THE ENHANCEMENT OF THE OXIDATIVE COUPLING OF METHANE ON OXIDE/SiO_2 CATALYSTS BY TETRACHLOROMETHANE

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The introduction of carbon tetrachloride to the feed stream in the conversion of methane to C_2 hydrocarbons over a variety of silica-supported oxides is shown to alter both the conversion and selectivity, but, notably with oxides of Ba, Cs and Mn produces remarkable increases in the yield and selectivity to C_2H_4 and C_2H_6, particularly the former.

1. Introduction

The oxidative coupling of methane, the major component of natural gas, to ethane and ethylene is currently a subject of intensive research interest [1]. Since the pioneering work of Keller and Bhasin [2] a wide variety of catalytic substances, supported or bulk, doped or undoped, has been studied as heterogeneous catalysts in the coupling reaction. At the present time, the more effective catalysts include alkaline earth oxides promoted with alkali elements [3–7], some rare earth oxides especially Li-doped Sm_2O_3 [8], transition metal oxides such as those of Mn and Ni after addition of LiCl [9], alkali metal promoted manganese oxide supported on silica [10] and layered bismuth oxyhalides [11].

Although the addition of chlorine or chloromethanes to the feed stream is well documented to have a positive influence on many catalytic processes particularly on the selective oxidation of ethylene [12] and in hydrocarbon reforming processes [13], very little is known on the effects of these additives in methane conversion processes. Sofranko et al. [14,15] have reported that higher selectivities to C_2^+ hydrocarbons can be obtained in methane conversion on sodium/manganese/silica catalyst in the presence of gaseous CH_3Cl or HCl. However this work was primarily concerned with the aforementioned catalyst operating in redox cycle.

In our recent studies [16–18] on the conversion of methane by nitrous oxide on silica supported heteropoly oxometalates, it was shown that the addition of a small quantity of dichloro- or tetrachloromethane to the feed stream has a profound influence on the conversion of methane and selectivities to different

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products. The presence of the additive significantly enhanced the activity of 12-molybdophosphoric acid and of 12-tungstophosphoric acid supported on silica. While over 12-molybdophosphoric acid a large increase in the yield of oxygenated hydrocarbon (HCHO) was noted, over 12-tungstophosphoric acid monochloromethane was produced with a high selectivity and a reasonable yield with little or no effect on the yield of HCHO.

In the light of these positive effects of a chloroadditive on the partial oxidation of methane as observed with heteropoly oxometalates in this laboratory we have undertaken an extensive study of the effect of these chlorocompounds on the direct oxidative coupling of methane to higher hydrocarbons using a variety of catalytic materials. In the present communication the result of the addition of a small quantity of tetrachloromethane to the feed on the oxidative dimerization reaction with a number of silica supported metal oxides is reported.

2. Experimental

The catalysts used were prepared by impregnating the support (Grace-Davison, grade 407, 740 m^2/g) with aqueous solutions of metal acetates or nitrates at 80–90 ° C, followed by a drying in air at 110 ° C for 3 h and finally calcining in air at 750 ° C for 4 h. The metal salts were impregnated to give nominally 5 wt% metal loadings. For Mn, Co, Bi and Pb, the corresponding nitrates were used for impregnation. For the remaining catalysts, acetates were used. The tests of catalysts was carried out using a laboratory scale fixed-bed reactor operated in a flow mode at atmospheric pressure. The reactor consisted of a 8 mm-id and 35 mm length quartz tube sealed to 4 mm-id quartz tubes on two sides (total length of the reactor was 200 mm). The catalyst was placed in the 8 mm-id portion of the reactor whose length was just enough to accommodate the catalyst particles. The reactor was designed in this manner to keep the dead space of the reactor at a minimum in the hottest zone with the aim of minimizing the contribution of non-catalytic homogeneous reactions as far as possible. The additive, CCl_4, was admitted to the main flow of reactants (CH_4, O_2, and He) by passing a separate stream of helium through a gas dispersion tube in a glass saturator containing the liquid at ice-water temperature. The flow of helium was so adjusted that after dilution following introduction to the main flow of feed the appropriate concentration of the additive in the flow was achieved. The reaction conditions used were as follows: $W = 1.5$ g, $F = 30$ ml/min; $T = 775\,°C$, $P(CH_4) = 220$ torr, $P(O_2) = 210$ and 35 torr, $P(CCl_4) = 0$ or 1.1 ± 0.1 torr, balance to the atmospheric pressure was provided by helium.

The reactants and products were analyzed on a gas chromatograph (TCD) with MS 5A and Porapak T column packings. The main products of reaction were CO, CO_2, C_2H_4, C_2H_6, CH_3Cl and H_2O. C_3 hydrocarbons, H_2CO and CH_3OH were, at most, produced in trace quantities and have been neglected. The conversion of methane was calculated on a carbon-account-for basis. The selectivities were calculated on the basis of the conversion of methane (expressed as mole percentage) to each product. For example, the selectivity to ethylene was calculated as 100 × [2 × moles of ethylene produced]/(moles of methane converted).

3. Results

Tables 1 and 2 summarize the results in terms of conversion, selectivities and yields of C_2 hydrocarbons obtained with two different compositions of reactants in the feed mixture. In the following M/SiO_2 (M = metal) refers to the oxide of

Table 1
Conversion and selectivity for $CH_4/O_2 \approx 7$ [a]

Catalyst	CCl_4	Conv. (%)		Selectivity (mol%)					C_2 yield (mol%)
		CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	CH_3Cl	
None [b]	A	0.95	~15	40	4.0	8.5	47.5	–	0.55
None [b]	P	1.15	~15	9.0	8.0	38.5	34.5	10	0.85
Silica	A	0.90	~10	67.5	5.5	0.5	26.0	–	0.25
Silica	P	2.1	~15	26.5	11	26	26	10.5	1.1
Ba/SiO_2	A	4.8	45	79	8.0	6.2	6.8	–	0.60
Ba/SiO_2	P	11.9	85	37.5	5.0	41.0	13.5	2.5	6.5
Cs/SiO_2	A	3.9	40	87.5	9.0	10	2.0	–	0.45
Cs/SiO_2 [c]	P	13.3	95	37	4.0	43.5	15.5	t	7.85
Mn/SiO_2 [d]	A	11.8	~ 93	10	75	5.0	10	–	1.8
Mn/SiO_2 [d]	P	14.5	~100	32.5	29.5	25.5	6.0	6.5	4.55
K/SiO_2	A	0.50	~ 5	67	4.0	4.0	25	–	0.15
K/SiO_2	P	3.2	~15	11	7.0	30	28	21	1.85
Ca/SiO_2	A	6.3	65	67	12.5	10	10	–	1.25
Ca/SiO_2	P	8.7	95	58.5	8.0	28.5	4.5	0.5	2.85
Co/SiO_2	A	5.9	90	31	57	3.5	8.5	–	0.70
Co/SiO_2	P	20.5	100	92.5	4.5	t	3.0	t	0.60
Bi/SiO_2	A	1.0	10	35.5	29	4.5	31	–	0.35
Bi/SiO_2	P	5.6	70	27.5	35.5	12.5	10.5	t	1.3
Pb/SiO_2	A	5.4	35	2.0	18.5	23.5	56.5	–	4.25
Pb/SiO_2	P	1.4	~ 5	12	8.0	37.5	33	10	1.0
		(4.1)	(25)	(2.0)	(15.5)	(22.5)	(60)	(–)	(3.4)
Tl/SiO_2 [c]	A	14.9	~100	11	14.5	30.5	43.5	–	11.0
Tl/SiO_2 [c]	P	5.0	55	47.5	7.0	17.0	13.5	14.5	1.5

[a] CH_4 = 220 Torr, O_2 = 25–30 Torr, W = 1.5 g, F = 30 ml/min, T = 775 °C, CCl_4 = 1.1 ± 0.1 Torr when present; conversion and selectivities are at near steady state unless otherwise stated.

[b] reactor packed with quartz wool.

[c] conversion and selectivities measured at ~1/2 hr. of onstream time.

[d] for Mn/SiO_2 $CH_4 \cong 220$ Torr and $O_2 \cong 60$ Torr were used.

( ) data obtained following elimination of CCl_4 from feed stream.

A and P = Absent and Present respectively.

Table 2
Conversion and selectivity for $CH_4/O_2 \approx 1$[a]

Catalyst	CCl_4	Conv. (%)		Selectivity (mol%)					C_2 yield (mol%)
		CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	CH_3Cl	
None[b]	A	4.0	15	72.5	5.0	5.5	16.5	–	0.90
None[b]	P	5.0	20	55.5	6.0	21	11.5	6.0	1.6
Silica	A	4.9	20	75	10	4.0	11	–	0.75
Silica	P	8.3	25	70	5.0	13.0	6.5	5.5	1.6
Ba/SiO_2	A	9.5	15	85.5	8.0	1.0	4.0	–	0.50
Ba/SiO_2	P	20.0	32	55.5	6.0	30.5	6.0	2.5	7.3
Cs/SiO_2	A	12.2	17	80	17.5	0.5	2.0	–	0.30
Cs/SiO_2[c]	P	36.5	57	79.5	7.0	12	1.5	t	5.0
Mn/SiO_2	A	22.2	42	16.5	70	6.0	7.5	–	3.0
Mn/SiO_2	P	45	75	39.5	39	18	2.0	2.0	9.0
Ca/SiO_2	A	19.8	27	62.5	24.5	6.5	7.0	–	2.7
Ca/SiO_2	P	26	43	81.5	10	5.5	1.0	1.0	1.7
Pb/SiO_2	A	13.3	25	6.5	50	19.5	24	–	5.8
Pb/SiO_2	P	4.5	12	56	5.0	19	12.5	7.0	1.4
		(10.6)	(22)	(6.5)	(44)	(20)	(30)	(-)	(5.3)

[a] $CH_4 = 205–220$ Torr, $O_2 = 180–190$ Torr $W = 1.5$ g. $F = 30$ ml/min, $T = 775\,^\circ C$. $CCl_4 = 1.1 \pm 0.1$ Torr when present; conversion and selectivities are at near steady state unless otherwise stated.
[b] reactor packed with quartz wool.
[c] conversion and selectivities measured at ~1/2 hr. of on stream time.
( ) data obtained following elimination of CCl_4 from feed stream.
A and P = Absent and Present respectively.

the metal supported on SiO_2. It should be noted that the presence of the corresponding carbonate cannot be ruled out when acetates are used for impregnation. In addition to the catalysts tabulated here, Cd/SiO_2, Zn/SiO_2, Ni/SiO_2 were also tested. With these catalysts, however, there was no significant effect of the CCl_4 additive on the reaction features and selectivities to C_2 products were quite low, although, of these catalysts, Ni/SiO_2 showed the highest activity.

It is evident from the tables that the effect of the presence of CCl_4 on the conversion and selectivity is most strikingly reflected with Ba/SiO_2, Cs/SiO_2 and Mn/SiO_2. A dramatic increase in the yield of C_2 hydrocarbons is observed with these three catalysts. In addition, with Ba/SiO_2 and Cs/SiO_2 a remarkable increase in the selectivity to C_2 products was observed. However, with Mn/SiO_2, the increase in the selectivity to products was not so profound. The conversion of CH_4 and the corresponding yield of C_2 products observed in the absence of the catalyst or over the silica support under otherwise identical conditions, as shown in tables 1 and 2 clearly demonstrate that the contributions of the non-catalytic reaction or of the support to conversions and yields observed in the presence of these three catalysts are quite small. However in the absence of the catalyst when the conversion of methane was very low, the selectivity to C_2 products was quite high, particularly in the presence of CCl_4 in the feed (table 1).

It is interesting to note that with each of the aforementioned three catalysts (Mn/SiO_2, Cs/SiO_2, Ba/SiO_2), in the presence of CCl_4 in the feed, ethylene is produced in larger quantities than that of ethane. Increase in the oxygen pressure, as evident from a comparison of tables 1 and 2, results in an increase in the conversion but produces a decrease in the selectivity to hydrocarbons while the ratio of C_2H_4 to C_2H_6 in the product stream increases.

It should be pointed out that, unlike with Ba/SiO_2 and Cs/SiO_2, with other oxides of these groups (Ca/SiO_2, K/SiO_2) the introduction of CCl_4 is less effective in enhancing the formation of C_2 products. In fact, on Ca/SiO_2 at higher oxygen pressure no increase in the yield of C_2 products in the presence of CCl_4 was observed.

Table 1 shows that introduction of CCl_4 in the feed resulted in large increases in the conversion also over Co/SiO_2 and Bi/SiO_2, but did not promote coupling of methane. It is interesting to note that over Co/SiO_2, the product of the reaction is almost entirely CO. However since the quantity of water produced was much too small to account for the stoichiometry $CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$ it is suspected that substantial amounts of H_2 were produced over Co/SiO_2.

It may be noted that in the absence of CCl_4, Pb/SiO_2 and Tl/SiO_2 showed very high selectivity to C_2 products. Both selectivity and yield of C_2 products observed over Tl/SiO_2 were, in fact, even higher than those observed on CCl_4 modified Ba/SiO_2, Cs/SiO_2 or Mn/SiO_2. Interestingly, however, on both these oxides the oxidation of methane was strongly inhibited by the presence of CCl_4 in the feed. On Pb/SiO_2, the effect was temporal in the sense that upon elimination of CCl_4 from the feed the activity of the catalyst was gradually reestablished and the conversion and selectivities approached those observed before the sample was exposed to CCl_4 (data in parentheses in tables 1 and 2 refer to values observed after several hours of reaction following elimination of CCl_4 from the feed stream). On the other hand, over Tl/SiO_2, the inhibition of oxidation induced by the exposure of the catalyst to CCl_4 appeared to be permanent since the activity of the catalyst was not permanent since the activity of the catalyst was not regained after elimination of CCl_4 from the feed.

In fig. 1 yields of C_2 hydrocarbons and selectivities to individual C_2 products are compared in the presence and absence of CCl_4 for the three catalysts showing the more favourable results. The dramatic influence of the presence of a small quantity of CCl_4 in the feed in enhancing the yields of hydrocarbon as discussed above is very clearly demonstrated in this figure. It may be mentioned that the ratios of C_2 hydrocarbons produced to CCl_4 added in the feed for the conditions of the experiments described in fig. 1 are 18, 23 and 6 for Ba/SiO_2, Cs/SiO_2 and Mn/SiO_2 respectively. From fig. 1 it is evident that for Ba/SiO_2, Cs/SiO_2, the presence of CCl_4 increases the selectivity to both ethane and ethylene, but more so for ethylene. However, for Mn/SiO_2, the presence of CCl_4 increases the selectivity to ethylene but, somewhat suppresses that to ethane. These trends are also reflected in the data of tables 1 and 2 obtained for two reactant compositions.

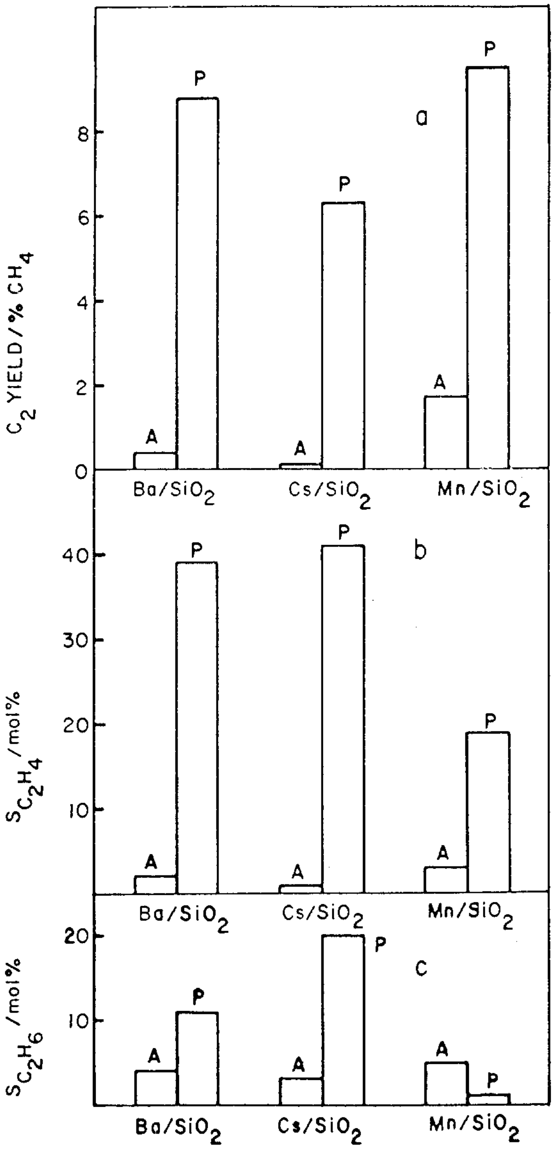

Fig. 1. C_2 yields and selectivities on three favourable catalysts. A and P indicates the Absence and Presence of CCl_4, respectively. $W = 1.5$ g, $F = 30$ ml/min, $T = 775°C$, $CCl_4 = 1.1 \pm 0.1$ Torr
For Ba/SiO_2: $O_2 \sim 62$ Torr, $CH_4 \sim 210$ Torr
For Cs/SiO_2: $O_2 \sim 30$ Torr, $CH_4 \sim 370$ Torr
For Mn/SiO_2: $O_2 \sim 60$ Torr, $CH_4 \sim 63$ Torr
Values are obtained for near steady state with Ba and Mn; for Cs in the absence of CCl_4 values are for steady state and in the presence of CCl_4 are at time on stream $\sim 1/2$ hr. M/SiO_2 (M = metal) refers to the oxide of the metal supported on SiO_2.

Figure 2 compares time on stream effects for these three catalysts under similar experimental conditions (high oxygen concentration chosen so that conversion is not limited by the availability of gas phase oxygen although this sacrifies

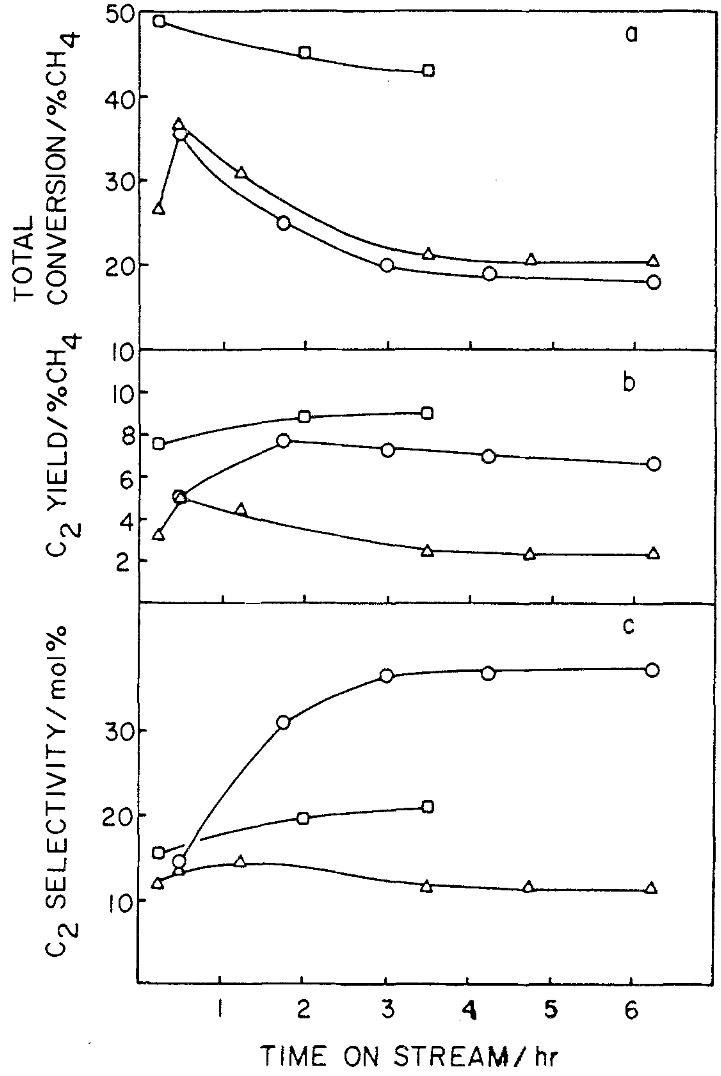

Fig. 2. Effect of time on stream on conversion, selectivity and yield. $W = 1.5$ g, $F = 30$ ml/min; $CH_4 \sim 210$ Torr, $O_2 \sim 185$ Torr, $CCl_4 \sim 1.1 \pm 0.1$ Torr, $T = 775$ °C. ○ Ba/SiO_2, △ Cs/SiO_2, □ Mn/SiO_2

a. Total conversion of methane
b. Yield of C_2 ($C_2H_4 + C_2H_6$)
c. Selectivity to C_2 ($C_2H_4 + C_2H_6$)

M/SiO_2 (M = metal) refers to the oxide of the metal supported on SiO_2.

selectivity to C_2 products). Evidently, Mn/SiO_2 shows the highest activity, Ba/SiO_2 and Cs/SiO_2 having about the same activity. Over Ba/SiO_2 and Cs/SiO_2, a substantial increase in the yield of C_2 hydrocarbons is noted in the initial hours of reaction. Over Cs, however, this increase in the yield of C_2 hydrocarbons is not maintained with further process time. On Ba/SiO_2 a large increase in the selectivity to C_2 hydrocarbon in the initial periods of reaction is observed as well.

4. Discussion

In this communication a potentially new route to promote the oxidative coupling of methane on heterogeneous catalysts is described. The process involves the introduction of a small quantity of a chloromethane to the feed stream. The results presented show that among the catalysts examined the addition of CCl_4 to the oxides of Ba, Cs and Mn supported on silica strikingly enhanced the formation of C_2 hydrocarbons by oxidative dehydrogenation of methane. It is evident that the manner in which the oxidation process is affected by the presence of CCl_4 depends very much on the nature of the oxide used. For example, in addition to oxides which facilitate the coupling reaction, there are some oxides such as Ni/SiO_2, Cd/SiO_2, and Zn/SiO_2 which appear to have little effect on the oxidation process and some such as Pb/SiO_2, and Tl/SiO_2 with which the addition of CCl_4 strongly inhibits the reaction. None the less, there are also some oxides which strongly accelerate the oxidation process but do not promote the coupling reaction in the presence of CCl_4. In view of such diverse behaviour where CCl_4 has been added, it is reasonable to suspect that CCl_4 is modifying the oxide surface in a number of ways. The observed effects may, among others, depend upon the manner in which the acidity and/or basicity of the oxide surface is altered by CCl_4, whether chlorine is incorporated into or retained by oxide, the strength of the metal-chlorine bond if it is formed at all and the ability of the oxide surface to decompose CCl_4 and form Cl atoms or radicals.

At the present stage, very little can be said about the mechanism of the reaction. The fact that an increase in oxygen concentration increases the ratio of C_2H_4 to C_2H_6 appears to indicate as suggested by others in the absence of CCl_4 [5,10,19], that C_2H_6 is the primary C_2 product and C_2H_4 is produced by the subsequent oxidative dehydrogenation of C_2H_6. The relatively high ratio of C_2H_4 to C_2H_6 observed in the presence of CCl_4 in the feed suggests that halogen radicals supplied from CCl_4 are catalyzing the dehydrogenation of C_2H_6 to C_2H_4. It may be noted that in the absence of any catalyst the ratio of C_2H_4/C_2H_6 was also much higher when the experiment was conducted with CCl_4 in the feed. It is difficult therefore to separate the heterogeneous from the homogeneous involvement in the enrichment of C_2H_4 to C_2H_6 ratio in the presence of CCl_4. In fact, at high temperatures, chlorine radicals have been shown to catalyze formations of C_2H_4 from CH_4 in the gas phase [20,21]. It may be noted that with CCl_4 in the feed, in addition to CO, CO_2, C_2H_4 and C_2H_6, CH_3Cl is formed although in very small quantities. This suggests that products apart from being formed directly from CH_4, may have resulted from the formation of CH_3Cl and its subsequent oxidation. The low selectivity of CH_3Cl is not surprising in view of the high temperature used.

While it is realized that the yields and selectivities obtained for C_2 products are not as high as those reported in the literature obtained with some alkali promoted alkaline earth and rare earth oxides, nevertheless, in view of the remarkable increase observed both in the yield and selectivity of dimerized product, it is believed that further studies will provide valuable practical and mechanistic information on the conversion process and the nature of the additive effect. Detailed studies are currently in progress.

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References

[1] J.S. Lee and S.T. Oyama, Catal. Rev. Sci. and Eng. 30 (1988) 249.
[2] G.E. Keller and M.M. Bhasin, J. Catal. 73 (1982) 9.
[3] J.H. Lunsford, in: *Methane Conversion*, Studies in Surf Sci. Catal. eds. D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, Vol. 36 (Elsevier, Amsterdam, 1988) p. 359.
[4] C.H. Lin, J.-X. Wang and J.H. Lunsford, J. Catal. 111 (1988) 302.
[5] T. Ito, J.-X. Wang, C.-H. Lin and J.H. Lunsford, J. Amer. Chem. Soc. 107 (1985) 5062.
[6] E. Iwamatsu, T. Moriyama, N. Takasaki and K. Aika, J. Catal. 113 (1988) 25.
[7] R. Burch, G.D. Squire and S.C. Tsang, Appl. Catal. 43 (1988) 105.
[8] K. Otsuka, Q. Liu, M. Hatano and A. Morikawa, Chem. Lett. 467 (1986).
[9] K. Otsuka, M. Hatano and T. Komatsu, in: *Methane Conversion*, Studies Surf. Sci. Catal., eds. D.M. Bibby, C.D. Chang, R.F. Howe and S. Yurchak, Vol. 36 (Elsevier, Amsterdam, 1988) p. 383.
[10] C.A. Jones, J.J. Leonard and J.A. Sofranko, J. Catal. 103 (1987) 311.
[11] W. Ueda and J.M. Thomas, *Proc. 9th Int. Cong. Catal.* eds. M.J. Phillips and M. Ternan, Vol. 2 (Chemical Institute of Canada, Ottawa, 1988) p. 960.
[12] S.A. Tan, R.B. Grant and R.M. Lambert, J. Catal. 100 (1986) 383.
[13] J.M. Grau, E.L. Jablonski, C.L. Dieck, R.J. Verderone and J.M. Parera, Appl. Catal. 36 (1988) 109.
[14] J.A. Sofranko and C.A. Jones, U.S. Patent 4, 544, 784, 1985.
[15] C.A. Jones, J.J. Leonard and J.A. Sofranko, Energy & Fuels 1 (1987) 12.
[16] S. Ahmed and J.B. Moffat, Catalysis Letts. 1 (1988) 141.
[17] S. Ahmed and J.B. Moffat, J. Phys. Chem., in press.
[18] S. Ahmed and J.B. Moffat, J. Catal., in press.
[19] P.F. Nelson, C.A. Lukey and N.W. Cant, J. Phys. Chem. 92 (1988) 6176.
[20] J.A. Hawari, S. Davis, P.S. Engel, B.C. Gilbert and D. Griller, J. Am. Chem. Soc. 107 (1985) 4721, and references therein.
[21] M. Weissman and S.W. Benson, Int. J. Chem. Kinet. 19 (1984) 307.