Chemisorption of methane over Ni/Al$_2$O$_3$ catalysts

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Abstract

Adsorption of methane as well as co-adsorption of methane and O$_2$ on Ni/Al$_2$O$_3$ catalyst have been studied by in situ FT-IR spectroscopy. The reaction start temperature measurements indicate that the methane partial oxidation occurs at 230°C. As the reduced Ni/Al$_2$O$_3$ was exposed to pure CH$_4$, two bands for adsorbed methane were observed at 3005 and 2998 cm^{-1}, respectively, which was confirmed by the appearance of two bands at 2242 and 2237 cm^{-1} when CD$_4$ was used. During temperature programmed (TP) dynamic process (in the presence of CH$_4$), the intensities of the bands at 3005 and 2998 cm^{-1} increased with increase in temperature, indicating that the amount of adsorbed methane increases with increasing temperature, which is indicative of chemisorption of methane. During TP dynamic process (in the co-presence of CH$_4$ and O$_2$), two forms of chemisorbed methane are observed. The amount of chemisorbed methane increased with increasing temperature. At 250°C, the intensity of the band at 3015 cm^{-1} for gaseous methane decreased remarkably and at the same time, CO, H$_2$, CO$_2$ and H$_2$O were detected in the gas phase, indicating that the partial oxidation of CH$_4$ occurs, which is in good agreement with the reaction start temperature observed above. These results suggest that the dissociation of chemisorbed methane in the participation of chemisorbed oxygen is a key step for methane partial oxidation. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ni/Al$_2$O$_3$ catalyst; Chemisorption of methane

1. Introduction

Partial oxidation of methane to syngas has been an active subject of recent research. Unlike the highly endothermic catalytic steam reforming of methane [1], which is the dominant process currently employed in industry, methane partial oxidation is not energy intensive and also yields syngas with H$_2$/CO mole ratio of 2.0, which is suitable for the methanol and Fisher–Tropsch synthesis processes. Thus, partial oxidation of methane is a promising way of producing syngas on alternative syngas generation by steam reforming of methane. The mildly exothermic partial oxidation of methane to synthesis gas was first investigated in the 30s and 40s [2,3] and has been virtually ignored for the last 50 years. In the recent years, industrial and academic interest in the catalytic partial oxidation of methane to synthesis gas was reawakened [4]. In methane catalytic partial oxidation, supported group VIII metal [5–20], metal-coated

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monoliths [21–29] have been used as catalysts. Most of them gave high methane conversion and CO and H_2 selectivities.

The reaction pathway of methane partial oxidation to syngas is still not elucidated. There are two possible pathways for CH_4 partial oxidation: (1) direct oxidation to CO and H_2 or (2) total oxidation to CO_2 and H_2O followed by CO_2 and H_2O reforming. Hickman and Schmidt [21,25,27,29], Torniainen et al. [22], Schmidt and Huff [23], Bharadwaj and Schmidt [24], Hickman et al. [28] and Choudhary et al. [6,9,16–18] claimed that carbon monoxide and hydrogen are the products of the direct and selective oxidation of methane with oxygen on catalyst surface. The oxidation steps are as follows: methane pyrilyzes on the catalyst surface and H atoms dimerise to H_2 and the carbon is oxidized to CO. In contrast to direct oxidation pathway, other authors [6,14,15,19,30,31] maintain that the mechanism of methane partial oxidation on catalyst surface involve total oxidation of a part of the methane feed to CO_2 and H_2O followed by steam reforming, CO_2 reforming and water–gas shift reactions. The details of adsorption of methane as well as the interaction of methane with oxygen on catalyst surface are still not clear. Ni-based catalysts were proved to be highly effective for methane partial oxidation to syngas and widely studied [5,6,10,12–18,20]. However, only a few studies dealing with the chemisorption of CH_4 over Ni-based catalyst has been made. Erkelens and Wosten [32] studied methane adsorption on a Ni/SiO_2 catalyst using the low-field magnetic method and infrared measurements. Comparing the initial slopes of the methane and hydrogen isotherms, both measured at 25°C, they calculated that four or five surface bonds were formed by each methane molecule chemisorbed. But no IR spectra of the adsorbed species were obtained at −20° or 25°C in their IR measurements. Kuijpers et al. [33] studied the interaction of methane with a silica-supported nickel catalyst at temperature between 30° and 347°C, in both continuous-flow and pulse-flow experiments. They found that even at 30°C chemisorption of methane was observed and the activation energy for chemisorption was estimated to be at 6 kcal/mol. The low-field magnetic method and infrared spectroscopy were also applied to measure the adsorption of methane on silica-supported nickel catalyst at various constant temperature (30°C < 100°C) and at increasing temperature (30°C < 300°C) by Kuijpers et al. [34]. In the entire temperature range, the chemisorbed methane was found to dissociate according to the reaction.

$$CH_4 + 7Ni \rightarrow Ni_3C(\text{'surface nickel} - \text{carbide'})$$
$$+ 4Ni-H.$$
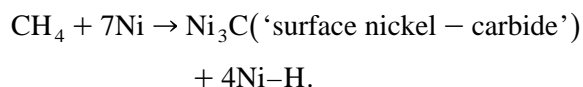
In the infrared spectrum, no CH_x adsorption bands were observed. Several authors [35,36] claimed that the chemisorption of methane on nickel involves the direct breaking of a C–H bond with no adsorbed molecule as precursor. Details of how methane interacts with the surface of nickel catalyst were much less known. In this paper, adsorption of methane and co-adsorption of methane with O_2 over Ni/Al_2O_3 catalyst is investigated with a hope to know the details of the chemisorption of methane as well as the interaction of methane with oxygen on catalyst surface.

2. Experimental

δ-Al_2O_3 was obtained by treatment of γ-Al_2O_3 (200 m^2/g) at 900°C for 4 h and used as support for catalysts.

Ni/Al_2O_3 catalysts was prepared by the impregnation of δ-Al_2O_3 (110 m^2/g) with a solution of nickel nitrate and subsequent heating at 100°C for 3 h and calcination in air at 600°C for 3 h. The resulting catalyst contained 10 wt.% nickel.

The determination of the reaction start temperature for methane partial oxidation over Ni/Al_2O_3 was performed with a quartz-fixed reactor (I.D. 4 mm) containing 20 mg catalyst.

A tubular furnace (I.D. 8 mm) was used to heat the reactor. The catalyst was reduced in a flow (40 cm^3/min) of H$_2$ at 600°C for 4 h. The temperature was measured by a Chromel–Alumel thermocouple located in the catalyst bed. The feed and product gases were analyzed by an on-line gas chromatograph equipped with a thermal conductivity detector and carbon molecular sieve column. After reducing Ni/Al$_2$O$_3$ in H$_2$ at 600°C for 4 h, the temperature was lowered to a certain value in H$_2$ flow and then the H$_2$ flow was switched to reaction mixture of CH$_4$ and O$_2$ (CH$_4$/O$_2$ = 2:1, GHSV = 6.9 × 10^5 cm^3/g h). If the reaction took place, above run with fresh catalyst is repeated at lower temperature until the reaction start temperature for methane partial oxidation is confirmed.

For FT-IR studies the sample was pressed into a self-supporting disk with a weight of about 20 mg. An IR quartz cell with CaF$_2$ window connected to a gas handling and a high vacuum system was used. The sample disk in the cell can be treated in various ways such as degassing, oxidation, and reduction at a wide temperature range from room temperature to 500°C. The temperature of the cell was controlled by temperature programmer. The pretreatment of the sample disk was performed in the cell as follows (1) the sample was reduced in flowing H$_2$ (40 cm^3/min) at 400°C for 2 h, and (2) evacuated for 30 min and then cooled down to 20°C.

IR spectra of the adsorbed methane were recorded with a Nicolet 170 SX FT-IR Spectrometer at experiment temperature. The parameters of 50 scan and 2 cm^{-1} resolution over the total spectral range (4000–200 cm^{-1}) were established by a 680-computer IR work station.

CH$_4$ adsorption–TP (in the presence of 140 Torr methane)–IR dynamic process procedure. As 140 Torr (1 Torr = 133.3 Nm^{-2}) of methane was admitted into the cell, IR spectrum was recorded after standing of 15 min at 20°C. Then the temperature was raised from 20° to 400°C at the rate of 7°C/min while IR spectra were

recorded at 20°, 100°, 200°, 250°, 300°, 350° and 400°C, respectively.

The co-adsorption of CH$_4$ with O$_2$–TP (in the presence of 280 Torr of gas mixture of CH$_4$ and O$_2$)–IR dynamic process procedure. As gas mixture of CH$_4$ and O$_2$ (280 Torr, CH$_4$/O$_2$ = 2:1) was admitted into the cell, IR spectrum was recorded after standing of 15 min at 20°C. Then the temperature was raised from 20° to 450°C at the rate of 7°C/min while IR spectra were recorded at 20°, 100°, 200°, 250°, 300°, 350°, 400° and 450°C, respectively.

3. Results and discussion

3.1. The reaction start temperature for methane partial oxidation over reduced Ni / Al$_2$O$_3$

Fig. 1 shows that the onset of activity for methane partial oxidation reaction over reduced Ni/Al$_2$O$_3$ occurred at 230°C. Below this temperature, methane partial oxidation does not proceed essentially. This result indicate that Ni/Al$_2$O$_3$ catalyst reduced at 600°C is very active for methane partial oxidation.

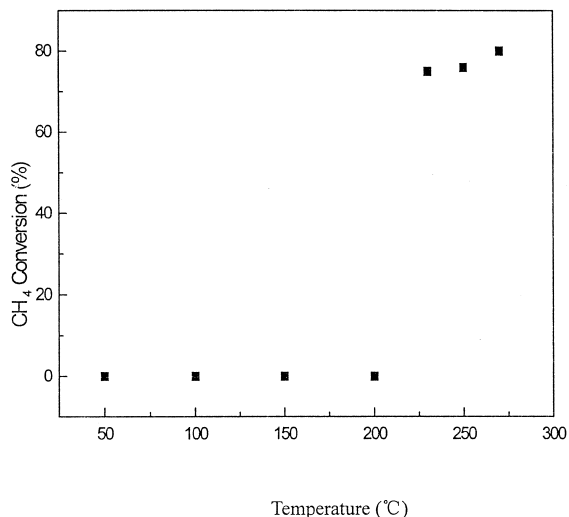Fig. 1. The reaction start temperature of methane partial oxidation on reduced Ni/Al$_2$O$_3$.

3.2. Chemisorption of CH_4 over reduced Ni / Al_2O_3

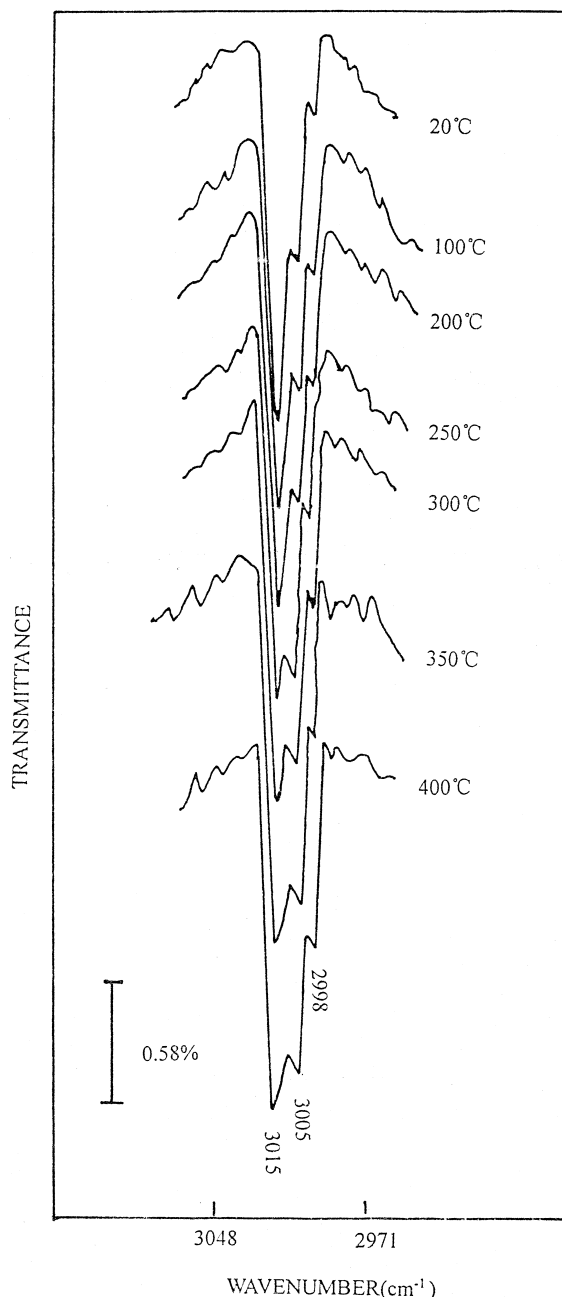Fig. 2 shows the results for the adsorption of CH_4–TP (in the presence of 140 Torr of CH_4)–

Fig. 2. IR spectra of adsorption of CH_4-TP (in 140 Torr CH_4) dynamic process on reduced Ni/Al_2O_3.

IR dynamic process over Ni/Al_2O_3 reduced at 400°C. It is shown that two adsorbed methane bands appear at 3005 and 2998 cm^{-1}, respectively, in addition to the bands at 3015 and 1305 cm^{-1} (1305 cm^{-1} is not included in Fig. 2) belonging to the bands ν_{CH} and δ_{CH} of gaseous methane, respectively, after 140 Torr CH_4 is exposed to the reduced and degassed Ni/Al_2O_3 catalyst at 25°C. During TP (in the presence of 140 Torr CH_4) process, the band at 3015 cm^{-1} for free methane kept unchanged in position and intensity over the whole temperature range from 20° to 400°C, and the bands at 3005 cm^{-1} increased in intensity with increasing temperature, and at 250°C, the band at 3005 cm^{-1} goes through a maximum and its intensity became almost equal with that of the band at 3015 cm^{-1} for free methane, and after 250°C the band at 3005 cm^{-1} stayed constant in intensity. The intensity of the band at 2998 cm^{-1} increased with increasing temperature and was roughly 1/3 that of the band for free methane at 250°C, and at 400°C, the intensity of the band at 2998 cm^{-1} reached about half that of the band of gaseous methane.

The result above indicates that there are two forms of adsorbed methane at 20°C on reduced Ni/Al_2O_3. This is confirmed by the IR spectra of CD_4 adsorption on Ni/Al_2O_3. Like in the case of CH_4, at 20°C, the band for gas CD_4 appears at 2255 cm^{-1} (Fig. 3) and two bands for adsorbed CD_4 appear at 2242 and 2237 cm^{-1}, respectively, in good agreement with the results of CH_4 adsorption on Ni/Al_2O_3. An increase in intensity of the bands at 3005 and 2998 cm^{-1} with increasing temperature during TP process shows that the amount of the adsorbed methane increased with increasing temperature. In general, physical adsorption, like liquefaction, require no activation and occur only at temperature close to the boiling-point of the adsorbate, and the amount of gas physical adsorbed always decrease monotonically as temperature is increased. While chemisorption, like most chemical processes, require activation, and should be capable of occurring at tempera-
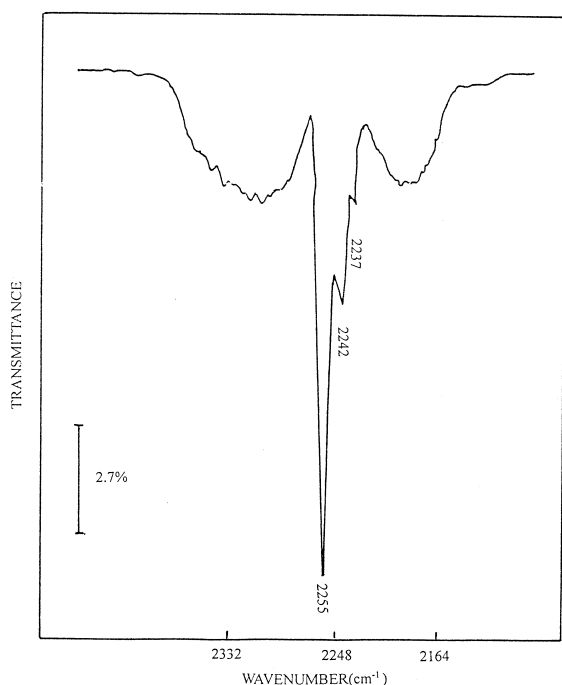
Fig. 3. IR spectrum of adsorption CD_4 on reduced Ni/Al_2O_3 at 20°C.

ture well above the boiling-point of the adsorbate. The boiling-point of methane is −164°C. Sheppard and Yates [37] have found that the bands for physically adsorbed methane on porous silica glass occurred at 3006, 2899 and 2819 cm^{-1} at −183°C. These bands were assigned to the ν_1 (2899 cm^{-1}), ν_3 (3006 cm^{-1}) and $\nu_2 + \nu_4$ (2819 cm^{-1}) modes of adsorbed methane. On well-outgassed MgO five bands at 3008, 3000, 2900, 2890 and ∼ 1306 cm^{-1} were observed at −100°C by Li et al. [38]. The bands were assigned to the ν_1 (2900, 2890 cm^{-1}), ν_3 (3008, 3000 cm^{-1}) modes of methane. Similar results were obtained on CeO_2 [39], HZSM-5 and Mo/HZSM-5 [40]. The above results have two common points: (1) the bands of adsorbed methane were observed at very low temperature (−183°C or −100°C and as temperature is increased the amount of adsorbed methane always decrease monotonically. (2) The infrared inactive ν_1 (2917 cm^{-1}) modes of gaseous methane became active and shifted to lower frequencies (2899 cm^{-1} [37], 2900 and 2890

cm^{-1} [38]) when methane was adsorbed. In the present paper, the temperature observed the bands of the adsorbed methane above is very much in excess of the boiling-point of methane and the amount of the adsorbed methane increased with increasing temperature in such large temperature range from 30° to 400°C. These results indicate that the bands at 3005 and 2999 cm^{-1} for the adsorbed methane are indicative of chemisorption of methane. During TP process, the behavior of the two bands are different. The band at 3005 cm^{-1} increased in intensity and reached its maximum at 250°C while the band at 2998 cm^{-1} increased in the intensity during the whole TP process indicating that the bands at 3005 and 2998 cm^{-1} are two different types of chemisorbed methane and experience different chemical processes during TP over the catalyst. The red shift of the bands at 3005 and 2998 cm^{-1} related to the bands of free methane indicate that the C–H bonds for chemisorbed methane have been activated in certain degree. But the red shifts related to the free methane band are only 10 and 17 cm^{-1}, respectively, indicating that chemisorbed methane are still in molecular form. Methane may be adsorbed on reduced Ni sites by one or two hydrogen atoms of methane.

3.3. Co-adsorption of CH_4 and O_2

To explore the interaction of CH_4 with O_2 over reduced Ni/Al_2O_3, co-adsorption of CH_4 and O_2 was carried out. When 280 Torr of CH_4 and O_2 gas mixture ($CH_4/O_2 = 2:1$) was co-adsorbed at 20°C on the reduced Ni/Al_2O_3, the band for gaseous methane appeared at 3015 and 1305 cm^{-1} (band at 1305 cm^{-1} is not included in Fig. 4), and two bands for adsorbed methane were observed, one appeared at 3010 cm^{-1} as a strong band whose intensity is about 2/3 that of the band at 3015 cm^{-1} for gaseous methane, and the other appeared at 3000 cm^{-1} as a shoulder. During TP (in the co-presence of CH_4 and O_2 gas mixture) dynamic process, the in-
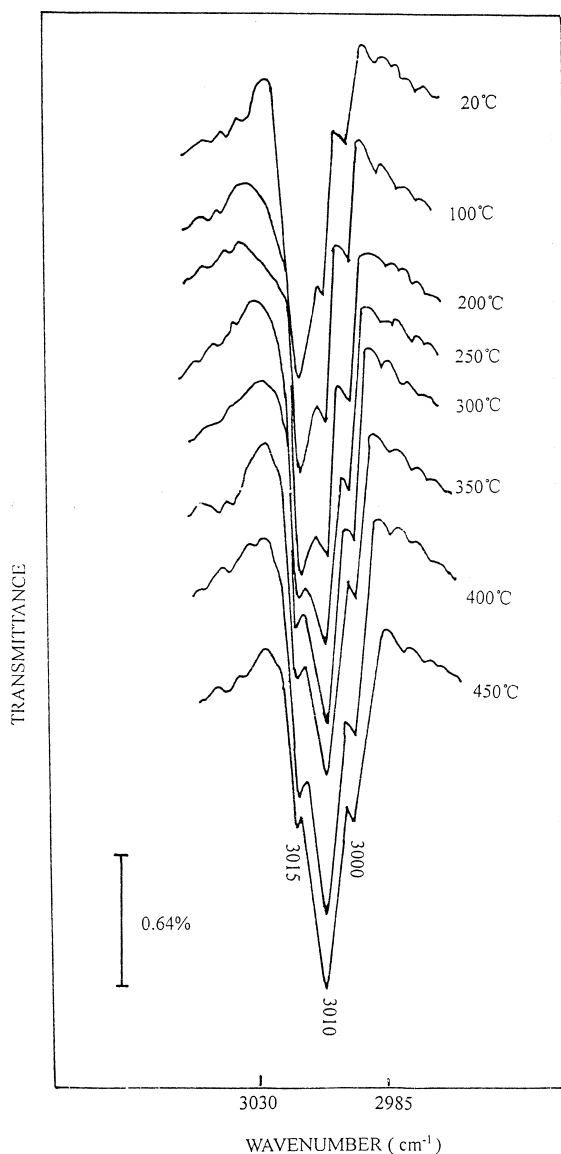
Fig. 4. IR spectra of co-adsorption of CH_4 and O_2-TP (in 280 Torr of gas mixture of CH_4 and O_2, $CH_4/O_2 = 2:1$) dynamic process on reduced Ni/Al_2O_3.

the same time, CO, H_2, CO_2 and H_2O were detected in gas phase, indicating that methane partial oxidation reaction has taken place. After 250°C, the 3015 cm^{-1} band for gaseous methane gradually attenuated in intensity, whereas the intensities of the 3010 and 3000 cm^{-1} bands for adsorbed methane gradually increased. At 450°C, the 3015 cm^{-1} band lost half of its intensity, and the bands of 3010 and 3000 cm^{-1} for adsorbed methane considerably increased. From a comparison of the spectra in Figs. 2 and 4, it is clear that the co-adsorption of CH_4 with O_2 at 20°C causes new bands appearing at 3010 and 3000 cm^{-1}, respectively. The bands at 3010 and 3000 cm^{-1} band can be assigned to the methane adsorbed on Ni/Al_2O_3 from their position. Because the chemisorption of O_2 on Ni is dissociative [41], surface sites located for the 3010 and 3000 cm^{-1} bands may be Ni sites influenced by surface oxygen species formed from chemisorption of O_2. This result reveals that oxygen participates directly in the chemisorption of methane over Ni/Al_2O_3. As the temperature was raised to 250°C, the 3015 cm^{-1} band for gaseous methane decreased in intensity and became a shoulder, and the intensity of the 3010 and 3000 cm^{-1} bands of adsorbed methane considerably increased, and at the same time, CO, H_2, CO_2 and H_2O were detected in the gas phase indicating that methane partial oxidation took place. This result is in agreement with the fact that the methane partial oxidation starts to occur at about 230°C observed above. After 250°C, following methane partial oxidation the band 3015 cm^{-1} for free methane gradually decreased in intensity, in the meantime the intensities of the bands at 3010 and 3000 cm^{-1} for adsorbed methane increased, and no adsorbed CH_3 species [42] were observed. The result shows that the dominant surface species are the chemisorbed methane over Ni/Al_2O_3 and methane partial oxidation is via the chemisorbed methane. Hickman et al. [28], Vernon et al. [30] and Choudhary et al. [16,18] suggested that the first step for CH_4 conversion to syngas is the pyrolysis of CH_4 on the catalyst

tensities of the bands at 3010 and 3000 cm^{-1} increased with increasing temperature. At 200°C, the band at 3010 cm^{-1} became equal in intensity with that of the band at 3015 cm^{-1} for free methane. At 250°C, the band at 3015 cm^{-1} for gaseous methane decreased in intensity and the band at 3010 cm^{-1} became a main peak, and the band at 3000 cm^{-1} increased in intensity, at

surface $CH_4 \rightarrow C_s + 4H_s$. Au and Wang [11] observed normal deuterium isotope effects on the overall reaction of methane partial oxidation as well as on the CO and CO_2 formation reaction over Rh/SiO_2 when CD_4 was used instead of CH_4 to perform the methane partial oxidation reaction and concluded that methane dissociation is a key step and CO and CO_2 are formed via the same common intermediates. Our results obtained above show that the dominant surface species are chemisorbed methane in the co-presence of CH_4 and O_2 especially over a reaction start temperature for methane partial oxidation. It can be concluded that the dissociation of chemisorbed methane in the participation of adsorbed oxygen is a key step for methane partial oxidation reaction.

4. Conclusion

The onset of activity for methane partial oxidation to CO and H_2 occurs at 230°C over reduced Ni/Al_2O_3, indicating that Ni/Al_2O_3 is very active for methane partial oxidation. As methane alone is exposed to reduced Ni/Al_2O_3, two types of adsorbed methane were generated. During TP dynamic process (in CH_4), the amount of adsorbed methane increase with increasing temperature, which is indicative of chemisorption of methane and chemisorption of methane appeared to be an activated process. The results obtained from the co-adsorption of methane with oxygen indicate that chemisorbed oxygen species participated directly in the activation of methane and the dissociation of chemisorbed methane in participation of chemisorbed oxygen species is a key step for methane partial oxidation.

Acknowledgements

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