Studies on the Reaction Mechanism of CH_4/CO_2 Reforming over Co/γ-Al_2O_3 Catalyst

Yong Lu, Changchun Yu, Jinzhen Xue, Yu Liu,* and Shikong Shen
*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, Lanzhou 730000, China*

(Received January 27, 1997; CL-970065)

XPS/AES and pulse reaction characterizations were combined to study the reaction mechanism of CH_4/CO_2 reforming to syngas over Co/γ-Al_2O_3. Surface carbide carbons formed from CH_4 dissociation were active C species for CO generation. Metallic Co species played an important role in dissociating CH_4 to form carbide carbon and H_2, abstracting an O atom from CO_2 molecule, and transferring O atom to carbide to form CO.

The CH_4/CO_2 reforming converts both CO_2 and CH_4 to useful feed stock (syngas) with H_2/CO ratio of 1, which is suitable for some special chemical processes, e.g., oxo synthesis.[1] Interestingly, this process exhibits certain potential to be used as thermochemical heat-pipe for recovery, storage and transmission of solar and other renewable energy sources.[2,3] The catalysts employed are mainly Ni and Pt metals.[4-9] Recently, we found that Co metal catalyst showed high activity (>92% for CH_4 and CO_2 conversions) and good stability for this reaction at 1023 K.[10] Many investigators have shown the occurrence of dissociative adsorption of CH_4 on Ni and Pt metals, but no further detailed studies were made to identify which of surface carbons is active for CO generation.[4-9] Especially, no any studies were made on the behaviors on Co metal for this reaction. The present work is focused on exploring the interactions of CH_4 and CO_2 molecule with metallic Co sites, and the reactions of surface intermediate species on Co/γ-Al_2O_3 catalyst.

Two Co/γ-Al_2O_3 catalysts with Co-loadings of 9.0 wt% (24-45 mesh) and 18.0 wt% (<60 mesh) were prepared by impregnation method. The impregnated samples were dried at 343 K and calcined at 673 K in air for 10 h. Pulse reaction was performed in the continuous flow quartz micro-reactor with an on-line Ion-Trap Detector (ITD) for analyzing exit gas. For each pulse reaction experiment, 300 mg of Co/γ-Al_2O_3 was reduced by H_2 at 973 K for 2 h, flushed in a He flow (20 ml/min) at this temperature for 2 h and cooled to 573 K. The pulse volumes of 10%CH_4+He and 10%CO_2+He were 0.3 ml. XPS/AES measurements were performed on VG ESCALAB 210 spectrometer, using Al anode source generated at a power of 300 watts. The 18.0 wt% Co/γ-Al_2O_3 were directly pressed into Φ13mm pellets. The pellets were reduced by H_2 at 973 K for 10 h and subsequently pretreated with CO_2, CH_4, first CH_4 then CO_2, and the mixture of CH_4/CO_2 in a specific quartz reactor (i.d. 20 mm) respectively. The treated samples were transferred into vacuum chamber for XPS/AES measurement under highly pure N_2 preventing. The morphology of coke formation in whiskers was examined by JEM-1200EX/9100EDAX TEM.

CH_4 TPPR (Temperature Programmed Pulse Reaction) on the reduced 9.0 wt% Co/γ-Al_2O_3 showed that C_2 and C_3 hydrocarbons were generated at 573-973 K. With increase of temperature, the amount of C_2 and C_3 hydrocarbons decreased markedly in contrast to the amount of dissociated CH_4. The results reflected that CH_4 showed a great tendency to dehydrogenate completely to form C species at high temperature.

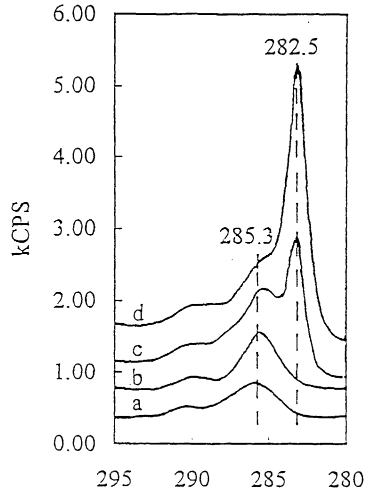

Figure 1. XPS spectra of 18.0 wt% Co/γ-Al_2O_3 in C1s region for (a) reduced sample in H_2 at 973 K for 10 h; sample (a) was treated at 973 K with: (b) mixture of CH_4/CO_2(=1) for 10 min, (c) first CH_4 for 5 min then CO_2 for 5 min, and (d) CH_4 for 5 min.

CO_2 TPPR on the reduced 9.0 wt% Co/γ-Al_2O_3 catalyst showed that the amount of remnant CO_2 decreased at >673 K. Meanwhile, gaseous CO was also detected at >873 K. These revealed that CO_2 dissociation occurred on reduced catalyst surface and CO desorption probably required higher temperature.

XPS/AES measurements were performed on the treated 18.0 wt% Co/γ-Al_2O_3 to acquire more information on intermediate species and their interactions. Binding energies of $Co2p_{3/2}$, O1s and C1s and assignments were summarized in Table 1.

An intense oxidative cobalt peak at 781.7 eV was observed on H_2-CO_2 treated catalyst surface. This was attributed to the oxidation of metallic cobalt with O atoms formed in dissociation of CO_2, further confirming the CO_2 dissociation on Co sites.

XPS spectra of the treated 18.0 wt% Co/γ-Al_2O_3 in C1s region were depicted in Figure 1. As may be seen, the C1s peaks at ~282 eV were observed on both H_2-CH_4 and H_2-CH_4-CO_2 treated catalyst surfaces. The C KVV peaks with the negative excursion at 250-280 eV (Kinetic energy) were also observed clearly, the peak shape of which was similar to carbide carbon on Ir.[12] Accordingly, the C1s peak at ~282 eV could be assigned adequately to the carbide in this work. The peak intensity of the carbide on the former was much stronger than that on the latter. The effluence of CO was detected by ITD in the case of H_2-CH_4 pretreated 18.0 wt% Co/γ-Al_2O_3 followed by CO_2 pulses at 973 K. The results revealed that the reaction of surface carbide with O atoms formed in CO_2 dissociation occurred on the H_2-CH_4-

Table 1. Binding energies of Co2p$_{3/2}$,[11] O1s and C1s on 18.0 wt% Co/γ-Al$_2$O$_3$ catalysts treated with various gases[a]

Peak	Assignment	Treating processes at 973 K					
		Fresh	H_2	H_2-CH_4	H_2-CO_2	H_2-CH_4-CO_2[b]	H_2-(CH_4/CO_2)[c]
Co2p$_{3/2}$	$Co^{(0)}$	none	779.5	779.6	none	779.5	779.5
Co2p$_{3/2}$	Co^{2+}	781.8	781.9	781.8	781.7	781.9	781.8
O1s	O^{2-}	531.9	531.9	531.9	531.8	531.7	531.8
C1s	Carbonates/CO	289.2	289.6	289.7	289.5	289.6	289.5
C1s	Adventitious/Whisker carbon	285.3	285.5(40.0)[d]	285.3(96.7)	285.5	286.1(100)	285.3(84.9)
C1s	Carbide carbon[e]	none	none	282.8	none	282.5	none

[a]Binding energies were calibrated against Al2p=74.7 eV; [b]The reduced catalyst was treated with CH_4, then with CO_2; [c]The reduced catalyst was treated with CH_4/CO_2(=1) feed gas; [d]Relative intensity defined as peak area ratio in bracket; [e]Graphite carbon had no contribution to C1s peak at ~282 eV in this work, due to appearance of the C KVV peak of the carbide at 250-280 eV (Kinetic energy).

CO_2 treated catalyst surface. A pronounced difference between H_2-(CH_4/CO_2) and H_2-CH_4-CO_2 or H_2-CH_4 treated surface was that C1s and C KVV peaks of the carbide disappeared on the H_2-(CH_4/CO_2) treated one. Additionally, no detectable increase in the intensity of the weak Co^{2+} peak at ~782 eV was detected on both H_2-CH_4-CO_2 and H_2-(CH_4/CO_2) treated surfaces, compared with that of unreducible $CoAl_2O_4$ spinel compound on H_2-CH_4 treated one. The results reflected that the reaction of the surface carbide with adjacent O atoms dissociated from CO_2 to CO was a fast step, which resulted in no detectable surface carbide on the H_2-(CH_4/CO_2) treated surface. From the above results, the conclusion could be drawn that surface carbide carbons were active species for CO production, by reacting immediately with O dissociated from CO_2 after its production.

As seen in Table 1, the relative intensity of the C1s peak at ~285 eV was larger on H_2-CH_4, H_2-CH_4-CO_2 or H_2-(CH_4/CO_2) treated surfaces than that of adventitious carbon on H_2 reduced one. In order to make the reason of the increase of the relative intensity of this peak clear, TEM examinations were conducted on H_2-CH_4 and H_2-(CH_4/CO_2) treated surfaces used in XPS measurements, and whiskers were observed on both surfaces. The results implied that the carbide could be also converted to whiskers, which were contributed to the increase of the relative intensity of the C1s peak at ~285 eV.

Based on the overall results, surface carbide carbons were active species for generating CO by reacting with O atoms dissociated from CO_2 molecule, and could be converted to whiskers. Note that the metallic Co species were corresponding for dissociating CH_4, abstracting an O atom from CO_2 molecule, and transferring O to carbide to form CO.

References and Notes

1 N. R. Udengaard, J. B. Hansen, D. C. Hanson, and J. A. Stal, *Oil & Gas J.*, **62**, March 9 (1992).

2 J. F. Muir, R. E. Hogan, R. D. Skocypec, and R. Buck, *Solar Energy,* **52**, 467 (1994).

3 R. D. Skocypec, R. E. Hogan, and J. F. Muir, *Solar Energy*, **52**, 479 (1994).

4 K. Seshan and J. A. Lercher, in "Carbon dioxide: Environmental issues," ed by J. Paul and C. Pradier, The Royal Soc. Chem., Cambridge (1994), p.16.

5 V. A. Tsipouriari, A. M. Efstathiou, Z. L. Zhang, and V. E. Verykios, *Catal. Today,* **21**, 579 (1994).

6 J. R. Rostrup-Nielsen and J-H. Bak Hansen, *J. Catal.,* **144**, 38 (1993).

7 A. Erdöhelyi, J. Cserényi, and F. Solymosi, *J. Catal.,* **141**, 287 (1993).

8 A. Erdöhelyi, J. Cserényi, E. Papp, and F. Solymosi, *Appl. Catal.*, **108**, 205 (1994).

9 M. C. J. Bradford and M. A. Vannice, *Appl. Catal.*, **142**, 97 (1996).

10 Yong Lu, Xuejia Ding, and Shikong Shen, *J. Catal.* (China), **16**, 447 (1995).

11 A. Satos, M. Menéndez, A. Monzón, J. Santamaria, E. E. Miró, and E. A. Lombardo, *J. Catal.*, **158**, 83 (1996).

12 J. W. Niemantaverdriet, in "Spectroscopy in Catalysis," ed by J. W. Niemantaverdriet, Weinheim, Germany (1993), Chap. 3, p. 70.