

# Studies of Catalysis in Partial Oxidation of Methane to Syngas( II ) \*

## — Chemisorbed Species, Energetics and Mechanism

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The characteristic study, by means of *in-situ* IR spectroscopy, of chemisorbed species on the Ni-catalysts for the partial oxidation of methane (POM) to syngas demonstrated the existence of  $\text{CH}_x(\text{a})$  and  $\text{H}_x\text{CO}(\text{a})$  adspecies on the functioning Ni-catalysts. Several designed experimental investigations on the reactivities of methane with  $\text{CO}_2$  and with  $\text{O}_2$ , respectively, over the Ni-catalysts, and of  $\text{CO}_2$  with the prerduced Ni-catalyst, as well as of the deposited carbon with  $\text{CO}_2$  and with  $\text{O}_2$ , respectively, have been carried out and the results were unfavorable to the two-step mechanistic interpretation proposed for the POM reaction. By means of the BOC-MP Approach, energetics of a set of elementary reactions, which may be involved in the POM process, on the clean (111) surface of Ni, Fe, Cu and Pd, respectively, has been studied. The results of the experiments and the calculation of the present work favor the direct catalytic dissociation-plus-surface oxidation-plus-further dehydrogenation mechanism as the dominant pathway making major contribution to the POM reaction.

**Keywords** Partial oxidation of methane, Syngas, Chemisorbed species, Energetics, Mechanism

### Introduction

Since the early work of Prettre *et al.*<sup>[1]</sup>, it has been accepted by many researchers that the catalytic partial oxidation of methane (POM) to syngas proceeds *via* a two-step reaction mechanism, *i. e.*, an initial combustion of a part of methane to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with complete conversion of oxygen followed by methane-steam, and  $-\text{CO}_2$  reforming and reverse shift reactions, leading to the equilibrium product distributions<sup>[1-5]</sup>. Various data have been advanced in support of this contention; one of the proofs proposed is that each reaction involved in the two-step mechanism can take place over the same POM catalysts.

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Another viewpoint is that  $H_2$  and CO are directly formed as primary products in methane oxidation, because any secondary reactions, such as methane steam reforming or water-gas shift are too slow<sup>[6,7]</sup>; these researchers considered that the surface reactions which produced  $H_2$  and CO occurred in an oxygen-depleted environment, and the major surface species were probably C or  $CH_x$  and H adsorbed on the surface. One of the experimental facts supporting this mechanistic interpretation is that  $CH_x$  adspecies were detected on the surface of Pd-catalysts<sup>[8]</sup>.

So far, a rather limited number of studies about the nature of the active site and the reaction mechanism has been reported. For better appraisal of the different mechanistic interpretations proposed, more detailed knowledge is needed about the nature of chemisorbed species and intermediates on the surface of the functioning catalysts as well as about the energetics of the surface reactions involved in the POM process.

Our recent investigations<sup>[9]</sup> on the catalytic performance of Ni, Co, and the other members in the first series of transition-metals for the POM reaction reveal that there is a correlation between the POM activity and the transition-metal sites with rapidly changeable valence,  $M^0/M^{2+}$  (*e. g.*,  $Ni^0/Ni^{2+}$ ) on the surface of the functioning catalysts; the zero-valence transition-metal sites seem to be responsible for activation and dehydrogenation of methane and the nature of rapidly changeable valence of the active sites is requisite for activation and rapid conversion of dioxygen.

In the present work, chemisorbed species on the surface of the functioning Ni-catalysts have been characterized using *in-situ* IR and Raman spectroscopies; the performances of the catalysts for  $O_2$ -reforming and for  $CO_2$ -reforming of methane were examined respectively; the interactions of  $CO_2$  with the surface of the reduced catalyst and of deposited carbon on the surface of the functioning catalyst with  $CO_2$  and with  $O_2$  were investigated, respectively; and energetics of a set of elementary reactions, which may be involved in the POM process, on clean (111) surface of Ni, Fe, Cu, and Pd, has been studied by using the Bond Order Conservation-Morse Potential (BOC-MP) Approach<sup>[10,11]</sup>. The results would provide significant implications concerning the general understanding of the dominant reaction pathway of the POM to syngas over the catalysts.

## Experimental

### 1 Preparation and Evaluation of Catalysts

The supported catalysts were prepared by impregnating with the solutions of the corresponding nitrate. The mixed metal oxides catalysts were prepared by thoroughly mixing, and finely grinding the corresponding nitrates. Both types of catalysts were calcined in air at 1073 K for at least 5 hours. The evaluation ex-

periment was performed in a fixed-bed continuous flow reactor-GC combination system operating under atmospheric pressure. The catalytic POM-to-syngas reaction over the catalysts was carried out at stationary state and under the following reaction conditions: the feed gas was a mixture of  $2\text{CH}_4/1\text{O}_2$ ; gas hourly space velocity (GHSV) at STP  $10^5 \text{ mL/h} \cdot \text{g} \cdot \text{catal.}$ ; temperature 973–1173 K. The detailed procedure of preparation and evaluation of the catalysts were described in our previous paper<sup>[9]</sup>.

## 2 Spectroscopic Characterization

### 2.1 FTIR

IR spectra were taken *in-situ* under the POM reaction conditions as well as *ex-situ* at room temperature using a Nicolet 740 FTIR spectrometer. Each spectrum was obtained by accumulation of 160 scans at a resolution of  $4 \text{ cm}^{-1}$ .

### 2.2 LRS

Laser Raman spectra were taken *in-situ* under the reaction conditions of 973 K and feedstream of  $2\text{CH}_4/1\text{O}_2$ , using a JY U-1000 Ramanor spectrometer with argon laser (488.0 nm, 200 mW) as the excitation source. Slit width settings corresponded to a resolution of  $4 \text{ cm}^{-1}$ . Spectral accumulation was necessary; up to 50 scans were accumulated to obtain an acceptable signal-to-noise ratio.

### 2.3 XPS

XPS measurements were done using a VG ESCA LAB MK-2 machine with Al- $K\alpha$  radiation (1487 eV) and UHV ( $1 \times 10^{-7} \text{ Pa}$ ), taking the Zr(4p) (B. E.) of  $\text{ZrO}_2$  at 182.3 eV or deposited carbon C(1s) (B. E.) at 284.6 eV, as the internal standard.

## Results and Discussion

### 1 *In-situ* IR and LR Spectra of Chemisorbed Species on the Surface of Catalysts

*In-situ* FTIR and LR spectroscopies have been applied to the investigation of the chemisorbed species on 4 wt% Ni/ $\text{ZrO}_2$  and Ni—Mg—O catalysts under the reaction conditions. Fig. 1 shows the IR transmittance spectra of NiO/ $\text{ZrO}_2$  during hydrogen prereduction. The absorption band appeared at  $1020 \text{ cm}^{-1}$ , which may be ascribed to the vibration of the Ni—O bond. The intensity of this band decreased gradually in the process of reduction and finally vanished, indicating that the Ni<sup>0</sup>-site was developed. It is evident from the result of Fig. 1 that the IR absorption by the reduced catalyst is relatively simple and weak, so that the background is quite low in the frequencies region for the IR observation.

As methane was introduced to the sample cell mounted with the prereduced 4 wt% Ni/ $\text{ZrO}_2$  catalyst, a series of new bands appeared soon, and subsequently, the infrared transmittance of the sample was rapidly getting poor due to carbon deposition on the surface of the reduced catalyst, most probably originating

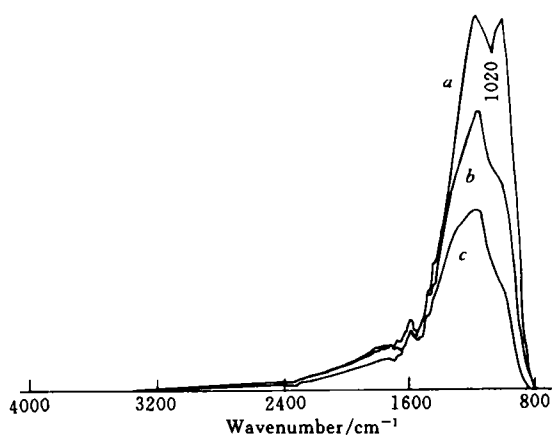


Fig. 1 IR transmittance spectra of 4 wt% Ni/ZrO<sub>2</sub> during temperature-programmed-hydrogen-reduction taken at a. 298 K, b. 573 K, c. 973 K.

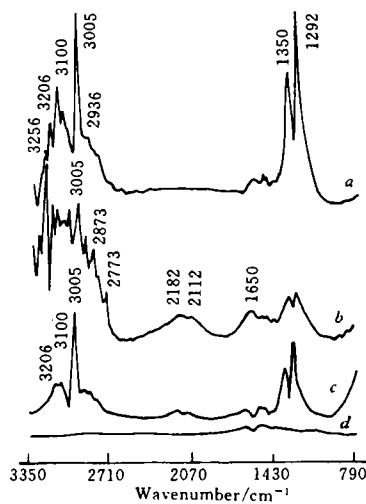


Fig. 2 IR absorption spectra of adsorption of methane on the prereduced 4 wt% Ni/ZrO<sub>2</sub> catalyst (a); chemisorbed species on the 4 wt% Ni/ZrO<sub>2</sub> catalyst after exposure to a flowing gaseous mixture of 2CH<sub>4</sub>/1O<sub>2</sub> at 973 K (b); chemisorbed species on the Ni-Mg-O catalyst after its exposure to a flowing gaseous mixture of 2CH<sub>4</sub>/1O<sub>2</sub> at 973 K (c); background of IR absorption of the prereduced Ni-Mg-O catalyst under atmosphere of helium (d).

from decomposition of methane. Fig. 2a shows the IR spectrum recorded in the initial two to three minutes in the region of 790—3350 cm<sup>-1</sup>. This result of spectroscopic measurement revealed activation and dehydrogenation of methane molecules on the surface of the prereduced 4 wt% Ni/ZrO<sub>2</sub> catalyst, perhaps on the Ni<sup>0</sup>-site, to fragments of hydrocarbon, mostly including such chemisorbed species as metal-methyl (2936, 2873, 1350 cm<sup>-1</sup>), metal-carbene (3100 cm<sup>-1</sup>), and metal-carbide (3206—3256 cm<sup>-1</sup>).

To gain information about adsorbed species which may exist on the 4 wt% Ni/ZrO<sub>2</sub> catalyst under reaction conditions associated with the POM, a sample of the H<sub>2</sub>-prereduced (973 K for 0.5 h) 4 wt% Ni/ZrO<sub>2</sub> catalyst was exposed at 973 K to a flowing gaseous mixture of 2CH<sub>4</sub>/1O<sub>2</sub>. After 1 minute of exposure, the IR spectrum of the functioning catalyst was recorded *in situ*. Fig. 2b shows the result of accumulation of 160 scans. Bands are present at 3005 cm<sup>-1</sup>(m), 3065—3193 cm<sup>-1</sup> region (m), 3256 cm<sup>-1</sup>(s), 2936 cm<sup>-1</sup>(mw), 2873 cm<sup>-1</sup>(mw) 2773 cm<sup>-1</sup>(mw), 2182 cm<sup>-1</sup>(w), 2112 cm<sup>-1</sup>(w), 1650 cm<sup>-1</sup>(m), 1350 cm<sup>-1</sup>(ms), and 1291 (s) cm<sup>-1</sup>. Surface adspecies, which may be tentatively assigned, in-

clude  $\text{CH}_3$  (2936, 2873, and  $1350\text{ cm}^{-1}$ ),  $\text{CH}_2$  ( $3100\text{ cm}^{-1}$ ),  $\text{CH}$  ( $3206\text{--}3256\text{ cm}^{-1}$ ),  $\text{H}_2\text{CO}$  ( $2773$ , and  $1650\text{ cm}^{-1}$ ),  $\text{CO(g)}$  ( $2182$ , and  $2112\text{ cm}^{-1}$ ).

Fig. 2d is the background of IR absorption of the prerduced Ni—Mg—O catalyst under atmosphere of helium, and Fig. 2c is the spectrum taken *in-situ* under the reaction conditions of 973 K, atmospheric pressure, and  $2\text{CH}_4/1\text{O}_2$  feedstream and in the two to three minutes after introduction of the feedstream. Fig. 3 shows IR spectra taken *in situ* under atmospheric pressure, and at 823, 873, 923, 973 K, respectively, on the prerduced Ni—Mg—O catalyst in the two to three minutes after introduction of feedstream of  $2\text{CH}_4/1\text{O}_2/4\text{N}_2$ . Information provided by these IR spectra about surface adspecies on the Ni—Mg—O catalyst is almost the same as that obtained on the 4 wt% Ni/ $\text{ZrO}_2$  catalyst. The assignment of IR bands for adsorbed species associated with the POM reaction on the 4 wt% Ni/ $\text{ZrO}_2$  and the Ni—Mg—O catalysts are summarized in Table 1. It is worthy of noting that the IR band at  $3730\text{ cm}^{-1}$  due to the surface hydroxyl was quite weak, implying low stationary state concentration of hydroxyl-ad-

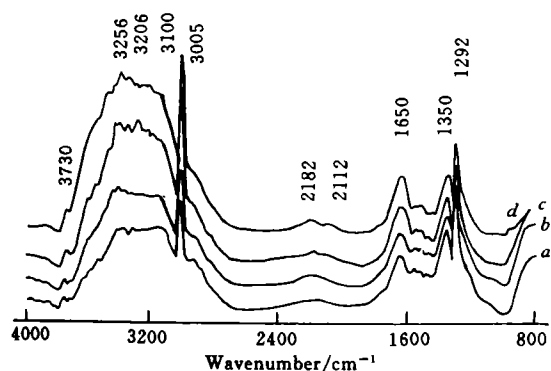


Fig. 3 *In-situ* IR spectra of the POM reaction system over the Ni—Mg—O catalyst under the reaction conditions of atmospheric pressure.

Feedstream:  $2\text{CH}_4/1\text{O}_2/4\text{N}_2$ ; temperature: a. 823 K, b. 873 K, c. 923 K d. 973 K.

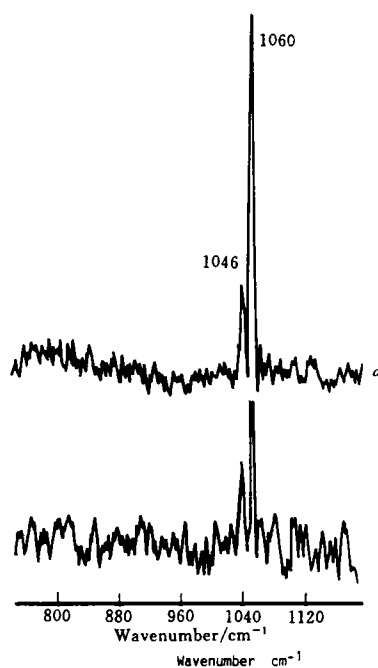


Fig. 4 *In-situ* Raman spectra taken on the functioning 4 wt% Ni/ $\text{ZrO}_2$  catalyst (a) and the functioning Ni—Mg—O catalyst (b).

The reaction conditions: 973 K, atmospheric pressure, and  $2\text{CH}_4/1\text{O}_2/4\text{N}_2$  feedstream; scanning number at 52 and 18, respectively.

species OH on the surface of functioning Ni-catalysts.

Laser Raman spectroscopy (LRS) was applied to the observation of vibrational spectra of adspecies on the catalysts in the wavenumber region below 1200  $\text{cm}^{-1}$ . Fig. 4 shows the Raman spectra taken on the functioning 4wt%Ni/ZrO<sub>2</sub> and Ni—Mg—O catalysts *in situ* under the conditions associated with the POM reaction, *i. e.*, 973K, atmospheric pressure, and 2CH<sub>4</sub>/1O<sub>2</sub>/4N<sub>2</sub> feedstream. Raman peaks are present at 1060  $\text{cm}^{-1}$  and 1046  $\text{cm}^{-1}$ , which are most probably originated from carbonate species adsorbed on the surface, perhaps at two kinds of adsorption sites with different micro-environments. Except the two peaks, no peak assignable to O—O vibrations of dioxygen adspecies was detected, implying that the activation and dissociation of dioxygen is quite fast on the surface of the functioning catalysts.

Absence of O<sub>2</sub><sup>-</sup> and O<sup>-</sup> in the observable concentrations was also identified by the EPR measurements. The EPR spectra obtained (unshown) were mainly characteristic and considerably complex absorption of *d*-electrons of nickel; no EPR signal assignable to O<sub>2</sub><sup>-</sup> or O<sup>-</sup> was detected.

Table 1 Assignment of IR bands for adsorbed species associated with the POM reaction on the 4wt%Ni/ZrO<sub>2</sub> and Ni—Mg—O catalysts

Band position ( $\text{cm}^{-1}$ )	Assignment	Reference
3730	O—H stretch of surface hydroxyl OH	[12]
3206—3256	C—H stretch of metal-carbide Ni≡CH	[12,13]
3100	C—H asym. stretch of metal-carbene Ni=CH <sub>2</sub>	[12,13,14]
3005	C—H asym. stretch of CH <sub>4</sub> (g)	[15]
2936	C—H asym. stretch of surface methyl CH <sub>3</sub>	[12,13]
2873	C—H sym. stretch of surface methyl CH <sub>3</sub>	[12,13]
2773	C—H stretch of H <sub>2</sub> CO	[16]
2182,2112	C—O vib.-rot. combination bands of CO(g)	[17]
1650	C—O stretch of H <sub>2</sub> CO	[18]
1350	C—H scissors of surface methyl CH <sub>3</sub>	[12,13]
1292	C—H scissors of CH <sub>4</sub> (g)	[15]
1020	Ni—O stretch of surface Ni=O bond	

## 2 Studies of Problems Associated with the Mechanism of the POM Reaction

So far, there has been no unified theory of mechanism, by which all the known important experimental facts can be adequately correlated and elucidated, and quite a few problems still remain to be solved. In order to get further information of the reaction-chemistry of the relevant reactant molecules and chemisorbed species on the Ni-based catalysts so as to appraise and distinguish various mechanistic interpretations proposed for the POM reaction, the following problems have been investigated by several designed experiments.

### 2.1 Reactivities of Methane with CO<sub>2</sub> and with O<sub>2</sub> over the Ni-based Catalysts

The performances of the two catalysts, Ni—Mg—O and 4wt%Ni/ZrO<sub>2</sub>, for the O<sub>2</sub>- and CO<sub>2</sub>-reforming reactions of methane have been evaluated, respective-

ly, and the results are presented in Table 2. It can be found that the difference in the reaction activities existed between the two processes over either catalyst: on the Ni—Mg—O catalyst, both reactions of O<sub>2</sub>-reforming and CO<sub>2</sub>-reforming proceeded in a considerably high rate—methane conversion being 96% for O<sub>2</sub>-reforming and 89% for CO<sub>2</sub>-reforming; whereas over the 4wt%Ni/ZrO<sub>2</sub> catalyst, methane conversion reached 93% for O<sub>2</sub>-reforming and less than 50% for CO<sub>2</sub>-reforming. Another significant finding is that for CO<sub>2</sub>-reforming reaction of methane, when the reaction proceeded for a few minutes, an apparent pressure drop in catalyst bed was observed due to heavy deposition of carbon on the surface of the catalyst. If the POM reaction proceeds *via* the two-step mechanism (*i. e.*, a part of methane was first combusted to CO<sub>2</sub> and H<sub>2</sub>O with complete conversion of O<sub>2</sub>, and then, both combusted products reacted with methane to produce CO and H<sub>2</sub>), it is difficult to rationalize that a poor catalyst for CO<sub>2</sub>-reforming reaction such as 4wt%Ni/ZrO<sub>2</sub> may be a good one for the POM reaction; furthermore, there could not be much less deposition of carbon on the surface of catalysts in the O<sub>2</sub>-reforming in comparison with that in the CO<sub>2</sub>-reforming.

Table 2 Results of activity assays of Ni—Mg—O and 4wt%Ni/ZrO<sub>2</sub> catalysts for O<sub>2</sub>-reforming and CO<sub>2</sub>-reforming of methane reaction (data taken at 10 min of reaction)

Catalysts	O <sub>2</sub> -reforming <sup>a</sup>		CO <sub>2</sub> -reforming <sup>b</sup>	
	C <sub>CH<sub>4</sub></sub> (%)	S <sub>CO</sub> (C%)	C <sub>CH<sub>4</sub></sub> (%)	C <sub>CO<sub>2</sub></sub> (%)
Ni—Mg—O	96	94	89	92
4wt %Ni/ZrO <sub>2</sub> <sup>c</sup>	93	97	<50	<50

a. Reaction conditions; Feed gases, 2CH<sub>4</sub>/1O<sub>2</sub>; Temp. , 1050K.

b. Reaction conditions; Feed gases, 1CH<sub>4</sub>/1CO<sub>2</sub>; Temp. , 1050K.

c. Deactivated in 70 minutes for CO<sub>2</sub>-reforming reaction.

## 2.2 Reactivity of CO<sub>2</sub> with the Prerduced Ni-catalyst

A sample of Ni—Ca—O catalyst was prerduced by a flow of hydrogen at 1050K for 1 hour, followed by cleaning the surface with a flow of pure nitrogen for a few minutes, and then followed by switching the gas-supply to CO<sub>2</sub>. The change in composition of gases in the exit of reactor with time was monitored by GC analyzer. Table 3 shows the results.

As shown in Table 3, during the time of testing, there was only a very little of CO detected in the products, and it disappeared after 50 minutes of time-on-CO<sub>2</sub> stream. The formation of CO indicated that an interaction must have occurred between CO<sub>2</sub> and the reduced catalyst, but in comparison with the interaction of O<sub>2</sub> with the reduced catalyst, it was considerably slow; in contrast, when O<sub>2</sub> contacted with the reduced catalyst, the latter would be very easy to be oxidized completely in a few minutes. Therefore, there was an obvious difference between CO<sub>2</sub> and O<sub>2</sub> in their reactivities with the reduced catalyst. Although in some cases, *e. g.*, on Ni—Mg—O catalyst, both reactions of CO<sub>2</sub>-reforming

and O<sub>2</sub>-reforming of methane may proceed in a comparable speed (see Table 2), it is doubtful that the oxygen source in CO<sub>2</sub>-reforming reaction is furnished by the redox of CO<sub>2</sub> with the surface of catalyst in reduction state.

Table 3 The change with time in composition of products for interaction of CO<sub>2</sub> with the prereduced Ni—Ca—O catalyst at 1050K

Time-on-CO <sub>2</sub> stream (min)	Composition of gases in the exit of reactor		Time-on-CO <sub>2</sub> stream (min)	Composition of gases in the exit of reactor	
	CO(%)	CO <sub>2</sub> (%)		CO(%)	CO <sub>2</sub> (%)
2.0	0.39	99.61	4.0	0.31	99.69
10.0	0.37	99.63	16.0	0.27	99.73
22.0	0.28	99.72	29.0	0.20	99.80
36.0	0.11	99.89	44.0	0.08	99.92
50.0	0.0	100			

XRD measurement provided further information about interaction of the prereduced Ni—Ca—O catalyst with CO<sub>2</sub> and with O<sub>2</sub>, respectively. Fig. 5 shows the XRD patterns taken on three different samples: (a) the precursor (oxidation state); (b) the H<sub>2</sub>-prereduced catalyst, followed by a O<sub>2</sub> treatment for 10 minutes at 1050K; (c) the H<sub>2</sub>-prereduced catalyst, followed by treatment with CO<sub>2</sub> for 60 minutes at 1050K. It is evident from the results that the patterns a and b are almost coincident, which demonstrate that the two samples possess the same composition of phase, NiO and CaO. In pattern b, no XRD peak assignable to Ni<sup>0</sup> was observed, indicating that the interaction of oxygen with the reduced catalyst is very easy to occur under the condition of 1050K. However, the appearance of pattern c is obviously different. Even though the time-on-CO<sub>2</sub> stream was as long as 60 minutes, the Ni<sup>0</sup>-phase still existed as one of the substantial components; the peak intensity ratio of Ni<sup>0</sup>/Ni<sup>2+</sup> remained about 73/100. These XRD results are in close agreement

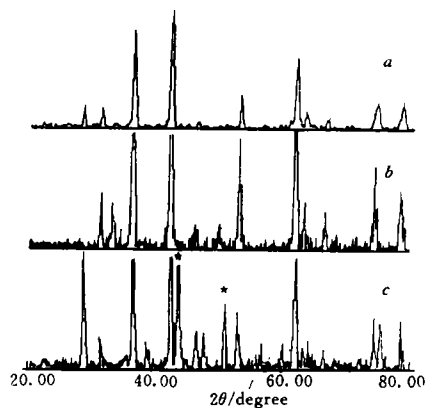


Fig. 5 XRD patterns taken on the precursor of Ni—Ca—O catalyst (oxidation state) (a), the H<sub>2</sub>-prereduced Ni—Ca—O catalyst, followed by a O<sub>2</sub> treatment for 10 minutes at 1050K (b), and the H<sub>2</sub>-prereduced Ni—Ca—O catalyst, followed by a CO<sub>2</sub> treatment for 60 minutes at 1050K (c).

with the above results of reactivity evaluation, and give a further support to the inference, *i. e.*, the dissociation of CO<sub>2</sub> on the prereduced Ni-catalyst in company with Ni<sup>0</sup>-site being oxidized, namely, CO<sub>2</sub> + Ni<sup>0</sup> = CO + NiO, proceeds much more slowly than the interaction of O<sub>2</sub> with Ni<sup>0</sup>-sites does, and therefore, it is



unlikely to be a necessary step in O<sub>2</sub>-reforming reaction of methane.

### 2.3 Reactivity of CO<sub>2</sub> with Deposited Carbon on the Surface of Catalyst

A sample of Ni—Ca—O catalyst was reduced by hydrogen at 1050K for 60 minutes, followed by switching the gas supply to methane-stream for 120 minutes and then followed by switching to a flow of purified nitrogen for a few minutes to clean the methane remaining in the reactor, and finally CO<sub>2</sub> feedstream was introduced. The change in composition of products with time was monitored using GC detector. Table 4 shows the results obtained.

As shown in Table 4, in the initial period of 6.6 minutes, the conversion of CO<sub>2</sub> kept above 70% and, during most of the time for testing, CO was the major product till the deposited carbon was depleted. These results indicate that the reaction of CO<sub>2</sub> with deposited carbon on the surface of catalyst is quite easy to occur under the condition associated with the CO<sub>2</sub>-reforming reaction, and the observed reaction rate may be comparable to overall rate of CO<sub>2</sub>-reforming under the same conditions. Therefore, this elementary step is probably involved in the reaction of CO<sub>2</sub>-reforming, as well as O<sub>2</sub>-reforming, of methane.

Table 4 The change with time in composition of products for interaction of CO<sub>2</sub> with deposited carbon on the Ni—Ca—O catalyst at 1050K

Time-on- CO <sub>2</sub> stream (min)	Composition of gases in the exit of reactor		Time-on- CO <sub>2</sub> stream (min)	Composition of gases in the exit of reactor	
	CO(%)	CO <sub>2</sub> (%)		CO(%)	CO <sub>2</sub> (%)
0.8	71.2	28.8	2.4	79.0	21.0
6.6	71.1	28.9	12.7	66.6	33.4
21.7	56.3	43.7	35.6	2.7	97.3

### 2.4 Reactivity of Deposited Carbon with O<sub>2</sub>

After a sample of prereduced Ni—Ca—O catalyst underwent a treatment by a flow of methane at 1050K for 1 hour, the feedstream was switched from methane to purified nitrogen so as to clean the testing system till no methane survived, followed by introducing a flow of pure oxygen and monitoring the change in the composition of products by GC. The results are shown in Fig. 6.

It can be seen from the results that at the initial stage of the reaction, the only product was carbon dioxide in a small amount. As time passed, conversion of oxygen and selectivity to carbon monoxide enhanced dramatically and both reached near to 100% at about 10 minutes, and afterwards, gradually dropped, whereas selectivity to CO<sub>2</sub> enhanced simultaneously, and finally, there was only CO<sub>2</sub> involved in the product but conversion of oxygen was getting less.

This experiment revealed the necessity of the activation of dioxygen on the surface of catalyst in the reaction of oxygen with deposited carbon (perhaps also in the POM reaction). It is conceivable that when the reaction began, the surface of catalyst was highly covered by deposited carbon, hampering the contact of oxygen with the surface of catalyst and resulting in the poor activity of reac-

tion. As reaction proceeded, a portion of the deposited carbon was consumed, and the chance of getting oxygen in touch with the catalyst surface and being activated would increase, thus, leading to the enhancement of O<sub>2</sub>-conversion. When most of deposited carbon was depleted, the catalyst was deeply oxidized, and the conversion of oxygen dropped, till completely stopped.

### 3 Reaction Energetics of the POM Process

We proposed<sup>[9]</sup> that there may exist two pathways for activation of methane on Ni-catalysts in the POM reaction, *i. e.*, dehydrogenation by homolytic splitting of the C—H bond on reduced Ni-sites (Ni<sup>0</sup>-sites) and oxygen-assisted dehydrogenation by heterolytic splitting of the C—H bond on oxidized Ni-sites, namely, Ni<sup>2+</sup>-O<sup>2-</sup> pair sites, and that under the conditions of rich-in-methane/poor-in-oxygen (*e. g.*, 2CH<sub>4</sub>/1O<sub>2</sub>) and high temperature (about 1000K), the former is probably the major pathway for the activation and conversion of methane with syngas as the dominant products. In order to gain the knowledge of the thermochemistry of the POM reaction, which can be applied to determine the most energetically favorable pathway for the reaction to proceed, the energetics of a set of elementary steps, which may be involved in the POM reaction, on the (111) surface of Ni, Fe, Cu and Pd single crystals have been examined by us. The heats of adsorption of all relevant ad-species and the activation barriers for all relevant elementary steps have been calculated by means of the BOC-MP Approach<sup>[10,11]</sup>. The results of these calculations are presented in Table 5 and Table 6. From these results, the following interesting inferences can be drawn.

On Cu(111) surface, the activation barrier for the dissociative chemisorption of methane is as high as 133.76 kJ/mol, and is higher than those for the surface-oxidation reaction of CH<sub>x</sub>(a) and the further dehydrogenation of the subsequent intermediates, H<sub>2</sub>CO(a), so that this step is most probably the rate-determining-step (*r. d. s.*) of the POM reaction; the rate of the overall reaction (conversion of methane) may expected to be comparatively low.

On the Fe(111) surface, the dissociative chemisorption of methane is expected to be fast (with an activation barrier of 45.98 kJ/mol for the first dehy-

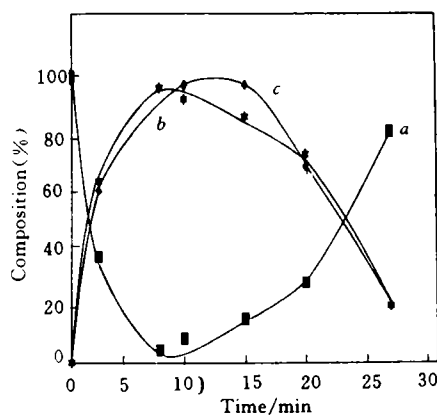


Fig. 6 The variance with time in the composition of products for interaction of O<sub>2</sub> with deposited carbon on the Ni—Ca—O catalyst at 1050K. a. Selectivity to CO<sub>2</sub>; b. selectivity to CO; c. conversion of O<sub>2</sub>.

drogenation), but the subsequent oxidation of  $\text{CH}_x(\text{a})$  would be slow due to the high activation barrier of at least 133.76 kJ/mol, so that the reaction,  $\text{CH}_x(\text{a}) + \text{O}(\text{a}) = \text{H}_x\text{CO}(\text{a})$ ; would become the rate-determining-step of the POM reaction. On the other hand, due to the low consuming rate of  $\text{O}_2$  and the larger negative potential of metallic iron, the surface of the functioning Fe-catalysts would be substantially oxidized under the POM reaction conditions, with the result that the major Fe-species on the surface of the functioning catalysts is  $\text{Fe}^{n+}$ , rather than  $\text{Fe}^0$ , as has been evidenced by our previous experimental results<sup>[9]</sup>.

On Ni(111) surface, the activation barriers for the dissociative chemisorption of methane and the surface-oxidation-reaction of  $\text{CH}_x(\text{a})$ , and for the further dehydrogenation of the subsequent intermediates,  $\text{H}_x\text{CO}(\text{a})$ , are all moderate, and, thus, the rate of the overall reaction may be expected to be much higher than that on Fe(111) or Cu(111) surface under the same reaction conditions, as has been evidenced by the results of our previous comparative study about the POM catalytic performance of the first series of transition-metals<sup>[9]</sup>. The activation barrier of the surface-oxidation of  $\text{CH}_x(\text{a})$  species, in comparison with that of the dissociative chemisorption of methane, is somewhat higher, making it probably to be the rate-determining-step of the overall reaction; on the other hand, not high enough rate of consumption of  $\text{O}_2$  would result in the co-existence of  $\text{Ni}^0$  with  $\text{Ni}^{n+}$  on the surface of functioning catalyst. Furthermore, the high activation barrier (146.30 kJ/mol) for the reaction,  $\text{C}(\text{a}) + \text{O}(\text{a}) = \text{CO}(\text{a})$ , would easily lead to deposition of carbon on the surface of functioning catalyst.

Table 5 Heats of chemisorption (Q) and total bond energies in the gas-phase (D) and chemisorption states (D+Q) for species involved in the partial oxidation of methane to syngas on Ni(111), Fe(111), Cu(111), and Pd(111) surface \*

Adsorbate	D	Ni		Fe		Cu		Pd	
		Q	D+Q	Q	D+Q	Q	D+Q	Q	D+Q
H	—	63	63	64	64	56	56	62	62
O	—	115	115	120	120	103	103	87	87
C	—	171	171	200	200	120	120	160	160
CH	81	116	197	142	223	72	153	106	187
CH <sub>2</sub>	183	83	266	104	287	48	231	75	258
CH <sub>3</sub>	293	48	341	60	353	25	318	42	335
CH <sub>4</sub>	398	9	407	10	408	8	406	9	407
OH	102	61	163	64	166	52	154	40	142
CO	257	27	284	32	289	12	269	34	291
HCO	274	50	324	65	339	27	301	44	318
H <sub>2</sub> CO	361	19	380	20	381	16	377	12	373
H <sub>3</sub> CO	383	65	448	67	450	55	438	43	426
CO <sub>2</sub>	384	6	390	8	392	5	389	4	388
H <sub>2</sub> O	220	17	237	19	239	14	234	10	230
H <sub>2</sub>	104	7	111	7	111	5	109	7	111

\* All energies in  $\times 4.18$  kJ/mol.

Table 6 Calculated activation barriers for forward ( $E_f^*$ ) and reverse ( $E_r^*$ ) directions of elementary reactions involved in partial oxidation of methane to syngas on Ni(111), Fe(111), Cu(111), and Pd(111) surface\*

Reaction	Ni		Fe		Cu		Pd	
	$E_f^*$	$E_r^*$	$E_f^*$	$E_r^*$	$E_f^*$	$E_r^*$	$E_f^*$	$E_r^*$
$\text{CH}_4(\text{a}) = \text{CH}_3(\text{a}) + \text{H}(\text{a})$	14	14	11	21	32	0	18	7
$\text{CH}_3(\text{a}) = \text{CH}_2(\text{a}) + \text{H}(\text{a})$	24	12	22	19	31	0	25	9
$\text{CH}_2(\text{a}) = \text{CH}(\text{a}) + \text{H}(\text{a})$	23	17	22	22	27	5	24	15
$\text{CH}(\text{a}) = \text{C}(\text{a}) + \text{H}(\text{a})$	5	42	4	45	8	31	5	40
$\text{CH}_3(\text{a}) + \text{O}(\text{a}) = \text{H}_3\text{CO}(\text{a})$	21	13	32	9	2	18	12	16
$\text{CH}_2(\text{a}) + \text{O}(\text{a}) = \text{H}_2\text{CO}(\text{a})$	24	23	40	15	0	42	6	34
$\text{CH}(\text{a}) + \text{O}(\text{a}) = \text{HCO}(\text{a})$	23	35	34	31	0	44	2	46
$\text{C}(\text{a}) + \text{O}(\text{a}) = \text{CO}(\text{a})$	35	33	52	22	5	51	6	50
$\text{CO}(\text{a}) = \text{CO}(\text{g})$	27	0	32	0	12	0	34	0
$\text{H}_3\text{CO}(\text{a}) = \text{H}_2\text{CO}(\text{a}) + \text{H}(\text{a})$	10	5	10	5	9	4	1	10
$\text{H}_2\text{CO}(\text{a}) = \text{HCO}(\text{a}) + \text{H}(\text{a})$	26	33	5	27	20	0	9	17
$\text{HCO}(\text{a}) = \text{CO}(\text{a}) + \text{H}(\text{a})$	0	23	4	18	0	24	0	34
$\text{HCO}(\text{a}) = \text{C}(\text{a}) + \text{OH}(\text{a})$	18	28	10	37	31	5	24	8
$\text{CO}(\text{a}) + \text{H}(\text{a}) = \text{C}(\text{a}) + \text{OH}(\text{a})$	29	16	18	31	51	0	51	0
$\text{CO}_2(\text{a}) = \text{CO}(\text{a}) + \text{O}(\text{a})$	6	15	1	27	28	11	34	24

\* All energies in  $\times 4.18$  kJ/mol.

On Pd(111) surface, the rate-determining-step of the POM reaction may be the dissociative chemisorption of methane, and the subsequent surface-oxidation of  $\text{CH}_x(\text{a})$  would be quite fast, and, thus, heavy coking was expectable to be avoided to a great extent. In a general way, Pd may be expected to have the best catalytic performance for the POM reaction among the four transition-metals investigated in the present work.

Based upon our results of the experiment and calculation, as well as upon known facts reported in literature, it can be inferred that the POM-to-syngas reaction over Ni-based catalysts may involve the following elementary processes:

(1) Dissociative chemisorption of methane by homolytic splitting of the C—H bond on the reduced Ni-sites, *i. e.*,  $\text{Ni}^0$ -sites:



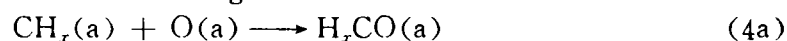
(2) Combination and desorption of adsorbed H atoms:



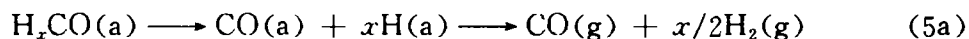
(3) Activation and dissociation of dioxygen on  $\text{Ni}^0$ -sites in company with the  $\text{Ni}^0$ -sites being oxidized:



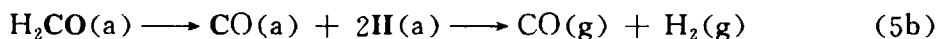
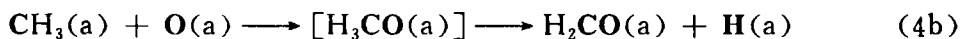
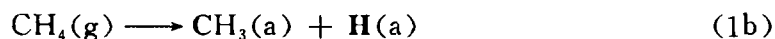
(4) Surface-oxidation-reaction of  $\text{CH}_x(\text{a})$  with  $\text{O}(\text{a})$  in company with the oxidized Ni-sites, *i. e.*,  $\text{Ni}^{2+}$ -sites, being reduced:



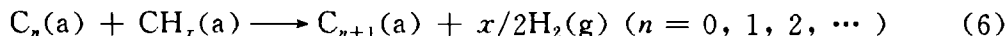
(5) Further dehydrogenation of the oxygenate-intermediates,  $\text{H}_x\text{CO}(\text{a})$ , and desorption of adsorbed CO and H:



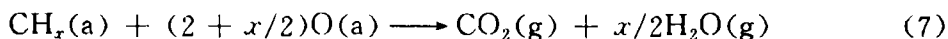
and the most energetically favorable pathway (also the dominant pathway making the major contribution to the POM reaction) over Ni-based catalysts was probably as follows:



Under the reaction conditions of poor-in-oxygen, the deposition of carbon was getting heavy:



and under the reaction conditions of rich-in-oxygen or low temperature, the products of deep-oxidation of methane ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) would dramatically increase:



Indeed, this is a preliminary suggestion. For the resolution of the mechanistic controversies, further work is needed.

## References

- [ 1 ] Prettre, M. , Eichner, C. , Perrin, M. , Trans. Faraday Soc. , **43**, 335(1946)
- [ 2 ] Ashcroft, A. T. , Cheetham, A. K. , Foord, J. S. , *et al.* , Nature, **344**, 319(1990)
- [ 3 ] Jones, R. H. , Ashcroft, A. T. , Waller, D. , *et al.* , Catal. Lett. , **8**, 169(1991)
- [ 4 ] Dissanayak, D. , Rosynek, M. P. , Kharas, K. C. C. , *et al.* , J. Catal. , **132**, 117(1991)
- [ 5 ] Choudhary, V. R. , Rane, V. H. , J. Catal. , **130**, 411(1991)
- [ 6 ] Hickman, D. A. and Schmidt, L. D. , J. Catal. , **138**, 267(1992)
- [ 7 ] Hickman, D. A. , Hauptfear, E. A. and Schmidt, L. D. , Catal. Lett. , **17**, 223(1993)
- [ 8 ] Lapszewicz, J. A. and Jiang, X. Z. , Prepr. Am. Chem. Soc. , Div. Pet. Chem. , **37**(1), 252 (1992)
- [ 9 ] Chen, P. , Zhang, H. B. , Lin, G. D. and Tsai, K. R. , Proc. 7th NCC (Dalian, 1994) p. 618
- [10] Shustorovich, E. , Acc. Chem. Res. , **21**, 183(1988)
- [11] Shustorovich, E. and Bell, A. T. , J. Catal. , **113**, 341(1988)
- [12] Galuszka, J. and Amenomiya, Y. , Proc. 9th ICC (Calgary, 1988), Eds. Phillips, M. J. and Ternan, M. , 1988: 697
- [13] Yates, D. J. C. and Lucchesi, P. J. , J. Chem. Phys. , **35**, 243 (1961)
- [14] Kazansky, V. B. , Shelimov, B. N. , Vikulov, K. A. , New Frontiers in Catalysis, Proc. 10th ICC (Budapest, 1992), Eds. Guzzi, L. , *et al.* , Elsevier, 1993: 515
- [15] Nakamoto, K. , Infrared and Raman Spectra of Inorganic and Coordination Compounds (3rd Ed. ) , New York, John Wiley & Sons, 1978:135
- [16] Tang Hui-tong, Spectroscopic Identification of Organic Compounds, Beijing, Perking University Press, 1992, 147
- [17] Drago, R. S. , Physical Methods in Chemistry, Philadelphia-London-Toronto, W. B. Saunders Company, 1977, 169
- [18] Collman, J. P. and Hegedus, L. S. , Principles and Applications of Organotransition Metal Chemistry, Mill Valley, California, Univ. Sci. Books, 1980, 80