Methane activation over unsupported and La_2O_3-supported copper and nickel catalysts

C.T. Au [a,1], Y.H. Hu [a,b] and H.L. Wan [b]

[a] Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon, Hong Kong
[b] Department of Chemistry and State Key Laboratory for Physical Chemistry, Xiamen University, Xiamen 361005, PR China

Received 20 September 1994; accepted 21 September 1995

Methane was pulsed over pure CuO and NiO as well as Cu/La_2O_3 and Ni/La_2O_3 catalysts at 600°C. Results indicate that the mechanisms for methane activation over copper and nickel are quite different. Over CuO, methane is converted to CO_2 and H_2O, most likely via the combustion mechanism; whereas metallic copper does not activate methane. Over NiO in the presence of metallic nickel sites, methane activation follows the pyrolysis mechanism to give CO, CO_2, H_2 and H_2O. Similar results were obtained over the Cu/La_2O_3 and Ni/La_2O_3 catalysts. XRD investigations indicate that copper and nickel existed as $CuLa_2O_4$ and $LaNiO_3$ respectively in the La_2O_3-supported catalysts. The effect of La_2O_3 on the activation of methane is discussed.

Keywords: methane activation; Cu/La_2O_3 and Ni/La_2O_3 catalysts

1. Introduction

Methane utilization has received much attention in the past years. Efforts have been devoted to converting it to transportable and/or value added products such as ethylene and methanol [1–4]. Besides the well-studied methane oxidative coupling process, partial oxidation of methane to syngas is another route being considered [4–8]. Most of the catalysts used in the latter case are supported transition metals. In order to disclose the mechanism of partial oxidation of methane to syngas, many researchers studied the activation of methane over transition metals by theoretical [9] as well as molecular beam [10] approaches. Not many of the studies were performed in practical catalytic conditions. In our previous work [11], pulse studies of the interaction of methane over NiO/Al_2O_3 catalysts at 500°C showed that the probability of methane being activated on nickel oxide was significantly lower than that observed on the reduced surface, indicating that methane adsorption and dissociation on reduced nickel sites is a key step for the oxidative conversion of methane. Recently, we studied the activation of methane over CuO, NiO as well as Cu/La_2O_3 and Ni/La_2O_3 catalysts at 600°C by pulse method. Some useful information was obtained.

2. Experimental

Catalyst preparation. CuO and NiO were prepared directly from CuO and $Ni(NO_3)_2$, while Cu/La_2O_3 and Ni/La_2O_3 catalysts were prepared by impregnating the proper nitrate solution on La_2O_3. The powder or paste generated was dried at 110°C and annealed at 400°C for decomposition. After being pressed and crushed, the material was sieved to a grain size of 20–40 mesh before calcination at 800°C in air for 4 h.

Pulse reaction. The reaction was carried out using a pulse microreactor system [11]. The reactor was made of a quartz tube with 4 mm i.d. For each study, 5 mg of catalyst was used. The pulse volume of methane was 1.1 ml. During the reaction, helium was the carrier gas (flow rate = 17 ml/min). Selectivities were calculated on the basis of carbon contents in the products. The amount of carbon C(s) accumulated on the surface during methane interaction with the catalysts was obtained based on 100% carbon balance. La_2O_3 as well as the blank runs show no activity whatsoever in the reaction conditions mentioned in this paper.

Catalyst characterization. Phase composition of catalysts was determined by X-ray diffraction (RU-200B, D/MAX-B, RIGAKU).

3. Results and discussion

3.1. CuO and NiO

Fig. 1 shows the variations of methane conversion and CO_2 selectivity over CuO at 600°C versus the ordinal number of methane pulses. One can see that CO_2 selectivity was 100% at all time while methane conversion declined from 81% at the 1st pulse to less than 2% at the 12th pulse.

Over NiO at 600°C, methane conversion was 90% at the 1st pulse and increased to reach 97% at the 2nd and 3rd pulses and then declined steadily to less than 4% at the 12th pulse. Between the 12th and 19th pulses,

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[1] To whom correspondence should be addressed.

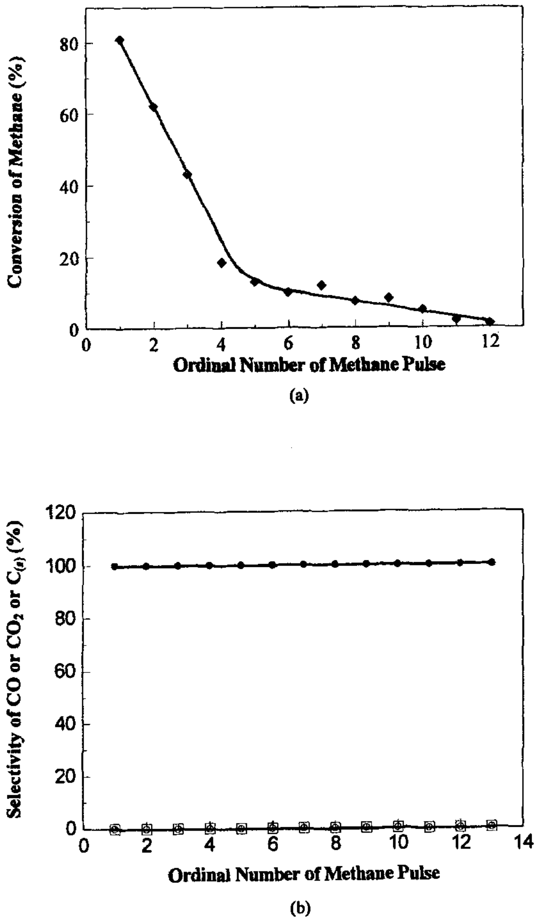

Fig. 1. The relationship of (a) CH_4 (◆) conversion and (b) C(s) (○), CO (□) and CO_2 (●) selectivities with the ordinal number of CH_4 pulsing over CuO at 600°C.

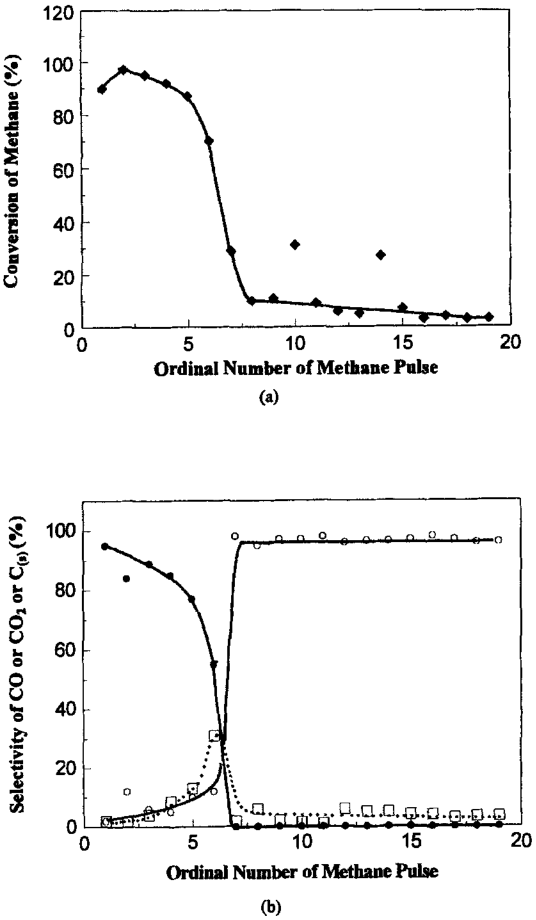

Fig. 2. The relationship of (a) CH_4 (◆) conversion and (b) C(s) (○), CO (□) and CO_2 (●) selectivities with the ordinal number of CH_4 pulsing over NiO at 600°C.

methane conversion remained at 4%. In the mean time, CO selectivity increased from the initial value of 2% to reach 31% at the 6th pulse before decline. After the 6th pulse, most of the methane converted ended up as carbon accumulated on the surface (fig. 2).

3.2. Cu/La_2O_3 and Ni/La_2O_3

Methane conversion over the 10 wt% Cu/La_2O_3 catalyst at 600°C was about 2.7% during the first two methane pulses and declined steadily to reach 0.1% at the 16th pulse. The selectivity of CO_2 stayed at 100% at all time (fig. 3).

Methane conversion was below 1% over the 10 wt% Ni/La_2O_3 catalyst initially. Further pulsing of methane would result in the increase of methane conversion that reached 31% at the 11th pulse and then decreased gradually and reached 13% at the 18th pulse. After the 18th pulse, methane conversion stayed at about 13%. In the mean time, a decrease in CO_2 selectivity from 98% at the 1st pulse to 0% at 7th pulse was observed. Carbon accumulation on the catalyst increased from the initial value of less than 2% to 97% at the 13th pulse and remained constant at about 97% afterwards. CO selectivity increased from the initial value of ca. 2% and reached 83% at the 5th pulse and then declined (fig. 4).

For the CuO catalyst, the conversion of methane decreased as the number of methane pulsing increased (fig. 1), indicating that surface reduction does not promote methane conversion, and metallic copper does not promote activated methane. As for NiO, the conversion of methane increased slightly in the first two pulses of methane (fig. 2), implying that the reduction of nickel would promote methane conversion. In other words, metallic nickel has better ability in methane activation than oxidized nickel.

It can be seen in fig. 2 that for NiO, following the reduction of surface oxygen, CO_2 selectivity decreased and CO selectivity as well as C(s) generation increased. However, over CuO (fig. 1), CO_2 selectivity was not affected by the reduction of copper on the surface and stayed at 100% all the time. Since no CO and surface carbon were generated over copper, one can conclude that CO and surface carbon were not intermediates in the generation of CO_2. The above results indicate that the mechanisms for methane activation over NiO are different from that

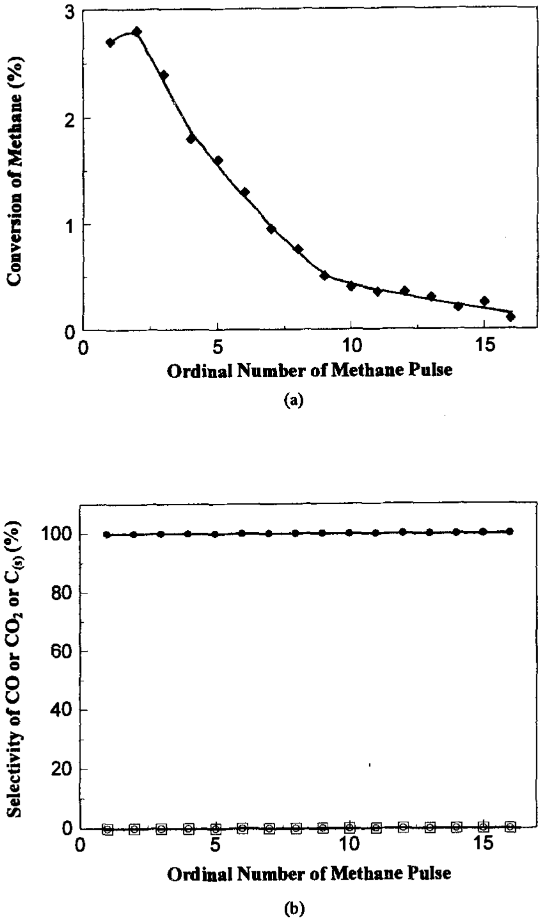

Fig. 3. The relationship of (a) CH_4 (◆) conversion and (b) C(s) (○), CO (□) and CO_2 (●) selectivities with the ordinal number of CH_4 pulsing over 10% Cu/La_2O_3 at 600°C.

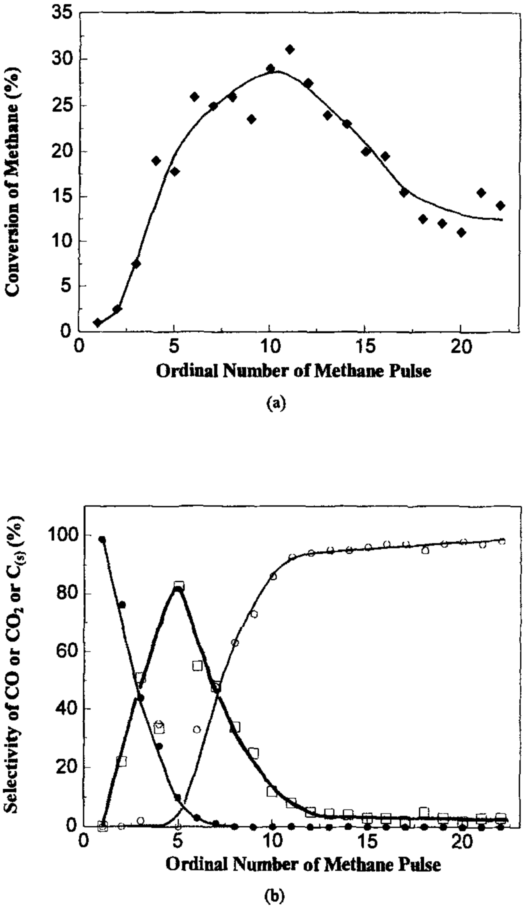

Fig. 4. The relationship of (a) CH_4 (◆) conversion and (b) C(s) (○), CO (□) and CO_2 (●) selectivities with the ordinal number of CH_4 pulsing over 10% Ni/La_2O_3 at 600°C.

over CuO: the former follows the pyrolysis mechanism [7,8] while the generation of CO_2 and H_2O over CuO is likely to be via the combustion–reform mechanism.

As shown in fig. 4, for the freshly prepared 10 wt% Ni/La_2O_3 catalyst, initial methane pulsing showed very low activation (methane conversion = 0.7%) but methane conversion increased with methane pulsing and reached 31% at the 11th pulse. Comparing with the NiO results (fig. 2), one can see that oxide in the Ni/La_2O_3 catalyst was more resistant to reduction. However, following the ordinal number of methane pulses, the changing profiles of methane conversion and prod-

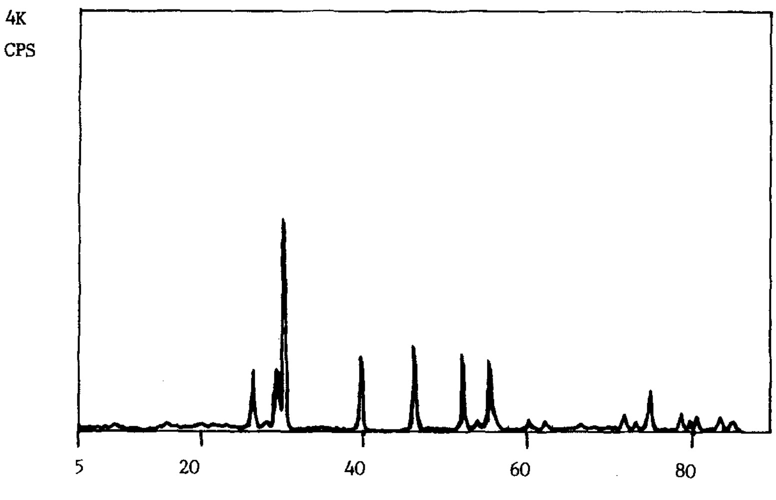

Fig. 5. XRD pattern of calcined La_2O_3.

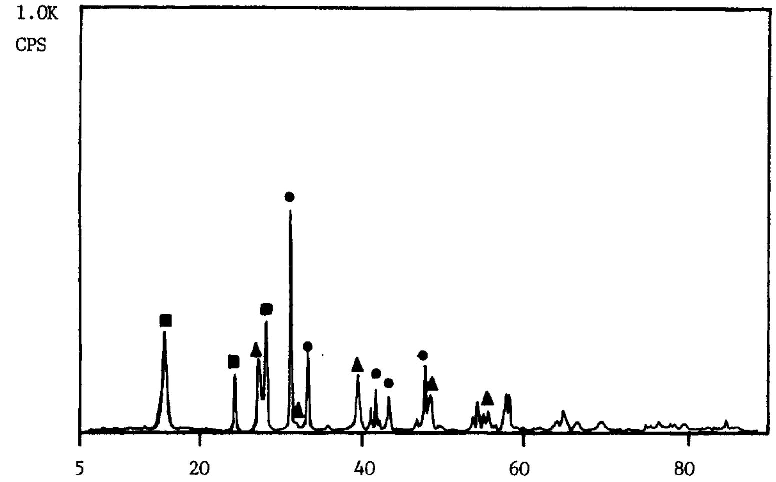

Fig. 6. XRD pattern of calcined 10% Cu/La_2O_3. (▲) Cubic La_2O_3 phase, (●) orthorhombic La_2CuO_4 phase, (■) unknown phase.

uct selectivities over Ni/La_2O_3 were similar to those over NiO. One can also see that the oxide in the Cu/La_2O_3 catalyst was also more resistant to reduction than those in CuO. Again, the changing profiles of methane conversion and product selectivities over Cu/La_2O_3 as related to the ordinal number of methane pulses were similar to those over CuO. XRD investigations revealed that the presence of Cu and Ni would cause La_2O_3 (hexagonal) to undergo structural transformation (figs. 5, 6 and 7). In the Cu/La_2O_3 catalyst, cubic La_2O_3, orthorhombic $CuLa_2O_4$ and an unknown phase were detected. In Ni/La_2O_3, besides cubic La_2O_3 and the same unknown phase, cubic $LaNiO_3$ was detected. Since the same unknown phase existed in both catalysts, it is considered to be an entity composed of La and O. Therefore, the difficulty in the reduction of Cu/La_2O_3 and Ni/La_2O_3 catalysts is due to phase changes. However, based on the similarities in reactivity profiles of the supported and unsupported catalysts, one can say that phase changes have no effect on the mechanism of methane activation over the copper and nickel catalysts.

In order to explain why metallic nickel is superior to metallic copper in methane activation, we have turned to BOC-MP calculations [12,13] and obtained the activation energies of the elementary steps for methane activation over the (111) crystal surfaces of the two metals (table 1). The results indicate that over nickel, the activation energies for the dehydrogenation of $CH_4(s)$ to give $CH_3(s) + H(s)$ and $CH_3(s)$ to give $CH_2(s) + H(s)$ are smaller than those over copper, particularly so in the former step. In other words, the dissociation of methane is thermodynamically more unfavorable on copper than on nickel.

4. Conclusion

In our investigation of the interaction of methane over unsupported and La_2O_3-supported copper and nickel catalysts at 600°C, we come to the following conclusions:

(i) Methane activation over CuO and 10 wt% Cu/

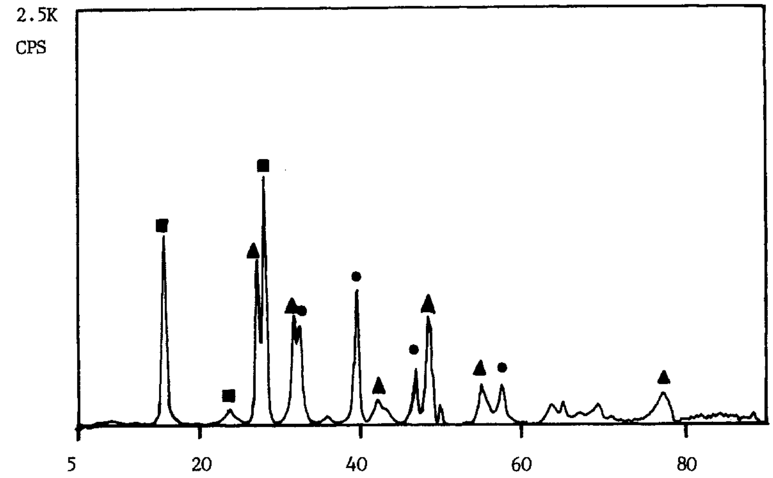

Fig. 7. XRD pattern of calcined 10% Ni/La_2O_3. (▲) Cubic La_2O_3 phase, (●) cubic La_2NiO_3 phase, (■) unknown phase.

Table 1
Activation barriers for elementary reaction for CH_4 dissociation

Reaction step	Ni(111) (kcal/mol)	Cu(111) (kcal/mol)
$CH_4(s) \rightarrow CH_3(s) + H(s)$	14	24
$CH_3(s) \rightarrow CH_2(s) + H(s)$	24	28
$CH_2(s) \rightarrow CH(s) + H(s)$	23	27
$CH(s) \rightarrow C(s) + H(s)$	5	8

La_2O_3 catalysts follows the complete combustion mechanism in which methane is oxidized by surface oxygen to give CO_2 and H_2O.

(ii) Methane activation over NiO and 10 wt% Ni/La_2O_3 catalysts follows the pyrolysis mechanism. Methane dissociation on the reduced sites is the key step for methane activation.

(iii) Results of BOC-MP calculations support the idea that methane activation is more feasible over metallic nickel than metallic copper.

Acknowledgement

We are grateful to Hong Kong RGC for financial support.

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