Unsteady oxidative conversion of methane to C_2-hydrocarbons over La_2O_3 catalyst

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Received 3 September 1991; accepted 11 August 1992

Unsteady reaction behaviour with periodic fluctuations in reaction temperature and concentration indicating symmetric oscillations in the oxidative coupling of methane over La_2O_3 (obtained from lanthanum acetate by thermal decomposition in air at 600°C and subsequently calcined in N_2 at 750°C) above 550°C but below 700°C has been observed.

Keywords: Lanthanum oxide; oxidative coupling of methane; oscillations; unsteady reaction; C_2-hydrocarbons

Earlier studies [1–5] showed that La_2O_3 is an active catalyst in the oxidative coupling of methane (OCM) to C_2-hydrocarbons. In this paper we would like to report our results on the unsteady oxidative methane coupling reaction involving temperature and concentration oscillations at above 550°C, but below 700°C, over La_2O_3 catalyst prepared by thermal decomposition of lanthanum acetate.

The La_2O_3 catalyst was prepared by decomposing lanthanum acetate (AR Grade) in static air at 600°C for 6 h, pressing and crushing to 22–30 mesh size particles. The OCM process was carried out at atmospheric pressure in a flow tubular reactor (made of quartz) packed with the catalyst particles (0.1 g) between quartz wool plugs. The reactor was kept in a vertical tubular furnace. The reaction temperature (controlled by a temperature controller) was measured by a chromel–alumel thermocouple located in the catalyst bed. The product gases were analysed by an on-line gas chromatograph using Porapak-Q and Spherocarb columns. Before the reaction, the catalyst was calcined in situ at 750°C in a flow of N_2 (20 cm^3 min^{-1}) for 1 h. The surface area of the catalyst (calcined at 750°C) was 4.5 m^2 g^{-1}. The reaction was carried out under the following conditions: amount of catalyst, 0.1 g; feed, a mixture of pure methane and O_2; CH_4/O_2 ratio, 3.0, 4.0, or 5.0; total gas flow rate (at STP), 200 cm^3 min^{-1}; and temperature, 550°–750°C. The concentration of O_2 in the product

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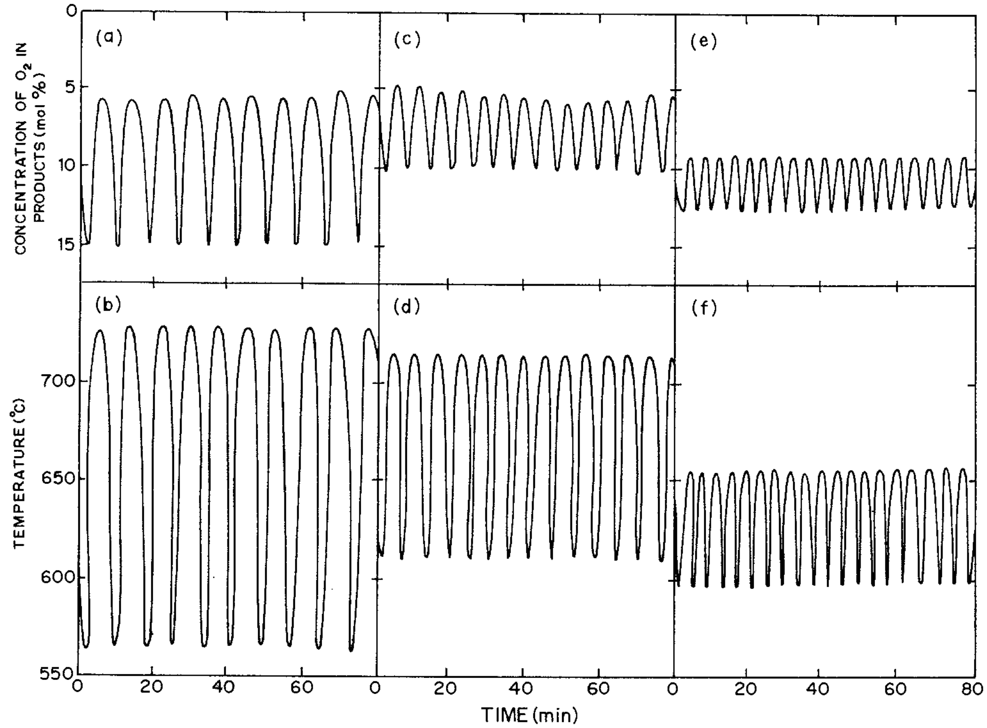

Fig. 1. Oscillations of reaction temperature and concentration of O_2 (in products) in the oxidative coupling of methane over the La_2O_3 catalyst at different CH_4/O_2 ratios. (T_s = reactor temperature setting.) (a, b) $CH_4/O_2 = 3$, $T_s = 600°C$; (c, d) $CH_4/O_2 = 4$, $T_s = 610°C$; (e, f) $CH_4/O_2 = 5$, $T_s = 610°C$.

stream (after separating by condensation) was measured/recorded continuously by an on-line paramagnetic O_2-analyser. There were no fluctuations in the feed rate and composition.

Fig. 1 shows symmetric temperature and O_2-concentration (in products) oscillations in the OCM reaction at different CH_4/O_2 ratios. The minimum and maximum of the O_2-concentration oscillation corresponds to the maximum and minimum, respectively, of the temperature oscillation. The cycle period and amplitude of both the oscillations are decreased with increasing the CH_4/O_2 ratio. For $CH_4/O_2 \geqslant 6.0$, no oscillation was observed. Also for $CH_4/O_2 = 3.0$ at $T_s \leqslant 560°C$ and $\geqslant 700°C$, for $CH_4/O_2 = 4.0$ at $T_s \leqslant 590°C$ and $\geqslant 700°C$ and for $CH_4/O_2 = 5.0$ at $T_s \leqslant 590°C$ and $\geqslant 630°C$, no sustained oscillation was observed.

The cycle period and amplitude of both the oscillation (except that at the temperature setting of 570°C for $CH_4/O_2 = 3.0$) are decreased with increasing the reaction temperature setting (fig. 2). In earlier studies, the amplitude and period of oscillations in the catalytic H_2 and CO oxidation reactions [6] and oxidative coupling of methane over $La_2O_3 \cdot BaO \cdot MgO$ catalyst [7] were found to decrease with increasing the reaction temperature.

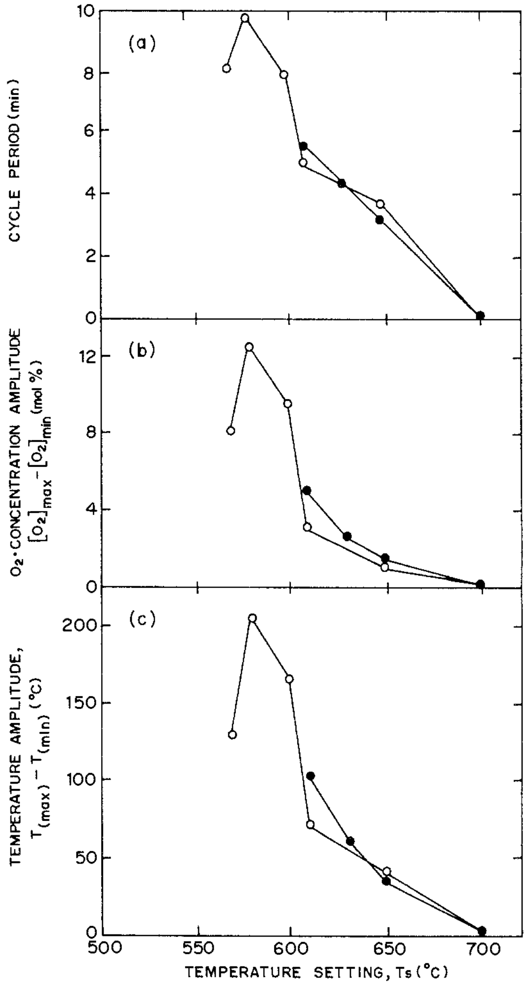

Fig. 2. Variation in the cycle period and amplitude of temperature and O_2-concentration (in products) oscillations in the oxidative coupling of methane with the reactor temperature setting. (○) $CH_4/O_2 = 3$; (●) $CH_4/O_2 = 4$.

Results on the catalytic activity and selectivity in the OCM process over the La_2O_3 catalyst for $CH_4/O_2 = 3.0$ under unsteady (i.e. oscillating) and steady state conditions are presented in table 1. The results under the unsteady conditions are just indicative of changes in the conversion and selectivity at around the minimum and maximum of the reaction temperature.

It is interesting to note that no unsteady behaviour in the reaction at 550–850°C over other La_2O_3 catalysts [8] obtained by the decomposition of other precursors for La_2O_3 (viz. nitrate, carbonate, hydroxide of lanthanum and hydrated La_2O_3) and subsequent calcination in the manner similar to that described above, has been observed. In the earlier studies on the OCM process over La_2O_3 [1–5], no oscillation has been observed.

Table 1
Results on the oxidative coupling of methane over the La_2O_3 catalyst for CH_4/O_2 ratio = 3, under unsteady and steady state conditions

Reactor temperature setting (°C)	Oscillating temperature (°C)	Oscillating O_2-concentration in products (mol%)	Methane conversion (%)	C_2-selectivity (%)
580	527 ± 5 (min)	18.0 ± 0.5	16.3	27.2
	732 ± 6 (max)	5.5 ± 0.4	28.6	43.0
600	565 ± 3 (min)	15.3 ± 0.2	18.9	29.1
	730 ± 2 (max)	5.6 ± 0.2	22.4	42.6
650	651 ± 2 (min)	8.7 ± 0.2	22.4	33.1
	691 ± 5 (max)	7.2 ± 0.2	23.4	37.6
700 [a]	700 ± 5	6.2 ± 0.1	24.4	40.9
750 [a]	750 ± 2	4.7 ± 0.1	28.6	44.0

[a] Oscillations not observed.

The observed unsteady reaction behaviour is likely to occur because of a large difference in the C_2-selectivity of the La_2O_3 catalyst in the OCM process at lower ($< 700°C$) and higher ($> 700°C$) temperatures (table 1). In the pulse reactions of methane over the La_2O_3 in presence of free O_2 ($CH_4/O_2 = 2.9$), the C_2-selectivity at lower temperatures (550–650°C) was much smaller (almost negligible small) than that at higher temperatures ($\geqslant 700°C$) [8]. The lower C_2-selectivity (i.e. the higher selectivity of carbon oxides) resulting in higher heat of reaction at the lower temperature is expected to cause an increase in the reaction temperature. When the temperature reaches a value at which the C_2-selectivity is high enough to cause no further increase in the reaction temperature, the transfer of reaction heat to the reactor surrounding (which is at lower temperature) results in a decrease in the reaction temperature. Thus the cycle is kept rotating and this leads to the observed temperature and concentration oscillations. However, for clearly understanding the unsteady reaction behaviour, further extensive studies covering various process and catalyst factors affecting the oscillating OCM process are essential.

In conclusion, the OCM process at temperatures above 550°C, but below 700°C, over the La_2O_3 obtained from the lanthanum acetate in the manner described above shows unsteady behaviour involving temperature and concentration oscillations.

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