JOURNAL OF CATALYSIS 135, 310–316 (1992)

Pulse Microreactor Studies on Conversion of Methane, Ethane, and Ethylene over Rare Earth Oxides in the Absence and Presence of Free Oxygen

Rare earth oxides (*1–6*) and rare earth promoted alkaline earth oxides (*7–9*) show high activity in the oxidative coupling of methane (OCM) to C_2 hydrocarbons. Oxidative coupling of methane has been covered in a number of recent reviews (*10–13*). In our recent studies (*6*), rare earth oxides have been compared for their acid/base strength distribution and catalytic activity of the OCM process, and a mechanism for the formation of methyl radicals involving acid–base pairs on the catalyst surface has been suggested. According to this mechanism, the formation of the methyl radical involves the transfer of an electron from CH_3^- to an oxygen molecule. Hence, for the rare earth oxide catalyst to be active in the OCM process, the presence of free oxygen is essential. Earlier, Lin *et al.* (*2*) have observed the requirement of free O_2 for the formation of methyl radicals on La_2O_3 (at 773 K) in substantial concentrations. It is therefore very interesting to compare the catalytic activity/selectivity of the rare earth oxides in the conversion of methane and also of ethane and ethylene (which are the desirable products of the OCM) in the absence and presence of free oxygen for understanding the catalytic process. These studies could be carried out very conveniently using a pulse microreactor. The present investigation was undertaken for this purpose.

The rare earth metal oxide catalysts (viz. La_2O_3, CeO_2, Sm_2O_3, Eu_2O_3, and Yb_2O_3) were prepared from high purity (99.9%) rare earth oxides by hydrothermal treatment (at 373 K for 4 h) followed by high temperature calcination in static air at 873 K for 6 h. The preparation and surface characterization (viz. surface area, acidity/basicity distribution) of the rare earth oxide catalysts have been given in detail in our earlier paper (*6*).

The conversion of methane, ethane, and ethylene over the catalysts in the absence and presence of free O_2 was investigated using a pulse microreactor (made up of quartz) connected to a gas chromatograph. The experimental arrangement was similar to that described earlier (*14*). Helium (99.99%) passed over the activated molecular sieves and Oxysorb to remove the traces of moisture and oxygen, respectively, were used as a carrier gas (flow rate, 30 cm^3 min^{-1}).

A known mass (0.1 g) of catalyst (particle size 22–30 mesh) was packed between two quartz wool plugs in the constant temperature zone (10 mm) of the quartz microreactor (i.d., 4.0 mm; o.d., 6.2 mm; and length, 30 cm). Before carrying out the pulse reaction, the catalyst was calcined *in situ* at 1223 K in a flow of helium (20 cm^3 min^{-1}) for 2 h.

The pulse reactions of methane, ethane, and ethylene over the catalysts in the absence of free O_2 were carried out by passing the pulses of pure methane, ethane, ethylene, and methane (following this sequence) one after another at an interval of 30 min over the catalysts at 1073 K. Similarly the pulse reactions in presence of free O_2 were carried out by passing pulses of methane, ethane, and ethylene, all mixed with O_2, over the fresh catalysts. The pulse reactions were carried out under the following conditions: amount of catalyst, 0.1g; He carrier

0021-9517/92 $3.00

gas flow rate, 30 cm^3 min^{-1}; temperature, 1073 K; pulse size and length, 0.3 cm^3 and 2.4 cm. The pulse reactions were also carried out in absence of catalyst (i.e., in an empty reactor) under similar conditions. The possibility of the coke formation in the pulse reactions was checked by passing an O_2 pulse over the La_2O_3 catalyst after the pulse reactions of methane, ethane, and ethylene and analyzing the oxides of carbon formed. The products formed in each pulse experiment were analyzed by the gas chromatograph using a Spherocarb column.

The activity (i.e., conversion) and selectivity data were calculated from the carbon balance in the pulse before and after the reaction, taking into consideration the reaction stoichiometry [e.g., conversion (%) of a particular reactant = $(R_i - R_o) \times 100/R_i$, where R_i and R_o are the moles of reactant in the pulse before and after the reaction, respectively, and selectivity (%) of a particular product = $(Z \times P \times R_i \times 100)/(R_i - R_o)$, where P is the moles of the product formed and $Z = C_P/C_R$ (C_P and C_R are the number of C-atoms in the product and reactant, respectively)]. The activity/selectivity data were reproducible within 6%.

High purity methane (99.995%), ethane (99.95%), ethylene (99.99%), and oxygen (99.99%) were used in the pulse experiments.

Results of the conversion of methane, ethane, and ethylene over the rare earth oxide catalysts in a pulse microreactor at 1073 K in the absence or the presence of gaseous oxygen are given in Tables 1–4. The conversion/selectivity data for the pulse reactions in absence of any catalyst (i.e., in the empty reactor) are also included in the respective table.

In the absence of free O_2, the methane conversion activity of all the rare earth oxides is very poor and there is no formation of C_2 hydrocarbons (Table 1); the activity of air-pretreated La_2O_3 is even lower than that of the He-treated one. The partially reduced rare earth oxide (except Sm_2O_3) catalysts (i.e., after the pulses of methane, ethane, and ethylene) showed higher methane conversion activity and all the reduced catalysts showed 100% selectivity for the CO_x formation. This reveals that the reactivity of the lattice oxygen of the rare earth oxides in the conversion of methane is very low and the reaction leads only to the combustion of methane (i.e., shows no selectivity for C_2 hydrocarbons). On the contrary, in the presence of free O_2 the rare earth oxides showed high methane conversion activity and, except for CeO_2, the catalyst also showed selectivity for C_2 hydrocarbons (Table 2). These observations are very much consistent with the earlier ones made by Lin *et al.* (*2*) for the formation of methyl radicals on La_2O_3 from methane in the presence and absence of O_2 in the feed; for the formation of methyl radicals in substantial concentrations, O_2 must be present in the reactant stream, even though the catalyst has been pretreated in O_2.

In presence of free O_2, the formation of methyl radicals from methane over the rare earth oxides is likely to follow the mechanism suggested earlier (*6*), which involves an acid–base pair on the catalyst surface in the abstraction of an H atom from the adsorbed methane molecule by its polarization, followed by heterolytic C–H bond rupture to form CH_3^- and the transfer of an electron from the carbanion to O_2, resulting in a methyl radical (which undergoes a coupling reaction in the gas phase) and O_2^- (which leads to regeneration of sites and formation of O^- species on the surface). Whereas, in absence of free O_2, since there is no possibiliy of the transfer of an electron from CH_3^- (which interacts strongly with surface acid, i.e., low coordinated metal cation on the surface, M_{LC}^{n+}), the CH_3^- seems to undergo a surface reaction leading to its combustion. This is supported by the fact that there is no formation of C_2 hydrocarbons, which indicates no release of methyl radicals (which could undergo coupling in the gas phase) from the catalyst surface to the gas phase, in the absence of free O_2.

TABLE 1

Oxidative Conversion of Methane over Rare Earth Oxides in Pulse Microreactor in the Absence of Free Oxygen

	Without catalyst (empty reactor)	Catalysts					
		La_2O_3	$La_2O_3^*$	CeO_2	Sm_2O_3	Eu_2O_3	Yb_2O_3
Data on fresh catalyst							
CH_4 conversion (%)	0.0	0.6	0.1	1.8	1.9	2.3	0.4
Selectivity for C_2 (%)	—	—	—	—	—	—	—
Selectivity for CO_x (%)	—	100	100	100	100	100	100
CO_2/CO ratio	—	2.5	0.0	0.4	0.1	0.0	0.0
Data on partially reduced catalyst (i.e., after the pulse of methane, ethane, and ethylene one after another)							
CH_4 conversion (%)	0.0	2.2	1.8	2.2	0.5	3.4	1.2
Selectivity for C_2 (%)	—	—	—	—	—	—	—
Selectivity for CO_x (%)	—	100	100	100	100	100	100
CO_2/CO ratio	—	0.0	0.0	0.4	0.0	0.0	0.0

Note. The catalysts were calcined in situ at 1223 K for 2 h in air. Amount of catalyst, 0.1 g; pulse, 0.3 cm^3 of pure methane; temperature, 1073 K; and He flow rate, 30 cm^3 min^{-1}.

In the catalytic pulse reaction in presence of free O_2, ethane is expected to be formed by gas phase coupling of methyl radicals (*15*). The ethane thus formed is likely to be converted to ethylene and carbon oxides by gas phase reactions or surface reactions or by both.

No coke deposition on the La_2O_3 catalyst in the methane pulse reaction in absence of free O_2 was detected. However, in the presence of free O_2, a deposition of coke on the catalyst to a very small extent was observed.

From the results in Table 3, the following observations on the ethane conversion in the pulse reactions could be made.

1. In the absence of a catalyst, the ethane conversion, with or without O_2 in the pulse, is quite high.

2. The presence of a rare earth oxide catalyst causes an increase in the ethane conversion but a decrease in the ethylene selectivity, in the presence or absence of O_2 in the pulse. In both the cases, a deposition of coke on the La_2O_3 catalyst to a small extent was observed.

3. An addition of O_2 in the pulse causes

TABLE 2

Oxidative Conversion of Methane over Rare Earth Oxides in Pulse Microreactor in the Presence of Free Oxygen

	Without catalyst (empty reactor)	Catalysts				
		La_2O_3	CeO_2	Sm_2O_3	Eu_2O_3	Yb_2O_3
CH_4 conversion (%)	<1.0	25.2	18.4	27.6	23.6	24.8
Selectivity for C_2 (%)	0.0	33.8	0.0	21.6	29.6	35.6
Selectivity for CO_x (%)	100	66.2	100	78.4	72.5	64.4
CO_2/CO ratio	—	4.4	11.1	3.8	10.4	2.1
C_2H_4/C_2H_6 ratio	—	1.3	—	3.1	1.8	3.3

Note. Amount of catalyst, 0.1 g; pulse, 0.3 cm^3 of a mixture of CH_4 and O_2; CH_4/O_2 ratio = 2.9; temperature, 1073 K.

TABLE 3

Oxidative Conversion of Ethane over Rare Earth Oxides in the Pulse Microreactor in the Absence and Presence of Free Oxygen

	Without catalyst (empty reactor)	Catalysts				
		La_2O_3	CeO_2	Sm_2O_3	Eu_2O_3	Yb_2O_3
Data in the absence of free oxygen (pulse: pure ethane)						
C_2H_6 conversion (%)	55.6	62.8	57.4	89.7	78.3	84.5
Selectivity for CH_4 (%)	2.9	7.1	2.7	16.1	21.5	11.2
Selectivity for C_2H_4 (%)	96.8	83.0	83.1	72.5	46.5	85.3
Selectivity for CO_x (%)	0.0	10.2	14.2	11.4	32.0	3.5
CO_2/CO ratio	—	0.09	0.5	1.8	0.0	0.0
Data in the presence of free oxygen (pulse: a mixture of ethane and O_2 with $C_2H_6/O_2 = 3.3$)						
C_2H_6 conversion (%)	67.9	73.3	66.4	95.8	78.5	91.8
Selectivity for CH_4 (%)	8.1	10.4	4.1	27.3	13.4	14.4
Selectivity for C_2H_4 (%)	81.2	75.9	77.5	28.4	60.4	71.1
Selectivity for CO_x (%)	10.7	13.7	18.8	44.3	26.2	14.5
CO_2/CO ratio	0.06	0.3	1.2	0.02	0.04	0.14

Note. Amount of catalyst, 0.1 g; pulse size, 0.3 cm^3; temperature, 1073 K; He flow rate, 30 cm^3 min^{-1}.

an increase in the ethane conversion, selectivity for CO and methane (except for Eu_2O_3), and CO_2/CO ratio (except for Sm_2O_3), but a decrease in the selectivity for ethylene (except for Eu_2O_3). These observations reveal that ethane undergoes both gas phase and surface reactions in presence or absence of O_2.

The results on the conversion of ethylene in the pulse reactions (Table 4) reveal the following.

1. The thermal cracking of ethylene (i.e., ethylene conversion in absence of catalyst and O_2) is negligibly small.
2. Ethylene undergoes gas phase oxidation with O_2 (in absence of catalyst) to a large extent.
3. Ethylene undergoes reaction on the rare earth oxides in the absence of O_2 (i.e., with lattice oxygen of the oxides) to an appreciable extent.
4. An addition of O_2 in the pulse causes an increase in the ethylene conversion, CO_x selectivity and CO_2/CO ratio, in both the catalytic and non-catalytic (i.e., homogeneous gas phase) reactions.
5. In the conversion of ethylene over the rare earth oxides in the presence or absence of O_2, the formation of methane and ethane is quite appreciable and there is also a deposition of coke on the La_2O_3 catalyst to a small extent.

Based on the observations on the heterogeneous (i.e., catalytic) and homogeneous (i.e., non-catalytic) pulse reactions of methane, ethane, and ethylene in the presence and absence of free O_2, the possible gas phase and surface catalyzed reactions involved in the oxidative coupling of methane to C_2 hydrocarbons over the catalysts in the presence of free O_2 are presented in Fig. 1. The reactions involved in the oxidative coupling process are very complex. The results (Table 4) indicate that the C_2 selectivity in the process is also expected to be controlled by the catalytic and/or non-catalytic oxidation of ethylene to CO_x in presence of

TABLE 4

Oxidative Conversion of Ethylene over Rare Earth Oxides in the Pulse Microreactor in the Absence and Presence of Free Oxygen

	Without catalyst (empty reactor)	Catalysts				
		La_2O_3	CeO_2	Sm_2O_3	Eu_2O_3	Yb_2O_3
Data in the absence of free oxygen (pulse: pure ethylene)						
C_2H_4 conversion (%)	0.3	5.5	18.2	14.8	15.3	7.1
Selectivity for CH_4 (%)	—	13.5	2.8	68.6	14.2	35.3
Selectivity for C_2H_6 (%)	—	59.8	8.2	14.5	43.8	43.0
Selectivity for CO_x (%)	—	26.5	89.0	16.9	42.1	21.7
CO_2/CO ratio	—	0.0	0.15	0.0	0.0	0.0
Data in the presence of free oxygen (pulse: a mixture of ethylene and O_2, $C_2H_4/O_2 = 5.1$)						
C_2H_4 conversion (%)	21.7	33.3	30.1	50.9	69.4	37.0
Selectivity for CH_4 (%)	5.8	24.1	7.4	17.4	21.8	26.5
Selectivity for C_2H_6 (%)	9.4	5.4	3.0	4.4	6.5	4.6
Selectivity for CO_x (%)	84.9	70.5	89.6	81.1	71.1	68.9
CO_2/CO ratio	0.2	0.2	0.5	0.0	0.01	0.1

Note. Amount of catalyst, 0.1 g; pulse size, 0.3 cm^3; temperature, 1073 K; He flow rate, 30 cm^3 min^{-1}.

free O_2. This is consistent with the earlier observation (*6*) that the selectivity in the oxidative coupling of methane over the rare earth oxide catalysts is increased to a large extent with increasing the CH_4/O_2 ratio in the feed.

The results (Tables 1–4) reveal that the rare earth oxides differ widely in their catalytic activity/selectivity and also in the activity of their lattice oxygen in the oxidative coupling of methane. The catalysts showed the following order for their activity/selectivity or product yield (i.e., conversion to the product) in the different pulse reactions.

For the activity of lattice oxygen. In the conversion of methane:

$$Eu_2O_3 > Sm_2O_3 \geq CeO_2 > La_2O_3 > Yb_2O_3 > La_2O_3^*.$$

For ethylene yield in the ethane conversion:

$$Yb_2O_3 > Sm_2O_3 > La_2O_3 > CeO_2 > Eu_2O_3.$$

For CO_x yield in the ethylene conversion:

$$CeO_2 > Eu_2O_3 > Sm_2O_3 > Yb_2O_3 \simeq La_2O_3.$$

For the catalytic activity in presence of free O_2. For C_2 yield in the methane conversion:

$$Yb_2O_3 > La_2O_3 > Eu_2O_3 > Sm_2O_3 >>> CeO_2.$$

For ethylene yield in the ethane conversion:

$$Yb_2O_3 > La_2O_3 > CeO_2 > Eu_2O_3 > Sm_2O_3.$$

For CO_x yield in the ethylene conversion:

$$Eu_2O_3 > Sm_2O_3 > CeO_2 > Yb_2O_3 > La_2O_3.$$

The results of the pulse reactions of methane, ethane, and ethylene lead to the following conclusions.

1. The presence of free (or gaseous) oxygen is very much essential for the rare earth oxide catalysts to be active in the OCM process.
2. In the OCM process over the rare earth oxides, ethane and ethylene undergo both the gas phase (homogeneous) and surface catalyzed (heterogeneous) reactions in O_2-rich or O_2-deficient conditions.
3. The rare earth oxides differ widely in

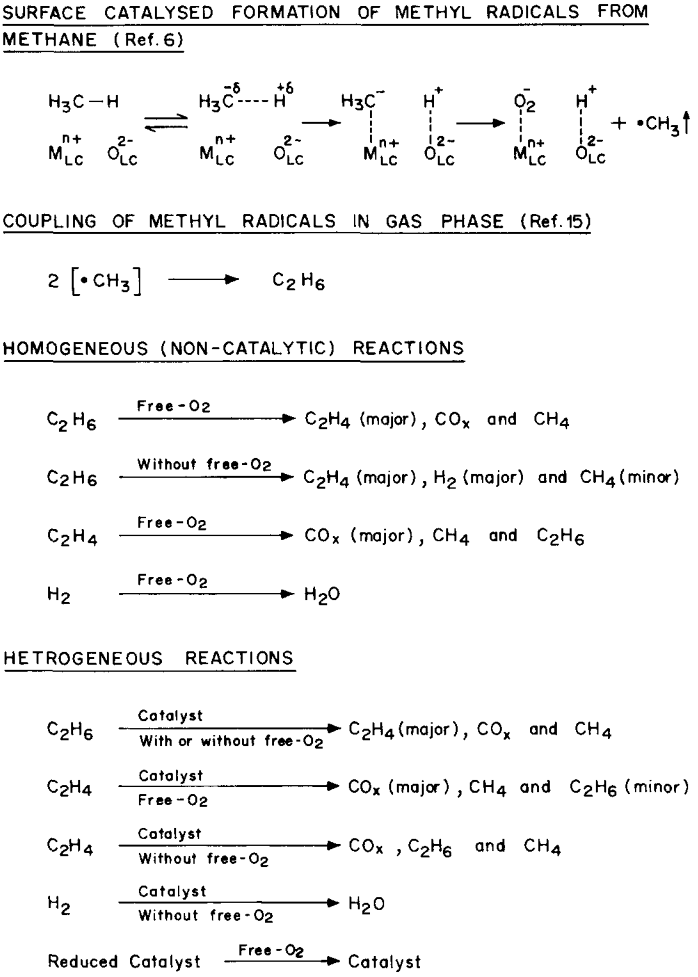

FIG. 1. Reactions occuring simultaneously in the oxidative coupling of methane over rare earth oxide catalysts.

their activity and selectivity in the conversion of methane, ethane, and ethylene in presence or absence of free O_2.

REFERENCES

1. Otsuka, K., Jinno, K., and Morikawa, A., *Chem. Lett.*, 499 (1985).
2. Lin, C.-H., Campbell, K. D., Wang, J.-X., and Lunsford, J. H., *J. Phys. Chem.* **90,** 534 (1986).
3. Otsuka, K., and Komatsu, T., *Chem. Lett.*, 483 (1987).
4. Campbell, K. D., Zhang, H., and Lunsford, J. H., *J. Phys. Chem.* **92,** 750 (1988).
5. Korf, S. J., Roos, J. A., Diphoorn, J. M., Veehof, R. H. J., van Ommen, J. G., and Ross, J. R. H., *Catal. Today* **4,** 279 (1989).
6. Choudhary, V. R., and Rane, V. H., *J. Catal.* **130,** 411 (1991).
7. Choudhary, V. R., Chaudhari, S. T., Rajput, A. M., and Rane, V. H., *J. Chem. Soc. Chem. Commun.*, 555 (1989); 605 (1989); 1526 (1989).
8. Choudhary, V. R., Chaudhari, S. T., Rajput, A. M., and Rane, V. H., *Catal. Lett.* **3,** 101 (1989).
9. Choudhary, V. R., Chaudhari, S. T., Rajput, A. M., and Rane, V. H., *Res. Ind.* **34,** 258 (1989).
10. Lee, J. S., and Oyama, S. T., *Catal. Rev. Sci. Eng.* **30,** 249 (1988).
11. Anderson, J. R., *Appl. Catal.* **47,** 177 (1989).

12. Garibyan, T. A., and Margolis, L. Ya., *Catal. Rev. Sci. Eng.* **31,** 355 (1989–1990).
13. Lunsford, J. H., *Catal. Today* **6,** 235 (1990).
14. Choudhary, V. R., Sansare, S. D., Rajput, A. M., and Akolekar, D. B., *Appl. Catal.* **69,** 187 (1991).
15. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Am. Chem. Soc.* **107,** 5062 (1985).

V. R. CHOUDHARY[1]
V. H. RANE

Chemical Engineering Division
National Chemical Laboratory
Pune-411 008, India

Received June 3, 1991; revised September 5, 1991

---

[1] To whom correspondence should be addressed.