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Nonequilibrium Oxidative Conversion of Methane to CO and H_2 with High Selectivity and Productivity over Ni/Al_2O_3 at Low Temperatures

Over the last few years, efforts have been made to develop the catalytic selective partial oxidation of methane to CO and H_2 (i.e., syngas), operating above 750°C at or very close to the reaction equilibrium (*1–4*). This process is not energy intensive, unlike the highly endothermic catalytic steam reforming of methane (*5*, *6*), and also yields syngas with H_2/CO mole ratio of 2.0, which is suitable for the methanol and Fischer–Tropsch synthesis processes. In methane oxidation, the formation of CO and H_2 over CO_2 and H_2O is thermodynamically favored at high temperatures (above 700°C) (*1*, *4*). By carrying out methane oxidation over Ni/Al_2O_3 at very low gas hourly space velocity (GHSV: 750 h^{-1}), Dissanayake *et al.* (*4*) obtained values of methane conversion and CO selectivity very close to that achievable at the reaction equilibrium, in a wide temperature range (450°–900°C). At temperature greater than or equal to 800°C, very high CO selectivity with almost complete methane conversion was obtained, but CO selectivity at low temperatures (below 700°C) was very poor. It has been shown that the reaction path for the process over Ni/Al_2O_3 at equilibrium involves a sequence of following reactions: a combustion of part of the methane to CO_2 and H_2O with complete conversion of O_2, followed by the highly endothermic steam and CO_2 reforming of unconverted methane to CO and H_2, and the shift reaction, establishing the equilibrium (*4*, *7*). We report here our preliminary results which reveal that much higher selectivity, with extremely high productivity for CO and H_2, than that obtained at equilibrium in the partial oxidation of methane over Ni/Al_2O_3 at low temperatures (300–700°C) can be obtained by carrying out the reaction far away from the equilibrium (i.e., using extremely high GHSV).

An 18.7 wt% Ni/Al_2O_3 catalyst was prepared by impregnating 22–30 mesh size particles of alumina (HARSHAW-AL-0104) with nickel nitrate and calcining at 930°C in air for 4 h. The catalytic reaction over the reduced (by 20 mol% H_2 in N_2 (80 cm^3 min^{-1})) at 500°C for 1 h before the reaction or unreduced catalyst (20 mg) was carried out in a quartz micro-reactor (i.d. 4 mm) at 1 atm. The reaction temperature was measured by a chromel–alumel thermocouple located in the catalyst bed. The water formed in the reaction was measured by condensing it from the product gases at 0°C. The feed and product gases were analyzed by an on-line gas chromatograph using a spherocarb column.

The results (Table 1) reveal that the performance of the reduced catalyst is better, and for both the reduced and unreduced catalysts, the CO selectivity (with H_2/CO ratio at 2.0) particularly at <700°C is very much higher than the equilibrium CO selectivity. This fact and the increase in the CO selectivity with the increase in GHSV show that the present process occurs far away from the equilibrium and the product selectivity is controlled mostly by the process kinetics, whereas the selectivity in the process at equilibrium (*4*) is controlled by its thermodynamics. Further, because of the higher selectivity, the methane conversion obtained at ≤500°C is higher and also the CO productivity at all the temperatures is very much higher (by about 2–3 orders of magnitude) than that obtained earlier (*4*) at the process equilibrium. A very small conver-

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TABLE 1

Results of Oxidative Conversion of Methane to CO and H_2 over Unreduced and Reduced Ni/Al_2O_3 (Feed: 67 mol% CH_4 and 33 mol% O_2)

Temp. (°C)	GHSV[a] × 10^{-5} (h^{-1})	CH_4 conversion (%)	Selectivity (%) H_2	Selectivity (%) CO	Selectivity (%) CO_2	H_2/CO mole ratio	CO STY[b] (mol g^{-1} h^{-1})	Equilibrium CO selectivity (%) (Ref. (4))
			Unreduced Ni/Al_2O_3					
800	4.95	85.8	97.7	96.8	3.2	2.02	13.41	95
700	4.95	78.6	94.8	94.0	6.0	2.02	11.93	92
500	4.95	67.7	87.0	85.7	14.3	2.03	9.37	25
300	4.95	56.4	77.3	75.0	25.0	2.06	6.83	<5[c]
			Reduced Ni/Al_2O_3					
800	4.95	87.2	98.0	97.6	2.4	2.01	13.75	95
700	4.95	86.4	96.6	95.8	4.2	2.02	13.67	92
500	4.95	72.7	91.1	90.0	10.0	2.02	10.57	25
300	4.95	63.5	86.3	83.6	16.4	2.06	8.57	<5[c]
700	0.91	59.0	92.0	86.6	13.4	2.12	1.51	92
500	0.91	47.8	76.1	52.2	47.8	2.92	0.743	25

[a] Volume of feed gas (measured in °C at 1 atm) per volume of catalyst per hour.
[b] Space-time-yield (or productivity).
[c] Approximate value.

sion of methane in its reaction with water and CO_2 (Table 2) indicates that the later are not the primary products formed in the methane oxidation over Ni/Al_2O_3 at the high GHSV (5.0 × 10^5 h^{-1}) and at low temperatures (≤700°). Thus, the process occurring under nonequilibrium conditions follows a reaction path completely different from that considered for the equilibrium process (*4*, *7*). Further work is necessary for understanding the reaction path for the nonequilibrium process at low temperatures.

The conclusion drawn from this study is as follows: partial oxidatoin of methane over Ni/Al_2O_3 at low temperatures (≤700°C) under nonequilibrium conditions using extremely high space velocities results in a much higher selectivity and productivity for CO and H_2 than that which can be obtained at the equilibrium, with a change in the reaction path.

TABLE 2

Results of Reactions of Water and CO_2 with Methane over reduced Ni/Al_2O_3 (Feed, Equimolar Mixture of CH_4 and H_2O or CO_2; GHSV, 5.0 × 10^5 h^{-1})

Reaction of water with methane				
Temp. (°C)	500	600	700	
CH_4 Conversion (%)	0.0	<0.5	10.4	
Reaction of CO_2 with methane				
Temp. (°C)	400	500	600	700
Conversion of CH_4 (%)	0.0	<0.5	2.0	13.4

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