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Energy efficient methane-to-syngas conversion with low H_2/CO ratio by simultaneous catalytic reactions of methane with carbon dioxide and oxygen

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By simultaneous reactions of methane with CO_2 and O_2 over NiO–CaO catalyst under certain reaction conditions, it is possible to convert methane into syngas with low H_2/CO ratio ($1 < H_2/CO < 2$) at above 95% conversion, with 100% CO selectivity and above 90% H_2 selectivity and also with very high CO productivity without catalyst deactivation due to coking for a long period, in a most energy efficient and safe manner, requiring little or no external energy.

Keywords: oxidation of methane to syngas; CO_2 reforming of methane; NiO–CaO catalyst; coupling of exothermic and endothermic reactions; reaction of methane with O_2 and CO_2

1. Introduction

Since last few years, research activities on the activation of carbon dioxide by its reaction with methane, commonly known as CO_2 reforming of methane to syngas (CO and H_2), using different catalysts [1–7] have got a lot of momentum because of a need for effective utilization of methane and CO_2 from natural gas and biogas. However, CO_2 reforming is highly endothermic ($\Delta H_r = 62.2$ kcal mol^{-1} at 800°C) and hence a highly energy intensive process. Further, it yields syngas with H_2/CO ratio of $\leqslant 1$ (which is not suitable for Fischer–Tropsch synthesis processes) and also involves rapid coke deposition, particularly on nickel catalyst. Recently, efforts have been made also for the direct oxidative conversion of methane to syngas (with $H_2/CO = 2.0$), which is an exothermic process and hence not at all energy intensive, using different catalysts [8–13]. However, the exothermic heat produced in this process is very strongly dependent upon the selectivity, which makes the process very difficult to control and thus highly hazardous or unsafe. In this communication, we show that, by carrying out the exothermic oxidative methane-to-syngas conversion simultaneously with the endothermic CO_2 reforming over NiO–

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CaO catalyst and manipulating the reaction conditions (viz. temperature and relative concentration of CH_4, CO_2 and O_2 in the feed), all the limitations of the CO_2 reforming process could be overcome.

2. Experimental

The preparation of the NiO–CaO (Ni/Ca = 3.0) catalyst is given earlier [10]. The simultaneous catalytic reactions of methane with CO_2 and O_2 were carried out at atmospheric pressure by passing continuously over the catalyst (0.3 g, particle size: 22–30 mesh) a mixture of pure methane, CO_2 and O_2 at different CH_4/O_2 and CH_4/CO_2 ratios in the feed, gas hourly space velocities (GHSV, measured at 0°C and 1 atm) and temperatures (measured by a Cr–Al thermocouple located in the catalyst bed) in a conventional fixed bed reactor (i.d.: 10 mm) made up of quartz. The product gases (after separating water by its condensation at 0°C) were analyzed by an on-line GC, using a Spherocarb column. The C, H, and O balances were within 5%.

3. Results and discussion

Results of the coupled process involving reactions of methane with CO_2 and O_2 over the same catalyst under different process conditions are summarized in figs. 1 and 3. In case of the CO_2 reforming alone, a very rapid coke deposition on the catalyst, causing development of high pressure drop across the reactor within a short reaction period (3 h), is observed. Whereas, in this coupled process, no catalyst deactivation due to coking is observed for a long period (fig. 1). The negative conversion of CO_2 observed at 700°C (fig. 2a), is just indicative of the formation of CO_2 in the coupled process. The net heat of reaction (ΔH_r) for the overall process is estimated by subtracting the heat of formation (at the process temperature) of the components in the feed from that of the components present in the product stream.

The ratios of the methane conversion by CO_2 reforming to that by oxidative conversion at the different temperatures (fig. 2a), estimated from mass balance, are given in table 1. The conversion of methane by CO_2 reforming relative to oxidative conversion is strongly dependent upon the temperature. At low temperature (<700°C), the oxidative conversion reactions,

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 + 5.2\ \text{kcal mol}^{-1} \tag{1}$$

and

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 191.5\ \text{kcal mol}^{-1}, \tag{2}$$

occur predominantly. However, at high temperatures, the CO_2 reforming reaction,

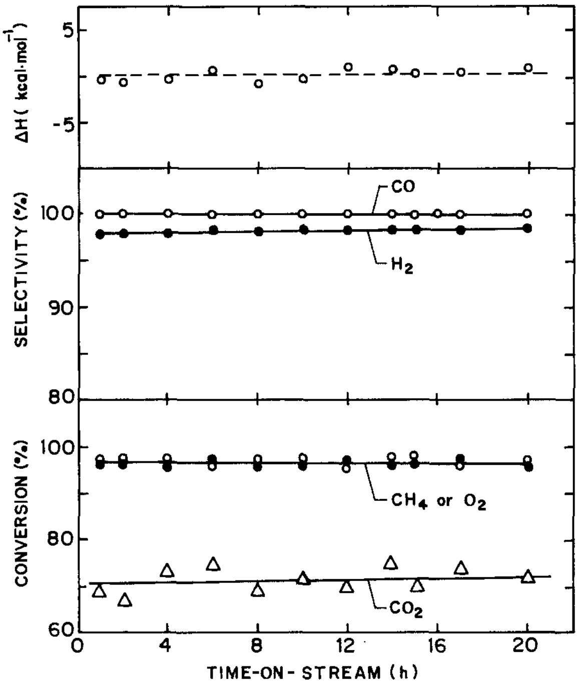

Fig. 1. Time-on-stream activity and selectivity of the catalyst in the coupled process at 850°C ($CH_4/O_2 = 2.1$; $CH_4/CO_2 = 10$; GHSV = 48000 $cm^3\ g^{-1}\ h^{-1}$).

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 - 62.2 \text{ kcal mol}^{-1} \qquad (3)$$

also occurs simultaneously with reactions (1) and (2). The CO_2 reforming/oxidative conversion ratio is found to be increased with increasing the temperature and/or the CH_4/O_2 ratio in the feed.

The results reveal that by coupling the endothermic CO_2 reforming with the exothermic oxidative methane conversion, the following advantages of great practical importance could be obtained.

(1) The coupled process can be made mildly endothermic, thermoneutral or mildly exothermic by manipulating the process conditions (particularly the reaction temperature and the CH_4/O_2 and CH_4/CO_2 ratios in the feed) and, therefore, can be operated with requiring little or no external energy. The ΔH_r for the process (i.e. process endothermicity) is increased markedly with increasing the reaction temperature (fig. 2a) and the CH_4/O_2 ratio (fig. 3a) but with decreasing the CH_4/CO_2 ratio (fig. 3b).

(2) The heat produced in the exothermic reactions of methane with O_2 (reactions (1) and (2)), is used instantly in the endothermic CO_2 reforming (reaction (3)), thus making the process most energy efficient, and also avoiding hot spot formation and consequently avoiding reaction runaway conditions and thereby making the process very safe to operate.

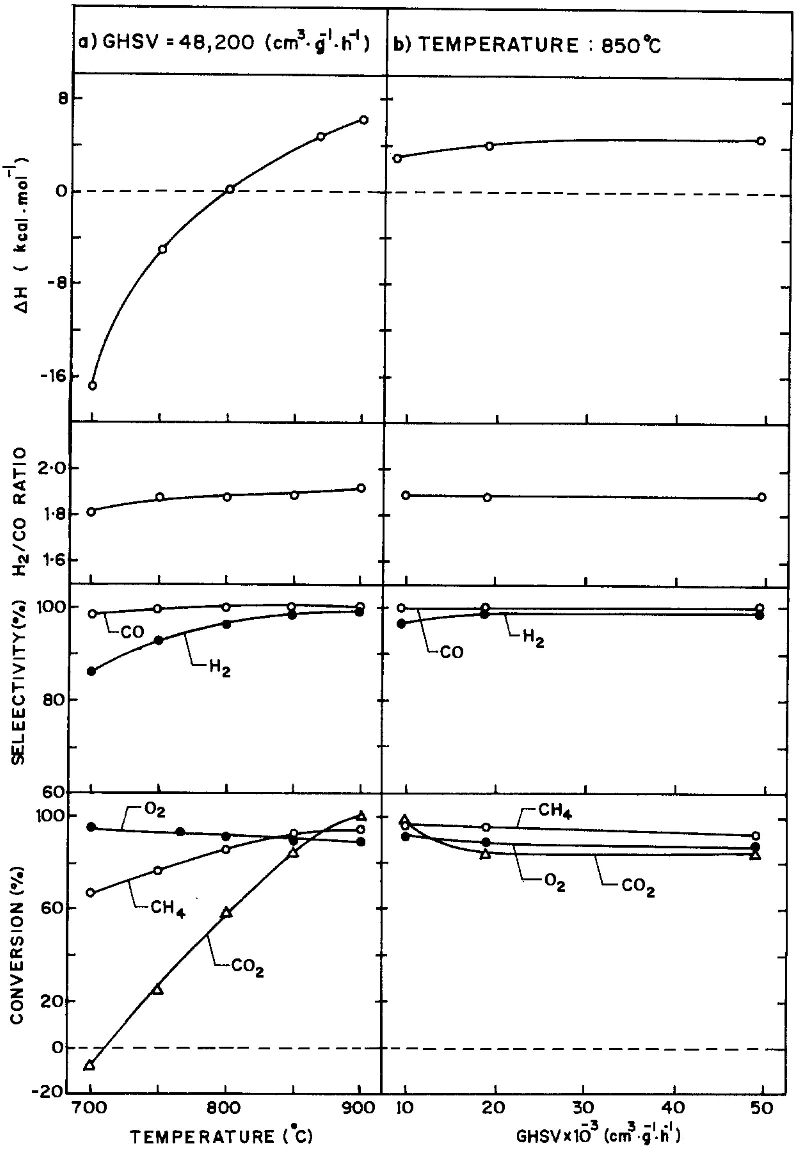

Fig. 2. Influence of (a) temperature and (b) gas hourly space velocity on the conversion, selectivity, H_2/CO product ratio and net heat of reaction (ΔH_r) in the coupled process ($CH_4/O_2 = 2.1$ and $CH_4/CO_2 = 8.0$).

(3) Further, in this coupled process, methane can be converted to syngas with a low H_2/CO ratio (between 1 and 2, which is required for Fischer–Tropsch synthesis) with very high conversion (even above 95%), CO selectivity (100%) and H_2 selectivity (above 90%) at very high space velocity (about 50 000 cm^3 g^{-1} h^{-1}) and consequently with very high CO productivity. The H_2 selectivity and or H_2/CO ratio can be increased by increasing and by manipulating the CH_4/O_2 and

Table 1
Ratio of methane conversion by CO_2 reforming to that by oxidative conversion at different temperatures

	Temperature (°C)				
	700	750	800	850	900
CO_2 reforming/oxidative conversion ratio	0.00	0.04	0.09	0.13	0.15

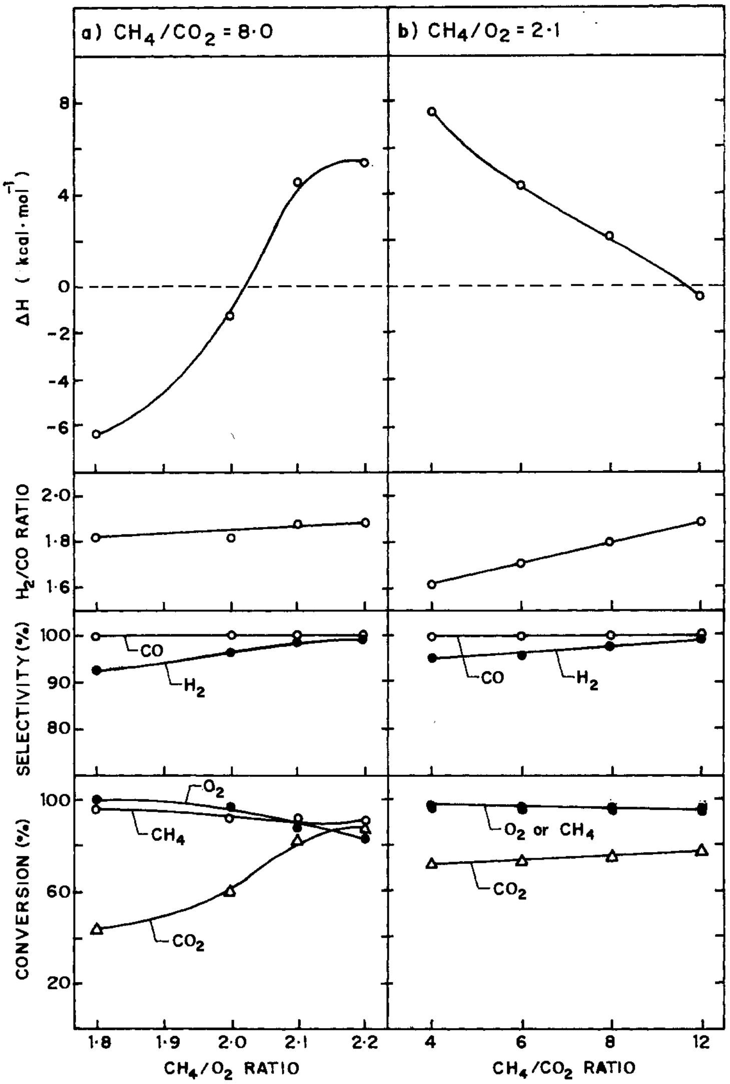

Fig. 3. Influence of (a) CH_4/O_2 and (b) CH_4/CO_2 ratios in the feed on the conversion, selectivity, H_2/CO product ratio and net heat of reaction (ΔH_r) in the coupled process at 850°C (GHSV = 49 000 cm^3 g^{-1} h^{-1}).

CH_4/CO_2 ratios in the feed (fig. 3). Coke formation on the catalyst is a serious problem in CO_2 reforming alone but not in the coupled process.

4. Conclusions

By coupling the endothermic and exothermic reactions of methane with CO_2 and O_2, respectively, over NiO–CaO catalyst and manipulating the process conditions, methane can be converted to syngas with low H_2/CO ratio required for Fischer–Tropsch synthesis, with very high conversion, selectivity and productivity without catalyst deactivation due to coking for a long period and also with requirement of little or no external energy, in a most energy efficient and safe manner.

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