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Low temperature oxidative conversion of methane to syngas over NiO–CaO catalyst

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Catalytic partial oxidation of methane over NiO–CaO (with or without its prereduction by H_2) at low temperatures ($\leqslant 973$ K) under non-equilibrium conditions yields syngas (H_2/CO ratio ≈ 2.0) with high conversion/selectivity and extremely high productivity. If required, the H_2/CO ratio can be increased by adding water vapour to the feed. Product selectivity is controlled by the process kinetics and also the reaction path is different from that observed for the high-temperature non-catalytic and catalytic processes operating at equilibrium.

Keywords: Methane conversion; synthesis gas; nickel–calcium oxide

1. Introduction

During the last decade considerable efforts have been devoted to the conversion of methane into easily transportable and/or value added products [1–5]. One of the most important means is the conversion of methane into petrochemicals and liquid hydrocarbon fuels by syngas conversion routes.

Syngas is produced from methane mostly by steam reforming [6,7] which suffers from the disadvantage of high energy requirements, high H_2/CO ratio (> 4, which is not suitable for methanol and Fischer–Tropsch synthesis) and poor selectivity ($\approx 60\%$) for CO. It can also be produced by the homogeneous non-catalytic oxidation of methane [6,7], but although this process is not energy intensive and yields syngas with the desired H_2/CO ratio (≈ 2.0), it operates at very high temperatures (> 1573 K) and, hence, is not commercially practiced. There is a need for an energy efficient but commercially feasible route for syngas from methane.

Recently, catalytic selective oxidation of methane to CO and H_2 (operating at or close to the thermodynamic equilibrium) over $Ln_2Ru_2O_7$ (Ln = lanthanide) [8], transition/noble metal supported Al_2O_3 [9], $Eu_2Ir_2O_7$ [9,10] and Ni/Al_2O_3

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[11,12] catalysts above 1023 K has been reported. The formation of CO and H_2 rather than CO_2 and H_2O in the process at equilibrium is favoured above 973 K [8,12]. Because of the operational problems and explosion hazards, the process will be much more practicable and commercially feasible if it were operated at lower temperatures, preferably below 873 K. However, at temperatures lower than 973 K poor selectivity for CO and H_2 over the above catalysts [8,9,12] has been observed. Because of the practical importance of the low-temperature process, the present investigation on oxidative methane-to-syngas conversion over a novel catalyst, NiO–CaO, using extremely high space velocities (i.e. operating under non-equilibrium conditions) for achieving much higher selectivity and productivity for syngas at lower temperatures ($\leqslant$ 973 K) was undertaken.

2. Experimental

The catalyst NiO–CaO (with different Ni/Ca ratios) was prepared by mixing thoroughly finely ground high purity nickel nitrate and calcium hydroxide (with the required Ni/Ca ratio) along with deionised water just sufficient to form a thick paste, drying and decomposing the mass at 873 K for 4 h, powdering, pressing and crushing to 22–30 mesh particles and calcining in air at 1200 K for 4 h. The catalytic reaction was carried out at atmospheric pressure in a continuous flow micro-reactor (i.d. 4 mm) made up of quartz, using 20 mg catalyst placed around the tip of a chromel–alumel thermocouple. The reactor was within a tubular furnace and reaction temperature was controlled by the thermocouple in the catalyst bed. The exothermic heat of reaction was removed by passing air through the furnace around the reactor. Before carrying out the reaction, the catalyst was heated in situ at 1200 K in a flow of moisture-free N_2 for 1 h and then reduced by H_2 in a flow (1.3 cm^3/s of 20% H_2 (balance N_2)) at 673 K for 1 h. The water formed in the reaction was condensed from the product gases at 273 K. The feed and product gases were analysed by an on-line gas chromatograph with thermal conductivity detector, using a spherocarb column. The reproducibility of results was checked by repeating the experiments. The C, O and H mass balances were better than 95%.

High purity gases [CH_4 (99.95%), CO_2 (99.995%), H_2 (99.99%), O_2 (99.9%) and N_2 (99.99%)] were used; their ratios are expressed as mole ratios. The space velocity (SV) of feed is defined as volume of gaseous feed (measured at 273 K and 1 atm) per gramme of catalyst per second.

3. Results and discussion

Results (table 1A, figs. 1 and 2) reveal that the reduced NiO–CaO (i.e. Ni–CaO) catalyst particularly with Ni/Ca ratio of 3.0, shows high activity and

Table 1
Results of oxidation of methane to syngas over reduced and unreduced NiO–CaO (Ni/Ca = 3.0) catalyst (feed: a mixture of CH_4 and O_2 with CH_4/O_2 ratio of 2.0, SV 145 $cm^3/g/s$)

Temp. (K)	CH_4 conversion (%)	Selectivity (%)			H_2/CO ratio in product	CO STY [a] (mmol/g/s)
		H_2	CO	CO_2		
(A) *reduced catalyst*						
973	83.4	92.0	93.9	6.1	1.96	3.33
823	75.7	90.3	90.1	9.9	2.00	2.89
673	67.9	85.5	84.8	15.2	2.02	2.44
573	62.3	78.3	80.7	19.3	1.94	2.17
(B) *unreduced catalyst*						
823 [b]	70.1	90.8	90.6	9.4	2.00	2.72
1023	82.4	93.4	95.2	4.8	1.96	3.39
1123	86.4	96.9	96.7	3.3	2.00	3.58
723	64.4	84.9	85.6	14.4	1.98	2.36
618	58.2	80.0	81.0	19.0	1.97	2.03

[a] Space–time–yield (or productivity) of CO.

[b] The run at 823 K was carried out for 15 h with no significant change in the time-on-stream activity/selectivity of the catalyst.

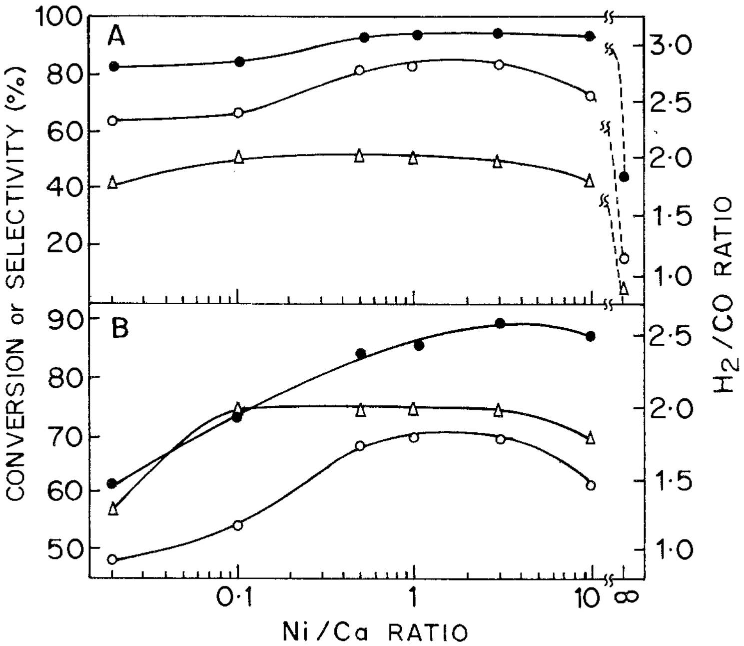

Fig. 1. Effect of Ni/Ca ratio on methane conversion (○), CO selectivity (●) and H_2/CO ratio (△) in the methane oxidation at 973 K (A) and 773 K (B) over reduced NiO–CaO (Feed: a mixture of CH_4 and O_2 with CH_4/O_2 ratio of 2.0, SV 145 $cm^3/g/s$. In the case of an empty reactor or pure CaO catalyst no oxidative conversion of methane at the above reaction conditions was observed).

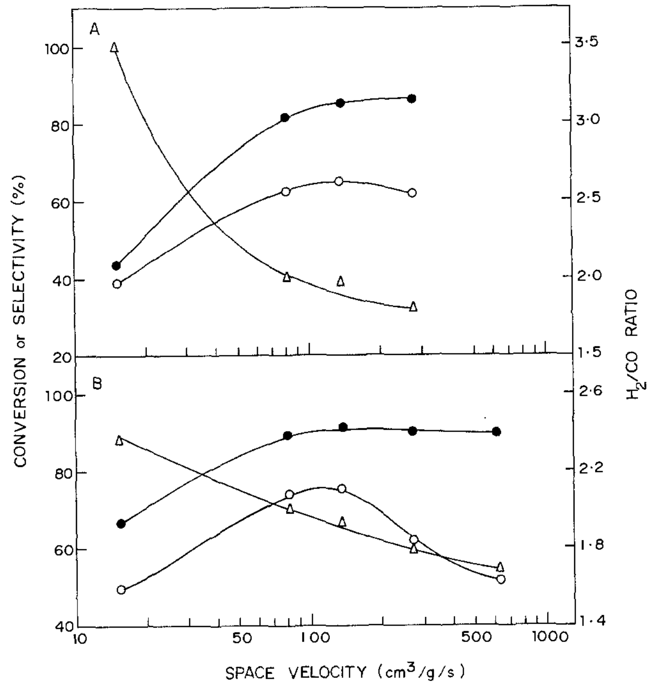

Fig. 2. Influence of space velocity on methane conversion (○), CO selectivity (●) and H_2/CO ratio (△) in the methane oxidation at 773 K (A) and 923 K (B) over reduced NiO–CaO (Ni/Ca = 3.0) catalyst (Feed: a mixture of CH_4 and O_2 with CH_4/O_2 ratio of 2.0).

selectivity (with H_2/CO ratio of about 2.0) and extremely high productivity in the oxidative conversion of methane to syngas, according to the reaction:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 + 22.6\ \text{kJ/mol}(CH_4) \qquad (1)$$

at low temperatures ($\leqslant 973$ K). The pre-reduction of the catalyst is, however, not essential; the reaction occurs even over unreduced catalyst (table 1B). However, the reaction on the unreduced catalyst does not occur below 823 K; the catalyst is activated by its reduction in the initial period of the reaction at higher temperatures ($\geqslant 823$ K) and then the reaction occurs at lower temperatures (below 823 K). Therefore, the catalyst in its active form is essentially Ni and/or partially reduced nickel oxide dispersed on CaO. The facts, that pure CaO is inactive and pure NiO shows very poor activity and selectivity in the reaction, and also that there is an optimum concentration of Ni (Ni/Ca $\approx$ 3.0) in the catalyst for achieving its best performance, reveal that the interactions between the reduced NiO and the CaO in the catalyst play an important role in creating desired active sites for the selective oxidation.

In the present case, the CO selectivity at lower temperatures ($\leqslant 973$ K) is much higher and also the CO productivity at all the temperatures is very much higher (by 1 to 3 orders of magnitude) than that obtained earlier using $Ln_2Ru_2O_7$

Table 2
Estimated values of CH_4 conversion and CO selectivity at the reaction equilibrium at 573–973 K (for CH_4/O_2 ratio of 1.78 and 1 atm pressure)

	$T = 973$ K	$T = 873$ K	$T = 773$ K	$T = 673$ K	$T = 573$ K
equilibrium CO selectivity (%)	92	67	25	4.5	very low
equilibrium CH_4 conversion (%)	96	84	58	35	≈ 20

[8] and Ni/Al_2O_3 [12] catalysts. Also, the activation of unreduced NiO–CaO catalyst occurs at much lower temperature ≈ 823 K than that (≈ 1023 K) required for unreduced Ni/Al_2O_3 [12].

In the partial oxidation of methane, the formation of CO over CO_2 is thermodynamically favoured at higher temperatures ($\geqslant 973$ K) [8,12]. The decrease in the CO selectivity with decreasing temperature (table 1) is consistent with this. However, the selectivity at lower temperatures (below 973 K) (table 1, figs. 1 and 2) is very much higher than that achieved at the reaction equilibrium. For the purpose of comparison, the estimated values of CH_4 conversion and CO selectivity at the reaction equilibrium (for CH_4/O_2 ratio of 1.78 and 1 atm pressure) at 573–973 K [12] are given in table 2. At $\leqslant 773$ K, the CH_4 conversion observed in the present work (even for CH_4/O_2 ratio $= 2.0$) is higher than the equilibrium one. Thus, the comparison of the observed conversion and selectivity with the equilibrium ones clearly shows that the reaction in the present case occurs under non-equilibrium conditions. This fact and the increase in the CO selectivity with increasing space velocity (fig. 2) reveal that the low temperature formation of CO and H_2 in the present process is controlled by its kinetics rather than its thermodynamics and, hence, favoured at very low contact times (or very high space velocities), unlike the earlier catalytic processes [8,9,12] operating at or close to the equilibrium.

An addition of water in the feed results in a large decrease in the CO selectivity and also an increase in the H_2/CO ratio (fig. 3). Thus, if required, H_2/CO ratio higher than 2.0 can be obtained by adding water in the feed. The increase in the H_2/CO and CO_2/CO ratios with increasing H_2O/CH_4 ratio in the feed indicates occurrence of the shift reaction simultaneously with the oxidative methane conversion.

For the high-temperature non-catalytic [7] and catalytic [8,12,13] oxidative methane-to-syngas conversion processes, operating at or close to the equilibrium, the reaction path involves the following sequence of reactions: a highly exothermic combustion of part of methane to CO_2 and H_2O with complete conversion of O_2, followed by the endothermic steam- and CO_2-reforming of the unconverted methane and the shift and reverse shift reactions, with the establishment of reaction equilibrium. In the present case, the reaction path is

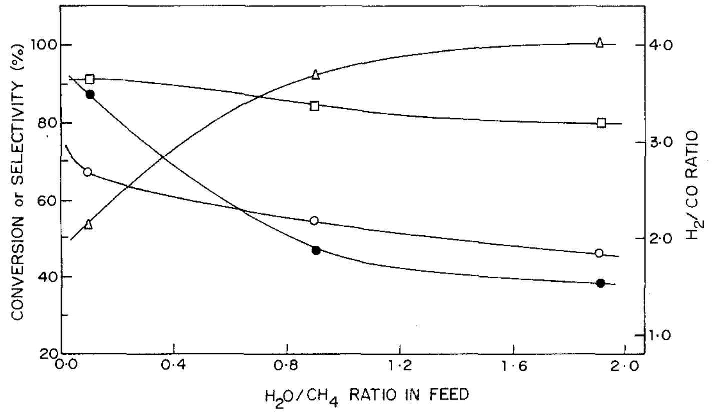

Fig. 3. Influence of addition of water vapours in the feed on methane conversion (○), selectivity for CO (●) and H_2 (□) and H_2/CO ratio (△) in the methane oxidation at 923 K over reduced NiO–CaO (Ni/Ca = 3.0) (Feed: a mixture of CH_4, O_2 and steam, CH_4/O_2 ratio of 2.0, SV 145 $cm^3/g/s$).

expected to be completely different from the above because of the following reasons. At the lower temperatures ($\leqslant$ 873 K), the methane conversion in the steam reforming is negligibly small with a poor selectivity for CO (table 3A) and also the CO_2 reforming of methane occurs only to a very small extent (table 3B). This fact and the increase in the CO selectivity with increasing space velocity (fig. 2) suggest that, in the present process, syngas is formed directly from methane without involving formation of CO_2 and H_2O as primary products, quite unlike the high temperature equilibrium process.

The results in table 3C indicate that CO_2 hydrogenation over the reduced catalyst occurs to a considerable extent with high selectivity for CO and methane formation at higher and lower temperatures, respectively. This reveals a possibility of occurrence of the reverse shift and methanation reactions in the present process.

Based on the above results, the possible reactions occurring in the present process are:

oxidation of methane

$$CH_4 \xrightarrow{[O_2]} CO \text{ and } H_2 \xrightarrow{[O_2]} CO_2 \text{ and } H_2O, \tag{2}$$

$$CH_4 \xrightarrow{[O_2]} CO_2 \text{ and } H_2O; \tag{3}$$

shift and reverse shift reactions

$$CO + H_2O \rightleftharpoons CO_2 + H_2; \tag{4}$$

methanation reaction

$$CO \text{ and } CO_2 \xrightarrow{[H_2]} CH_4 \text{ and } H_2O. \tag{5}$$

Table 3
Results of reactions occurring simultaneously with the oxidative conversion of methane over reduced NiO–CaO (Ni/Ca = 3.0)

(A) Reaction of water with methane [a]

Temp. (K)	CH_4 conversion (%)	Selectivity (%)	
		CO	CO_2
773	< 0.1	–	–
873	0.6	2.9	97.1
1078	6.6	34.9	65.5

(B) Reaction of carbon dioxide with methane [b]

Temp. (K)	CH_4 conversion (%)
773	0.3
873	2.2
973	7.1
1073	16.4

(C) Reaction of H_2 with CO_2 [c]

Temp. (K)	CO_2 conversion (%)	Selectivity (%)	
		CO	CH_4
723	29.9	53.1	46.9
1073	32.4	99.6	0.4

[a] Feed: an equimolar mixture of methane and water vapours, SV 150 $cm^3/g/s$.
[b] Feed: an equimolar mixture of CH_4 and CO_2, SV 150 $cm^3/g/s$.
[c] Feed: a mixture of CO_2 and H_2 with H_2/CO_2 ratio of 2.0, SV 145 $cm^3/g/s$.

The exact mechanism of formation of H_2 and CO from methane still remains unclear and further investigation is necessary.

4. Summary

We report here our preliminary studies disclosing the use of NiO–CaO catalyst in oxidative conversion of methane to syngas (H_2/CO) ratio ≈ 2.0) with high conversion, selectivity and productivity at low temperatures ($\leqslant 973$ K) and extremely high space velocities. The process occurs far away from the reaction equilibrium and involves a reaction path different from that in the high temperature equilibrium processes reported earlier. The product selectivity is controlled by kinetics rather than thermodynamics of the process. The H_2/CO ratio can be increased by adding water in the feed. The side reactions occurring simultaneously with the selective methane to CO and H_2 oxidation are a total combustion of methane, an oxidation of CO and H_2 and the shift, reverse shift and methanation reactions.

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