

CHAPTER II

LITERATURE REVIEWS

Studies of the ethanol decomposition process have used a variety of test apparatus and catalysts. The catalysts reported in the literature can be categorized into three groups: metal single crystals, metal oxide or supports, and supported metal.

2.1 Ethanol reaction on metal single crystals

Among metal single crystal catalysts, mechanisms of ethanol decomposition over Pd (111) and Ni (111) have been proposed, as follows:

2.1.1 Mechanism of ethanol decomposition on Pd (111)

The mechanism of ethanol decomposition on Pd (111) single crystal metal catalyst has been studied by Davis and Barteau [2] using high resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) under a standard ultra-high vacuum (1×10^{-10} Torr). They revealed that the reaction proceeded through a decarbonylation pathway. The reaction was initiated by dissociative adsorption of ethanol to adsorbed ethoxy species and hydrogen. The mechanism is demonstrated in Figure 2.1. The adsorbed ethoxy species, which is relatively unstable on the clean Pd (111) surface, then decomposed below -73°C to acetaldehyde and a surface acetyl species. Finally, at temperature above 7°C the acetyl species decomposed to carbon monoxide, hydrogen, and methane. Acetaldehyde desorption was not observed in TPD experiments. This indicated that it was only a surface intermediate. Methane was formed from hydrogenation of surface methyl. The temperature at which methane was detected was about 73°C . A small amount of surface carbon was observed. Davis suggested that it was from the decomposition of the surface methyl which competed with the hydrogenation.

2.1.2 Mechanism of ethanol decomposition on Ni (111)

The reaction on a Ni (111) single metal crystal catalyst has been studied by Gates and coworkers [3] using scanning kinetic spectroscopy (SKS), temperature programmed desorption (TPD), and auger electron spectroscopy (AES). The proposed sequence of bond breaking is shown in Figure 2.2. The first step is the breaking of the O-H bond to form an adsorbed ethoxy and hydrogen. The second step is the dehydrogenation of the methylene group (-CH₂-), followed by the carbon-carbon bond breaking, and dehydrogenation of the methyl group (-CH₃). The mechanism proposed is illustrated in Figure 2.3. The products observed were acetaldehyde, hydrogen, methane, carbon monoxide, and surface carbon whose formation was similar to that on Pd (111).

The mechanism was confirmed by using infrared absorption spectroscopy (IRAS), x-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Xu and coworkers [4] reported that ethanol decomposition on Ni (111) originated with O-H bond cleavage of adsorbed ethanol to form an ethoxy group in the temperature range between -108 to -73°C. This occurred while the O-H bond was almost parallel to the surface and caused the O-H stretching mode in IRAS spectra to disappear during the dissociative adsorption. In addition, during the decomposition of ethanol to the surface ethoxy group, the methyl group in the ethoxy species oriented itself to have a C-H bond nearly parallel to the Ni (111) surface before cleaving to form acetaldehyde. Then carbon-carbon bond breaking occurred. In the presence of hydrogen, methane was formed and desorbed. However, this reaction competed with the decomposition of methane to form surface carbon, which decreased surface activity. The formation of diethyl ether and ethylene were not reported.

The mechanism of ethanol dehydration on active sites has been studied by Shinohara and coworkers [5]. The mechanism is demonstrated in Figure 2.4. The surface hydrogen (H_S) and active sites (*) were proposed to interact concertedly with the oxygen (O_E) and H_B of ethanol, respectively, and ethylene and water are formed.

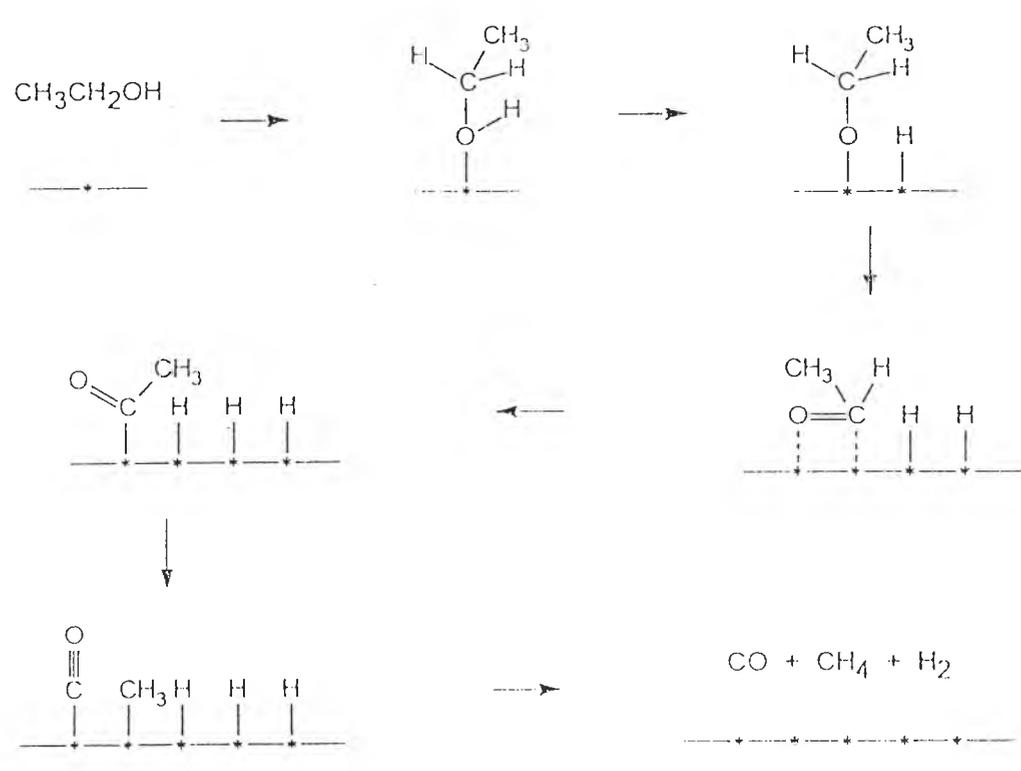


Figure 2.1 Mechanism of ethanol decomposition over Pd (111).

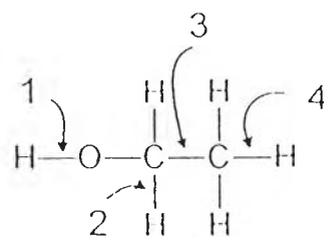


Figure 2.2 The sequence of ethanol bond breaking on Ni (111).

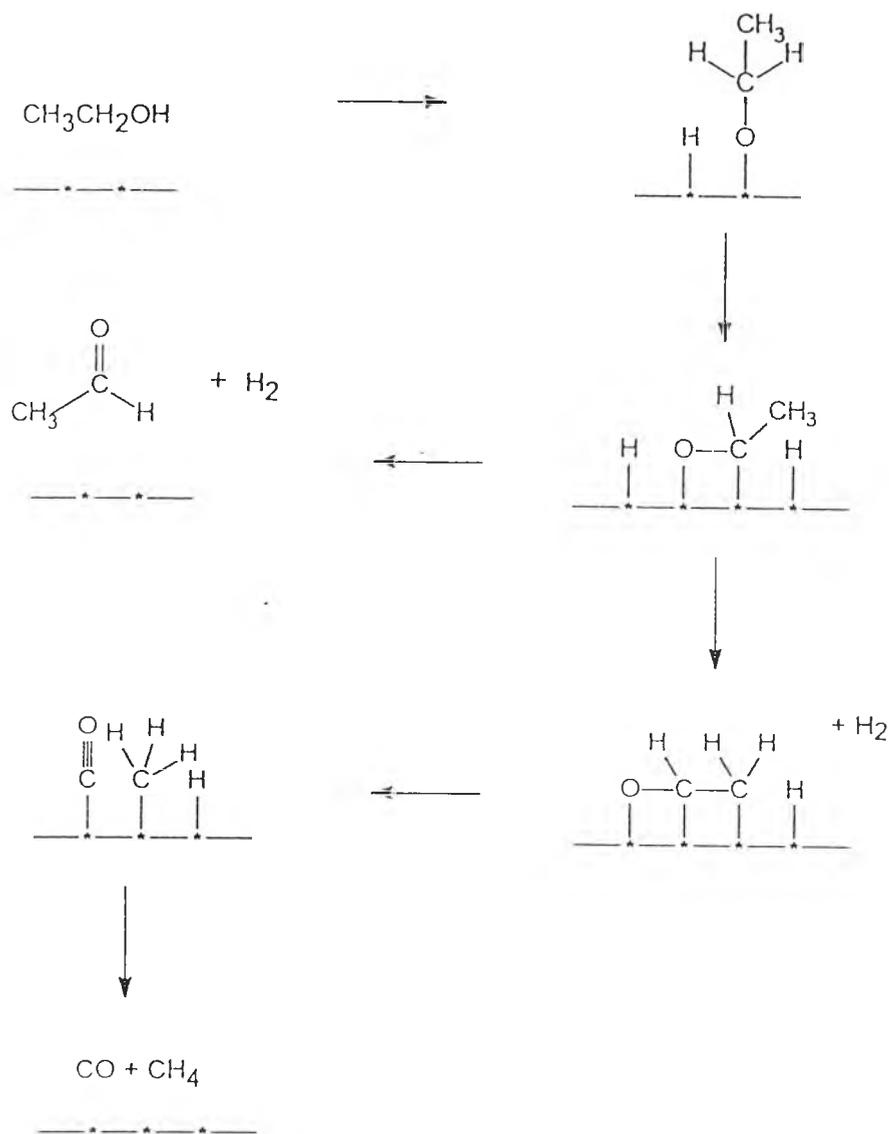


Figure 2.3 Mechanism of ethanol decomposition over Ni (111).

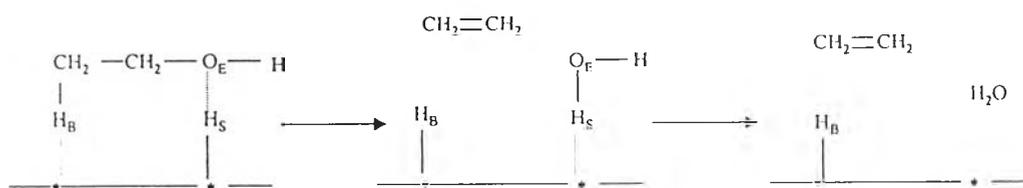


Figure 2.4 Mechanism of ethanol dehydration on active sites.

2.2 Ethanol reaction on metal oxide supported

Two metal oxide supports will be discussed in this section, Al_2O_3 (alumina) and SiO_2 (silica). These two supports have been widely used as catalytic supported due to their high mechanical strength, thermal stability, and high surface area. Active sites and reactivity on both supports are discussed.

2.2.1 Ethanol reaction on alumina

Diddams [6] reported that ethanol reaction could be performed on alumina. Hydrated alumina was activated by calcination at 500°C . Activated alumina was amphoteric, containing both acidic and basic sites as illustrated in Figure 2.5. These sites are active for the dissociative adsorption of ethanol. By using infrared spectroscopy to study ethanol decomposition on alumina, it was reported by Soma and coworkers [7] that in the temperature range of $120\text{--}180^\circ\text{C}$, ethanol dissociatively adsorbs as ethoxy groups and surface hydrogen. Then the surface ethoxy reacts through one of the two pathways as shown in Figure 2.6. The first pathway, which occurs above 220°C , involves the formation of diethyl ether and water from two ethoxy groups, since the adsorbed species can migrate all over the surface. This is substantiated by the fact that diethyl ether dissociatively adsorbs as surface ethoxy groups. Above 180°C , the reaction products were only ethylene and water from the reaction between the adsorbed ethoxy species and surface hydroxyl. The overall process is referred to as ethanol dehydrogenation. The rate of decomposition is independent of ethanol pressure, i.e., it is zero order in the ethanol.

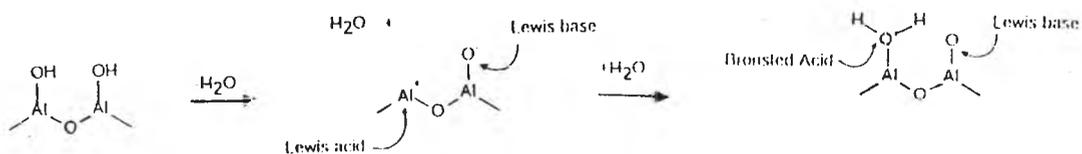


Figure 2.5 Basic and acidic sites on alumina.

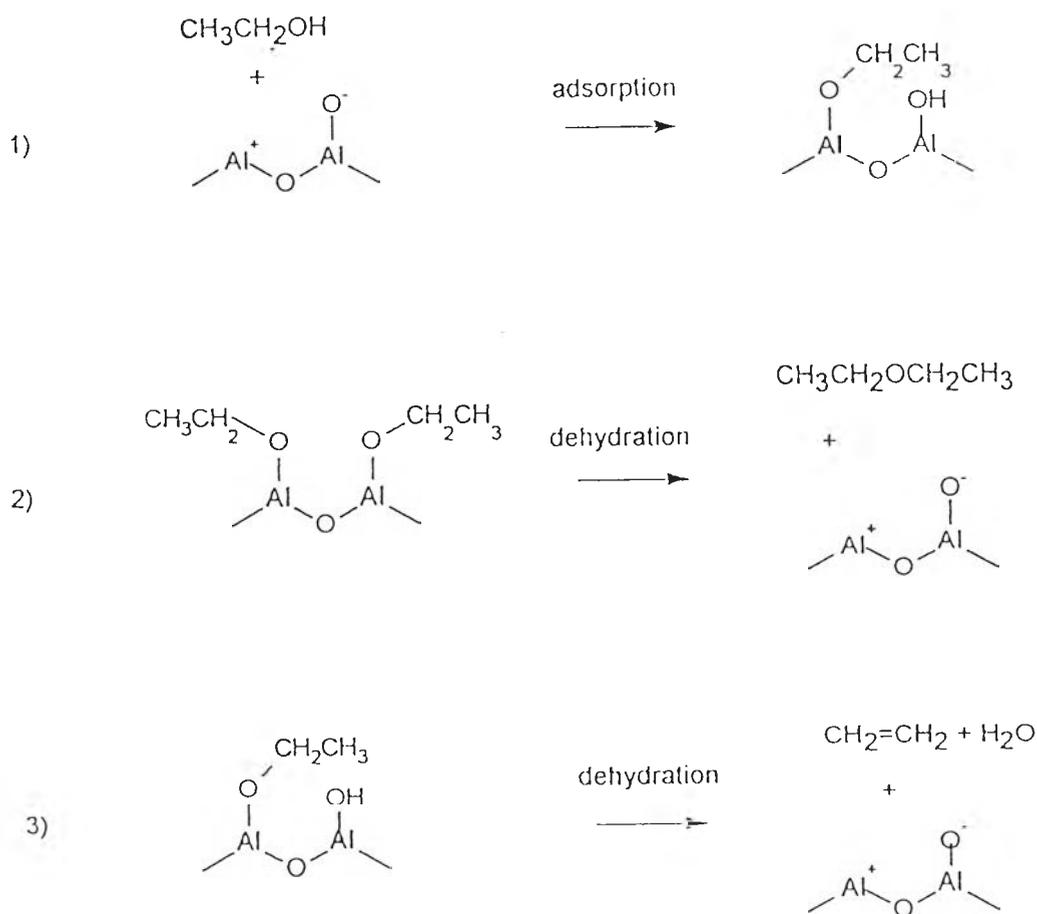


Figure 2.6 Ethanol reaction on alumina.

2.2.2 Ethanol reaction on silica

Diddams [6] reported that ethanol reaction could be performed on silica. The surface of amorphous silica consists of siloxane (Si-O-Si) and silanol (Si-OH) groups. In Figure 2.7, silanol groups are identified as a weak Brønsted acid. From the study of hydrogen bonding of ethanol on silica by Metcalfe and Shankar [8], alcohols such as ethanol can adsorb by two different pathways as illustrated in Figure 2.8. An esterification of surface hydroxyl groups occurs at high temperature was studied by Jeziorowski and coworkers [9] while a surface alkylation taking place through opening of strained siloxane bonds occurs at low temperature and may be completed at room temperature.

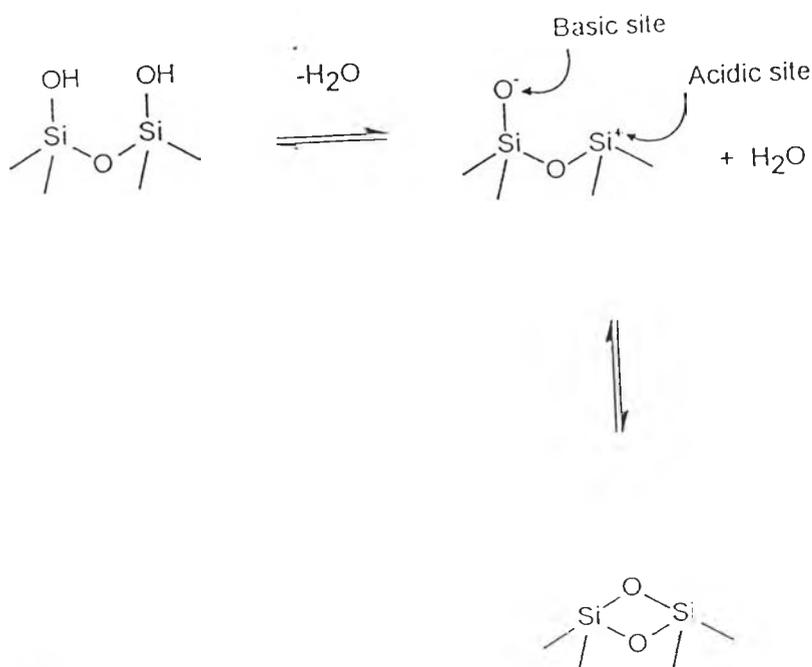


Figure 2.7 Basic and acidic sites on silica.

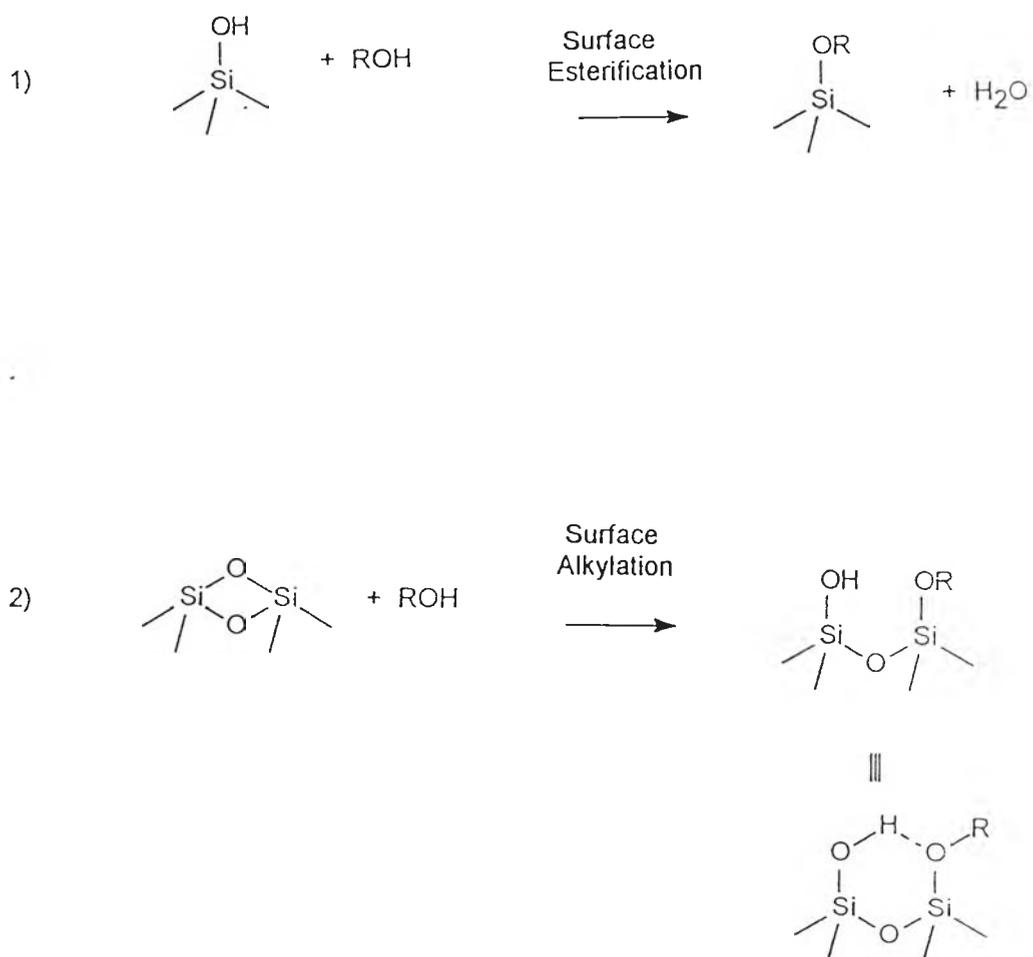


Figure 2.8 Alcohol adsorption on silica.

2.3 Ethanol reaction on supported metal

The ethanol decomposition discussed below was studied on two catalysts, zinc oxide-supported palladium and alumina-supported palladium.

2.3.1 Ethanol reaction on zinc oxide-supported palladium (Pd/ZnO)

On Pd/ZnO, Mokawa and coworkers [10] revealed that ethanol decomposition was observed through two reaction pathways: dehydrogenation to acetaldehyde and hydrogen written in equation 2.1 and dehydration to ethylene and water written in equation 2.2.



These reactions were similar to that observed on the ZnO surface [11]. However, at a higher coverage of Pd, acetaldehyde decomposes to carbon monoxide and methane as shown in equation 2.3. This reaction was dominant over reaction 2.1 and 2.2.

2.3.2 Ethanol reaction on alumina-supported palladium (Pd/Al₂O₃)

For palladium on alumina, the reaction was studied by Davisson and coworkers [12]. It was conducted as steady-state flow experiments in a Bertly reactor at 180-230°C. This temperature range was selected because the dehydration of ethanol on alumina was negligible below 230°C. It was reported that ethanol decomposition was a two-step reaction. The first step is ethanol dehydrogenation to acetaldehyde and hydrogen (equation 2.1) and second step is acetaldehyde decomposition (equation 2.3). The main products are hydrogen, methane, and carbon monoxide with a trace of acetaldehyde, ethylene, diethyl ether and carbon dioxide. Carbon dioxide was attributed to the reaction between carbon monoxide and water

(equation 2.4). This reaction is referred to as the water-gas shift or steam reforming reaction.



2.4 Lanthana-modified supported

Acidic sites in solid support promote the dehydration reaction. In order to reduce the acidity of support, the support should be coated by a basic material. Lanthanum oxide (La_2O_3 or Lanthana) has been reported as a good candidate [13].

2.4.1 Lanthana modified silica and ceria supported

Catalytic behavior and surface properties of supported lanthana have been studied by Castiglioni and coworkers [13] using thermogravimetric analysis (TGA), mass spectrometry (MS), x-ray diffraction (XRD), and high resolution electron microscopy (HREM). They deal with the role of dispersed lanthana as an active phase in several catalytic reaction: CO hydrogenation, CO oxidation, and oxidative dimerization of methane. Characterization of the prepared catalysts indicates that lanthana can be effectively dispersed on silica and ceria. While in the case of silica-supported catalysts lanthana appears at the surface, leading to an almost full coverage for loading higher than 40%, in the case of ceria-based systems, lanthana forms a solid solution with the support. The results of CO hydrogenation reaction indicate that the addition of lanthana improves the catalytic properties of the bare silica and ceria supports. For $\text{La}_2\text{O}_3\text{-SiO}_2$, the conversion towards hydrocarbons increased with La_2O_3 loading. For $\text{La}_2\text{O}_3\text{-CeO}_2$, the selectivity towards branched C_4 compounds is also increased. Results from the CO oxidation reaction indicate that La_2O_3 leads to an increase in the oxidative properties of SiO_2 and to decrease in the oxidative properties of CeO_2 . The catalytic results for the $\text{CH}_4 + \text{O}_2$ reaction indicate that the addition of lanthana to both silica and ceria supports increase in the activities towards CH_4 dimerization products.

2.4.2 Lanthana modified alumina supported

The Lanthana-modified alumina supported has been studied by Bernard and coworkers [14] by using BET, x-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive x-ray (EDX). They disclosed that the addition of lanthana content or an atomic ratio of lanthana-to-alumina showed the effects of a stabilization of alumina towards thermal sintering, and phase transfer catalysts. With the addition of low lanthana contents, it behaved better thermal stability below 1050°C. In contrast, with an atomic ratio of lanthanum-to-alumina close to 0.01 did not prevent the formation of α -Al₂O₃ associated with a drastic loss of specific area. By increasing the lanthanum-to-alumina ratio until a value of 0.05, thermal stability toward sintering was observed even at 1220°C. The positive effect of lanthanum was assigned to the formation of microdomains of lanthanum aluminate on the alumina surface. In the perovskite structure, aluminium ions were stabilized in octahedral coordination. Lanthanum ions must be presented at a sufficient concentration to ensure the complete LaAlO₃ formation from the more reactive surface aluminium ions. The formation of the La₂O₃, 11Al₂O₃ phase (lanthanum β Al₂O₃) observed at high temperature was associated with the loss of the stabilizing effect. This phase might be formed by a solid state reaction between Al₂O₃ and LaAlO₃.

Hiromichi and Masato [15] studied thermal stabilization of supported catalysts for development of high-temperature combustion catalyst. By the addition of BaO, La₂O₃, SiO₂, Li₂O or K₂O, their results showed that large surface area of alumina was retained because the additive cations occupied the surface site or bulk sites, prevented atomic diffusion (surface diffusion and bulk diffusion) which brought the α phase transformation. Lanthanum is most widely investigated as a stabilizer of transition alumina. The study of this matter was dosed on alumina originally surface area ca. 200m²/g. After the calcination at 1100°C, for instance, the surface area of 5 mole % La₂O₃/Al₂O₃ was ca. 50 m²/g, whereas that of net alumina was less than 10 m²/g. They attributed the surface area loss to the sintering of transition alumina by surface diffusion, which was retarded by the formation of surface lanthanum aluminate. The

thermal stability of alumina was assumed to be related to the strong interaction resulting from coherency.

2.5 Catalyst deactivation by coking

An important feature of the catalytic reforming is that the catalysts deactivate in the course of the process. The main cause of that deactivation is the deposition of coke on the active sites of metal and the support, producing a lowering of the activity and change in selectivity [16,17].

2.5.1 Deactivation by coking of supported palladium catalysts

Marecot and coworkers [18,19] studied deactivation by coking of supported palladium. The coking reaction with cyclopentane was investigated on silica supported palladium catalysts in the temperature range 400–500°C at various times. After reaction, the catalysts were characterized by temperature programmed oxidation by the fouling effect of coke on the reaction of cyclohexane dehydrogenation and by infrared spectroscopy of chemisorbed CO. The results obtained by TPO and by infrared spectroscopy of chemisorbed CO bears out that the TPO peak at ca. 250°C would correspond to the coke deposited on the (111) planes whereas the peak at ca. 400°C would involve palladium atoms of lower coordination number like corners, edges or Pd(100) planes. As for the peaks at ca. 550°C, it corresponds to the coke on the support. These palladium atoms of low coordination number are more resistant to coke deposition than palladium atoms of high coordination number which are strongly poisoned by carbon deposits whatever the temperature or the time of the coking reaction. However, an increasing time on temperature of reaction enhances the deposition of coke on the low coordinated palladium atoms and therefore, their deactivation.

2.6 Comment on previous works

According to the above review ethanol decomposition on single crystal metal has been successfully studied over Pd(111) and Ni(111) and reasonable mechanisms on these catalysts have been proposed. However, those were done under an ultra-high vacuum, which is not practical in industry. To decrease energy consumption and increase practicability, the reaction was conducted at atmospheric pressure. To increase the metal surface area, palladium is deposited on a solid supported. Silica was considered to be the best candidate for a solid support because it is thermally stable, porous, and inert. However, it contains acidic sites which promote the dehydration reaction. In order to reduce the support acidity, the support was coated with a basic material. Lanthanum oxide (La_2O_3 or lanthana) has been reported as a good candidate. However, there has been no report about using metal deposited on lanthana-modified supported in ethanol decomposition reaction. Hence, to investigate the effect of lanthana on catalytic activity of lanthana-modified Pd/SiO₂ for ethanol decomposition is the aim of the study.