

Raney Ni Catalysts Derived from Different Alloy Precursors Part II. CO and CO₂ Methanation Activity

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Abstract—Catalytic activity, in conjunction with reaction mechanism, was studied in the methanation of CO and CO₂ on three Raney Ni catalysts derived from different Ni-Al alloys using different leaching conditions. Main products were CH₄ and CO₂ in CO methanation, and CH₄ and CO in CO₂ methanation. Any other hydrocarbon products were not observed. Over all catalysts, CO methanation showed lower selectivity to methane and higher activation energy than CO₂ methanation. The catalyst derived from alloy having higher Ni content using more severe leaching conditions, namely higher reaction temperature and longer extraction time, showed higher specific activity and higher selectivity to methane both in CO and CO₂ methanation. In CO and CO₂ methanation on Raney Ni catalyst, catalytic activity was seen to have close relation with the activity to dissociate CO.

Key words: Raney Ni Catalysts, CO and CO₂ Methanation, Leaching Condition, Selectivity to Methane, Activation Energy

INTRODUCTION

The methanation of carbon oxides over transition metal catalysts is important in some chemical reactions, such as the purification of ammonia feeds and the production of synthetic fuels [Kim et al., 2003], and has been studied extensively.

Recently, carbon oxide methanation has attracted much attention due to the crisis in natural resources and environmental concerns [Hwang et al., 2003]. As methanation catalyst, nickel is still the most studied catalyst due to its high activity and relatively low price [Lee et al., 2000], and it is most selective to methane [Hu et al., 1999; Chang et al., 2003]. Although the methanation of carbon oxides is a comparatively simple reaction, its mechanism appeared to be difficult to establish. From earlier studies, several mechanisms have been proposed for both CO and CO₂ methanation [Vannice, 1976]. In the case of CO methanation, proposed mechanisms can be divided into two major categories concerning reaction intermediates. One involves the formation of a CH₃O complex, and the other regards surface carbon as an intermediate. The reaction mechanisms proposed for CO₂ methanation also fall into two main categories. The first one involves the conversion of CO₂ to CO, followed by CO methanation, while the second involves the direct hydrogenation of CO₂ to methane by a mechanism different from that for CO methanation.

Recently, several generalizations concerning both CO and CO₂ methanation were established [Fujita and Takezawa, 1997]. In general, CO₂ methanation, which exhibits lower activation energy, shows higher selectivity, higher reaction rate and lower reaction temperature compared to CO methanation. CO₂ methanation is generally considered to proceed via dissociation of CO₂ to form CO fol-

lowed by CO methanation.

As mentioned above, Ni is currently one of the most studied catalysts for methanation. Raney nickel, one kind of nickel catalyst, is known as an active catalyst in hydrogenation and appears to have high activity in methanation [Rehmat and Randhava, 1970; Yang et al., 1984]. Raney nickel catalyst is usually obtained from Ni-Al alloy using alkaline dissolution of Al. The precursor alloy is generally made of several phases and a portion of each phase can be varied with the Ni/Al ratio and the preparation method of alloy [Sane et al., 1984]. These phases have different reactivity to alkaline solution. It can be expected, therefore, that different Raney nickels are obtained from alloys having different composition; consequently, the catalyst properties depend on the phase composition of precursor alloy. However, there are some discrepancies in considering the effect of origin of catalyst on its catalytic activity [Sane et al., 1984; Nakabayashi et al., 1983; Savelov and Fasman, 1985]. In the present work, catalytic activities, in conjunction with reaction mechanism, were studied in CO and CO₂ methanation on three Raney Ni catalysts derived from different Ni-Al alloys using different leaching conditions.

EXPERIMENTAL

The precursor Ni-Al alloys were obtained from the Davison Chemical Division, W.R. Grace Co. (Baltimore, Maryland, USA). Atomic absorption spectroscopy analysis showed that the nickel contents of three precursor alloys were 41.3, 49.2 and 59.9 wt%. Catalysts were prepared from 300-500 μ m alloy particles obtained by crushing and screening the alloy pieces. Leaching of Al was carried out by reaction of 5 g of alloy powder with 250 g of 20 wt% aqueous NaOH solution. Different leaching conditions were used for three alloys because each alloy showed different reactivity to alkaline solution. Ni 41.3 and 49.9 wt% alloys were leached at same temperature, 50 °C, but different leaching time, 4 h and 10 h for Ni 41.3 and 49.2 wt% alloy, respectively. Ni 59.9 wt% alloy, which shows very low reactivity toward alkaline solution, was leached at 107 °C

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for 125 h. After a complete reaction had taken place, the catalysts were thoroughly washed with distilled water to pH 7. The nickel content in the leached material was also analyzed by atomic absorption spectroscopy.

The surface area of catalyst was determined by nitrogen adsorption at -195°C with a Micromeritics ASAP 2000. The Raney catalysts were transferred to the adsorption vessel under water, which was removed by evacuation. The samples were evacuated for 4 h at room temperature and then at 130°C for additional 5 h. Samples were weighed by difference in adsorption vessel on the completion of each experiment. Separate samples were also used for CO adsorption. The CO adsorption isotherms were measured according to the method in the literature [Wainwright et al., 1980]. The samples were evacuated by the procedure used for the adsorption of N_2 . The chemisorption of CO was taken as the difference of the isotherm on the original evacuated catalyst at -195°C and a second isotherm at -195°C following evacuation at -78°C for 2 h.

The catalytic activity measurements were carried out by using a 1/4" stainless steel reactor, surrounded with heating block and equipped with thermocouples in the catalyst bed. Prior to activity measurement, the catalyst was dried at 130°C for in flowing H_2 and reduced at 350°C for 4 h. Catalyst loadings were 0.05–0.07 g. Helium, 50% in total reactant feed, was used as a diluent to reduce temperature rising during activity measurement and reactant mole ratios were $\text{H}_2/\text{CO}=3/1$ for CO methanation and $\text{H}_2/\text{CO}_2=4/1$ for CO_2 methanation. The total gas flow rates used were 32–740 cc/min, corresponding to gas hourly space velocities (GHSV) of 38,000–880,000 h^{-1} . Products were analyzed by Shimadzu GC-8A gas chromatograph and Porapak Q column. The activation energies were calculated from the results obtained at low conversion.

RESULTS

Atomic absorption analysis showed that the nickel contents in catalysts obtained from Ni 41.3, 49.2 and 59.9 wt% alloys (designated as Ni 42, Ni 50 and Ni 60 catalysts, respectively) were 77.7, 75.3 and 84.6 wt%, respectively.

As can be seen Table 1, total surface areas of Ni 42, Ni 50 and Ni 60 catalysts were found to be 101.67, 100.84 and 35.81 m^2/g , respectively.

Table 1 also presents CO adsorption results. Ni 60 catalyst revealed lower chemisorption amounts. However, if we calculate the chemisorption amount per unit surface area, Ni 60 catalyst would show a little higher value compared to the other catalysts.

Figs. 1(a) and 1(b) show the change of selectivity to methane in CO and CO_2 methanation on Ni 42 catalyst as a function of conversion (space velocity). In CO methanation, main products were CH_4 and CO_2 . From the result in Fig. 1(a), it is apparent that selectivity to methane decreases with increasing conversion (decreasing space velocity). At the same time, the yield of CO_2 increases with increas-

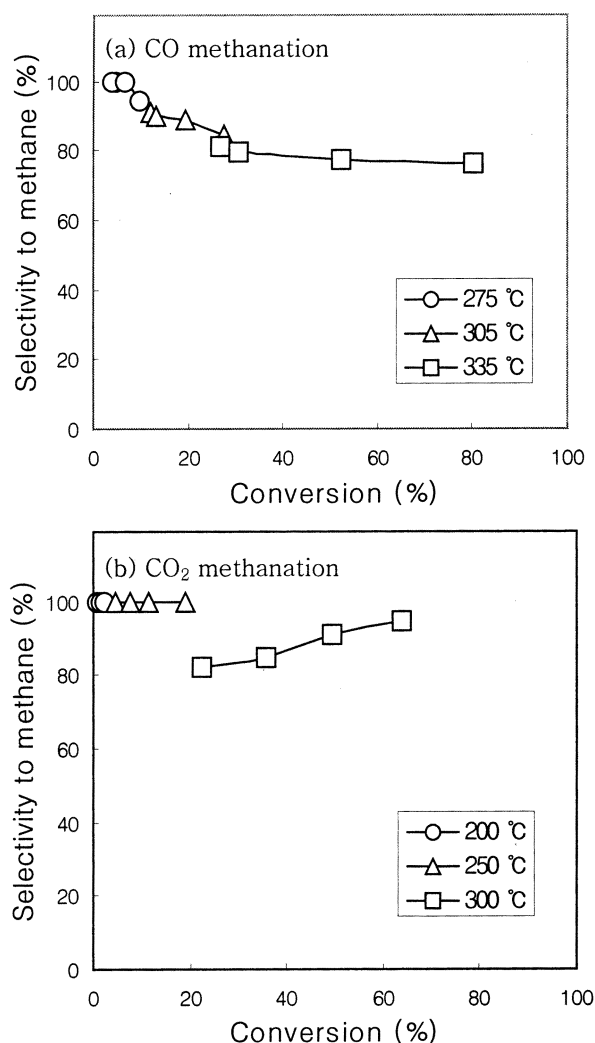


Fig. 1. Selectivity as a function of conversion on Ni 42 catalyst.

ing conversion. At lower reaction temperature, CO conversion and CO_2 production were lower and methane production was higher.

In CO_2 methanation, CH_4 and CO were formed as main products and reaction could take place at much lower temperature than in CO methanation. At 200°C , CO_2 was methanated at a measurable rate, while no CO conversion occurred under present reaction conditions.

As shown in Fig. 1(b), an opposite behavior to CO methanation was observed in CO_2 methanation in which the selectivity to methane increased with decreasing space velocity (increasing conversion). At lower reaction temperature, for example 200 and 250°C , the selectivity to methane was almost unity over wide range of space velocity.

Figs. 2 and 3 show the results of CO and CO_2 methanation selectivity on Ni 50 and Ni 60 catalysts as a function of conversion (space

Table 1. Properties and CO adsorption on Raney Ni catalysts

Catalyst	Surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter ($\text{\AA}$)	CO adsorption at -195°C ($\text{ml STP}/\text{g}$)
Ni 42	102	0.110	44	10.75
Ni 50	101	0.097	38	11.12
Ni 60	36	0.146	163	4.36

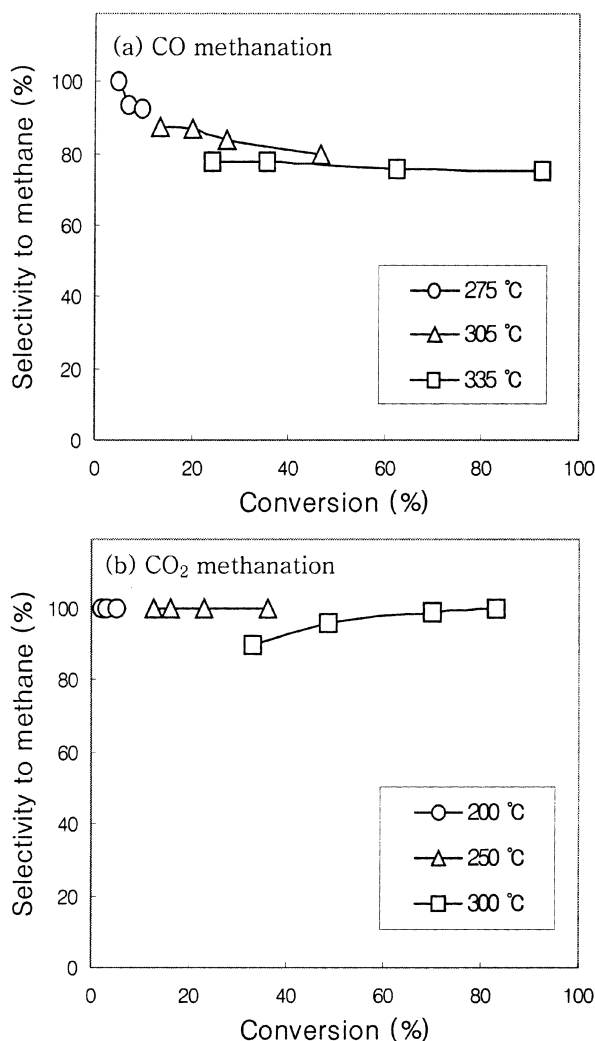


Fig. 2. Selectivity as a function of conversion on Ni 50 catalyst.

velocity). On both catalysts, selectivity to methane changed with conversion in same manner as that on Ni 42 catalyst. However, among three catalysts, Ni 60 catalyst showed the highest selectivity to methane both in CO and CO₂ methanation.

Arrhenius plots for CO and CO₂ methanation on the three catalysts are shown in Fig. 4. The activation energies for CO methanation on Ni 42, Ni 50 and Ni 60 catalysts were found to be 170, 151, 155 kJ/mole, respectively. Ni 60 catalyst showed higher specific reaction rate than the other catalysts (under reaction conditions). Fig. 4 shows the activation energies for CO₂ methanation on Ni 42, Ni 50 and Ni 60 catalysts to be 88, 91, 90 kJ/mole, respectively. In CO₂ methanation, Ni 60 catalyst also revealed the highest specific activity among three catalysts. From both the plots, it can be seen that at higher temperature Arrhenius plots for CO and CO₂ methanation on each catalyst intersect, which suggests that the specific rate of CO methanation could be larger than that of CO₂ methanation at high temperature.

DISCUSSION

Three Raney nickel catalysts, obtained from different precursor

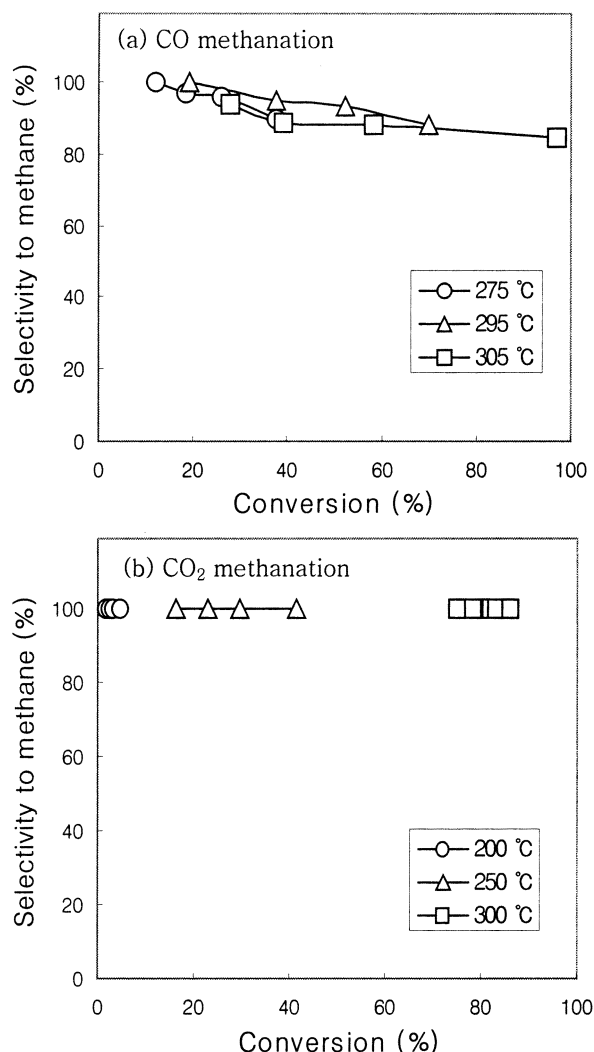


Fig. 3. Selectivity as a function of conversion on Ni 60 catalyst.

alloys using different leaching conditions, revealed differences in some properties.

High extraction temperature favors low surface area [Freel et al., 1969], and consequently the Ni 60 catalyst, leached at the boiling temperature of alkaline solution, showed the lowest surface area, and Ni 42 and Ni 50 catalysts, leached at same temperature of 50 °C, revealed similar surface areas.

The surface area of Raney Ni catalyst is usually composed of alumina and metallic Ni [Freel et al., 1970]. In CO chemisorption measurements, Ni 60 catalyst revealed a little larger amount of chemisorbed volume per unit surface area than the other two catalysts. Therefore, it can be deduced that in the case of Ni 60 catalyst comparatively large portion of surface is metallic Ni.

In this work, main products from CO methanation were CH₄ and CO₂. Any other hydrocarbon products were not observed.

CH₄ is produced by following reaction.



However, there are two possibilities to form CO₂, namely disproportionation or water gas shift reaction [Araki and Ponec, 1976; Van Ho and Harriot, 1980].

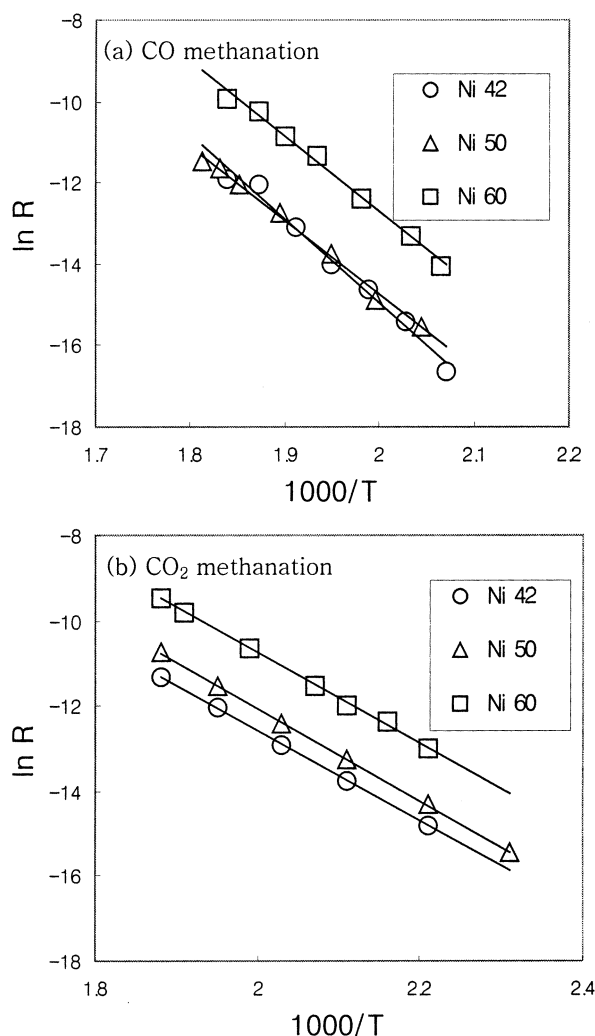


Fig. 4. Arrhenius plots for CO and CO₂ methanation on Raney Ni catalysts.

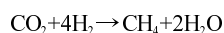


or



As shown in Fig. 1(a), at lower space velocity (higher conversion), more CO₂ was produced and therefore lower selectivity to methane appeared. This observation, together with the fact that the water gas shift reaction rate is a positive function of partial pressure of water [Mirodatos et al., 1987], suggests that a more possible reaction route to produce CO₂ is water gas shift reaction, because at higher conversion (lower space velocity) more water can be produced; consequently, it can react to produce more CO₂ and nickel is known to have high catalytic activity in water gas shift reaction [Grenoble et al., 1981].

In CO₂ methanation, CH₄ and CO were formed as main products. It is known that CH₄ is easily synthesized from CO₂ with H₂ [Hashimoto et al., 2001], and the reaction equation of methanation of CO₂ is as follows.



From the data in Fig. 1(b), it can be seen that at lower reaction temperatures (200 and 250 °C) the selectivities to methane are almost 100% over wide range of space velocity. It was also observed that, at the reaction temperature of 200 °C, the methanation of CO₂ proceeds with selectivities over 99% on unsupported Ni and various supported Ni and Rh catalysts [Fujita and Takezawa, 1997]. At a higher reaction temperature (300 °C), however, the selectivity to methane increases with decreasing space velocity (increasing conversion). Similar behavior was reported previously in CO₂ methanation on supported Ni catalyst and it was proposed that the production of CO is determined by an equilibrium phenomenon, while the production of methane is kinetically determined [Weatherbee and Bartholomew, 1981]. In addition, it was also seen from the equilibrium composition in CO₂ methanation reaction that higher temperature favors the higher production of CO [Anderson et al., 1976]. CO₂ methanation is generally thought to proceed through the mechanism involving dissociative adsorption of CO₂ to CO and surface oxygen, followed by hydrogenation of CO via carbon intermediate to methane [Yesgar and Sheintuch, 1991]. Therefore, it can be anticipated that the selectivity to methane decreases with increasing space velocity (decreasing conversion) at relatively high reaction temperature. It is seen from Figs. 1(a) and 1(b) that CO₂ methanation has higher selectivity to methane than CO methanation.

The difference in activity and product distribution between CO and CO₂ methanation has been reported in relation to their mechanisms [Weatherbee and Bartholomew, 1981]. It is usually thought that higher activity in CO₂ methanation, compared to CO methanation, is ascribed to lower concentration of adsorbed CO, because CO adsorbs very strongly and can act as a poison for H₂ adsorption, while adsorption of CO₂ is weaker [Takenaka et al., 2004]. In addition, higher concentration of surface oxygen can be expected in CO₂ dissociation compared to in CO dissociation, and this higher concentration of surface oxygen could change the rate of CO dissociation [Weatherbee and Bartholomew, 1982]. Similar observation was demonstrated in CO methanation on supported Rh catalyst, which revealed that oxidized catalyst has much higher activity than a reduced one [Iizuka et al., 1982].

In the study of CO and CO₂ methanation over Raney nickel catalyst, it was found that CO₂, at low concentration, has positive reaction order while CO has negative order [Lee and Anderson, 1979]. The activities and selectivities in CO and CO₂ methanation on Ni 50 and Ni 60 catalysts are shown in Figs. 2 and 3. Ni 60 catalyst revealed higher activity and selectivity both in CO and CO₂ methanation, as compared with other two catalysts. From these facts, it can be suggested that high activity and selectivity of Ni 60 catalyst is due to its high activity to dissociate CO because the dissociation of CO is essential step in synthesis of hydrocarbon from carbon oxides [Araki and Poniec, 1976].

The Ni 60 catalyst, which revealed the highest activity in CO methanation, showed almost no CO production from CO₂ methanation even at high temperature and high space velocity (low conversion). From consideration of the mechanism for CO₂ methanation, it can be expected that the formation of CO in CO₂ methanation has some relation with the ability of catalyst to dissociate CO. Above facts support the idea that adsorbed CO₂ and CO on Ni 60 catalyst easily dissociate to form carbon and oxygen.

As can be seen in Figs. 4(a) and 4(b), the activation energies of

CO and CO₂ methanation on the three catalysts, calculated from Arrhenius plot, show significantly high value both in CO and CO₂ methanation as compared with the previous reported results, 105–139 and 80 kJ/mole for CO and CO₂ methanation on Ni catalysts, respectively [Vannice, 1976; Weatherbee and Bartholomew, 1981]. However, the activation energy for the same reaction can be changed by many factors, for example reaction condition, active metal component and support [Goodman, 2003]. In this study, a quite different type of catalyst and reaction conditions were used. The results in Figs. 4 show that CO methanation involves higher activation for CH₄ production than does CO₂ methanation and Arrhenius plots for both reactions may intersect at higher temperature. Hence, CO methanation proceeds at higher rate than CO₂ methanation at elevating temperature.

What is not yet clear is why the Ni 60 catalyst shows the highest specific activity among the three catalysts. It was reported that CO can be dissociated only on places where carbon atoms can be bound to several Ni atoms, and therefore the addition of small amount of inactive compound to Ni strongly reduces the rate of methanation by diluting active Ni sites [Aksoylu et al., 1998]. From CO adsorption measurement, it was revealed that Ni 60 catalyst has comparatively large portion of surface metallic Ni. Therefore, it can be deduced that higher catalytic activity of Ni 60 catalyst for CO and CO₂ methanation is ascribed to the higher ability to dissociate CO, resulting from higher density of surface Ni. The results in Fig. 3(b) reveal, in CO₂ methanation, that CO is not formed over a wide range of space velocity and temperature, also supporting the above idea. From the above results, it can be concluded that, in CO and CO₂ methanation on Raney Ni catalyst, catalytic activity has close relation with the ability to dissociate CO.

CONCLUSIONS

Main products were CH₄ and CO₂ in CO methanation, and CH₄ and CO in CO₂ methanation on Raney Ni catalysts. Over all catalysts, CO₂ methanation proceeded highly selectively with lower activation energy as compared with CO methanation. The catalyst derived from alloy having higher Ni content using more severe leaching conditions showed higher specific activity and higher selectivity to methane in both CO and CO₂ methanation. The increase in specific activity and selectivity can be explained with the higher ability of catalyst to dissociate CO. Thus, in CO and CO₂ methanation on Raney Ni catalyst, catalytic activity seems likely to have close relation with the activity to dissociate CO.

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