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Kinetic studies of oxidative coupling of methane on samarium oxide

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Abstract

Kinetic behaviour of three samples of samarium oxide (cubic (Sm-1), monoclinic (Sm-3) and mixed cubic-monoclinic (Sm 2)) were studied in the oxidative coupling of methane using a gradientless flow circulation system. The specific rate of C_2-product formation differed by a factor of 6–8 for Sm-1 and Sm-3. The specific activity for CO formation did not depend upon the crystal structure of samarium oxide while the rate of formation of CO_2 was different for the samples studied. It is proposed that formation of CO and CO_2 occurs via different reaction routes. The rate of CO_2 formation at high CH_4/O_2 ratio is limited by oxidant activation or surface CO_2-complex decomposition.

1. Introduction

The oxides of the rare-earth elements (REE) are promising catalysts for the oxidative coupling of methane (OCM) to ethane and ethylene and have been intensively studied for the last few years. It was shown that strong correlation exists between the crystal structure of OCM catalysts and the catalytic activity in OCM reaction [1–3]. Difference in selectivity for REE based catalysts was interpreted in terms of the variation in oxygen environment in the crystal structures [2] or was attributed to the degree of defectness of the lattice [3] though the influence of the lattice structure on the individual reaction steps and the rates of formation of products remains unknown.

The present study was undertaken with the objective to examine in detail the role of the crystal structure of samarium oxide in OCM reaction and to clarify the activity–structure relationship.

2. Experimental

Three samples of samarium oxide (cubic Sm-1, 8.7 m^2/g; monoclinic Sm-3, 1.3 m^2/g and mixed cubic-monoclinic Sm-2, 6.9 m^2/g) were studied in the OCM reaction using a recirculation gradientless reactor (Fig. 1). The reactor (alumina tube 6 mm inner diameter) was equipped with a 10 cm long pre-heater. A sample of samarium oxide (0.01–0.05 g) was placed in the center of isothermal hot zone (about 1.5 cm long). The partial pressures of reactants used in the circulation system were: $pCH_4 = 2–55$ kPa, $pO_2 = 0.2–12$ kPa in helium, the total flow-rate of the feed mixture (Q_1) was 16 cm^3 (STP)/min. The rate of circulation flow (Q_2) was 900 cm^3/min. The reactants and reaction products were analyzed by

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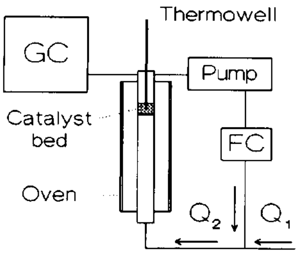

Fig. 1. Schematic diagram of the apparatus used for kinetic experiments. GC, gas chromatograph; FC, flow controller; Q_1, feed flow; Q_2, circulation flow.

an on-line gas chromatograph using TCD and Carbosieve S-II chromatographic column.

A separate set of experiments was performed to obtain the dependencies of the reaction rate $R(CO_x)$, $R(C_2)$ upon the oxygen or methane partial pressures. In each experiment the partial pressure of only one component was changed (methane or oxygen) keeping the total flow-rate and the partial pressure of the second component in the circulation loop constant. Each kinetic curve was repeated at least twice, first changing from higher to lower concentration and then changing from lower to higher. The results were reproducible indicating minor to negligible loss of catalyst activity during the time of the run.

3. Results and discussion

A blank experiment showed that the conversion of methane in the empty reactor at 740°C ($pCH_4 = 38.8$ kPa and $pO_2 = 15.8$ kPa) was 0.4%. Hence, under the experimental conditions used pure gas phase conversion of methane is negligible. However, this does not exclude the possibility that some surface initiated gas phase reactions can take place in the presence of catalysts.

The specific rate of methane conversion for Sm-1 was found to be twice that Sm-3, while the rates of C_2-product formation for Sm-1 and Sm-3 differed by a factor of 6–8 depending upon experimental conditions. Sm-2 had an intermediate level of activity. The specific activity for carbon monoxide formation did not depend upon the crystal structure of samarium oxide and had the same dependencies upon methane and oxygen partial pressures for all the samples (Fig. 2, Table 1).

Equal specific rates of CO formation for all three Sm_2O_3 samples and difference in the pressure dependencies for $R(CO)$ and $R(CO_2)$ mean that CO and CO_2 are formed via different reaction routes. On the basis of H_2/CO ratios observed one can assume that carbon monoxide is formed by the decomposition of oxygen containing species which are probably produced by the reaction of the hydrocarbons with lattice O_s^{-2}. The H_2/CO ratio decreased with increasing pCH_4 (from 1.8 to 1.2 for Sm_2O_3-1 and from 1.3 to 1.1 for Sm_2O_3-3 over the range of pCH_4 values studied) and there was a slight increase of H_2/CO ratio from 1.0 to 1.2 with increasing pO_2. The reaction pathway for CO formation possibly includes gas phase reac-

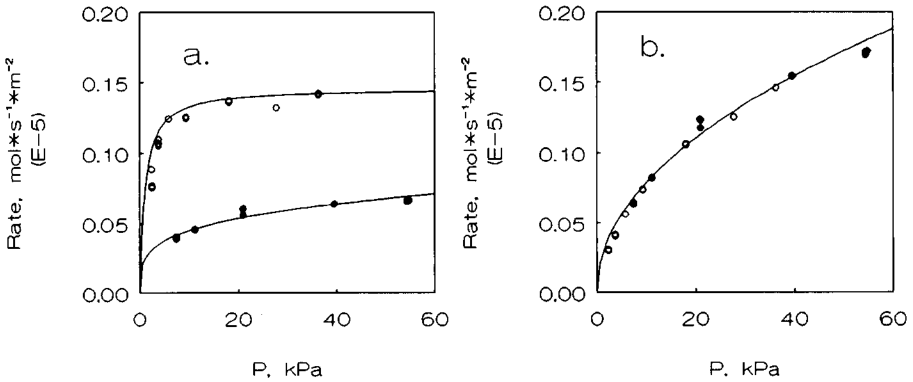

Fig. 2. Variation in the rate of CO_2 (a) and CO (b) formation as a function of methane partial pressure (740°C, $pO_2 = 1.7$ kPa). Open symbols, cubic Sm-1; solid symbols, monoclinic Sm-3.

Table 1
Apparent orders of OCM reaction for C_2, CO, CO_2 formation and CH_4 conversion calculated from $R(i) = k_i \cdot P^m_{CH4} \cdot P^n_{O2}$

Sample	n				m			
	CH_4	C_2	CO	CO_2	CH_4	C_2	CO	CO_2
Sm1	0.74	0.45	0.70	1.34	0.5	1.0	0.49	*
Sm2	1.0	0.60	0.70	1.58				
Sm3	0.68	0.44	0.70	0.86	0.5	1.0	0.49	*

* - can not be described by power equation;
R(i) - rate of product formation (methane conversion);
P_{O2},P_{CH4} - partial pressure of oxygen and methane in circulation loop.

tion or decomposition of oxygen-containing surface species such as CH_3O or CH_2O.

The rate of CO_2 formation does not depend on methane pressure at $pCH_4 > 5$ kPa for the samples studied. This observation may be explained by the limited availability of oxidant on the surface because the slow step of oxygen activation is followed by the rapid reaction of the active oxygen species with hydrocarbons or by slow desorption of carbon dioxide releasing an active site. An addition of 15 kPa of carbon dioxide to feed mixture (Sm_2O_3-2, T = 740°C) results in decrease of the total methane conversion and CO_2 formation by a factor of 1.4 whereas only a very slight decrease of C_2 formation rate occurs and no change of the rate of CO formation is observed. Despite there is no evidence for strong adsorption of CO_2 from transient isotope experiments at OCM condition over Sm_2O_3 [4] some quantity of carbon dioxide may be held on the Sm_2O_3 surface under reaction conditions. This is confirmed by the observation that there is a pronounced delay in the evolution of CO_2 after switching from O_2–CH_4 mixture to O_2–He mixture at 700°C [5]. Thus strong influence of CO_2 on the CO_2 formation rate may be connected with slow desorption of carbon dioxide from the surface of catalyst.

4. Conclusions

A kinetic study of the oxidative coupling of CH_4 over cubic and monoclinic samarium oxide shows:

(1) Formation of carbon monoxide and carbon dioxide occurs via different reaction routes, rates of formation of CO_2 and C_2 are different for cubic and monoclinic modification of Sm_2O_3, whereas rate of CO formation is independent of the type of structure.

(2) The reaction pathway for formation of CO possibly includes gas phase or surface decomposition of oxygen containing species such as CH_3O or CH_2O.

(3) Rate of CO_2 formation at high CH_4/O_2 ratio is limited by CO_2 desorption from the Sm_2O_3 surface.

5. References

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