

CHARTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Methane Dry Reforming

Synthesis gas (syngas), which is a mixture of CO and H₂, is an important feedstock for the chemical industry. The established commercial method employed for synthesis gas production is the steam reforming of methane:



which is achieved by the use of a nickel/ α -Al₂O₃ catalyst at temperatures around 900 °C and at pressures of 15-30 atm (Rostrup-Nielson *et al.*, 1984).

The product mixture can then be introduced to a methanol synthesis reactor. Demand for this process has increased markedly due to the rapid expansion of MTBE (methyl tert-butyl ether) use in the automotive fuel sector. Alternatively, the initial syngas mixture can be further modified with water to enhance the hydrogen concentration by the water-gas shift reaction (Ghiotti *et al.*, 1987).



This latter mixture is then suitable for use in an ammonia synthesis industrial reactor. A critical parameter for subsequent reaction of the synthesis gas is the H₂/CO ratio that must be adjusted close to unity for some syntheses such as the manufacture of oxo-alcohols and acetic acid (Wender *et al.*, 1996).

These latter issues have stimulated research into the formation of synthesis gas by the carbon dioxide reforming of methane (dry reforming). The carbon dioxide reforming of methane, in fact, has been of interest for a long time, dating back to as early as the 1920's (Fischer and Tropsch, 1928), but it is only in recent years that interest in it has rapidly increased for both environmental and commercial reasons. This reaction can be represented as



This process has many desirable advantages over steam reforming (Chubb *et al.*, 1980): (a) Synthesis gas has an H₂/CO ratio of unity without further, post-reformer reactions. (b) The use of CO₂ means that it is an attractive route toward CO₂ mitigation in stationary anthropogenic sources. (c) It allows the conversion of methane, previously a waste component of oil reserves, into an economically attractive feedstock.

This process can also be used as a chemical energy storage and an energy transmission system. Figure 1.1 shows that solar energy is used to drive the endothermic forward reaction, and the energy thus stored can be transported via pipelines such as syngas and liberated at will by the reverse reaction at any location or time. The highly endothermic reaction could be an option to store solar energy in hot regions (Richardson and Paripatyadar, 1990).

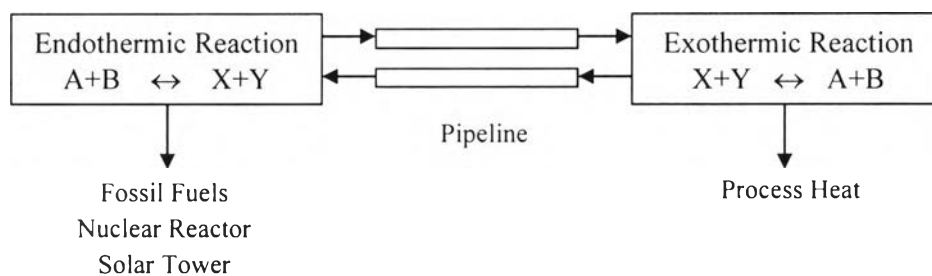


Figure 2.1 Schematic diagram of the chemical energy transmission system (CETS).

The main reaction (1) is accompanied by several secondary processes, of which the reverse water-gas shift reaction appears to be the most important one because of its dependence on the product hydrogen of reaction (1) (Rostrup-Nielsen and Bak Hansen, 1993).

Reverse water-gas shift:



It can be seen that water always formed in the reactions system. The formation of water is reflected by lower hydrogen concentration than CO due to the reverse water-gas shift reaction which is the main water formation route then the amount of CO is always higher than that of hydrogen.

Moreover, depending on the reaction conditions and on the composition of feed gas, carbon build up can occur due to the Boudouard reaction and methane cracking (Gadalla and Bower, 1988).

Methane cracking:



Boudouard:



Thus, the CH₄/CO₂ reforming reaction (1) can be seen as consisting of reaction (5) and the reverse of reaction (6). Ideally the carbon formed in the reaction (5) should be rapidly consumed by the reverse of reaction (6) and, to a lesser extent, by the steam/carbon gasification reaction (7).

Steam/Carbon gasification:



Reaction (7) can play a role in CH₄/CO₂ reforming because steam is almost always formed via the reverse water-gas shift (RWGS) reaction (4). If reaction (5) is faster than the carbon removal rates (6,7), there will be a net build-up of carbon to pose serious problem in the overall reaction concept which in practice would lead to catalyst deactivation and reaction blockage. Apart from

reaction (5), reaction (6) and the reverse of reaction (7), both of which are favored at low temperatures, are also potential sources of carbon (Edward and Maitra, 1995).

A number of studies have been made on this reaction, but there is still no process for the CO₂ reforming currently considered to be commercially feasible. The major obstacle preventing commercialization of the process is that, owing to the endothermic nature of the process, high temperatures are required to reach high conversions. These conditions are conducive to carbon deposition, and severely deactivated the catalyst. Hence, the main concern of many CO₂-reforming studies is to develop suitable catalysts and optimize the lifetime stability of the catalysts used.

2.1.2 Application of Sol-Gel in Catalyst Preparation

Sol-gel processing in which metal organic precursors is mixed with metal precursor to form a homogeneous solution. The metal organic precursor is hydrolyzed through the addition of water while carefully controlling the pH and reaction temperature. As hydrolysis and polymerization occur, colloidal particles or micelles with approximate diameter of 10 nm are formed. These particles continue to increase the size until a metal oxide gel is formed (Gonzalez *et al.*, 1997).

The hydrolysis and condensation reactions can be expressed as follows:

In aqueous phase:

Hydrolysis:



Condensation:

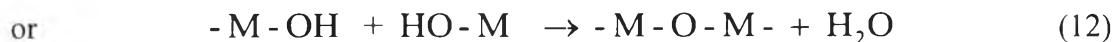


In organic phase:

Hydrolysis:



Condensation:



Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.

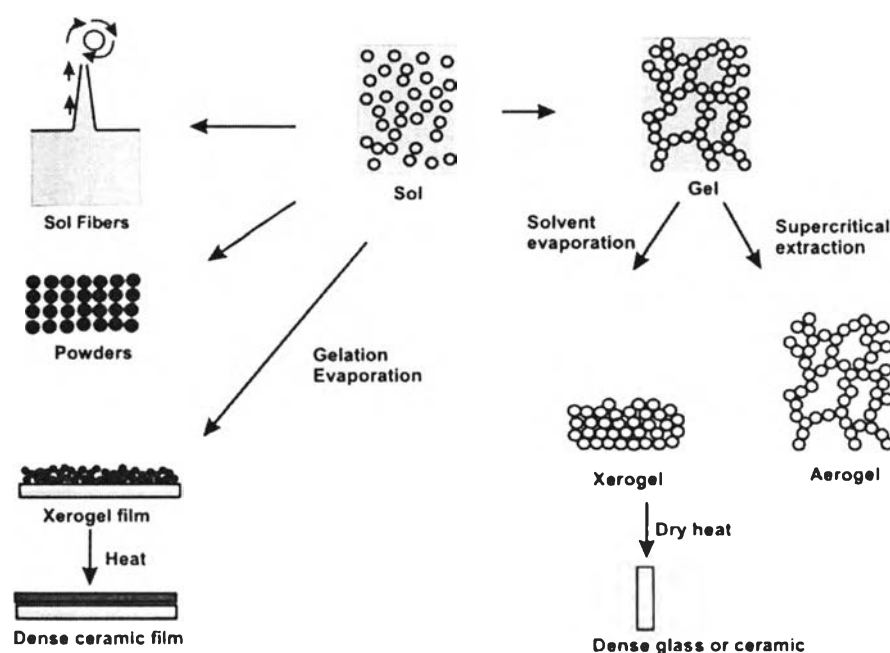


Figure 2.2 Sol-gel processing options (<http://www.gitam.edu>).

The size and the degree of branching of inorganic polymer, and the extent of cross-linking have strong influence on porosity of the gel, and latter, the surface area, pore volume, pore size distribution, and thermal stability of the final oxide after calcinations. In general, macropores and mesopores structures of oxides are achieved through the gel contained large void regions; resulted from gel contained polymeric chain with high branching and cross-linking. If the gel that has smaller void region, is structurally weak, and thus collapses readily upon calcinations. The resulting oxide has mostly micropores and low surface area.

2.1.3 Acidic and Basic Properties of Catalyst

Acid and base are paired concepts; a number of chemical interactions have been understood in terms of acid-base interaction. Among chemical reactions which involve acid-base interactions are acid catalyzed and base-catalyzed reactions which are initiated by acid-base interactions followed by catalytic cycles. In acid-catalyzed reactions, reactants act as bases toward catalysts which act as acids. In base-catalyzed reactions, on the contrary, reactants act as acids toward catalysts which act as bases.

In homogeneous systems, a huge number of acid catalyzed reactions and base-catalyzed reactions are known. In heterogeneous systems, a limited number of reactions are recognized as acid- or base-catalyzed reactions. In particular, base-catalyzed reactions have been studied to a lesser extent as compared to acid-catalyzed reactions in heterogeneous systems.

Heterogeneous acid catalysis attracted much attention primarily because heterogeneous acidic catalysts act as catalysts in petroleum refinery and are known as a main catalyst in the cracking process which is the largest process among the industrial chemical processes. Extensive studies of heterogeneous cracking catalysts undertaken in the 1950's revealed that the essential nature of cracking catalysts are acidic, and generation of acidic sites on the solids was extensively studied. As a result, amorphous silica-alumina was utilized as a cracking catalyst, and then crystalline aluminosilicate (zeolite) was used afterward.

Four reasons for recognizing certain materials as heterogeneous basic catalysts are as follows.

(1) Characterization of the surfaces indicates the existence of basic sites: Characterizations of the surfaces by various methods such as color change of the acid-base indicators adsorbed, surface reactions, adsorption of acidic molecules, and spectroscopies (W, IR, XPS, ESR, etc.) indicate that basic sites exist on the surfaces.

(2) There is a parallel relation between catalytic activity and the amount and/or strength of the basic sites: The catalytic activities correlate well with the amount of basic sites or with the strength of the basic sites measured by various methods. Also, the active sites are poisoned by acidic molecules such as HCl, H₂O, and CO₂.

(3) The material has similar activities to those of homogeneous basic catalysts for “base-catalyzed reactions” well-known in homogeneous systems: There are a number of reactions known as base-catalyzed reactions in homogeneous systems. Certain solid materials also catalyze these reactions to give the same products. The reaction mechanisms occurring on the surfaces are suggested to be essentially the same as those in homogeneous basic solutions.

(4) There are indications of anionic intermediates participating in the reactions: Mechanistic studies of the reactions, product distributions, and spectroscopic observations of the species adsorbed on certain materials indicate that anionic intermediates are involved in the reactions.

2.1.4 Temperature-Programmed Desorption

This method is frequently used to measure the number and strength of basic sites. The strength and amount of basic sites are reflected in the desorption temperature and the peak area, respectively, in a TPD plot. However, it is difficult to express the strength in a definite scale and to count the number of sites quantitatively. Relative strengths and relative numbers of basic sites on the different catalysts can be estimated by carrying out the TPD experiments under the same conditions. If the TPD plot gives a sharp peak, the heat of adsorption can be estimated. TPD plots of carbon dioxide desorbed from alkaline earth oxides are compared in Figure 2.2 in which adsorption of carbon dioxide and the following treatment before the TPD run were done under the same conditions. The strength of basic sites is in the increasing order of $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$. The number of basic sites per unit weight that can retain carbon dioxide under the adsorption conditions increases in the order $\text{BaO} < \text{SrO} < \text{MgO} < \text{CaO}$. Enhancement of basic strength by addition of alkali ions to X-zeolite in excess of the ion exchange capacity was demonstrated by TPD plots of carbon dioxide as shown in Figure 2.2. The peak areas are larger for the alkali ion-added zeolites (solid lines) than for the ion-exchanged zeolites (dotted lines). In particular, desorption of carbon dioxide still continues at the desorption temperature of 673 K for ion-added zeolites.

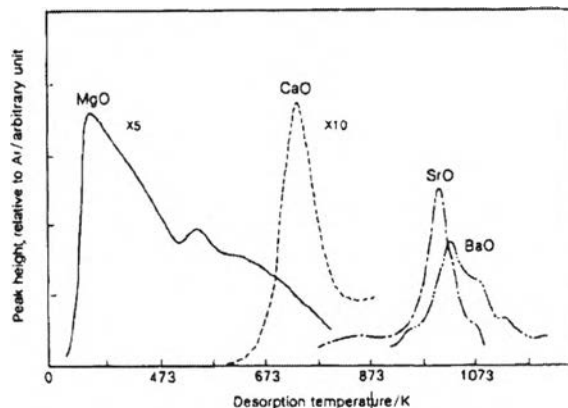


Figure 2.3 TPD plots of carbon dioxide desorbed from alkaline earth oxides (Zhang *et al.*, 1988).

2.2 Literature Review

2.2.1 Catalysts used in Reforming

Numerous materials have been tested as potential catalysts for reforming of CH_4 with CO_2 , and most of them have been focused on Group VIII metals on a variety of supports. The metals studied include Co, Ni, Ru, Rh, Pd and Pt, La and Zr have also been used. Oxides such as CeO_2 , Al_2O_3 , La_2O_3 , MgO, CaO, SiO_2 ; TiO_2 and ZrO have been employed as support materials. Among the catalysts examined, nickel-based catalysts, as well as supported noble metal catalysts, have been found to exhibit promising catalytic activities in terms of methane conversion and selectivity to synthesis gas. Encouraging stability results have been obtained using noble metal-based catalysts. However, it was observed that carbon deposition cannot be avoided over nickel-supported catalysts and for a CO_2/CH_4 molar ratio of unity (Ashcroft *et al.*, 1991). In this part, there are two head line concluding about an interaction of MgO on supports and activity and stability of catalyst.

2.2.1.1 *Interaction of MgO on Supports*

In recent year, the deactivation is the main problems of the Ni-based catalyst. The carbon deposition on the nickel-based catalyst and the sintering of metallic nickel at high temperature are reported for this problem. Therefore, there have had many attentions to improve the stability of the catalysts by

modifying the properties of support or adding some additives to improve the stability of the catalyst. MgO is the one of additive that exhibits the ability to reduce the coke formation and also the sintering of metal at reaction temperature.

Jang *et al.* (2013) studied H₂ and CO production over a stable Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ catalyst from CO₂ reforming of CH₄. They reported that Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ exhibited higher catalytic activity and stability (CH₄ conversion > 95% at 800 °C for 200 h). The outstanding catalytic performance is mainly due to the basic nature of MgO and an intimate interaction between Ni and MgO. Ni-Ce_{0.8}Zr_{0.2}O₂ and Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ catalysts were investigated for H₂ production from CO₂ reforming of CH₄ reaction at a very high gas hourly space velocity of 480,000 h⁻¹.

Wanga *et al.* (2009) studied durable Ni/MgO catalysts for CO₂ reforming of methane. They found that a complete incorporation of NiO into the MgO “support” to form NiO-MgO solid solution during the calcination stage of the catalyst preparation was identified essential for the formation of stable Ni/MgO catalysts, and the presence of readily reducible “free” NiO in the calcined (unreduced) NiO/MgO samples was shown to produce the deactivating Ni/MgO catalysts during the CO₂/CH₄ reaction. The reactivities of CO₂/CH₄ were found sensitive to the particle size (or dispersion) of metallic Ni; the catalytic activity by CH₄ turnover frequency (TOF) decreased with increasing the Ni particle size. The reduced catalysts showed two H₂-TPD peaks and the nickel sites corresponding to H₂-TPD peak at higher temperature showed a higher activity than those associated with the peak at lower temperature. Their data demonstrate that the support in the stable catalysts was actually a kind of Ni_xMg_{1-x}O ($x = 0.02-0.15$) solid solution and the stable catalytic sites were associated with nano-sized Ni particles (3-20 nm) in strong interaction with the solid solution support.

Xu *et al.* (2007) studied Nano-MgO: novel preparation and application as support of Ni catalyst for CO₂ reforming of methane. They found that Primary application of the MgO nanocrystals for support of nickel catalyst was successful and gave promising results for highly active as well as very stable Ni/MgO catalysts for the dry reforming of methane to produce syngas. The sizes of

MgO nanocrystals (10-12 nm) those are able to resist “sintering” up to 650 °C without significant loss of the surface area.

Nagaraja *et al.* (2011) studied the effect of potassium on the activity and stability of Ni-MgO-ZrO₂ catalysts for the dry reforming of methane to give synthesis gas. They found that the addition of 0.5 wt% potassium to a catalyst consisting of 8 wt% Ni supported on a MgO-ZrO₂ support prepared by co-precipitation improved both the activity and stability of this material for the dry reforming of methane. Increasing the content of potassium caused a decrease in the catalytic activity but the stabilities of the resultant catalysts were still higher than those for the undoped catalyst. The BET surface areas of the catalysts increased with potassium content.

Sato *et al.* (2010) studied preparation and characterization of active Ni/MgO in oxidative steam reforming of n-C₄H₁₀. They reported that Ni/MgO prepared at pH 7 exhibited considerably higher activity than Ni/MgO prepared from a conventional acidic aqueous precursor solution (pH 3.5). The H₂ formation rate for the modified Ni/MgO was up to 2.3 times that for conventional Ni/MgO under a high space velocity of 1660 l(hg)⁻¹. Furthermore, after reduction at high temperature (1273 K), the modified Ni/MgO showed a higher H₂ formation rate than did Rh/MgO. The superior performance of the modified Ni/MgO was ascribed to stronger resistance to oxidation of NiO due to the formation of relatively large NiO particles. The Ni/MgO catalysts were prepared by the impregnation method from aqueous Ni(NO₃)₂ precursor solutions at two pH values.

Kong *et al.* (2012) studied catalytic performance of Ni/MgO in carbon dioxide reforming of toluene. They reported that either higher reaction temperatures or higher CO₂/toluene mole ratios made Ni/MgO more stable and efficient. Ni/MgO at 550 °C and a high CO₂/toluene mole ratio of 28 had a better activity with less coke than that at 570 °C but low CO₂/toluene mole ratios, which suggested the activation of carbon intermediates from the dissociation of toluene by abundant oxidizing CO₂ species played a crucial role in having a better catalytic performance. At a high toluene feed rate (0.48 ml/h), Ni/MgO had an inferior activity due to the comparatively insufficient active Ni; moreover, it had a worse stability because of a large amount of coke.

Kima *et al.* (2010) studied catalytic activity of promoters on Ni/MgO catalyst in C_8H_{18} autothermal reforming in solid oxide fuel cell system. They found that the formation of NiO-MgO solid solution was accomplished during calcination of the Ni/MgO catalyst at 900 °C, resulting in loss of the active Ni metal and very low catalytic activity. Therefore, all catalysts were treated by a reduction process without calcination in order to prevent the formation of NiO-MgO solid solution. Among Ni/MgO catalysts combined with various promoters such as Ag, Cr, and Cu, Ni-Cr/MgO catalyst showed the most desirable characteristics in the aspects of its activity, stability, and resistance to carbon deposition.

Nagaoka *et al.* (2007) studied catalytic activity of Ni/MgO in oxidative steam pre-reforming of n-butane for fuel cell application. They found that the higher activity of Ni/MgO (pH 7) was ascribed to stronger resistance against oxidation of NiO due to the formation of relatively large NiO particles. When the Ni/MgO was prepared from an aqueous $Ni(NO_3)_2$ solution with pH 7, H_2 formation rate of Ni/MgO (pH 7) at a high space velocity ($SV=1660 \text{ l}(\text{h}\cdot\text{g})^{-1}$) was 2.3 times as high as that of conventional Ni/MgO.

2.2.1.2 Activity and Stability of Catalyst

Due to activity and stability of catalyst, most studies propose to improve performance of catalyst which have many different challenges (Zhaoyin Hou *et al.*, 2003; Adriana D. *et al.*, 2005; Rogatis *et al.*, 2009; Mari'a Martha Barroso-Quiroga *et al.*, 2010; P. Sutthumporn *et al.*, 2011; K. Fronteraa *et al.*, 2012) in order to use as the catalyst in the methane dry reforming.

Hou *et al.* (2003) studied characterization of Ca-promoted Ni/ α - Al_2O_3 catalyst for CH_4 reforming with CO_2 . They found that small amounts of Ca increased the activity and stability of Ni/ α - Al_2O_3 . The Ca-promoted Ni/ α - Al_2O_3 catalysts indicated that Ca improved the dispersion of Ni, strengthened the interaction between Ni and Al_2O_3 , and retarded the sintering. A higher amount of Ca covered the surface of α - Al_2O_3 and enhanced the decomposition of CH_4 .

Adriana *et al.* (2005) investigated effects of supports on the Pt-supported catalysts via reforming of CH_4 with CO_2 . They found that Pt/Na (0.3 wt%)- Al_2O_3 and Pt/ ZrO_2 catalysts showed both a good activity and selectivity with a

very high catalytic stability at 1073 K. The Pt/K (0.3 wt%)-Al₂O₃ catalyst showed a good performance but a slightly lower conversion level than Pt/Na (0.3 wt%)-Al₂O₃. On the other hand, the Pt/Al₂O₃ catalyst displayed an important decrease of the methane conversion through the reaction time at 1073 K and hence, a lower catalytic stability due mainly to the carbon deposition. It can be concluded that either Na or K addition to Pt/Al₂O₃ enhances the catalytic stability since they provide basic sites, which favor the dissociation reaction of CO₂ into CO and O. The O species can react with the carbon deposited on the Pt, thus cleaning the metallic phase of the doped catalysts.

Barroso-Quiroga *et al.* (2010) studied catalytic activity and effect of modifiers on Ni-based catalysts for the dry reforming of methane. They found that the catalyst supported on ZrO₂ showed the highest stable activity during the period of time studied.

Sutthiumporn *et al.* (2011) evaluated effects of alkaline earth over Ni/ La₂O₃ catalyst for CO₂ reforming of CH₄. They found that the Sr-doped Ni/La₂O₃ catalyst not only yields the highest CH₄ and CO₂ conversions (~78% and ~60%) and highest H₂ production (~42% by vol.) but also has the lowest carbon deposition over the catalyst surface. The excellent performance over the Sr-doped Ni/La₂O₃ catalyst is attributed to the presence of a high amount of lattice oxygen surface species which promotes C/H activation in dry reforming of methane (DRM) reaction, resulting in high H₂ production. Moreover, these surface oxygen species on the Ni-SDL catalyst can adsorb CO₂ molecules to form bidentate carbonate species, which can then react with the surface carbon species formed during DRM, resulting in higher CO₂ conversion and lower carbon formation.

Fronteraa *et al.* (2012) studied catalytic dry-reforming on Ni-zeolite supported catalyst. They found that the silylation of the support surface leads to the formation of smaller and more reducible Ni-oxide species that not only improve the CH₄ and CO₂ conversion but also reduce the deactivation of the catalyst due to coke deposition and the obtained H₂/CO value is 1.04.

2.2.2 Co-Precipitation Method

Recently, there have been studies of the co-precipitation method to prepare a support for catalytic reaction. The various preparation methods, catalytic performance and carbon formation resistivity have been investigated for properties of catalysts prepared by this method (Montoya *et al.*, 2000; Koo *et al.*, 2008; Chen *et al.*, 2012).

Montoya *et al.* (2000) studied H₂ and CO production over a stable Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ catalyst from CO₂ reforming of CH₄. They tried Ni-based catalysts on a tetragonal Ce-ZrO₂ support for CDR. However, the problem of support sintering at 800 °C could not be addressed completely. In their previous results, a co-precipitated Ni-Ce_{0.8}Zr_{0.2}O₂ catalyst exhibited higher activity and higher stability than an impregnated catalyst with the same composition at the gas hourly space velocity (GHSV) of 108,000 h⁻¹ in CDR.

Koo *et al.* (2008) studied coke formation on MgO-promoted Ni/Al₂O₃ catalyst in combined H₂O and CO₂ reforming of methane for gas to liquid (GTL) process. They found that the co-precipitated stable Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ catalyst exhibited the highest activity as well as stability among supported Ni catalysts for CDR in the literature. In addition, it was reported that the addition of MgO improved the activity and stability of catalysts for combined steam and carbon dioxide reforming of methane (CSCRM) resulting from enhanced steam adsorption and a strong metal to support interaction.

2.2.3 Acid and Basic Properties of Catalysts

The modifications of the support basic function depend on the amount and acid/base properties of the solid-solution supported. Many researchers have investigated acid/base properties (Nia *et al.*, 2012; Chen *et al.*, 2012).

Nia *et al.* (2012) studied carbon deposition on borated alumina supported nano-sized Ni catalysts for dry reforming of CH₄. They found that the formation of strong Lewis acid sites causes severe carbon deposition on 1 wt% and 10 wt% B₂O₃ loaded Ni catalysts, hence decreasing catalytic activity and stability. The formation of weak Lewis acid sites and O-H groups on 5 wt% B₂O₃ promoted Ni catalysis found to significantly facilitate carbon removal and improve the stability of the catalysts. The reaction mechanism of dry reforming of methane over

borated-alumina supported Ni catalysts is proposed, especially the promotional effect of OH groups on the suppression of carbon formation being emphasized.

Chen *et al.* (2012) studied the effect of surface acidic and basic properties on the hydrogenation of laurionitrile over the supported nickel catalysts. They found that Ni was to be relatively easier to reduce in Ni/MgO and Ni/SiO₂ than in Ni/Al₂O₃, while nickel was higher dispersed in Ni/SiO₂ than in Ni/Al₂O₃ and Ni/MgO. Thus, the reducibility and dispersion of nickel in Ni/MgAlO and Ni/SiAlO were significantly enhanced, leading to the high active nickel surface areas (75 m²/g-catalyst). Acetonitrile was found to be adsorbed on the reduced nickel and acidic sites. The strong surface basicity of Ni/MgO was found to favor the selectivity to the primary amine, but inhibited the conversion of laurionitrile. On the other hand, the conversion of laurionitrile was high over the Ni/SiO₂, Ni/Al₂O₃ and Ni/SiAlO with strong surface acidity, but the selectivity to the prime amine was relatively low. The Ni/MgAlO with intermediate strengths of surface acidity and basicity exhibited the high conversion of laurionitrile and high selectivity to the prime amine.

Guo *et al.* (2012) studied effect of support's basic properties on hydrogen production in aqueous-phase reforming of glycerol and correlation between WGS and APR. They found that the overall catalytic activities for APR of glycerol decreased in the following order for Pt based catalysts: Pt/MgO > Pt/Al₂O₃ > Pt/CeO₂ > Pt/TiO₂ > Pt/SiO₂. The WGS reactions were also examined over these five catalysts. The relationship between WGS and APR was discussed and found that WGS played a key role in the process of APR, both are related to the surface properties: the basic sites are prefer for water-gas shift and further enhanced the APR process. Typical solid basic magnesium and alumina mixed oxides supporting Pt catalysts were also tested and exhibited the best APR activity.

In addition, they showed the results of support on TPD profiles of CO₂ adsorbed on different supports are presented in Fig. 2.3. The basic surface sites were classified according to their basic strengths. In these three peaks, α and β are usually related to the occurrence of the weak basic surface sites. Meanwhile, γ is taken as a distinct distribution of surface centers with relatively strong basic sites. The SiO₂ support showed only one very weak α peak of CO₂ desorption. The TiO₂ support

exhibited two weak α and β peaks. For CeO_2 , there was a narrow β peak with high intensity of MS signal. Besides, a shoulder α peak could also be observed in the profile of CeO_2 . It is worth to remark that there was a broad and strong peak in the temperature range from 50 to 400 °C with a peak of 100 °C in the profile of Al_2O_3 , indicating that all of the three kinds of basic surface sites existed and the weak basic sites were dominant in Al_2O_3 support. Although there were also three kinds of basic surface sites for the MgO support as Al_2O_3 , the dominant basic sites were contributed by the stronger one. From these data, a basicity scale of oxides used in this research can be established, according to the CO_2 -TPD, as follows: $\text{MgO} > \text{Al}_2\text{O}_3 > \text{CeO}_2 > \text{TiO}_2 > \text{SiO}_2$.

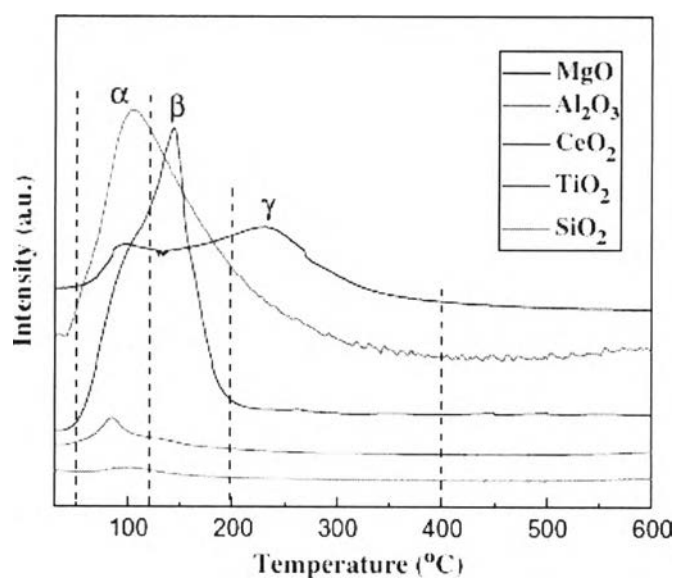


Figure 2.4 TPD profiles of CO_2 adsorbed on the support (Guo *et al.*, 2012).