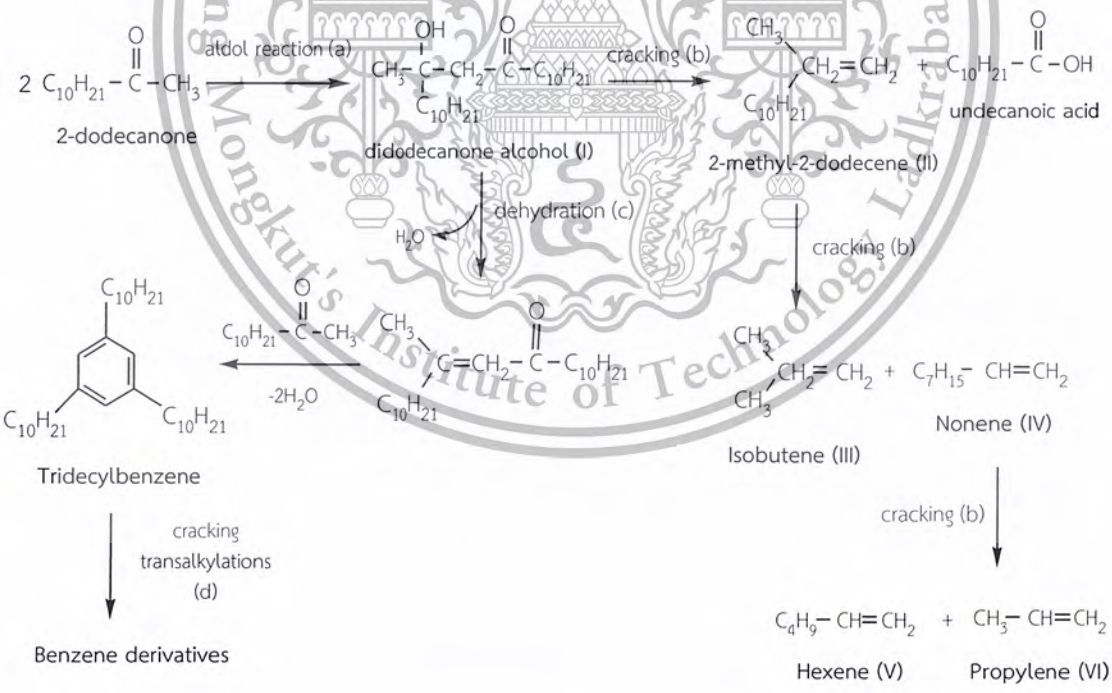
| | Catalyst | | | | |
|---|---|---|---|---|---|
| | HZSM-5 | $CeO_2$(HSA) | $CeO_2$(com) | Alumina | Silica |
| **Conversion** | 99.6 | 39.1 | 2.1 | 3.7 | 3.0 |
| **Product yield (%)** | | | | | |
| **Total Hydrocarbon** | **99.6** | **0.1** | **trace** | **2.6** | **trace** |
| Ethylene | 2.8 | - | - | - | - |
| Propylene | 26.9 | - | - | - | - |
| C4 | 26.0 | - | - | - | - |
| C5 | 12.3 | - | - | - | - |
| C6 alkanes | - | - | - | - | - |
| C6 alkenes | 6.5 | - | - | - | - |
| C7 alkanes | 0.9 | - | - | - | - |
| C7 alkenes | 5.9 | - | - | - | - |
| C8 alkanes | - | trace | - | trace | - |
| C8 alkenes | 1.7 | - | - | trace | - |
| C9 alkanes | 0.6 | trace | - | trace | - |
| C9 alkenes | - | trace | - | 0.1 | - |
| C10 alkanes | - | trace | - | trace | - |
| C10 alkenes | - | trace | - | trace | - |
| C11 alkenes | - | - | - | trace | - |
| C12 alkane | - | trace | trace | 0.3 | trace |
| C12 alkenes | - | 0.1 | trace | 2.0 | trace |
| C13 alkenes | - | trace | - | 0.1 | - |
| C7 aromatic | 3.5 | - | - | - | - |
| C8 aromatics | 6.6 | - | - | - | - |
| C9 aromatics | 4.6 | - | - | - | - |
| C10 aromatics | 1.3 | - | - | - | - |
| **Total Ketone** | **0.0** | **26.9** | **1.3** | **0.9** | **1.8** |
| C3 ketone | - | - | - | trace | - |
| C8 ketone | - | - | - | trace | - |
| C9 ketone | - | - | - | trace | - |
| C10 ketone | - | 0.1 | trace | trace | - |
| C11 ketone | - | 0.2 | 0.1 | 0.7 | 0.1 |
| C12 ketone | - | trace | trace | 0.1 | trace |
| C13 ketone | - | 0.1 | 0.1 | 0.1 | 0.1 |
| C15 ketone | - | 0.5 | trace | - | - |

| | | | | | |
|---|---|---|---|---|---|
| C17 ketone | - | 1.5 | trace | - | trace |
| C19 ketone | - | 0.7 | trace | - | 0.1 |
| C21 ketone | - | 6.1 | 0.2 | - | 1.1 |
| C24 ketone | - | 17.6 | 0.8 | - | 0.4 |
| C24 dihydrofuran | - | 12.4 | 0.8 | - | 1.2 |
| Alcohol | - | 0.1 | trace | 0.2 | trace |

*(Reaction conditions: 400°C, contact time 50 g·h/mol, 6 h after the reaction)*

The main hydrocarbon product obtained from 2-dodecanone over HZSM-5 are propylene, C4 and C5 hydrocarbons. By contrast, the main products from 2-dodecanone over $CeO_2$ (HSA) are C21 ketone (didecylketone), C24 ketone and C24 dihydrofuran.

The transformation of 2-dodecanone into hydrocarbons over HZSM-5 is a complex reaction network which seems to takes place via aldol condensation and dehydration, followed by cyclization, aromatization and cracking [44-46]. **Scheme 4.1** shows some possible reaction pathway of 2-dodecanone conversion over HZSM-5.



**Scheme 4.1** Some of the possible reaction pathway in the 2-dodecanone conversion to hydrocarbon over HZSM-5

The presence of propylene and tridecylbenzene in the aliphatic and aromatic fractions, suggested that 2-dodecanone molecules are successively reacted and condensed via aldol reaction as the primary reaction. Thus, 2-dodecanone dimerization can give rise to didodecanone alcohol (I) that would 2-methyl-2-dodecene and undecanoic acid after cracking. After that, cracking of 2-methyl-2-dodecene (II) can give isobutene (III) and propylene (IV) that as the main products by cracking process.

To demonstrate that the hydrocarbon products observed are derived from the cracking of high molecular weight hydrocarbon precursor, dodecane was chosen as model hydrocarbon compound for the catalytic cracking activity over HZSM-5 (Si/Al=180). The conversion and product yield of dodecane over HZSM-5 at 400°C as a function of contact time (W/F), as shown in **Figure 4.5**.

**Figure 4.5** The conversion of dodecane and the yields of products over HZSM-5 (Si/Al = 180) at various contact times

*(Reaction conditions: reaction temperature 400°C, under $N_2$ atmosphere, data collected every 60 mins and up to 6 h)*

The conversion of dodecane over HZSM-5 is increased with contact time. The yield of major products is similar to those observed in cracking of 2-dodecanone. The propylene yield increases from 30% to 71%, C4 hydrocarbons yield increase from 37% to 75% and C5 hydrocarbons yield increase from 18% to 23%. Other products (less than 8%) are ethylene, C6 alkene, C8 alkene and C8 aromatic [47].

To better comparison the selectivity of the hydrocarbon products from the two different feeds over HZSM-5, data at a similar conversion are shown in **Table 4.3**.

**Table 4.3** Product distribution of 2-dodecanone and dodecane over HZSM-5 at similar level of conversion

| | Feed | |
|---|---|---|
| | 2-Dodecanone | Dodecane |
| Contact time (g.h/mol) | 50 | 200 |
| Conversion (%) | 99.6 | 93.9 |
| Product yield (%) | 99.6 | 93.9 |
| Product selectivity (%) | | |
| Ethylene | 2.8 | 3.6 |
| Propylene | 27.0 | 37.8 |
| C4 | 25.5 | 39.8 |
| C5 | 12.3 | 11.9 |
| C6 alkane | - | 2.7 |
| C6 alkenes | 6.5 | - |
| C7 alkane | 0.9 | 2.4 |
| C7 alkenes | 5.9 | - |
| C8 alkane | - | 1.7 |
| C8 alkenes | 1.7 | - |
| C9 alkane | 0.6 | - |
| C7 aromatic | 3.6 | - |
| C8 aromatics | 6.6 | - |
| C9 aromatics | 4.7 | - |
| C10 aromatics | 1.3 | - |

*(Reaction conditions: 400°C, 6 h after the reaction)*

It can be seen that at similar conversion, a lower contact time can be used for 2-dodecanone. This is because 2-dodecanone possesses carbonyl group that is very active for aldol condensation over HZSM-5 catalyst.

The main products when using either dodecane or 2-dodecanone as the feed are propylene, C4 and C5 hydrocarbons. However, the selectivity of propylene and C4 from 2-dodecanone are lower than these from dodecane. This is because aromatics were also produced from 2-dodecanone.

However, the products from the reaction of 2-dodecanone over $CeO_2$ (HSA) are different from the products of 2-dodecanone over HZSM-5 catalyst (Table 4.2). This result suggests that $CeO_2$ processes no acid site for 2-dodecanone conversion. To demonstrate the lack of acidity over $CeO_2$. The $CeO_2$ (HSA) and $CeO_2$ (com) were tested for cracking dodecane, as shown in **Figure 4.6**.

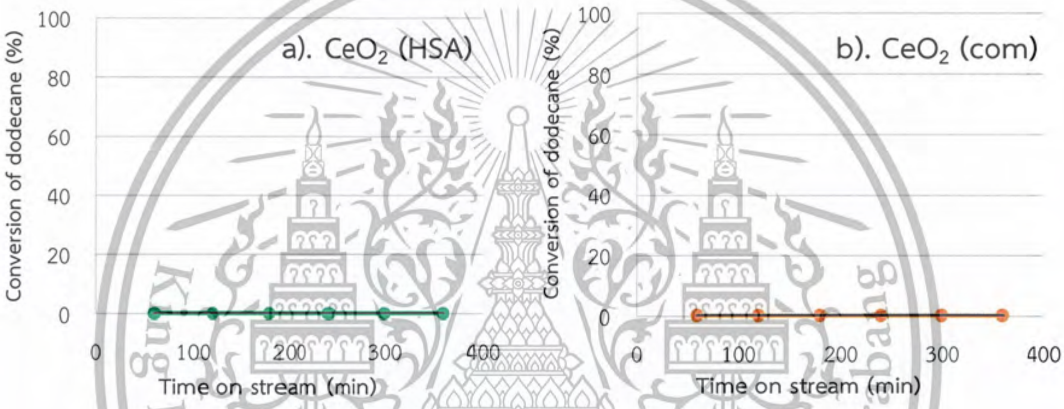


**Figure 4.6 (a)** The conversion of dodecane over $CeO_2$ (HSA)

**(b)** The conversion of dodecane over $CeO_2$ (commercial)

*(Reaction conditions: reaction temperature 400°C, contact time* 400 g·h/mol *under* $N_2$ *atmosphere, data collected every 60 mins and up to 6 h)*

It can be seen that no conversion of dodecane over $CeO_2$ (HSA) and $CeO_2$ (commercial) can be obtained even at higher contact time (400 g·h/mol), as compared to that used for HZSM-5 (50-200 g·h/mol). These results confirm that $CeO_2$ do not possess the acid site that is active for the cracking of hydrocarbon.

To verify the reaction pathway for 2-dodecanone conversion over $CeO_2$, the reaction of 2-dodecanone were tested as a function of the contact time, as shown in **Figure 4.7**.

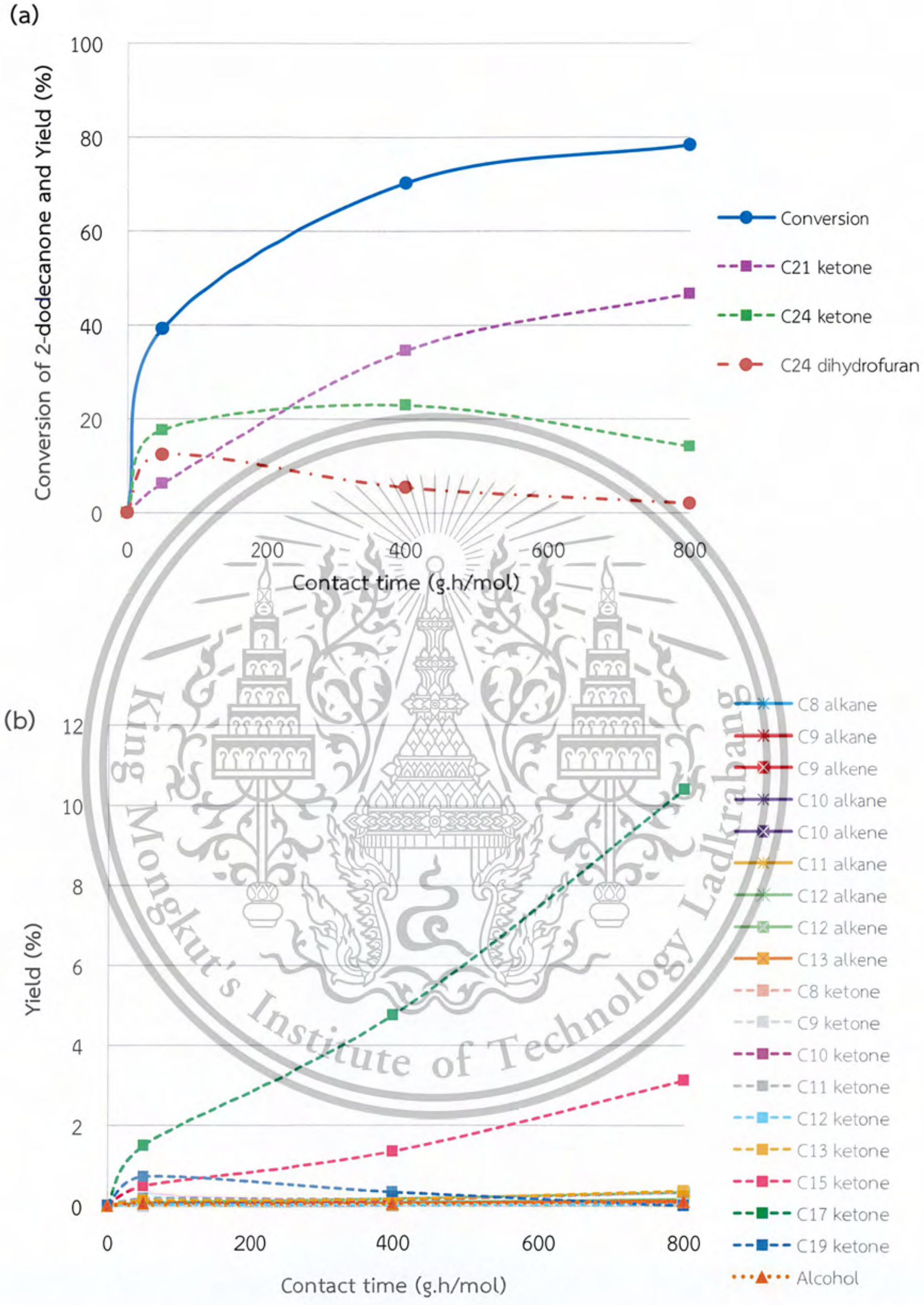
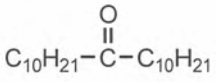


**Figure 4.7** The conversion of 2-dodecanone and yield of major products (a) and yield of minor products (b) at different contact times

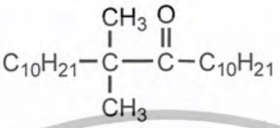
*(Reaction conditions: $CeO_2$ (HSA), reaction temperature 400°C, reduction temperature 450 °C, under atmospheric $N_2$ at 60 mins time on stream)*

The conversion of 2-dodecanone is increased from 39 to 78% when the contact time is increased from 50 to 800 g·h/mol. The increased conversion at higher contact time is understandable, because 2-dodecanone spends a longer time in contact with the active sites on the surface of a catalyst. The major products are didecylketone (C21 ketone), C24 ketone and C24 dihydrofuran (**Figure 4.9a**), of which the structures were confirmed by GC-MS as shown below.



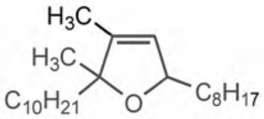
$C_{10}H_{21}-\overset{\overset{O}{\|}}{C}-C_{10}H_{21}$

**C21 ketone**



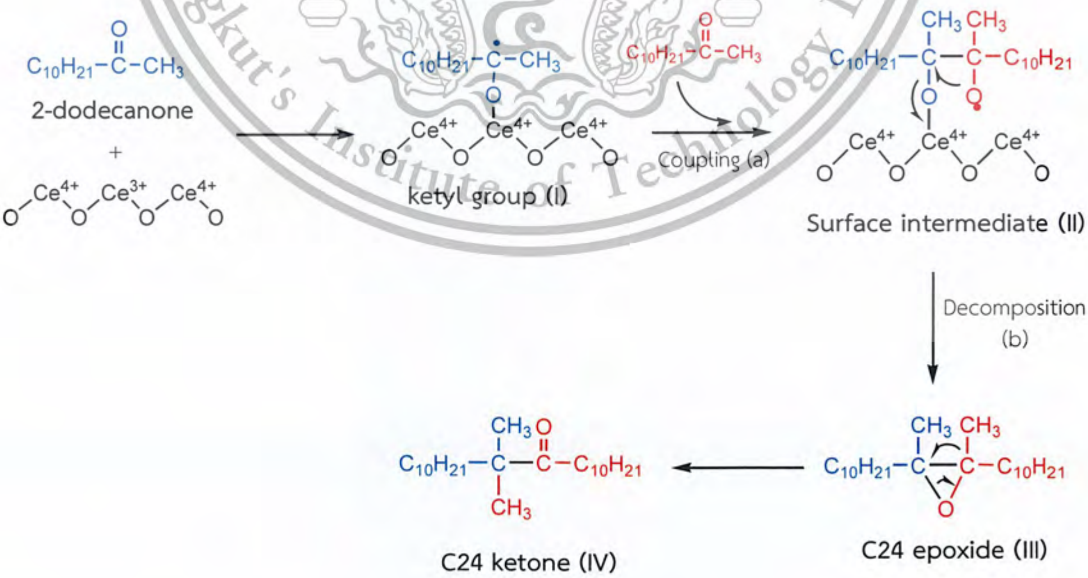
$C_{10}H_{21}-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\overset{O}{\|}}{C}-C_{10}H_{21}$

**C24 ketone**



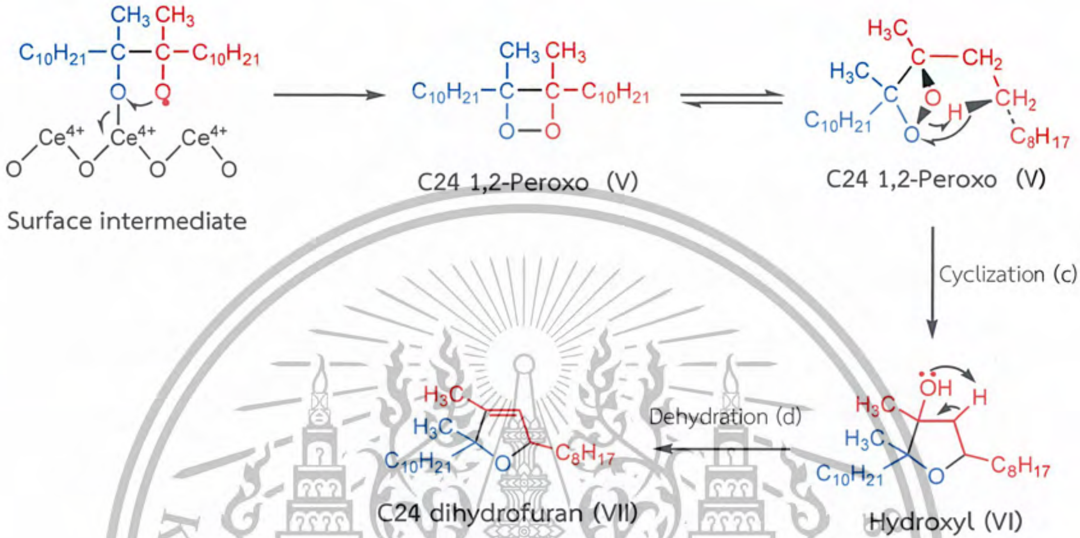
**C24 dihydrofuran**

It can be seen that yields of C24 ketone and C24 dihydrofuran are increased at the early contact time. C24 ketone (IV) is produced from coupling of 2-dodecanone. It is likely that 2-dodecanone is reduced by $Ce^{3+}$ on the surface of $CeO_2$ to form ketyl radical species (I). This radical couples with another 2-dodecaone over $Ce^{4+}$ site, forming surface intermediate (II). The surface intermediate can then decompose to C24 epoxide (III) that is rearranged to C24 ketone (IV), as shown in **Scheme 4.2**.



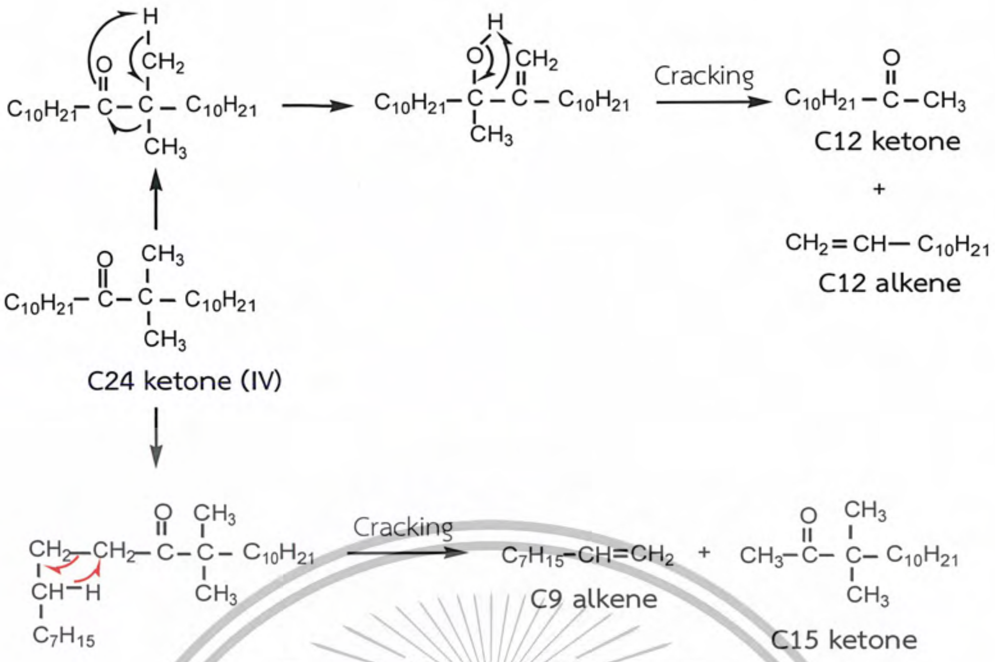
**Scheme 4.2** Production of C24 ketone from 2-dodecanone

For C24 dihydrofuran (VII), it is likely derived from the same surface intermediate as C24 ketone. However, the surface intermediate decomposes to C24 1,2-peroxo (V) that is followed by the cyclization (c) and dehydration (d), as shown in **Scheme 4.3**.

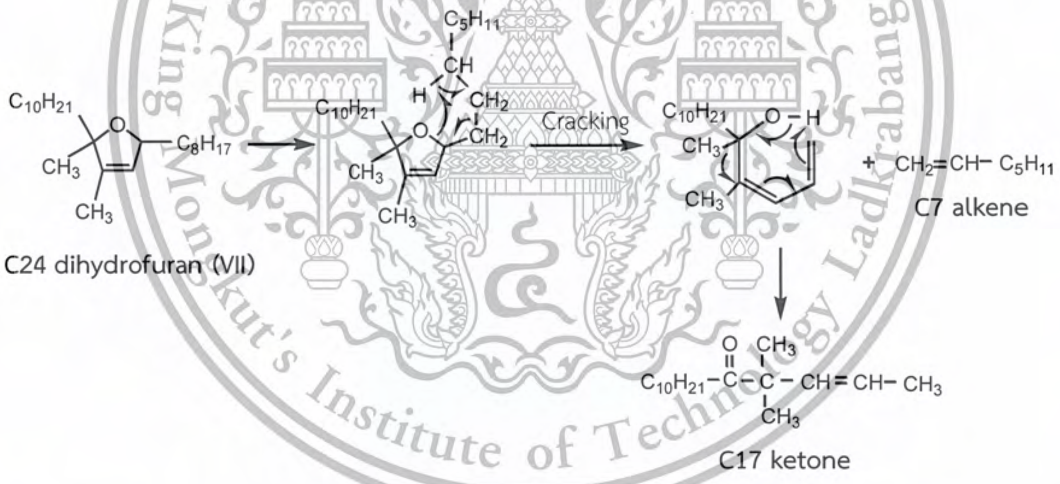


**Scheme 4.3** Production of C24 dihydrofuran from 2-dodecanone

Form **Figure 4.7a** C24 ketone and C24 dihydrofuran are decreased with contact time. On the other hand, the yield of C15 and C17 ketone (**Figure 4.7b**) are gradually increased. Accordingly, one can infer that both C24 ketone and C24 dihydrofuran are not stable and cracked to smaller ketone and hydrocarbons. The C24 ketone (IV) can be cracked to C12 ketone, C15 ketone, C9 alkene and C12 alkene while C24 dihydrofuran can be cracked to C17 ketone and C7 alkene, as shown in **Scheme 4.4 and 4.5**.

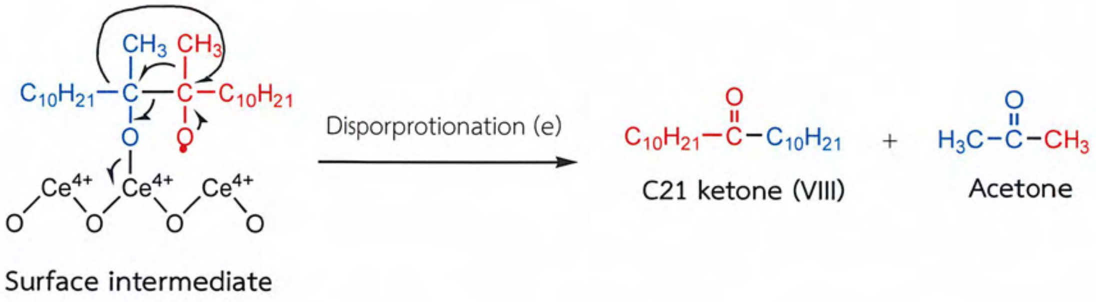


Scheme 4.4 The cracked ketone and hydrocarbon products from C24 ketone



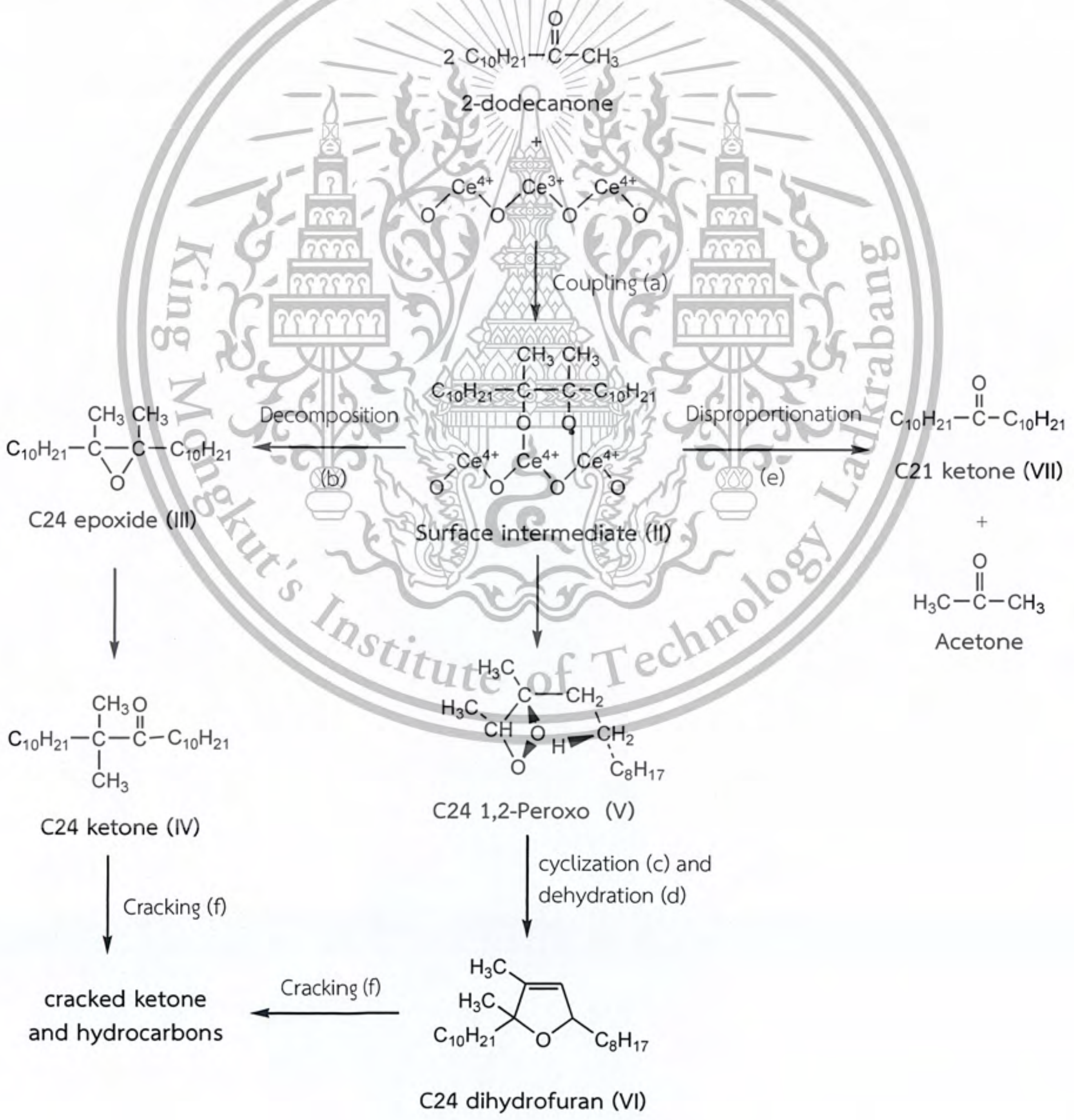
**Scheme 4.5** The cracked ketone and hydrocarbon products from C24 dihydrofuran

However, yield of C21 ketone (didecylketone) is increased from 6 to 46% when the contact time is increased. It is suggested that C21 ketone (IV) is a relatively stable symmetric ketone and not decomposed at higher contact time. It can be produced from the same surface intermediate (II) as C24 ketone and C24 dihydrofuran, but followed by disproportionation (e) over $CeO_2$ catalyst, as shown in **Scheme 4.6**.



Scheme 4.6 Production of C21 ketone from 2-dodecanone

The reaction pathway for the conversion of 2-dodecanone over $CeO_2$ (HSA) is depicted in **Scheme 4.7**.



**Scheme 4.7** Reaction pathway of the conversion of 2-dodecanone over $CeO_2$ (HSA)

The main products are probably produced from the same surface intermediate (II) followed by decomposition (b), cyclization (c), disproportionation (d) and cracking (f) over redox active sites of $CeO_2$ (HSA).

The hydrocarbon observed from the cracking of 2-dodecanone are secondary products from cracking of the primary products mentioned above.

Considering that 2-dodecanone was first coupled to form a symmetrical ketone, the second order reaction was assumed, i.e., "$\mathrm{A} + \mathrm{A} \rightarrow \textbf{products}$", while A is 2-dodecanone. The rate law for the second order reaction (see also Appendix B) is $-r_A = kC_A^{\,2} = -dC_A/dt$. Using the integral method, **Eq.4.1** can be obtained, where ($C_{A0}$) is the initial concentration of 2-dodecanone, ($C_A$) is the concentration of 2-dodecanone at any reaction time, k is the second order rate constant, and t is the reaction time. The plot of the left-hand side of equation 4.1 versus the time over $CeO_2$ (HSA) catalyst is shown in **Figure 4.8**. The linearity of this plot supports the second order nature of this reaction where 2-dodecanone was coupled over a ceria catalyst. The obtained rate constant k is 996 L/mol•s. More details can be found in Appendix B.

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \qquad \textbf{Eq. 4.1}$$

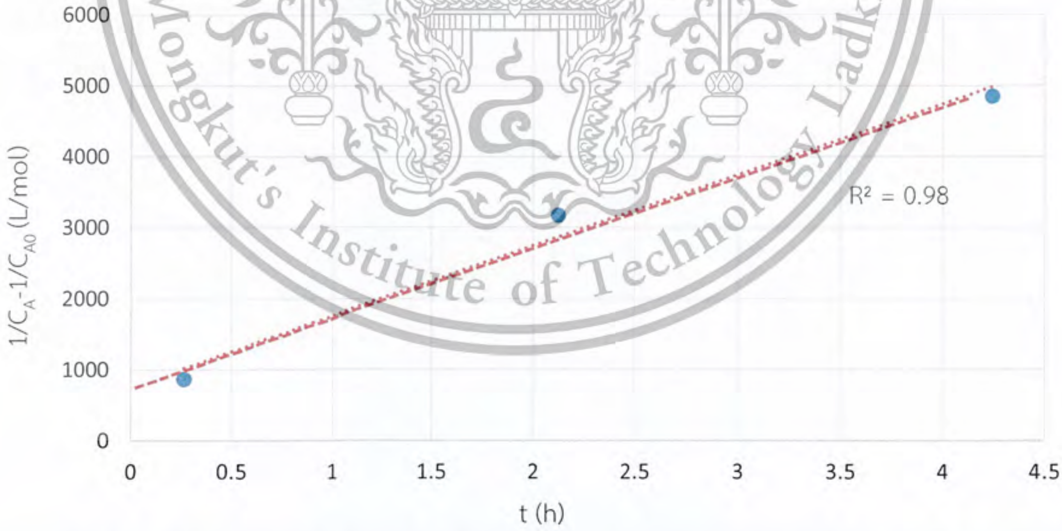


**Figure 4.8** The plot showing the second order nature of the coupling of 2-dodecanone over the $CeO_2$ (HSA) catalyst.

*(Reaction conditions: $CeO_2$ (HSA), reaction temperature 400°C, reduction temperature 450 °C, under atmospheric $N_2$ at 60 mins time on stream*

# CHAPTER 5
# CONCLUSION AND SUGGESTION

## 5.1 Conclusion

The high surface area (HSA) ceria was successfully prepared by the coprecipitation method, assisted by CTAB surfactant to obtain the nanosized-particles. According to the PXRD pattern, a fluorite structure was obtained similar to the commercial one. The small crystallite size of 8 nm was calculated from FWHM. In agreement with this result, $N_2$ adsorption/desorption shows a relatively high surface area of 158 m$^2$/g. Raman spectroscopy confirms the cubic fluorite structure of high surface ceria (a peak at 460 cm$^{-1}$) and suggests the presence of oxygen vacancy sites (a broad peak at 600 cm$^{-1}$).

Different catalysts were tested for cracking of 2-dodecanone and dodecane. It was found that HZSM-5 (Si/Al=180) showed 99% conversion of 2-dodecanone at the contact time of 50 g·h/mol and the reaction temperature of 400 °C, while $CeO_2$ (HSA) gave only 39% conversion. Other catalysts including $CeO_2$ (com), alumina and silica were inactive for the cracking of 2-dodecanone at the same contact time. For HZSM-5, 2-dodecanone was converted to propylene, C4 and C5 hydrocarbons as the major products by acid sites. By contrast, the major products over $CeO_2$ (HSA) are C21 ketone, C24 ketone and C24 dihydrofuran and the minor products are smaller ketones and some hydrocarbons by redox active sites. Dodecane was chosen as model hydrocarbon compound to study the catalytic cracking activity over HZSM-5 and $CeO_2$ (HSA). It was found that HZSM-5 is the only active catalyst for the cracking of hydrocarbon by acid sites. To get similar conversion of dodecane relative to 2-dodecanone, the contact time of dodecane has to be increased. This result can be explained considering the inert nature of alkanes. The carbonyl group in 2-dodecanone is very active for aldol condensation over HZSM-5 catalyst such that high molecule ketones are formed over the acid sites, followed by cyclization, aromatization and cracking. The major products over HZSM-5 from 2-dodecanone or dodecane as the feed are propylene, C4 and C5 hydrocarbons but the selectivities of propylene and C4 from 2-dodecanone are lower than those from dodecane. This is because aromatics were also produced from 2-dodecanone. For $CeO_2$ (HSA) and $CeO_2$ commercial, they are not active for the cracking of hydrocarbon because $CeO_2$ does not possess the acid site. The conversion of 2-dodecanone over $CeO_2$ (HSA) is increased to 78% when the contact time was increased to 800 g•h/mol. The higher conversion in this case can be ascribed to the larger concentration of active sites in contact with 2-dodecanone. In addition, it was found that the yields of C24 ketone and C24 dihydrofuran is significantly increased at the initial contact time, and then decreased at longer contact time. It can be inferred that both C24 ketone and C24 dihydrofuran are not stable and cracked to C15 and C17 ketone. In agreement with this claim, the yields of both ketones (C15 and C17 ketone) increased with the contact time. Also, the yield of C21 ketone steadily increased with the contact time. It is suggested that C21 ketone is a relatively stable symmetric ketone and does not decomposed with the increase in contact time. 2-Dodecanone was converted to the major products via coupling (surface intermediate), followed by decomposition, cyclization, disproportionation and cracking over redox active sites of $CeO_2$ (HSA).

## 5.2 Suggestion

5.2.1 It is interesting to load a metal as an additional active site on ceria catalyst to study the possible reaction pathways of chemicals in the oxygenate pool generated from the reaction of 2-dodecanone.

5.2.2 Since a lot of coke was found on ceria catalysts, the effect of hydrogen on coke removal from ceria catalysts could be investigated.

# REFERENCES

[1] D. Chalinee, K. Teerapong and S. Surachet. 2011 "**Deoxygenation of palmitic acid over cerium-metal oxide**" *Faculty of science*, KMITL 1.

[2] Tu N. Pham, S. Tawan, Steven P. Crossley, and Daniel E. 2013 "**Ketonization of Carboxylic Acids: Mechanisms, Catalysts, and Implications for Biomass Conversion**" **Acscatalysis** 2456.

[3] A. Trovarelli. 1996 "**Catalytic properties of Ceria and $CeO_2$-Containing materials**", *Catalysis reviews* 439.

[4] D. Casanave, J.-Luc Duplan and E. Freund. 2007 "**Diesel fuels from biomass**" *Pure Appl. Chem*, vol. 79, 2071–2081.

[5] Greg Breining. 2014. *Biomass Diesel:* **Rising Star of the Renewable Fuel Standard.** [Online] : http://bioenergyconnection.org/article/biomass-diesel-rising-star-renewable-fuel-standard.

[6] Z. Zhang, S. Sui, F. Wang, Q. Wang and Charles U. Pittman. 2013 "**Catalytic Conversion of Bio-Oil to Oxygen-Containing Fuels by Acid-Catalyzed Reaction with Olefins and Alcohols over Silica Sulfuric Acid**" *Energies*, vol. 6, 4531-4550.

[7] J. Lu, S. Behtash, M. Faheem and A. Heyden. 2013 "**Microkinetic modeling of the decarboxylation and decarbonylation of propanoic acid over Pd (1 1 1) model surfaces based on parameters obtained from first principles**" *Journal of Catalysis,* vol. 305, 56–66.

[8] M. Ahmadi, Eugenia E. Macias, Jacek B. Jasinski, P. Ratnasamy and Moises A. Carreon. 2014 "**Decarboxylation and further transformation of oleic acid over bifunctional, Pt/SAPO-11 catalyst and Pt/chloride $Al_2O_3$ catalysts**" *Journal of Molecular Catalysis A: Chemical*, vol. 386, 14–19.

[9] Thomas M. Yeh, Ryan L. Hockstad, S. Linic and Phillip E. Savage. 2015 "**Hydrothermal decarboxylation of unsaturated fatty acids over $PtSn_x$/C catalysts**" *Fuel*, vol.156, 219–224.

[10] *Ketonic decarboxylation*. [Online] :https://en.wikipedia.org/wiki/Ketonic_decarboxylation

[11] V.N. Panchenko, Yu.A. Zaytseva, M.N. Simonov, I.L. Simakova and E.A. Paukshtis. 2014 "**DRIFTS and UV–vis DRS study of valeric acid ketonization mechanismover $ZrO_2$ in hydrogen atmosphere**" *Journal of Molecular Catalysis A: Chemical*, vol.388–389, 133–140.

[12] *Renewable hydrocarbon fuels via decarboxylation / decarbonylation*. [Online]: https://en.wikipedia.org/wiki/Renewable_hydrocarbon_fuels_via_decarboxylation / decarbonylation

[13] J. Carlos, S.-Ruiz and James A. Dumesic. 2012 "**Catalytic Production of Liquid Hydrocarbon Transportation Fuels**" *Catalysis for Alternative Energy Generation.*

[14] A. Arthur, W. Madden ,R. Percy and E. Soliman. 2013 "**Ethylene to Linear Alpha Olefins**". *University of Pennsylvania*, Spring.

[15] Elif I. Gu¨ rbu¨ z, Edward L. Kunkes, James A. Dumesic "**Integration of C–C coupling reactions of biomass-derived oxygenates to fuel-grade compounds**" *Applied Catalysis B: Environmental* 94 (2010) 134–141

[16] *Cracking*. [Online] : https://en.wikipedia.org/wiki/Cracking_(chemistry).

[17] *Acid–basecatalysis*.[Online]:http://global.britannica.com/science/acid-base catalysis.

[18] *Acid catalysis*. [Online] : https://en.wikipedia.org/wiki/Acid_catalysis.

[19] ZSM-5. [Online] : https://en.wikipedia.org/wiki/ZSM-5.

[20] S. Sang, F. Chang, Z. Liu, C. He, Y. He and L. Xu. 2004 "**Difference of ZSM-5 zeolites synthesized with various templates**" *Catalysis Today*, 729–734.

[21] [Online] : https://engineering.purdue.edu/~thomsonk/projects.html.

[22] Jose A. Jiménez, Laila Fillali1,2, Sol López-Andrés, Isabel Padilla and A. López-Delgado. "**Characterization of the aluminas formed during the thermal decomposition of boehmite by the Rietveld refinement method**"

[23] V. Coelho, Rocha, S. Santos and Kiyohara. 2008 "**Specific surface area and structures of aluminas from fibrillary pseudoboehmite**" Revista Matéria, v. 13, n.2, 329 – 341.

[24] N. S. FIGOLI and M. P ARERA. 1970 "**acidity of oxide catalysts in the presence of reactants**" *journal of the research institute for catalysis hokkaido university*, vol.18. 142-149.

[25] "**Kinetics of the Catalytic Dehydration of 2-Propanol in an Aqueous Medium**" *Department of Chemical and Materials Engineering, Edmonton,* Alberta. 2000.

[26] P. Souza Santos, H. Souza Santos and S.P. Toledo. 2000 "**Standard Transition Aluminas. Electron Microscopy Studies**" *Materials Research*, Vol. 3, No. 4, 104-114.

[27] Bruce C. Gates. *Catalytic Chemistry*. Singapore : John Wiley & Sons; 1991.

[28] *Cerium (IV) oxide*. [Online] : https://en.wikipedia.org/wiki/Cerium(IV)_oxide

[29] Jolla Kullgren. 2012 "**Oxygen Vacancy Chemistry in Ceria**" *Acta Universitatis Upsaliensis Uppsala*. 9-14.

[30] Yunyun Zhou. 2015 "**Nanostructured Cerium Oxide Based Catalysts: Synthesis, Physical Properties, and Catalytic Performance**" *University of Nebraska-Lincoln*.

[31] S.A. Hassanzadeh-Tabrizi. 2011 "**Optimization of the synthesis parameters of high surface area ceria nanopowder prepared by surfactant assisted precipitation method**". *Applied Surface Science* 257, 10595– 10600.

[32] F. Billaud ,A.K. Tran Minh ,P. Lozano and D. Pioch. 2001 "**Catalytic cracking of octanoic acid**" Journal of Analytical and Applied Pyrolysis, 605–616.

[33] Z. Guo, S. Wang, Y. Zhu, X. Li and Z. Luo. 2010 "**Catalytic cracking of ketone components in biomass pyrolysis oil**" *Zhejiang University*, China.

[34] S. Wang, Q. Cai, X. Wang, Z. Guo and Z. Luo. 2013 "**Bio-gasoline production from co-cracking of hydroxypropanone and ethanol**" *Fuel Processing Technology,* 111, 86–93.

[35] T.An Le, H. Vu Ly, J. Kim, S.-Soo Kim, J. Hyung Choi, H.-Chul Woo and M. Roslee Othman. 2014 "**Hydrodeoxygenation of 2-furyl methyl ketone as a model compound in bio-oil from pyrolysis of Saccharina Japonica Alga in fixed-bed reactor**" *Chemical Engineering Journal*, 250, 157–163.

[36] Y. Wang, X. Xian, X. Hou, X. Zhang, L. Wang and G. Liu. 2015 "**Catalytic cracking of binary hydrocarbons of n-dodecane and iso-dodecane under supercritical conditions**" *Journal of Analytical and Applied Pyrolysis*, 113, 133–136.

[37] Y. Wang, T. Yokoi, S. Namba, Junko N. Kondo and T. Tatsumi. 2016 **“Improvement of catalytic performance of MCM-22 in the cracking of n-hexane by controlling the acidic property”** *Journal of Catalysis,* 333, 17–28.

[38] Sandeep D. Randery, Jack S. Warren, Kerry M. Dooley **“Cerium oxide-based catalysts for production of ketones by acid condensation”** *Applied Catalysis A: General* 226 (2002) 265–280.

[39] Edward L. Kunkes, Elif I. Gürbüz, James A. Dumesic **“Vapour-phase C–C coupling reactions of biomass-derived oxygenates over Pd/CeZrO$_x$ catalysts”** *Journal of Catalysis* 266 (2009) 236–249.

[40] N. Laosiripojana and S. Assabumrungrat. 2006 **“Catalytic dry reforming of methane over high surface area ceria”** *Applied catalysis* 108.

[41] A.I.Y. Tok , F.Y.C. Boey, Z. Dong and X.L. Sun. 2007 **“Hydrothermal synthesis of CeO$_2$ nano-particles”** *Journal of materials processing technology* 220.

[42] Y. Lee, G. He, Austin J. Akey, R. Si, Maria Flytzani-Stephanopoulos and Irving P. Herman. 2011 **“Raman Analysis of Mode Softening in Nanoparticle CeO$_2$ $\delta$ and Au-CeO$_2$ $\delta$ during CO Oxidation”** *Journal of the American Chemical Society* B.

[43] Z.-Ying Pu, J.-Qing Lu, M.-Fei Luo and Y.-Long Xie. 2007 **“Study of Oxygen Vacancies in Ce$_{0.9}$Pr$_{0.1}$O$_2$-$\delta$ Solid Solution by in Situ X-ray Diffraction and in Situ Raman Spectroscopy”** *Journal of Physical Chemistry C* 18697.

[44] A. J. Cruz-Cabeza , D. Esquivel, C. Jiménez-Sanchidrián and F. J. Romero-Salguero, **“Metal-Exchanged β Zeolites as Catalysts for the Conversion of Acetone to Hydrocarbons”**, *materials ISSN 1996-1944* (2011) 129.

[45] T. Tsutsui, S. Mitsuyoshi, I. Endo and K. Mizuta, **“conversion of ethylmethylketone and levulinic acid into petrochemicals over zsm-5 as a biorefinery technology”**, *International Journal ofbiomass & renewables* (2012) 22-24.

[46] T. Danuthai, S. Jongpatiwut, T. Rirksomboon, S. Osuwan and Daniel E. Resasco, **“Conversion of methylesters to hydrocarbons over an H-ZSM5 zeolite catalyst”**, *Applied Catalysis A: General 361* (2009) 99–105.

[47] Z. Diao, L. Wang, X. Zhang and G. Liu. 2015 **“Catalytic cracking of supercritical n-dodecane over meso-HZSM-5@Al-MCM-41 zeolites”** *Chemical Engineering Science* 457.

# APPENDICES

# APPENDIX A

# CATALYSTS CHARACTERIZATION

## 1. Powder X-ray diffraction

**Figure A1** XRD pattern of H-ZSM-5 (Si/Al 180)

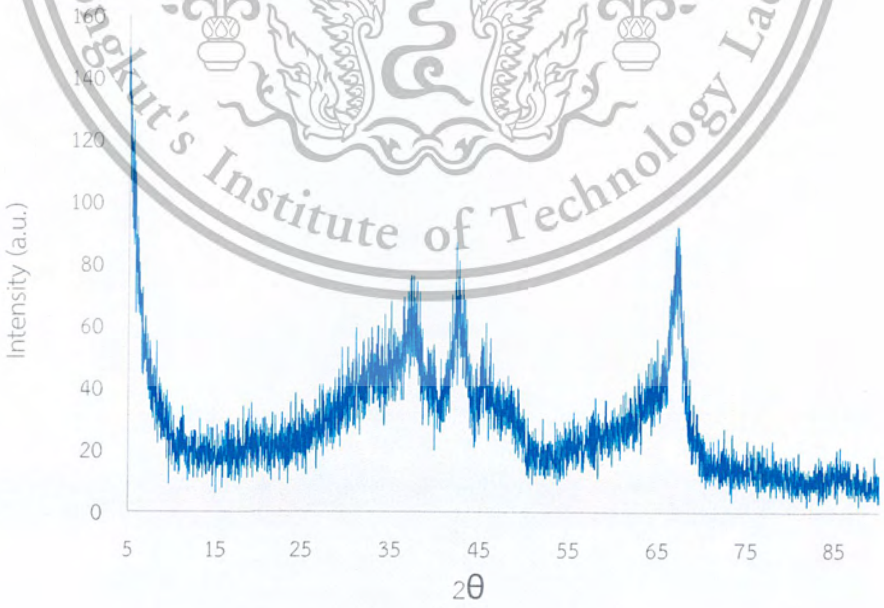


**Figure A2** XRD pattern of $Al_2O_3$

## 2. Scanning electron microscopy (SEM)

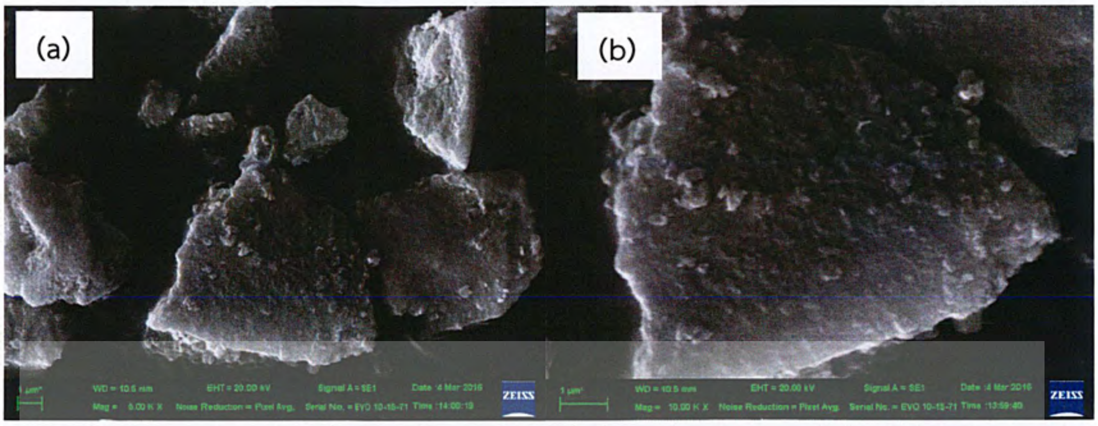


**Figure A3** SEM images of $CeO_2$ (HSA) 5.00 K (a) and 10.00 K (b)

**Figure A4** SEM images of $CeO_2$ (com) 5.00 K (a) and 10.00 K (b)

## 3. Gas adsorption analysis

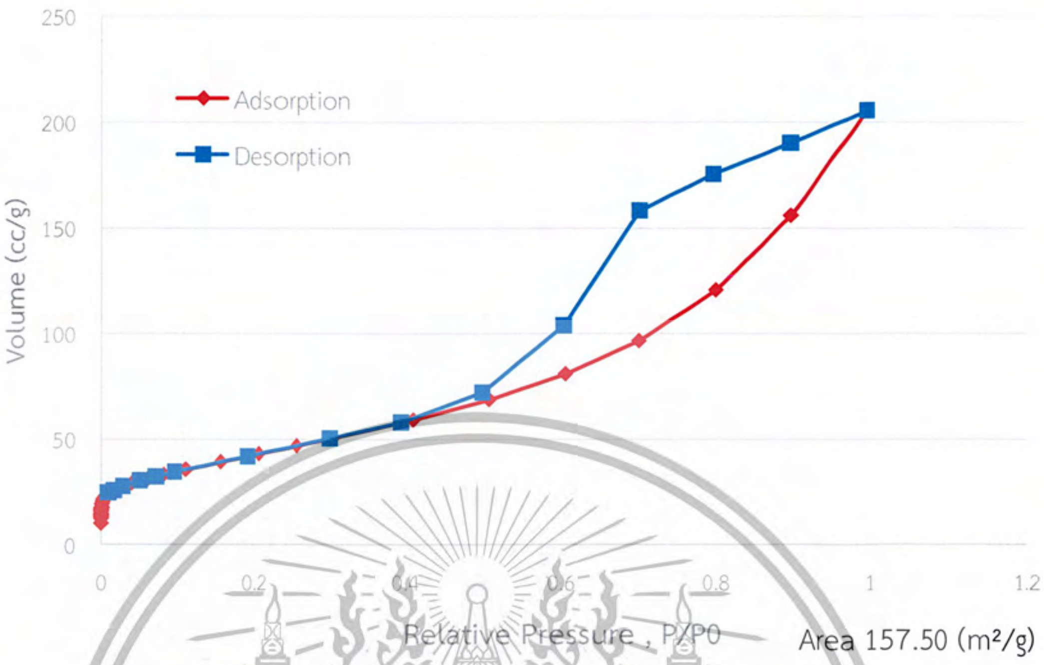


**Figure A5** Adsorption-desorption isotherm of $CeO_2$ (HSA)

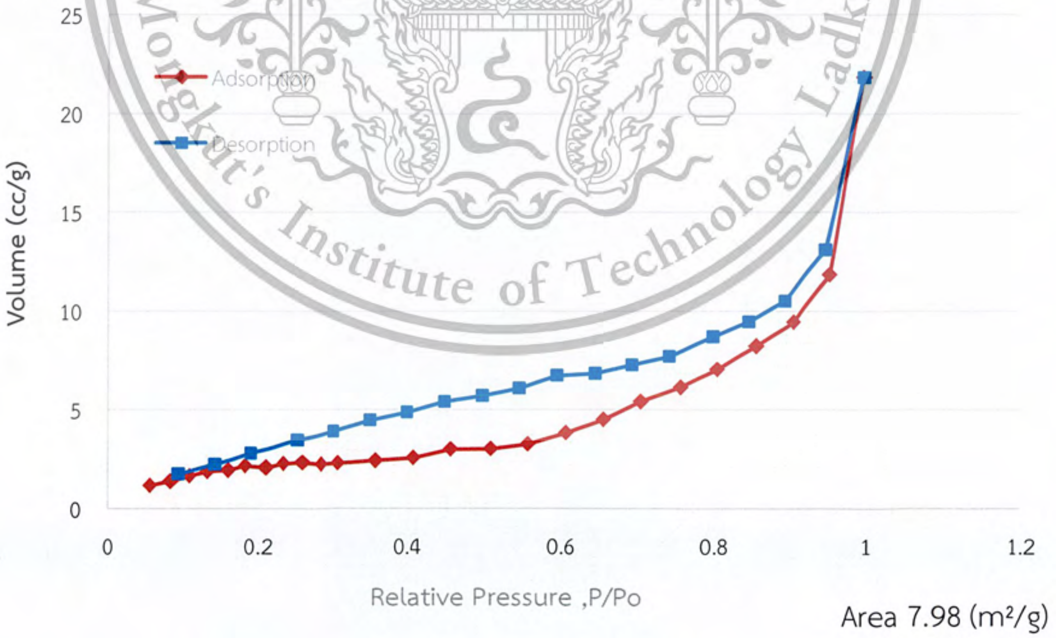


**Figure A6** Adsorption-desorption isotherm of $CeO_2$ (commercial)

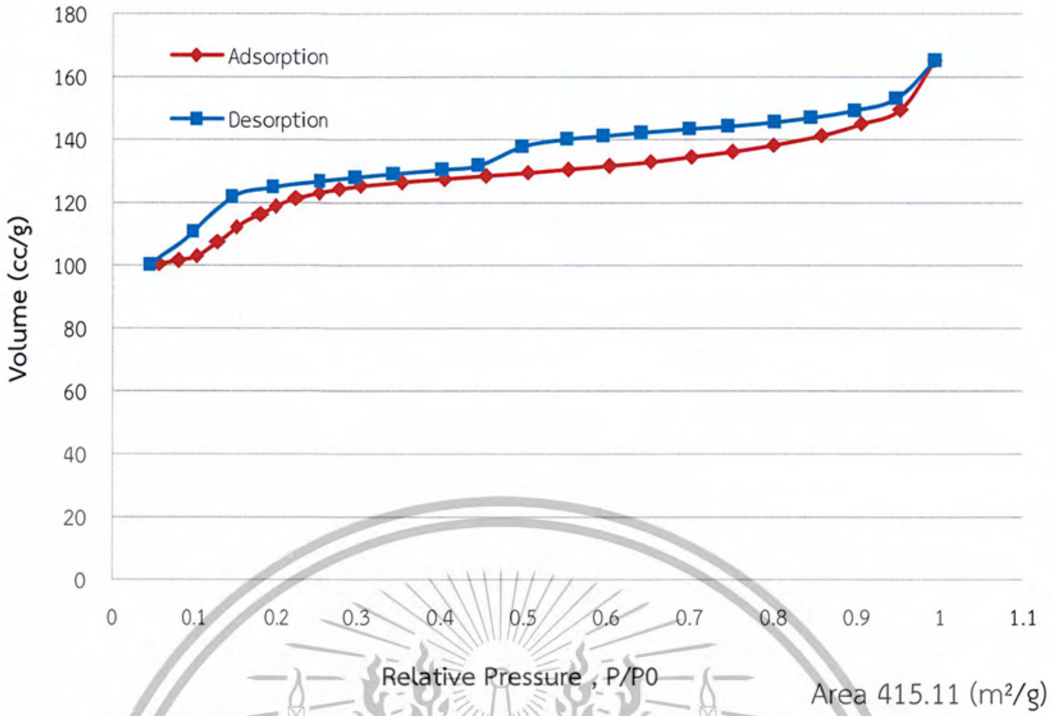


**Figure A7** Adsorption-desorption isotherm of HZSM-5 (Si/Al 180)

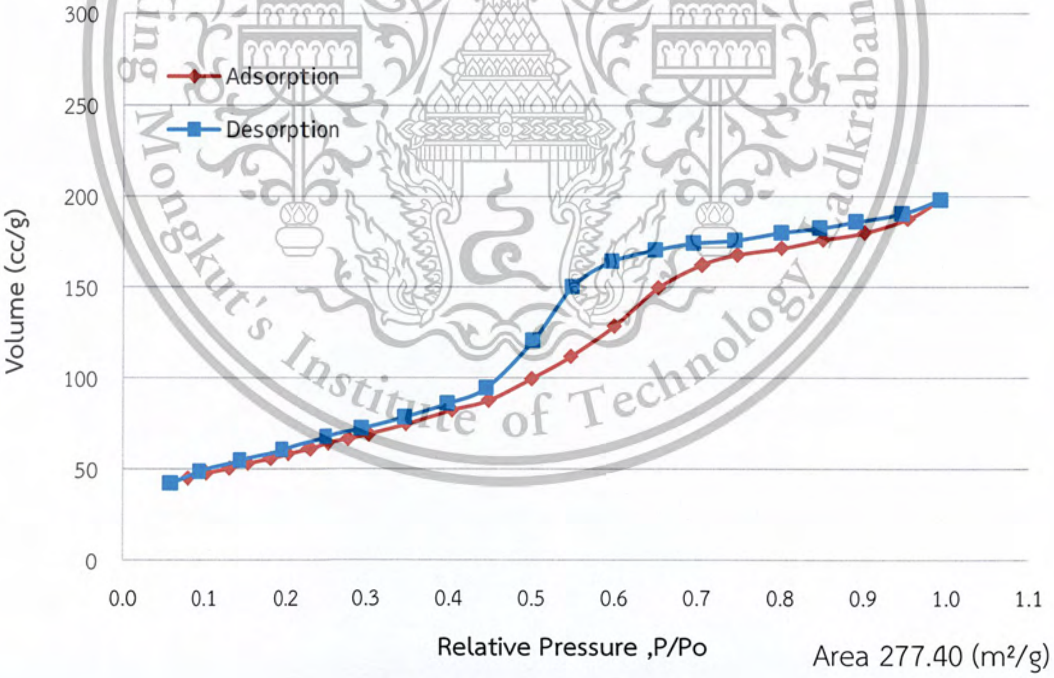
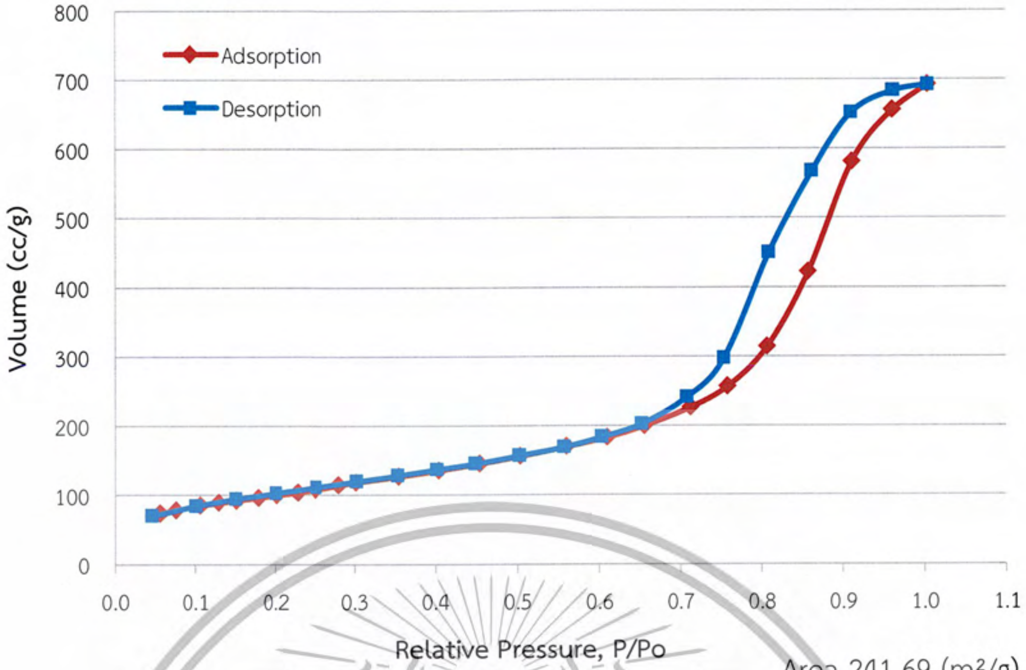


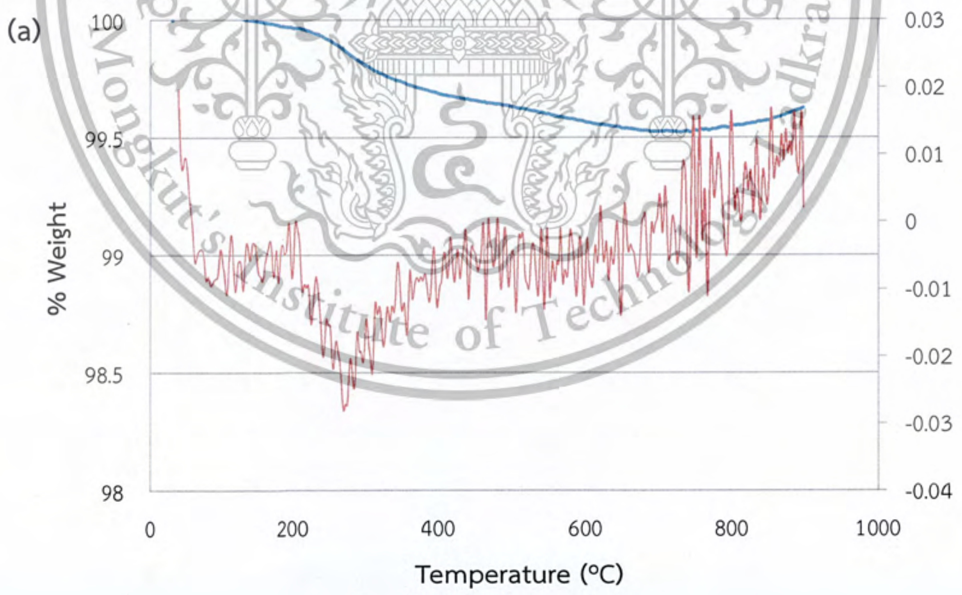
**Figure A8** Adsorption-desorption isotherm of $Al_2O_3$



Area 241.69 ($m^2/g$)

Figure A9 Adsorption-desorption isotherm of $SiO_2$

## 4. Thermogravimetric analysis



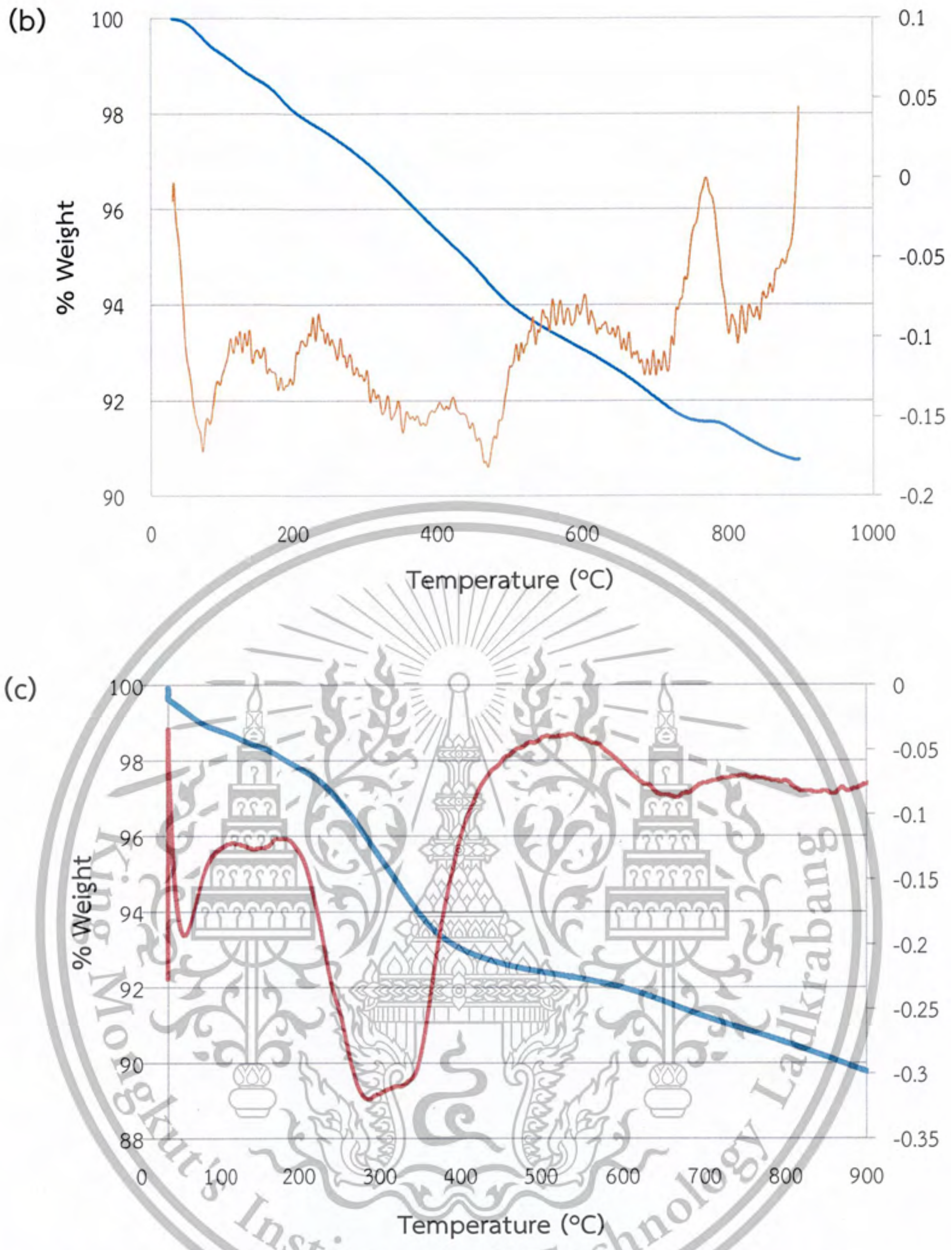


**Figure A10** The mass loss curve (ascribed to coke) on spent catalysts after the conversion of 2-dodecanone over different catalysts/contact times: (a) commercial $CeO_2$ (0.45%, W/F = 50 g·h/mol), (b) HSA $CeO_2$ (9.24%, W/F = 50 g·h/mol), and (c) HSA $CeO_2$ (10.29%, W/F = 800 g·h/mol).

# APPENDIX B
# CALCULATION

**Contact time, W/F**

$$W/F = \frac{\text{Weight of catalysts (g)}}{\text{Mole of reactant feed (mol/h)}}$$

This parameter can be tuned by varying the mass of catalyst, keeping the feed rate unchanged. The reactant feed rate is fixed at 0.0027 mol/h for 2-dodecanone or 0.0026 mol/h for dodecane.

For example;

In the reaction using 0.0027 mol/h of 2-dodecanone in feed and using 0.1350 grams of catalyst, the W/F is calculated as follow:

$$W/F = [0.1350\ (g) / 0.0027\ (mol/h)]$$

$$= 50\ g{\cdot}h/mol$$

In similar manner; W/F of catalyst with different catalyst weight and different feed rate are calculated.

**Yield** - the products that are obtained after reaction

Calculation of % yield of products from gas chromatography by normalization method. In normalization method, the areas of all eluted peak were computed areas for differences in the detector response to different compound types. The concentration of the analyzed was found from the ratio of its area to the total area of all peaks.

**Table B1** the summation of the peak area for products.

| Product | Peak area |
|---|---|
| C8 | 119.6 |
| C9 | 152.7 |
| C10 | 513.6 |
| C12 | 1797.8 |
| C13 | 561.9 |
| 2-octanone | 73.0 |
| 2-decanone | 1098.4 |
| 2-undecanone | 3047.6 |
| 5,9-dimethyl-2-decanone | 600.2 |
| C13 ketone | 2227.1 |
| 2-pentadecanone | 8869.0 |
| 9-heptadecanone | 39356.0 |
| 10-nonadecanone | 8382.8 |
| C21 ketone | 8818.5 |
| C24 ketone | 293990.5 |
| C24 dihydrofuran | 138918.5 |
| Alcohol | 1934.9 |
| 2-Dodecanone (Feed) | 379804.0 |
| Total | 890266.1 |

**In formation of $CeO_2$(HSA) , Reaction temperature 400 °C, Reduced 450 °C, Contact time 50 g·h/mol, time on steam = 120 minutes*

Calculate the percent yield of each component in sample as follows:

$$\%\text{Yield in each product} = \frac{\text{Peak area of A x 100}}{\text{Total area}}$$ ; When A is each product.

<u>For example</u>;

$$\%\text{Yield of C24 ketone} = \frac{293990.5 \times 100}{890266.1}$$

$$= 33.02$$

The percent yield of each product obtained from above calculation is shown in **Table B2**.

**Table B2** %Yield of product derived by normalization method.

| Product | % Yield |
|---|---|
| C8 | 0.01 |
| C9 | 0.02 |
| C10 | 0.06 |
| C12 | 0.20 |
| C13 | 0.06 |
| 2-octanone | 0.01 |
| 2-decanone | 0.12 |
| 2-undecanone | 0.34 |
| 5,9-dimethyl-2-decanone | 0.07 |
| C13 ketone | 0.25 |
| 2-pentadecanone | 1.00 |
| 9-heptadecanone | 4.42 |
| 10-nonadecanone | 1.05 |
| C21 ketone | 0.99 |
| C24 ketone | 33.02 |
| C24 dihydrofuran | 15.60 |
| Alcohol/Aldehyde | 0.22 |
| 2-Dodecanone (Feed) | 42.66 |
| Total | 100 |

**In formation of $CeO_2$(HSA) , Reaction temperature 400 °C, Reduced 450 °C, Contact time 50 g·h/mol, time on steam = 120 minutes*

**Conversion** - the feed changed after the reaction.

%Conversion can be calculated from the following equation:

$$\%\text{Conversion} = \frac{(\text{Total area} - \text{Feed}_{\text{rest}}\text{ area x } 100)}{\text{Total area}}$$

For example;

$$\%\text{Conversion} = \frac{(890266.1 - 293990.5) \text{ x } 100}{890266.1}$$

$$= 57.34$$

**Order of reaction**

Assumption:

1. $2^{nd}$ order elementary reaction

2. Integral method

3. $-r_A = kC_A^2 = -\frac{dC_A}{dt}$

**Table B3** kinetic analysis data.

| contact time (g·h/mol) | catalyst weight (g) | WHSV ($h^{-1}$) | Space time (h) | conversion ($X_A$) | $C_A$ ($\times10^{-4}$ mol/L) | $1/C_A$ (L/mol) | k (L/mol•s) |
|---|---|---|---|---|---|---|---|
| 50 | 0.1350 | 3.68 | 0.27 | 0.3905 | 4.56 | 2191.39 | 995.98 |
| 400 | 1.0552 | 0.47 | 2.12 | 0.7033 | 2.22 | 4501.69 | |
| 800 | 2.1104 | 0.23 | 4.24 | 0.7838 | 1.62 | 6177.85 | |

Solution;

$$-\frac{dC_A}{C_A^2} = kdt$$

$$-\int_{C_{A0}}^{C_A} \frac{1}{C_A} dC_A = k\int_0^t dt$$

$$-\left(-\frac{1}{C_A}\Big|_{C_{A0}}^{C_A}\right) = kt$$

$$-\left[-\left(\frac{1}{C_A} - \frac{1}{C_{A0}}\right)\right] = kt$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

Mathematical of $2^{nd}$ order reaction is $\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$

# APPENDIX C

# GAS-CHROMATOGRAM

## Analysis product from gas chromatography

Prior to analysis, the products were identified by GC-MS (Gas chromatography equipped with Mass Spectrometer detector). Then, quantitative analysis of products was determined by GC-FID (Gas chromatography equipped with Flame Ionization Detector). The analytical conditions of products from the conversion of 2-dodecanone and dodecane are shown in **Table C1**.

**Table C1** GC conditions for products analysis from the catalytic cracking of 2-dodecanone and dodecane

| | |
|---|---|
| Column | DB-1, 30 m × 0.32 mm i.d., 5 Micrometer |
| Temperature program | 40 °C for 5 min to 280 °C at rate 15 °C/min for 24 min |
| Carrier gas | Nitrogen gas flow rate 2.4 mL/min (40 cm/sec) |
| Injector | 275 °C (split ratio 80:1) |
| Sampling loop | 250 microliter |
| Detector | FID (275 °C) |

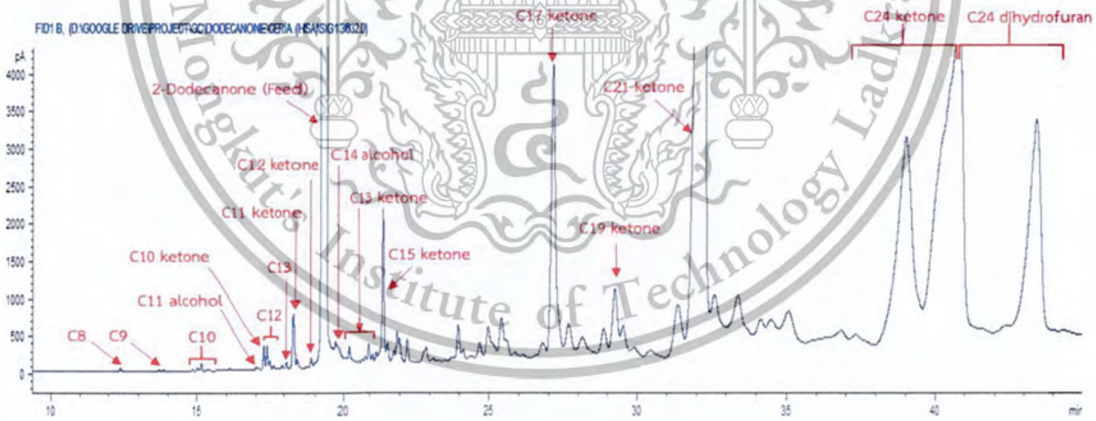


**Figure C1** Chromatogram of products from the conversion of 2-dodecanone over $CeO_2$ (HSA).

**Reaction conditions: Temperature 400°C, Reduced 450°C , Contact time 50 g·h/mol at time on stream 120 mins.*

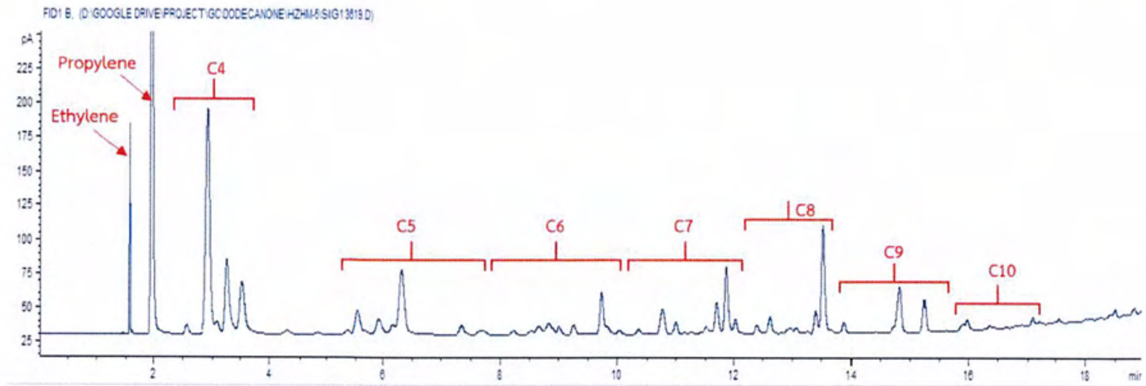


**Figure C2** Chromatogram of products from the conversion of 2-dodecanone over HZSM-5

**Reaction conditions: Temperature 400°C, Contact time 50 g·h/mol at time on stream 60 mins.*

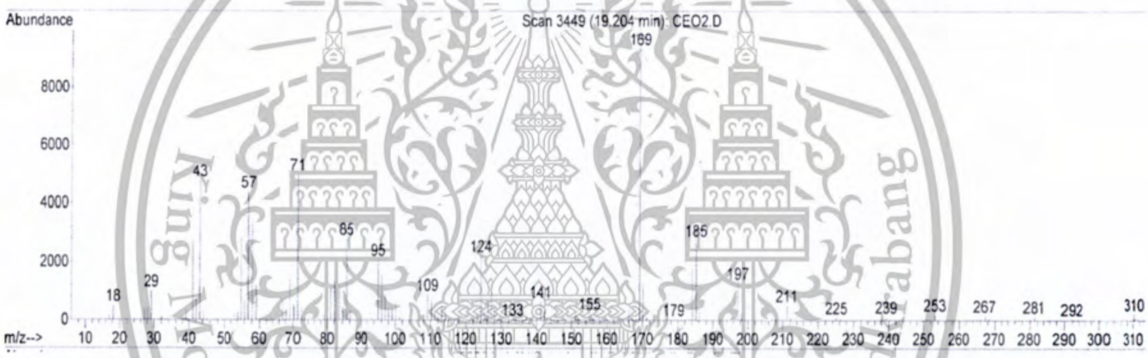


**Figure C3** GC-MS of C21 ketone from the conversion of 2-dodecanone over $CeO_2$ (HSA)

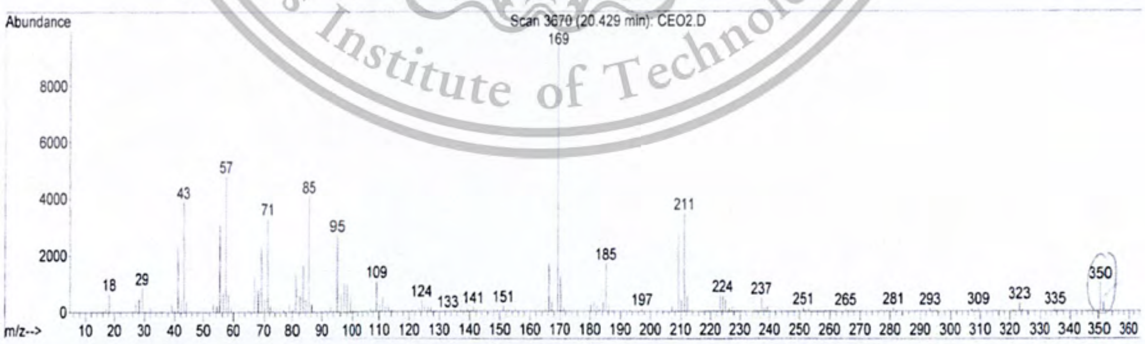


**Figure C4** GC-MS of C24 ketone from the conversion of 2-dodecanone over $CeO_2$ (HSA)

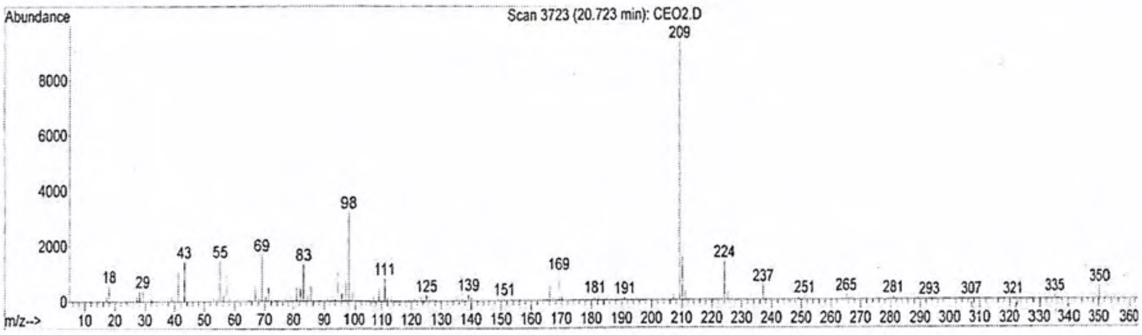


**Figure C5** GC-MS of C24 dihydrofuran from the conversion of 2-dodecanone over $CeO_2$ (HSA)

The products from the catalytic cracking of 2-dodecanone over $CeO_2$ (HSA) and HZSM-5 were identified by comparing the retention time to that of the known substances as listed in **Table C2** and **Table C3** respectively.

**Table C2** Products distribution from the conversion of 2-dodecanone over $CeO_2$ (HSA)

| **Feed or products** | **Retention time (min)** |
|---|---|
| **C8** : Octane | 12.4 |
| **C9** | |
| • 1-Nonene | 13.7 |
| • Nonane | 13.9 |
| **C8 Ketone** : 2-Octanone | 14.8 |
| **C10** | |
| • 1-Decene | 15.0 |
| • Decane | 15.2 |
| • 2-Decene | 15.4 |
| **C11 Alcohol** : 1-Undecanol | 17.0 |
| **C10 Ketone** : 2-Decanone | 17.2 |
| **C12** | |
| • 1-Dodecene | 17.3 |
| • Dodecane | 17.4 |
| • 4-Dodecene | 17.6 |
| **C11 Ketone** : 2-Undecanone | 18.3 |
| **C13** | |
| • 2-Methyl-1-dodecene | 18.4 |
| • 2-Methyl-2-dodecene | 18.6 |
| **C12 Ketone** | |
| • 5,9-Dimethyl-2-decanone | 18.8 |

| | |
|---|---|
| • 2-Dodecanone (Feed) | 19.4 |
| **C14 Alcohol** : 2-Tetradecanol | 19.7 |
| **C13 ketone** | |
| • 3-Tridecanone | 20.1 |
| • 11-Methyl-4-dodecanone | 20.9 |
| **C15 Ketone** : 2-Pentadecanone | 21.4 |
| **C17 Ketone** : 9-Heptadecanone | 27.1 |
| **C19 Ketone** : 10-Nonadecanone | 29.2 |
| **C21 Ketone** | 31.9 |
| C24 Ketone | 41.0 |
| C24 Dihydrofuran | 43.5 |

**Table C3** Products distribution from the conversion of 2-dodecanone over HZSM-5

| Feed or products | Retention time (min) |
|---|---|
| **C2** : Ethylene | 1.5 |
| **C3** : Propylene | 1.9 |
| **C4** | 2.5 – 3.5 |
| **C5** | 5.5 – 7.6 |
| **C6** | |
| • 2-Hexene | 8.6 |
| • 4-Methyl,2-pentene | 8.8 |
| • 3-Methyl,2-pentene | 9.0 |
| • 1-Methyl cyclopentene | 9.2 |
| • Cyclohexene | 9.7 |
| C7 | |
| • 1,3-Dimethyl cyclopentane | 10.3 |
| • 3,5-Dimethyl cyclopentane | 10.7 |
| • 1,5-Dimethyl cyclopentane | 10.9 |
| • Methylcyclohexane | 11.5 |
| • 4-Methylcyclohexene | 11.7 |
| • Toluene | 11.9 |
| • 1-Methyl cyclohexene | 12.0 |
| C8 | |
| • 3,5-Dimethyl cyclohexene | 12.3 |
| • 1-Ethyl-2-methylcyclopentene | 12.6 |
| • Ethylbenzene | 13.3 |

| | |
|---|---|
| • p-Xylene | 13.5 |
| C9 | |
| • Nonane | 13.8 |
| • 1-Ethyl-2-methyl-benzene | 14.8 |
| • 1,3,5-trimethylbenzene | 15.2 |
| C10 | |
| • 1,3-Diethylbenzene | 15.9 |
| • 1-Methyl-2-propenylbenzene | 17.0 |

# APPENDIX D
# REACTION DATA

## D1. The catalytic activity of 2-dodecanone

**Table D1** The product distribution from the conversion of 2-Dodecanone over HZSM-5 at contact time 50 g·h/mol

| Time on stream (min) | 60 | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|---|
| Conversion (%) | 100.00 | 100.00 | 100.00 | 99.45 | 99.29 | 98.93 |
| | | | Yield of Product (%) | | | |
| Ethylene | 3.12 | 2.92 | 2.79 | 2.75 | 2.56 | 2.41 |
| Propylene | 27.55 | 27.41 | 27.08 | 27.37 | 26.37 | 25.68 |
| C4 | 26.02 | 26.05 | 25.93 | 26.16 | 25.79 | 26.06 |
| C5 | 11.05 | 11.58 | 11.40 | 12.80 | 13.08 | 13.82 |
| C6 alkenes | 6.01 | 6.43 | 6.44 | 6.03 | 6.93 | 7.26 |
| C7 alkanes | 0.84 | 0.80 | 0.92 | 0.88 | 0.88 | 0.88 |
| C7 alkenes | 5.55 | 5.92 | 5.97 | 5.83 | 6.07 | 6.17 |
| C7 aromatic | 3.94 | 3.72 | 3.63 | 3.49 | 3.25 | 3.16 |
| C8 alkenes | 1.60 | 1.68 | 1.69 | 1.47 | 1.77 | 1.84 |
| C8 aromatics | 7.31 | 6.88 | 7.03 | 6.31 | 6.26 | 5.84 |
| C9 alkane | 0.67 | 0.65 | 0.67 | 0.55 | 0.61 | 0.52 |
| C9 aromatics | 5.01 | 4.74 | 5.04 | 4.43 | 4.49 | 4.10 |
| C10 aromatics | 1.32 | 1.22 | 1.41 | 1.37 | 1.24 | 1.20 |

*(Reaction conditions: reaction temperature 400°C, at contact time 50 g·h/mol, Feed flow rate 0.6 ml/h, under $N_2$ atmosphere 60 ml/min data collected every 60 mins and up to 6 h, catalyst was activated 550°C for 2h)*

**Table D2** The product distribution from the conversion of 2-Dodecanone over $CeO_2$ (HSA) at contact time 50 g•h/mol

| Time on stream (min) | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|
| Conversion (%) | 57.34 | 55.35 | 30.02 | 25.49 | 27.07 |
| Yield of product (%) | | | | | |
| C8 alkane | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| C9 alkane | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| C9 alkene | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| C10 alkane | 0.04 | 0.01 | 0.01 | 0.01 | 0.01 |
| C10 alkene | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 |
| C12 alkane | 0.05 | 0.01 | 0.02 | 0.02 | 0.02 |
| C12 alkene | 0.15 | 0.04 | 0.05 | 0.05 | 0.06 |
| C13 alkene | 0.06 | 0.02 | 0.01 | 0.02 | 0.01 |
| C8 ketone | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| C10 ketone | 0.12 | 0.05 | 0.04 | 0.05 | 0.05 |
| C11 ketone | 0.34 | 0.12 | 0.12 | 0.16 | 0.14 |
| C12 ketone | 0.07 | 0.02 | 0.02 | 0.03 | 0.02 |
| C13 ketone | 0.25 | 0.10 | 0.08 | 0.08 | 0.08 |
| C15 ketone | 1.00 | 0.55 | 0.34 | 0.31 | 0.25 |
| C17 ketone | 4.42 | 1.04 | 0.64 | 0.61 | 0.77 |
| C19 ketone | 0.94 | 0.30 | 0.18 | 0.17 | 0.19 |
| C21 ketone | 0.99 | 13.01 | 5.76 | 5.06 | 5.88 |
| C24 ketone | 33.02 | 23.66 | 10.76 | 10.32 | 10.31 |
| C24 dihydrofuran | 15.60 | 16.36 | 11.97 | 8.59 | 9.24 |
| Alcohol | 0.22 | 0.02 | 0.02 | 0.02 | 0.02 |

*(Reaction conditions: reaction temperature 400°C, at contact time 50 g·h/mol , Feed flow rate 0.6 ml/h, under $N_2$ atmosphere 60 ml/min data collected every 60 mins and up to 6 h, catalyst was activated 450°C for 2h and reduced 450°C for 2h)*

**Table D3** The product distribution from the conversion of 2-Dodecanone over $CeO_2$ (com) at contact time 50 g·h/mol

| Time on stream (min) | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|
| Conversion (%) | 2.18 | 2.91 | 3.16 | 1.36 | 0.98 |
| Yield of product (%) | | | | | |
| C12 alkane | 0.01 | 0.02 | 0.01 | 0.02 | 0.03 |
| C12 alkene | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 |
| C10 ketone | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C11 ketone | 0.08 | 0.09 | 0.06 | 0.07 | 0.08 |
| C12 ketone | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 |
| C13 ketone | 0.03 | 0.06 | 0.05 | 0.06 | 0.07 |
| C15 ketone | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 |
| C17 ketone | 0.03 | 0.04 | 0.03 | 0.03 | 0.08 |
| C19 ketone | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 |
| C21 ketone | 0.38 | 0.29 | 0.21 | 0.10 | 0.12 |
| C24 ketone | 0.83 | 1.16 | 1.38 | 0.47 | 0.27 |
| C24 dihydrofuran | 0.71 | 1.12 | 1.32 | 0.52 | 0.23 |
| Alcohol | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 |

*(Reaction conditions: reaction temperature 400°C, at contact time 50 g·h/mol , Feed flow rate 0.6 ml/h, under $N_2$ atmosphere 60 ml/min data collected every 60 mins and up to 6 h, catalyst was activated 450°C for 2h and reduced 450°C for 2h)*

**Table D4** The product distribution from the conversion of 2-Dodecanone over $Al_2O_3$ at contact time 50 g•h/mol

| Time on stream (min) | 60 | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|---|
| Conversion (%) | 6.73 | 4.20 | 3.10 | 2.80 | 2.96 | 2.37 |
| | | | Yield of Product (%) | | | |
| C8 alkane | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 |
| C8 alkene | 0.04 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| C9 alkane | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 |
| C9 alkene | 0.13 | 0.07 | 0.05 | 0.04 | 0.03 | 0.03 |
| C10 alkane | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C10 alkenes | 0.08 | 0.05 | 0.04 | 0.03 | 0.03 | 0.03 |
| C11 alkene | 0.06 | 0.03 | 0.02 | 0.02 | 0.02 | 0.01 |
| C12 alkane | 0.56 | 0.33 | 0.22 | 0.20 | 0.20 | 0.16 |
| C12 alkenes | 4.03 | 2.40 | 1.66 | 1.49 | 1.45 | 1.18 |
| C13 alkenes | 0.13 | 0.08 | 0.05 | 0.05 | 0.06 | 0.05 |
| C3 ketone | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 |
| C8 ketone | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 |
| C9 ketone | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C10 ketone | 0.04 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 |
| C11 ketone | 1.08 | 0.78 | 0.62 | 0.53 | 0.71 | 0.48 |
| C12 ketone | 0.13 | 0.09 | 0.09 | 0.07 | 0.09 | 0.08 |
| C13 ketone | 0.07 | 0.04 | 0.05 | 0.05 | 0.05 | 0.05 |

*(Reaction conditions: reaction temperature 400°C, at contact time 50 g·h/mol , Feed flow rate 0.6 ml/h, under $N_2$ atmosphere 60 ml/min data collected every 60 mins and up to 6 h, catalyst was activated 550°C for 2h)*

**Table D5** The product distribution from the conversion of 2-Dodecanone over $SiO_2$ at contact time 50 g•h/mol

| Time on stream (min) | 60 | 120 | 180 | 240 | 300 |
|---|---|---|---|---|---|
| Conversion (%) | 4.55 | 2.83 | 1.33 | 1.38 | 1.20 |
| **Yield of product (%)** | | | | | |
| C12 alkane | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| C12 alkene | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C11 ketone | 0.07 | 0.06 | 0.06 | 0.05 | 0.05 |
| C12 ketone | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| C13 ketone | 0.07 | 0.12 | 0.11 | 0.10 | 0.09 |
| C17 ketone | 0.02 | 0.07 | 0.03 | 0.03 | 0.02 |
| C19 ketone | 0.08 | 0.19 | 0.09 | 0.11 | 0.11 |
| C21 ketone | 2.96 | 1.40 | 0.42 | 0.29 | 0.20 |
| C24 ketone | 0.63 | 0.48 | 0.21 | 0.33 | 0.31 |
| C24 furan | 0.63 | 2.31 | 0.97 | 1.00 | 0.85 |
| Alcohol | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 |

*(Reaction conditions: reaction temperature 400°C, at contact time 50 g·h/mol , Feed flow rate 0.6 ml/h, under $N_2$ atmosphere 60 ml/min data collected every 60 mins and up to 6 h, catalyst was activated 550°C for 2h)*

**Table D6** The product distribution from the conversion of dodecane over HZSM-5 (Si/Al 180) at contact time 50 g·h/mol

| Time on stream (min) | Conversion (%) | Yield of product (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Ethylene | Propylene | C4 | C5 | C6 alkane | C7 alkane | C8 alkane |
| 60 | 50.50 | 0.74 | 16.26 | 19.53 | 9.95 | 1.60 | 1.36 | 1.07 |
| 120 | 46.45 | 0.69 | 14.79 | 18.64 | 8.71 | 1.44 | 1.22 | 0.96 |
| 180 | 47.11 | 0.71 | 14.94 | 18.88 | 8.86 | 1.47 | 1.28 | 0.98 |
| 240 | 46.33 | 0.74 | 16.05 | 16.13 | 9.48 | 1.57 | 1.34 | 1.02 |
| 300 | 44.06 | 0.66 | 14.03 | 17.49 | 8.26 | 1.40 | 1.24 | 1.00 |
| 360 | 47.53 | 0.71 | 15.09 | 18.93 | 8.92 | 1.51 | 1.32 | 1.06 |

*(Reaction conditions: reaction temperature 400°C, under $N_2$ atmosphere 60 ml/min, Feed flow rate 0.6 ml/h, data collected every 60 mins and up to 6 h, catalyst was activated 550°C for 2h)*

**Table D7** The product distribution from the conversion of dodecane over HZSM-5 (Si/Al 180) at contact time 100 g·h/mol

| Time on stream (min) | Conversion (%) | Yield of product (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Ethylene | Propylene | C4 | C5 | C6 alkane | C7 alkane | C8 alkane |
| 60 | 61.36 | 1.35 | 21.57 | 25.34 | 8.55 | 1.75 | 1.58 | 1.22 |
| 120 | 66.31 | 1.46 | 23.30 | 27.01 | 9.39 | 1.95 | 1.81 | 1.38 |
| 180 | 60.73 | 1.33 | 21.47 | 24.58 | 8.46 | 1.81 | 1.73 | 1.35 |
| 240 | 70.14 | 1.56 | 24.89 | 28.35 | 9.74 | 2.11 | 1.94 | 1.55 |
| 300 | 71.97 | 1.58 | 25.38 | 29.19 | 10.07 | 2.16 | 2.04 | 1.54 |
| 360 | 71.61 | 1.56 | 25.24 | 29.00 | 10.05 | 2.17 | 2.03 | 1.56 |

*(Reaction conditions: reaction temperature 400°C, under $N_2$ atmosphere 60 ml/min, Feed flow rate 0.6 ml/h, data collected every 60 mins and up to 6 h, catalyst was activated 550°C for 2h)*

**Table D8** The product distribution from the conversion of dodecane over HZSM-5 (Si/Al 180) at contact time 200 g·h/mol

| Time on stream (min) | Conversion (%) | Yield of product (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Ethylene | Propylene | C4 | C5 | C6 alkane | C7 alkane | C8 alkane |
| 60 | 95.73 | 3.41 | 35.30 | 38.47 | 12.53 | 2.44 | 2.12 | 1.46 |
| 120 | 95.10 | 3.43 | 35.50 | 38.56 | 11.49 | 2.45 | 2.15 | 1.53 |
| 180 | 94.36 | 3.44 | 35.40 | 37.63 | 11.40 | 2.57 | 2.27 | 1.65 |
| 240 | 93.73 | 3.42 | 35.66 | 37.20 | 11.01 | 2.58 | 2.23 | 1.64 |
| 300 | 92.34 | 3.33 | 35.24 | 36.19 | 10.85 | 2.62 | 2.35 | 1.75 |
| 360 | 92.37 | 3.37 | 35.64 | 36.45 | 9.98 | 2.63 | 2.51 | 1.78 |

*(Reaction conditions: reaction temperature 400°C, under $N_2$ atmosphere 60 ml/min, Feed flow rate 0.6 ml/h, data collected every 60 mins and up to 6 h, catalyst was activated 550°C for 2h)*

**Table D9** The product distribution from the conversion of 2-Dodecanone over $CeO_2$ (HSA) at contact time 400 g•h/mol

| Time on stream (min) | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|
| Conversion (%) | 67.84 | 74.10 | 64.40 | 74.12 | 71.18 |
| Yield of product (%) | | | | | |
| C8 alkane | 0.03 | 0.02 | 0.02 | 0.02 | 0.01 |
| C9 alkane | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| C9 alkene | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| C10 alkane | 0.06 | 0.04 | 0.03 | 0.03 | 0.03 |
| C10 alkene | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 |
| C12 alkane | 0.10 | 0.07 | 0.06 | 0.08 | 0.06 |
| C12 alkene | 0.21 | 0.18 | 0.14 | 0.18 | 0.13 |
| C13 alkene | 0.07 | 0.06 | 0.04 | 0.04 | 0.03 |
| C8 ketone | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 |
| C9 ketone | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C10 ketone | 0.18 | 0.14 | 0.12 | 0.14 | 0.10 |
| C11 ketone | 0.21 | 0.17 | 0.15 | 0.16 | 0.13 |
| C12 ketone | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| C13 ketone | 0.23 | 0.15 | 0.13 | 0.11 | 0.13 |
| C15 ketone | 1.90 | 1.15 | 1.12 | 1.15 | 1.40 |
| C17 ketone | 5.74 | 5.02 | 4.85 | 4.74 | 3.44 |
| C19 ketone | 0.43 | 0.39 | 0.32 | 0.33 | 0.23 |
| C21 ketone | 38.34 | 38.99 | 32.01 | 34.86 | 28.89 |
| C24 ketone | 17.53 | 22.70 | 20.55 | 25.49 | 28.52 |
| C24 dihydrofuran | 2.63 | 4.88 | 4.73 | 6.70 | 7.96 |
| Alcohol | 0.06 | 0.05 | 0.04 | 0.02 | 0.03 |

*(Reaction conditions: reaction temperature 400°C, under $N_2$ atmosphere 60 ml/min, Feed flow rate 0.6 ml/h, data collected every 60 mins and up to 6 h, catalyst was activated 450°C for 2h and reduced 450°C for 2h)*

**Table D10** The product distribution from the conversion of 2-Dodecanone over $CeO_2$ (HSA) at contact time 800 g•h/mol

| Time on stream (min) | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|
| Conversion (%) | 77.17 | 81.57 | 81.26 | 74.66 | 77.22 |
| Yield of product (%) | | | | | |
| C8 alkane | 0.05 | 0.04 | 0.03 | 0.03 | 0.02 |
| C8 alkene | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C9 alkane | 0.03 | 0.03 | 0.02 | 0.02 | 0.01 |
| C9 alkene | 0.04 | 0.03 | 0.03 | 0.03 | 0.02 |
| C10 alkane | 0.11 | 0.08 | 0.06 | 0.06 | 0.05 |
| C10 alkene | 0.04 | 0.03 | 0.03 | 0.02 | 0.02 |
| C11 alkane | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 |
| C12 alkane | 0.25 | 0.16 | 0.14 | 0.13 | 0.12 |
| C12 alkene | 0.50 | 0.34 | 0.29 | 0.29 | 0.26 |
| C13 alkene | 0.21 | 0.13 | 0.07 | 0.10 | 0.10 |
| C8 ketone | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| C9 ketone | 0.04 | 0.02 | 0.02 | 0.02 | 0.02 |
| C10 ketone | 0.50 | 0.34 | 0.30 | 0.30 | 0.25 |
| C11 ketone | 0.56 | 0.34 | 0.28 | 0.26 | 0.27 |
| C12 ketone | 0.07 | 0.02 | 0.02 | 0.02 | 0.03 |
| C13 ketone | 0.59 | 0.38 | 0.34 | 0.33 | 0.18 |
| C15 ketone | 4.56 | 3.90 | 3.26 | 1.38 | 2.53 |
| C17 ketone | 15.44 | 12.09 | 8.75 | 7.92 | 7.77 |
| C19 ketone | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| C21 ketone | 44.79 | 49.39 | 49.09 | 44.54 | 45.45 |
| C24 ketone | 8.81 | 12.66 | 16.21 | 16.28 | 16.70 |
| C24 dihydrofuran | 0.31 | 1.39 | 2.16 | 2.72 | 3.27 |
| Alcohol | 0.14 | 0.09 | 0.07 | 0.11 | 0.07 |

*(Reaction conditions: reaction temperature 400°C, under $N_2$ atmosphere 60 ml/min, Feed flow rate 0.6 ml/h, data collected every 60 mins and up to 6 h, catalyst was activated 450°C for 2h and reduced 450°C for 2h)*