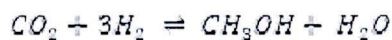


CHAPTER III

THEORY

3.1 CO₂ Hydrogenation Reactions

In recently, several reaction mechanisms for the CO₂ hydrogenation have been proposed. First, the catalytic hydrogenation over promoted Cu-ZnO catalysts under pressurized conditions produces mainly CH₃OH, CO and H₂O. A small amount of CH₄ was produced. At higher temperature, a very small amount of CH₃OCH₃ was also produced. Therefore, main reactions are shown in the following equations [Arakawa et al., 1992].



An in situ F-IR observation of surface species over 5 wt% Cu-ZnO/SiO₂ as model catalyst showed the presence of bidentate carbonate species on both Cu and ZnO at the condition of 3MPa, 30°C and 100 ml/min. Also a small amount of adsorbed CO on Cu site was observed. These bidentate carbonate species were rapidly transformed to the bidentate formate species with the increase of reaction temperature up to 150°C under 3 MPa. However, a small amount of adsorbed CO species has diminished at 100°C and it was never observed under the reaction conditions. The experimental dynamic in situ FT-IR spectra of adsorbed species over the catalyst at various reaction conditions, this observation also suggests the direct formation of CH₃OH from CO₂ via bidentate carbonate species, formate species and methoxy species as shown in Figure.

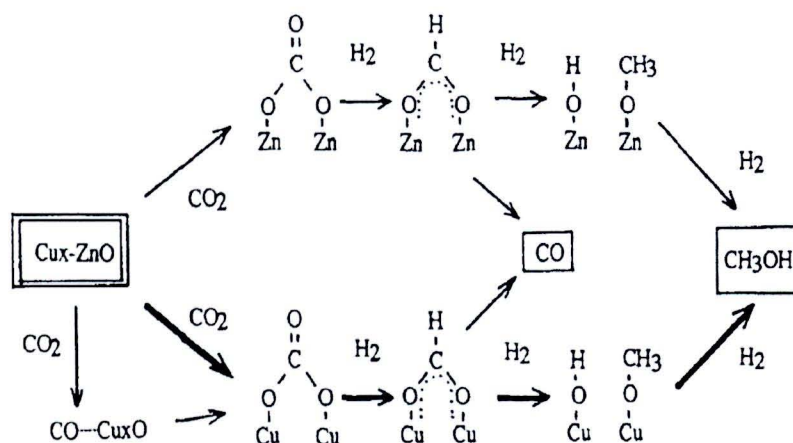


Figure 3.1 Reaction mechanisms for CH_3OH formation from H_2/CO_2 over Cu-ZnO/SiO_2 catalyst [Arakawa et al., 1992].

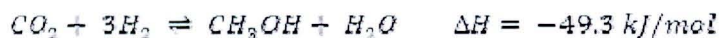
The fibrous Cu/Zn/Al/Zr catalyst showed high activity for producing methanol from CO_2 hydrogenation [Xin et al., 2009]. Thus, there are three independent reactions present in methanol synthesis from CO_2 , namely Methanol synthesis from CO :



Reverse water gas shift:



Methanol synthesis from CO_2 :



3.2 Silica dioxide

In its many forms, silica has been used in all stages of civilization, from the ancient flints of the Stone Age to the modern silica laboratory ware. Because of its many uses, and of the many varied forms in which it occurs, silica has been called by more name than any other mineral. Many of the older names of flints are now so obsolete that repetition is needless, but many of the present-day names for quartz gems are unknown save to a few jewelers. Then, the exact research of the modern laboratory has shown

several distinct crystallographic varieties of silica; some of which are closely connected with the temperature experienced in their life-history.

Table 3.1 Physical properties of silica

Other name	Silica
Molecular formula	SiO ₂
Molar mass	60.0843 g/mol
Appearance	White powder
Density	2.643 g/cm ³
Melting point	1650(±75) °C
Boiling point	2230 °C
Solubility in water	0.012 g/ 100mL



The many different names, and their different connotations, which are now in use for silica minerals, call for a classification and arrangement in a more ample, yet more concise manner than is to be found in the usual discussion of the varieties of silica. This article is written with the hope of making a scientific classification of these names, so that the use of the different terms will no longer be a cause for tedious searching for definitions.

These varieties are named in the order formed with descending temperature. Recrystallization changes occur at the temperature noted when ample time is allowed for the action, often in the laboratory only in the presence of catalysts. Besides the changes at these critical temperatures, there are probably similar changes from unstable forms towards quartz at atmospheric temperature, especially after long time intervals. With fairly rapid cooling or heating intermediate forms may not occur in their stable zone, but a direct change from one to another without the intermediate product may take place.



Most of the recrystallization changes noted is found to occur at ascending and descending temperatures.

(A) SILICA GLASS – amorphous, a true non-crystalline glass, stable below the melting point and above the “gc” temperature. Quartz Glass Fused Silica, fused Quartz, are the other names for this supercooled liquid. In most forms at atmospheric temperature there are traces of cristobalite.

(B) CRISTOBALITE – isomeric, or pseudo-isometric, “gc” range is at 1710°C where cristobalite changes to glass as temperature rise or glass to cristobalite as they fall. Cristobalite, an alternate spelling, Beta Cristobalite, also called High Cristobalite, is the high temperature product, forming in the “gc” range in cooling. It is isometric, and in cooling recrystallizes to Alpha Cristobalite, or Low Cristobalite, at 200-275°, providing cooling through the “ct” and “tq” ranges has been too rapid for recrystallization. It is tetragonal.

(C) TRIDYMITE – hexagonal, bipyramidal. “ct” range is at 1470°, where cristobalite changes to tridymite on cooling. Glass may crystallize as tridymite at 1670° if the cooling was too rapid through the “gc” range. Beta Second Tridymite, or Upper High Tridymite, is the high temperature product, forming in the “ct” range in cooling, and which recrystallizes to Beta First Tridymite, also called Lower High Tridymite, at 163° if cooling was too rapid for the “tq” transformation. This in turn alters to Alpha Tridymite, or Low Tridymite, at 117°C, which is the usual tridymite of nature.

- | | | |
|-----------|---|---|
| Asmanite | - | a meteoric tridymite, relate to the above series. |
| Vestan | - | a doubtful silica mineral, probably to be ascribed to tridymite. |
| Granuline | - | a doubtful pulverescent mineral which seems allied to tridymite on optical grounds. |

(D) QUARTZ – hexagonal, forms from tridymite in the “tq” range at 870° in cooling. Glass may change to crystalline quartz at about 1400 ° providing cooling was too rapid for the “gc”, “gt” and “ct” transformations. Beta Quartz, or High Quartz, is the high temperature product, forming at the “tq” point. It is hemihedral. On cooling it recrystallizes to Alpha Quartz, also called Low Quartz, at 573°, yielding the stable low temperature mineral. It is tetartohedral, showing polarity along the c axis and is devisable into Right Hand Quartz and Left Hand quartz

(E) CHALCEDONY – a cryptocrystalline, or very finely fibrous mineral, which has not been successfully located in the thermal equilibrium diagram. Heating to 725-850° usually results in an alteration to tridymite, which thereafter acts as normal tridymite. Chalcedony is usually found as a deposit from solutions, and may be a mixture of glass and quartz, or more probably an intermediate product in the dehydration of the opal colloid. Various subdivisions of chalcedony have been made on optical grounds.

Chalcedony	-	biaxial, positive, elongation positive.
Chalcedonite	-	biaxial, negative.
Lussatite	-	biaxial, positive, parallel, elongation.
Quartzine	-	biaxial, positive, negative, elongation pseudochalcedonite, Lutecite.
Jenzschite	-	differently soluble, but of same S. G. as chalcedony.
Melanophlogite	-	possibly impure chalcedony.
Sulfuricin	-	probably a chalcedony rich in sulphur.

(F) COLLOIDAL SILICA – is usually hydrous, and is commonly described under opal. Silicon occurs in nature combined with oxygen in various forms of silica and silicates. Silicates have complex structures consisting of SiO₄ tetrahedral structural units incorporated to a number of metals. Silicon is never found in nature in free elemental form. Among all elements silicon forms the third largest number of compounds after hydrogen and carbon. There are well over 1000 natural silicates including clay, mica, feldspar, granite, asbestos and hornblende. Such natural silicates have structural units

containing orthosilicates, SiO_4^{4-} , pyrosilicates $\text{Si}_2\text{O}_7^{6-}$ and other complex structural units, such as, $(\text{SiO}_3)_n^{2n-}$ that have hexagonal rings arranged in chains or pyroxene $(\text{SiO}_3^{2-})_n$ and amphiboles, $(\text{Si}_4\text{O}_{11})_n^{6-}$ in infinite chains. Such natural silicates include common minerals such as tremolite, $\text{Ca}_2\text{Mg}_5(\text{OH})_2\text{Si}_8\text{O}_{22}$; diopsid, $\text{CaMg}(\text{SiO}_3)_2$; kaolin, $\text{H}_8\text{Al}_4\text{Si}_4\text{O}_{18}$; montmorillonite, $\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12}$; tale, $\text{Mg}_3[(\text{OH})_2\text{SiO}_{10}]$; muscovite (a colorless form of mica), $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$; hemimorphite, $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$; beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; zircon, ZrSiO_4 ; benitoite, $\text{BaTiSi}_3\text{O}_9$; feldspars, KAlSi_3O_8 ; zeolites, $\text{Na}_2\text{O} \cdot 0.2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$; nephrite, $\text{Ca}(\text{Mg},\text{Fe})_3(\text{SiO}_3)_4$; enstatite, $(\text{MgSiO}_3)_n$; serpentine, $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_{10}$; jadeite, $\text{NaAl}(\text{SiO}_3)_2$; topaz, $\text{Al}_2\text{SiO}_4\text{F}_2$; and tourmaline, $(\text{H}, \text{Li}, \text{K}, \text{Na})\text{Al}_3(\text{BOH})_2\text{SiO}_{19}$. Silica, the other most important class of silicon compounds, exists as sand, quartz, flint, amethyst, agate, opal, jasper and rock crystal.

3.3 Alumina

Alumina which is Al_2O_3 in general form is a polymorphic material. Alumina can be easily synthesized small particles and obtained desirous surface area and pore distribution. Commercial alumina have surface area between 100-600 m^2/g . High porosity solid cause high intra surface area, good metal dispersion and increasable effective of catalytic. There are many forms of alumina (α -, γ -, δ -, η -, κ -, χ -, θ -, ρ -, and ι - Al_2O_3) but the α - Al_2O_3 is the only stable form. The thermodynamically stable phase is alpha alumina (α - Al_2O_3 , corundum) where all Al ions are equivalent in octahedral coordination in a hep oxide array. α - Al_2O_3 (corundum) powders are applied in catalysis as supports, for example, of silver catalysts for ethylene oxidation to ethylene oxide, just because they have low Lewis acidity, low catalytic activity, and conversely, they are mechanically and thermally very strong. All other alumina polymorphs are metastable [Evans, 1993].

The other forms are frequently termed 'transition' aluminas. These transition aluminas are frequently termed 'activated' or 'active' aluminas. ρ - Al_2O_3 is amorphous but the other forms have reasonably well-defined X-ray diffraction patterns. The activated aluminas use as an adsorbent. Even though the surface of an activated alumina

has a strong affinity for water, it makes very effective as a desiccant. Activated alumina can be used for removing water from a very wide range of compounds including acetylene, benzene, alkanes, alkenes and other hydrocarbons, air, ammonia, argon, chlorinated hydrocarbons, chlorine, natural gas and petroleum fuels, oxygen, sulfur dioxide and transformer oils [Evans, 1993].

Activated alumina can dry a gas to water content lower than that achievable with any other commercially available desiccant. In addition to water removal, activated alumina can be used selectively to adsorb certain other chemical species from gaseous or liquid streams. Polar molecules such as fluorides or chlorides are readily adsorbed and so activated alumina is used in petroleum refining to adsorb HCl from reformed hydrogen and organic fluorides from hydrocarbons produced by the HF-alkylation process [Evans, 1993].

Activated aluminas find widespread application as both catalysts in their own right and as catalyst substrates. The more significant applications are summarized as the claus catalyst for the removal of the hydrogen sulfide in natural gas processing, petroleum refining and coal treatment, as alcohol dehydration to give olefins or ethers, as hydrotreating to remove oxygen, sulfur, nitrogen and metal (V and Ni) impurities from petroleum feedstocks and to increase the H/C ratio, as reforming catalysts: Pt and Re catalysts on a γ - Al_2O_3 substrate are used to raise the octane-number of petrol, as automotive exhaust catalysts [Evans, 1993].

Activated alumina has a surface with both Lewis and Bronsted acidic and basic sites. Acidity is derived from the Al^{3+} ions and H_2O molecules coordinated to cationic sites, while basicity is due to basic hydroxide groups and O^{2-} anion vacancies [Evans, 1993].

If alumina contact to humidity, surface are adsorped water molecules and when alumina were dried at 100 °C to 150 °C, water molecules are desorbed but remain hydroxyl group (-OH) cause acidity of alumina are weak Bronsted acid (Figure 3.2).

Calcination temperatures below 300 °C, the acid strength and concentration of alumina are low and at 500 °C reduce Bronsted acid sites [Wittayakhun et al., 2004].

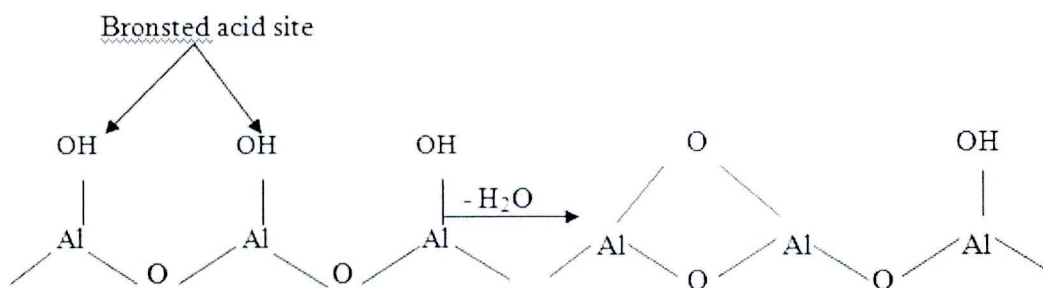


Figure 3.2 Desorption of water from alumina surface [Wittayakhun et al., 2004].

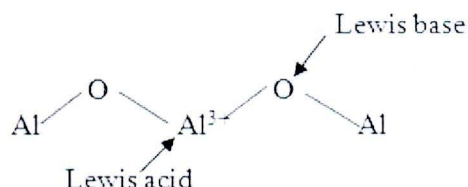


Figure 3.3 Lewis acid and Lewis basic sites on alumina [Wittayakhun et al., 2004].

As shown in Figure 3.3, further increasing temperatures above 600 °C, adjacent –OH combine and more emit H_2O and contribute to Al^{3+} are Lewis acid sites and O^{2-} are Lewis basic sites. Hardness of surface bring about no reaction between Lewis acid and Lewis base which both sites have high activity in various reaction such as Dehydration of alcohol and isomerization of alkene. The decline in acidity for calcination temperatures above 800 °C can be attributed to the collapse in surface area as the alumina is converted to its alpha form [Wittayakhun et al., 2004].

Table 3.2 Physical of aluminium oxide

Other name	Alumina
Molecular formula	Al_2O_3
Molar mass	101.96 g/mol
Appearance	White solid (very hygroscopic)
Density	3.95 – 4.10 g/cm ³
Melting point	2072 °C
Boiling point	2977 °C
Solubility in water	Insoluble
Solubility	Insoluble in diethyl ether practically insoluble in ethanol



The structure of α -alumina consists of close packed planes of the large oxygen ions stacking in A-B-A-B sequence, thus forming hexagonal close packed array of anions. The aluminium cations are located at octahedral sites of this basic array and from another type of close packed planes between the oxygen layers. To maintain neutral charge, however, only two third of the available octahedral sites are filled with cation. Figure 3.4 illustrates the packing of Al and O atom in the basal plane. Since the vacant octahedral sites also from regular hexagonal array, three different types of cation layer can be defined, namely a, b, and c layer, depending on the position of the vacant cation site within the layer. There layers are stacked in a-b-c-a-b-c sequence in the structure of alumina.

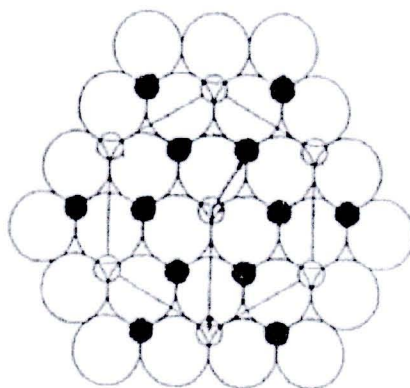


Figure 3.4 Illustration of Al and O atom packing the basal plan.

Alumina can exist in many metastable phase before transforming to the stable α -alumina (corundum form). There are six principle phase designated by The Greek letters chi, kappa, eta, theta, delta and gamma. The nature of the product obtained by calcinations depends on the starting hydroxide (Gibbsite, boehmit and others) and on the calcinations conditions. Normally, transition alumina starts to lose their surface areas even at temperature below 800°C due to the elimination of micro-pores. However, drastic loss occurs at temperature higher than 1000°C when the crystallization to the thermodynamically stable α -alumina occurs.

3.4 Cobalt

3.4.1 General

Cobalt, a transition series metallic element having atomic number 27, is similar to silver in appearance. Cobalt and cobalt compounds have expended from use colorants in glasses and ground coat frits for pottery to drying agents in paints and lacquers, animal and human nutrients, electroplating materials, high temperature alloys, hard facing alloys, high speed tools, magnetic alloys, alloys used for prosthetics and used in radiology. Cobalt is also as a catalyst for hydrocarbon refining from crude oil for the synthesis of heating fuel.

3.4.2 Physical Properties

The electronic structure of cobalt is $[\text{Ar}] 3d^7 4s^2$. At room temperature the crystalline structure of the α (or ϵ) form, is close-packed hexagonal (cph) and lattice parameters are $a = 0.2501 \text{ nm}$ and $c = 0.4066 \text{ nm}$. Above approximately 417°C , a face-centered cubic (fcc) allotrope, the γ (or β) form, having a lattice parameter $a = 0.3544 \text{ nm}$, becomes the stable crystalline form. Physical properties of cobalt are listed in Table 3.3.

The scale formed on unalloyed cobalt during exposure to air or oxygen at high temperature is double-layered. In the range of 300 to 900°C , the scale consists of a thin layer of mixed cobalt oxide, Co_3O_4 , on the outside and cobalt (II) oxide, CoO , layer next to metal. Cobalt (III) oxide, Co_2O_3 , may be formed at temperatures below 300°C . Above 900°C , Co_3O_4 decomposes and both layers, although of different appearance, are composed of CoO only. Scales formed below 600°C and above 750°C appear to be stable to cracking on cooling, whereas those produced at 600 - 750°C crack and flake off the surface.

Cobalt forms numerous compounds and complexes of industrial importance. Cobalt, atomic weight 58.933, is one of the three members of the first transition series of Group 9 (VIIB). There are thirteen known isotopes, but only three are significant, Co is the only stable and naturally occurring isotope, Co has a half-life of 5.3 years and is a common source of γ -radioactivity; and ^{57}Co has a 270-d half-life and provides the γ -source for Mossbauer spectroscopy.

Table 3.3 Physical properties of cobalt

Property	Value
Atomic number	27
Atomic weight	58.93
Transformation temperature, °C	417
Heat of transformation, J/ga	251
Melting point, °C	1493
Latent heat of fusion, ΔHfus J/ga	395
Boiling point, °C	3100
Latent heat of vaporization at bp, ΔHvap kJ/ga	6276
Specific heat, J/(g·°C) ^a	
15-100 °C	0.442
Molten metal	0.560
Coefficient of thermal expansion, °C ⁻¹	12.5
Cph at room temperature	14.2
Fcc at 417 °C	69.16
Thermal neutron absorption, Bohr atom	34.8
Resistivity, at 20 °C, 10 ⁻⁸ Ω·m	6.24
Curie temperature, °C	1121
Saturation induction, 4πIs, T ^c	1.870
Permeability, μ	
Initial	68
Max	245
Residual induction, T ^e	0.490
Coercive force , A/m	708
Young's modulus, Gpac	211

Cobalt exists in the +2 or +3 valance states for the major of its compounds and complexes. A multitude of complexes of the cobalt (III) ion exists, but few stable simple salt are known. Octahedral stereo chemistries are the most common for cobalt (II) ion as well as for cobalt (III). Cobalt (II) forms numerous simple compounds and complexes, most of which are octahedral or tetrahedral in nature; cobalt (II) forms more tetrahedral complex than other transition-metal ions. Because of the small stability difference between octahedral and tetrahedral complexes of cobalt (II), both can be found equilibrium for a number of complexes. Typically, octahedral cobalt (II) salts and complexes are pink to brownish red; most of the tetrahedral Co (II) species are blue.