JOURNAL OF CATALYSIS **172,** 471–474 (1997)
ARTICLE NO. CA971844

RESEARCH NOTE

Comparison of Praseodymium Oxide and SrF_2-Promoted Praseodymium Oxide Catalysts for Oxidative Coupling of Methane

Ruiqiang Long[1] and Huilin Wan[2]

Department of Chemistry and State Key Laboratory for Physical Chemistry of the Soild Surface, Xiamen University,
Xiamen, 361005, People's Republic of China

Received September 23, 1996; revised July 31, 1997; accepted August 1, 1997

The oxidative coupling of methane (OCM) to ethene and ethane is an attractive reaction to convert natural gas to more valuable chemicals. Since the pioneering work by Keller and Bhasin (1), OCM has become a subject of worldwide research in recent years. Almost all elements in the periodic table have been studied as OCM catalysts (2, 3). In rare earth oxide OCM catalysts, La_2O_3 and Sm_2O_3 have been extensively studied due to their high catalytic activities and selectivities as well as satisfactory thermal stabilities (4–7). However, poor C_2 selectivities were obtained over multivalent CeO_2, Pr_6O_{11}, and Tb_4O_7 (4, 5) due to their high oxidation reactivity to methyl radicals (5). From the work of Lunsford (5, 6) and other workers (2, 8, 9), it has been generally accepted that the major reaction path is as follows: methane molecule reacts with a surface oxygen species to produce a gaseous methyl radical, which may then couple with another methyl radical in the gas phase to give ethane, further dehydrogenation of ethane to form ethene takes place in the gas phase or on the surface of catalyst. Along with this major reaction path, methyl radicals and C_2 hydrocarbons also have a chance of being deeply oxidized to carbon dioxide or monoxide (CO_x) on catalyst surface, so it is necessary to minimize the secondary deep-oxidation reaction to acquire a good C_2 selectivity and yield for an OCM catalyst. Some researchers added several dopants, mostly alkali-metal compounds, e.g., Li_2CO_3 (10), Na_2WO_4 (11), to these nonstoichiometric rare earth oxide catalysts and found that C_2 selectivity was apparently increased. In the present study, we will report briefly the catalytic performance of SrF_2-doped praseodymium oxide catalyst for OCM reaction, along with the bulk composition and structure, surface composition, and reducibility of the catalyst. These results will provide us with some information for understanding the nature of the promotion effect of F^- in the catalyst.

Each of the catalyst samples was prepared by the method of grinding and calcining as described elsewhere (12). Different mole ratios of SrF_2/Pr_6O_{11} were mixed and carefully ground into fine powder. The solid mixture was then stirred with a certain amount of deionized water to a paste, followed successively by drying at 393 K for 4 h and calcining at 1173 K for 6 h. The resulting solid was crushed and sieved to 40–60 mesh particles. The pure Pr_6O_{11} (>99.9%) was also treated with the similar procedures as described above.

The catalytic performance evaluation was carried out in a fixed-bed continuous flow quartz microreactor (5.0 mm ID and 35 cm length) in atmospheric pressure, under the condition of $CH_4/O_2/N_2 = 3.4/1/1.8$ (mole ratio) with a flow rate of 60 ml/min. The data were obtained after 15 min on-stream. CH_4 (99.99%), O_2 (99.5%), and N_2 (99.99%) were used without further purification. In each experimental run, 0.20 g catalyst was used, and the effluent gas was analyzed at room temperature by an on-line Shang Fen 102GD gas-chromatograph equipped with thermal conductivity detector. Water and hydrogen were also present but were not measured. Other details were the same as reported previously (12).

The specific surface area of catalyst was measured by BET method with N_2 adsorption at 77 K on a Sorptmatic 1900 CARLOERBA instrument. The bulk composition and structure of the catalysts were measured by X-ray diffraction (XRD) method (12). The surface composition was analyzed by means of X-ray photoelectron spectroscopy (XPS). Spectra were recorded on a VG ESCALAB 210 XPS/AES instrument at room temperature, with Mg Kα as the excitation radiation. The base pressure of the XPS analysis chamber was about 7×10^{-11} Torr (1 Torr $= 133.3$ Nm^{-2}). All measured binding energies were

---

[1] Present address: Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109-2136.

[2] Correspondence author.

0021-9517/97 $25.00

TABLE 1

Electron Binding Energies of the Elements on the Fresh Catalysts as Measured by XPS

Catalyst	Binding energy (eV)				
	$Pr_{3d_{5/2}}$	$Sr_{3d_{5/2}}$	F_{1s}	O_{1s}	C_{1s}
Pr_6O_{11}	934.9 933.1	—	—	531.6, 530.3, 528.4	289.0, 284.6
SrF_2/Pr_6O_{11} (Sr/Pr = 1/2)	935.2 933.1	133.8	684.5	531.6, 530.4, 528.4	289.0, 284.6

calibrated with respect to C_{1s} energy at 284.6 eV due to adventitious carbon. Eclipse 1.7T software was used to resolve the experimental spectra. The surface compositions of the catalysts were estimated from peak areas using appropriate instrumental sensitivity factors. The temperature program reduction (TPR) experiment was carried out on a quartz microreactor, 11 mol% H_2/Ar at a flow rate of 15 ml/min was used as a reducing gas. In each of the experiments, the sample (40 mg, 80–100 mesh) was subjected to TPR from 298 to 1223 K at a heating rate of 20 K/min. A thermal conductivity detector was used for this purpose. The effluent gas was purified with KOH and 5A molecular sieve columns to get rid of HF (which might be produced on the SrF_2/Pr_6O_{11} sample during the TPR experiment) and H_2O before it got into the thermal conductivity detector.

The XRD results indicated that cubic SrF_2 and Pr_6O_{11} were observed in the fresh SrF_2/Pr_6O_{11} catalysts, and the diffraction peak intensity of SrF_2 phase in the catalysts was found to increase with the content of SrF_2. The specific surface areas of SrF_2/Pr_6O_{11} with Sr/Pr = 0, 1/6, 1/2, and 3/2 were 4.4, 2.3, 2.8, and 3.0 m^2/g, respectively.

The electron binding energies (BE) of the elements and the surface composition of the fresh Pr_6O_{11} and SrF_2/Pr_6O_{11} (Sr/Pr = 1/2) samples are summarized in Tables 1 and 2, respectively. The carbonate species can be detected on the surface of the catalysts with C_{1s} BE at 289.0 eV (13). All O_{1s} spectra in the catalysts could be resolved to three peaks locating at ca 531.6, 530.4, and 528.4 eV, respectively. The peaks at ca 528.4 eV can be attributed to lattice oxygen (O^{2-}) (14, 15), while the other peaks at ca 531.6 and 530.4 eV cannot be identified because the BE values of some oxygen species, e.g. OH^-, O_2^{2-}, and O^-, fall in the range of 530–532 eV (13–17). The $Pr_{3d_{5/2}}$ spectrum for Pr_6O_{11} displayed a broad signal. It could be resolved to two peaks with BE at 934.9 and 933.1 eV, which could be assigned to quadrivalent and trivalent praseodymium ions, respectively (13). On the fresh SrF_2/Pr_6O_{11} (Sr/Pr = 1/2) catalyst surface, a smaller amount of Pr^{4+} and Pr^{3+} ions were observed (Table 2), but the Pr^{3+}/Pr^{4+} ratio was found to increase apparently, suggesting that SrF_2 may play a certain role in stabilizing the surface Pr^{3+} oxidation state. Sr^{2+} and F^- ions were also detected on the surface of the fresh SrF_2/Pr_6O_{11} catalyst.

TABLE 2

Surface Composition of Various Elements in the Fresh Catalysts

Catalyst	Atomic concentration C_x[a] (%)							
	Pr^{4+}	Pr^{3+}	Sr^{2+}	F^-	O^{2-}	Other oxygen[b]	C[c]	Pr^{3+}/Pr^{4+}
Pr_6O_{11}	2.8	5.2	—	—	28.7	55.9	7.4	1.9
SrF_2/Pr_6O_{11} (Sr/Pr = 1/2)	0.4	2.2	13.4	11.6	24.3	40.7	7.4	5.5

[a] $C_x = (A_x/S_x)/(\Sigma A_i/S_i)$, where A = peak area; S = atomic sensitivity factor.

[b] Other oxygen refers to the oxygens in CO_3^{2-}, OH^-, O^-, O_2^{2-}, etc.

[c] C does not include the adventitious carbon.

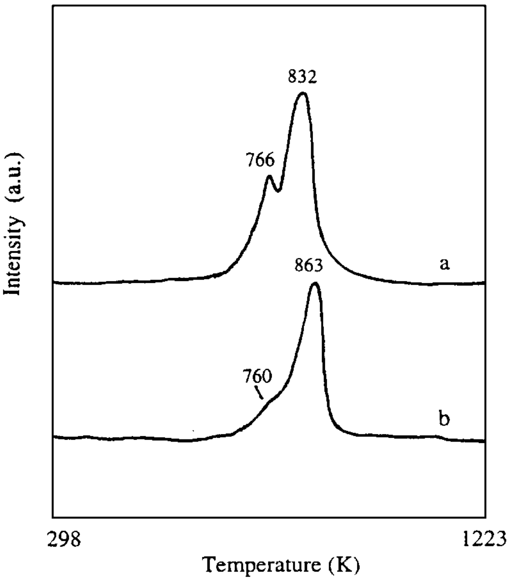

FIG. 1. The TPR spectra of (a) Pr_6O_{11} and (b) SrF_2/P_6O_{11} (Sr/Pr = 1/2) catalyst.

The TPR spectra of the fresh Pr_6O_{11} and SrF_2/Pr_6O_{11} (Sr/Pr = 1/2) are shown in Fig. 1. Two peaks at 766 and 832 K were observed on Pr_6O_{11} sample, which could probably be associated with reduction of the surface and bulk oxygen of Pr_6O_{11}, respectively. The color of praseodymium oxide reduced was changed to be light yellow-green from black, indicating that praseodymium oxide had been reduced to Pr_2O_3 (18). Comparatively, it could also be found that two reduction peaks at 760 and 863 K appeared on the SrF_2/Pr_6O_{11} sample, which could be attributed to the reduction of surface and bulk oxygen, respectively, but the reduction temperature of the latter increased. Moreover, the total reduction peak area of the SrF_2/Pr_6O_{11} catalyst was also a little smaller than that of Pr_6O_{11}, suggesting that the content of the reducible oxygen species decreased when a certain amount of SrF_2 was added to Pr_6O_{11} catalyst.

The catalytic performance evaluations of the SrF_2/Pr_6O_{11} catalysts with different Sr/Pr mole ratios are summarized

TABLE 3

The Catalytic Performance of the SrF_2/Pr_6O_{11} Catalysts with Different Sr/Pr Mole Ratios

		Conv. (%)		Rate $(mol/s/m^2)/10^{-6}$		Selectivity (%)							
Sr/Pr	Temp. (K)	CH_4	O_2	CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_2	C_2H_4/C_2H_6	C_2 yield (%)	C_2 yield $(mol/s/m^2)/10^{-6}$
0	1123	19.9	98.2	5.54	8.03	6.2	72.9	7.8	13.1	20.9	0.60	4.2	1.16
	1073	19.0	98.2	5.29	8.03	3.2	77.9	5.6	13.3	18.9	0.42	3.6	1.00
	1023	18.0	98.5	5.01	8.06	1.4	84.8	3.4	10.4	13.8	0.33	2.5	0.69
	973	17.1	98.0	4.76	8.02	0	89.1	2.2	8.7	10.9	0.25	1.9	0.52
	873	16.6	98.5	4.62	8.06	0	92.8	1.3	5.9	7.2	0.22	1.2	0.33
1/6	1123	29.2	98.1	15.5	15.4	0	42.0	31.4	26.6	58.0	1.2	16.9	8.99
	1073	29.4	98.4	15.6	15.4	0	41.9	28.8	29.3	58.1	0.98	17.1	9.06
	1023	28.2	98.6	15.0	15.4	0	44.5	26.0	29.5	55.5	0.88	15.7	8.33
	973	26.2	98.0	13.9	15.3	0	49.8	22.0	28.2	50.2	0.78	13.2	6.98
	873	4.3	25.6	2.29	4.01	0	100	0	0	0	—	0	0
1/2	1123	29.4	98.3	12.9	12.6	0	41.3	30.7	28.0	58.7	1.1	17.3	7.57
	1073	27.8	98.0	12.2	12.6	0	46.1	24.6	29.3	53.9	0.84	15.0	6.58
	1023	23.8	97.4	10.4	12.5	0	58.4	15.3	26.3	41.6	0.58	9.9	4.33
	973	22.1	97.9	9.66	12.6	0	66.2	11.7	22.1	33.8	0.53	7.5	3.27
	873	15.7	88.4	6.86	11.4	0	86.2	3.0	10.8	13.8	0.22	2.2	0.95
3/2	1123	26.8	86.8	10.9	10.4	0.1	38.4	35.4	26.1	61.5	1.4	16.5	6.70
	1073	26.2	98.2	10.7	11.8	0	50.2	21.7	28.1	49.8	0.77	13.0	5.33
	1023	23.8	98.5	9.71	11.8	0	58.6	15.0	26.4	41.4	0.57	9.9	4.02
	973	22.0	98.0	8.98	11.8	0	64.3	11.8	23.9	35.7	0.49	7.9	3.21
	873	3.7	20.1	1.51	2.41	0	100	0	0	0	—	0	0

Note. Conditions: 0.2 g catalyst; $CH_4/O_2/N_2 = 3.4/1/1.8$; total flow rate = 60 ml/min.

in Table 3. Under the condition of $CH_4/O_2/N_2 = 3.4/1/1.8$, over pure praseodymium oxide, only a very low C_2 selectivity and C_2 yield were observed, and the major product was carbon dioxide (>72% of selectivity) at the temperature range of 873–1123 K. When a certain amount of strontium fluoride, which showed poor activity for OCM (12), was added to praseodymium oxide, C_2 selectivity, methane conversion and C_2H_4/C_2H_6 ratio were found to improve apparently at higher temperatures. These facts indicate that strontium fluoride plays a significant promoting role for OCM with praseodymium oxide as host catalyst. No C_{2+} hydrocarbons were detected in this work. For all the catalysts, as the reaction temperature increased from 873 to 1123 K, the C_2 selectivity and C_2H_4/C_2H_6 ratio were found to increase, indicating that the formation of ethene is facilitated by higher temperature. In addition, the ratios of CO/CO_2 were very low (<0.1) on both Pr_6O_{11} and SrF_2-promoted Pr_6O_{11} catalysts, which might be attributed to the rapid surface reactions in which methyl radicals and/or CO were deeply oxidized to CO_2. A carbon balance of 100 ± 4% was obtained for every run over the catalysts.

The physical and chemical characteristics of the catalysts are reflected in their catalytic performance. When SrF_2 was added to praseodymium oxide, the concentration of the surface Pr^{4+} ion decreased as supported by the above XPS results (Table 2). Since Pr^{4+} ion was considered to have a high total oxidation reactivity to methane on praseodymium oxide (19), the addition of SrF_2 to Pr_6O_{11} may stabilize the surface Pr^{3+} oxidation state and suppress the Pr^{4+} ions that are associated with the labile oxygens, which will be favorable to the increase of C_2 selectivity in a certain extent. The similar result was also reported on the other catalysts, such as Li/PrO_x (10). On the other hand, the dispersion of F^- on the surface of catalysts will also be helpful to the isolation of the surface active centers and thus decreasing the chance of deep oxidation of methyl radicals and C_2 hydrocarbons. According to the TPR results (Fig. 1), it can be found that the reduction temperature of bulk lattice oxygen increased apparently when SrF_2 was added to Pr_6O_{11}. In the process of TPR of oxides, oxygen ions may be removed by inward diffusion of hydrogen or outward diffusion of oxygen ions from oxides to the reaction interface, the reduction temperature of bulk lattice oxygen may be used to compare the mobility of lattice oxygen in a certain extent for the same series oxides. The increase in reduction temperature of bulk lattice oxygen as a result of adding SrF_2 to Pr_6O_{11} reveals that the mobility of lattice oxygen decreased. Considering that the reducible oxygen species on praseodymium oxide may be responsible for the methane activation, leading to methyl radicals, and also for the further surface oxidation of these methyl radicals to CO_2 (20), the decrease in their concentration and mobility will also result in an increase of C_2 selectivity.

In short, it is reasonable to conclude that C_2 selectivity and yield over SrF_2/Pr_6O_{11} catalyst were much more than those of Pr_6O_{11} catalyst at high temperature in the continuous cofeed OCM reaction. When SrF_2 was added to Pr_6O_{11}, the decrease in the mobility of lattice oxygen and the surface concentration of Pr^{4+} ion as well as the dispersion of F^- on the surface of the catalysts will be favorable to the decrease in the secondary deep oxidation reaction and result in the increase of C_2 selectivity and yield.

ACKNOWLEDGMENTS

This work has been supported by the National Natural Science Foundation of China, and the Doctoral Foundation of State Education Commission of China.

REFERENCES

1. Keller, G. E., and Bhasin, M. M., *J. Catal.* **73**, 9 (1982).
2. Amenomiya, Y., Birss, V. I., Goledzinowski, M., Galuszka, J., and Sanger, A. R., *Catal. Rev.-Sci. Eng.* **32**(3), 163 (1990).
3. Maitra, A. M., *Appl. Catal. A: General* **104**, 11 (1993).
4. Otsuka, K., Jinno, K., and Morikawa, A., *Chem. Lett.*, 499 (1985).
5. Campbell, K. D., Zhang, H., and Lunsford, J. H., *J. Phys. Chem.* **92**, 750 (1988).
6. Lunsford, J. H., *Angew. Chem. Int. Ed. Engl.* **34**, 970 (1995).
7. Lacombe, S., Geantet, C., and Mirodatos, C., *J. Catal.* **151**, 439 (1994).
8. Inamatsu, E., and Aika, K., *J. Catal.* **117**, 416 (1989).
9. Nelson, P. F., Lukey, C. A., and Cant, N. W., *J. Phys. Chem.* **92**, 6176 (1988).
10. Gaffnery, A. M., Jones, C. A., Leonard, J. J., and Sofranko, J. A., *J. Catal.* **114**, 422 (1988).
11. Yu, Z., Yang, X., Lunsford, J. H., and Rosynek, M. P., *J. Catal.* **154**, 163 (1995).
12. Long, R. Q., Zhou, S. Q., Huang, Y. P., Weng, W. Z., Wan, H. L., and Tsai, K. R., *Appl. Catal., A: General* **133**, 269 (1995).
13. "Handbook of X-ray Photoelectron Spectroscopy," Φ Corporation, 1990.
14. Hedge, M. S., and Ayyoob, M., *Surf. Sci.* **173**, L635 (1986).
15. Sugiyama, S., Ookubo, T., Shimodan, K., Hayashi, H., and Moffa, J. B., *Bull. Chem. Soc. Jpn.* **67**, 3339 (1994).
16. Dubois, J. L., Bisiaux, M., and Mimoun, H., *Catal. Lett.*, 967 (1990).
17. Ayyoob, M., and Hedge, M. S., *Surf. Sci.* **133**, 516 (1983).
18. Ferguson, R. E., Guth, E. D., and Eyring, L., *J. Am. Chem. Soc.* **76**, 3890 (1954).
19. DeBoy, J. M., and Hicks, R. E., *Ind. Eng. Chem. Res.* **27**, 1577 (1988).
20. Poirier, M. G., Breault, R., Kaliaguine, S., and Adnot, A., *Appl. Catal.* **71**, 103 (1991).