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KINETICS OF METHANE PARTIAL OXIDATION TO SYNGAS OVER A LiLaNiO/γ-Al_2O_3 CATALYST

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Abstract

The kinetic behavior of partial oxidation of methane to syngas over a LiLaNiO/γ-Al_2O_3 catalyst was investigated under steady-state conditions. Under kinetic control, syngas, to a large extent, is formed *via* a direct partial oxidation (DPO) scheme. CO and CO_2 are formed in parallel by oxidation reaction over the catalyst. The active sites in the kinetically controlled regime are different from those in the non-kinetic regime, thus the CO selectivity in the former may not increase with temperature.

Keywords: Methane partial oxidation, syngas

INTRODUCTION

Partial oxidation of methane (POM) constitutes an interesting alternative process for the conversion of natural gas to synthesis gas. This reaction is slightly exothermic and leads to the production of syngas with a H_2/CO ratio of about 2, which is suitable for methanol and Fischer-Tropsh synthesis. In comparison, the steam reforming process over nickel-based catalysts is less energy-efficient and produces less desirable H_2/CO ratios. Thus, the POM process has attracted the attention of many research groups and has been investigated over various metal-based catalysts. Group VIII metals such as Rh, Ru, Pt, Ir, Pd and Ni are reported to be active and selective to partial oxidation of methane to synthesis gas [1].

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Ruckenstein *et al.* [2] investigated the kinetics of methane oxidation over a Ni/La_2O_3 catalyst, and reported that CO may be the primary product of the POM reaction, while CO_2 is subsequently generated from combustion of CO. Meanwhile, Verykios *et al.* [3] studied the kinetic behavior of NiO/La_2O_3 under steady-state conditions as a function of temperature and the partial pressures of CH_4 and O_2. They found that the POM reaction over the Ni/La_2O_3 is mainly the sequence of total oxidation of CH_4 to CO_2 and H_2O, followed by reforming reactions to synthesis gas. CO formation *via* direct route is possible at low oxygen partial pressures, and depends on the oxidation state of the Ni crystallites.

Recent studies conducted in this laboratory [4,5,6] showed that high reaction performance and good carbon-deposition resistance, combined with excellent stability can be achieved over the $LiLaNiO/\gamma\text{-}Al_2O_3$ catalyst. Meanwhile, the mechanism of the POM reaction over the catalyst was also performed [7]. In the present work, the kinetics of partial oxidation of methane to syngas over a $LiLaNiO/\gamma\text{-}Al_2O_3$ catalyst was investigated under steady-state conditions as a function of contact time, temperature and initial conditions.

EXPERIMENTAL

Preparation of the $LiLaNiO/\gamma\text{-}Al_2O_3$ catalyst was described previously [4]. The apparatus employed for kinetic measurements consist of a flow measuring system, a heated quartz tube reactor and an on-line analytical system. Feed flow rate was measured and controlled by the mass flow control. Analysis of the feed and the reaction mixtures was achieved by a gas chromatograph connected on-line to the reactor apparatus *via* a gas sampling valve.

The reactor was a 4 mm i. d. quartz tube, immersed in an electrically-heated furnace. Weighed amounts of catalyst (diluted with $\alpha\text{-}Al_2O_3$) were placed in the middle of the reactor, supported by quartz. The length of the catalyst bed was typically 4 mm. After the $LiLaNiO/\gamma\text{-}Al_2O_3$ catalyst was reduced *in situ* in H_2 (20 mL/min) at 850°C for 1 h, it was cooled to 700°C in a flow of N_2. The catalyst was then used in the $CH_4/O_2/He$ ($CH_4/O_2/He=4/2/94$) reaction. Contact time was altered by adjusting the total flow rate and amount of catalyst. Operating conditions with respect to total rate and average catalyst particle size were defined so as to eliminate intraphase and interphase transport resistances.

Two EU-2 thermocouples close to the catalyst bed were applied for temperature measurement and control. One inside a thermowell measured the temperature along the catalyst bed. Another one was placed at the exit of the catalyst bed to control the electrically heated furnace temperature (Tc), which was taken as the reaction temperature, while ΔT ($\Delta T = Tmax - Tc$) indicated the extent of overheating in the catalyst bed.

RESULTS AND DISCUSSION

Hot spots in the catalyst bed, mass transfer and heat elimination

When highly exothermic reactions, as in this case, are carried out in an experimental reactor, hot spots of significant magnitude can develop within the catalyst bed. Under such conditions, erroneous results concerning the kinetic behavior of the reaction system may be obtained. Several factors affecting the presence and magnitude of hot spots, the most important of these factors are contact time, solid dilution, gas dilution and metal loading of the catalyst [8]. The magnitude of hot spots was quantified by the temperature difference (ΔT), and the value of ΔT (<11^{o}C) became negligibly small, under the experimental conditions employed.

Operating conditions with respect to total feed flow rate and average catalyst particle size were defined so as to eliminate intraphase and interphase transport resistances. In preliminary experiments the catalyst particle size, for which intraphase transport of mass did not influence the observed rate, was determined, as can be seen in Table 1. Similarly, the minimum feed flow rate above which interphase transport resistance was minimized, was also determined following standard procedures (Fig. 1).

Table 1

Reaction performance as a function of particle size of the LiLaNiO/γ-Al_2O_3
(T =810^{o}C, W/F $_{total}$ = 5x10^{-5} g min/mL, CH_4/O_2/He=4/2/94)

Particle size (mm)	CH_4 conversion (%)	CO selectivity (%)
0.28-0.22	6.72	71.39
0.22-0.20	7.00	73.19
0.20-0.16	7.61	73.08
0.16-0.13	7.86	74.04
0.13-0.098	7.85	74.14

Taking into account the preceding results, the kinetic regime was characterized by a dilute reactant mixture, consisting of CH_4/O_2/He=4/2/94, total flow rates between 150 mL/min and 300 mL/min, and a catalyst of average particle size of 0.098 - 0.16 mm, diluted with 5 portions of α-Al_2O_3 (of the same particle size).

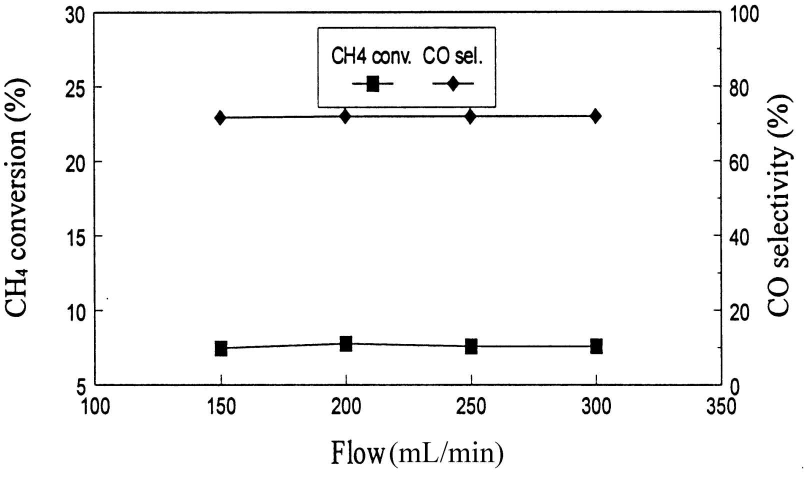

Fig. 1. Influence of total feed rate on CH_4 conversion and CO selectivity LiLaNiO/γ-Al_2O_3 (T=810°C, W/F $_{total}$ =5x10^{-5} g min/mL, $CH_4/O_2/He$=4/2/94)

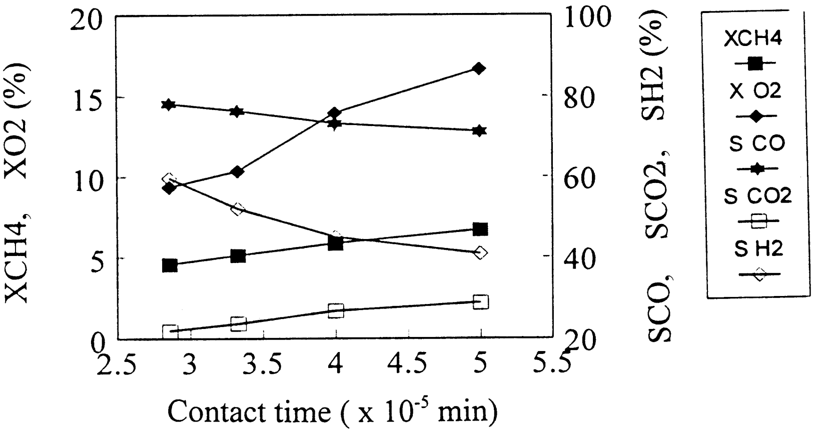

Fig. 2. Influence of contact time on the reaction performance of the LiLaNiO/γ-Al_2O_3 (790°C, $CH_4/O_2/He$ = 4/2/94)
*: XCH_4 is CH_4 conversion (%) and SCO is CO selectivity (%)

Influence of contact time on the reaction performance of the LiLaNiO/γ-Al_2O_3

Figure 2 shows the influence of contact time on the reaction performance of the LiLaNiO/γ-Al_2O_3, in the kinetic regime. A decrease in both H_2 and CO selectivities was observed with increasing contact time, while methane and oxygen conversions increased. Significantly, high CO selectivity (Fig. 4) was maintained even at very low methane conversions (T=650°C, CH_4 conversion = 0.4%, CO selectivity=58%). It can be concluded from these results that at low methane conversion, syngas (CO + H_2), to a large extent, is formed *via* the direct partial oxidation (DPO) scheme. The results shown in Fig.4 still indicate that both CO and CO_2 selectivities decrease to zero simultaneously (T=600°C). This conditions that CO and CO_2 are formed in parallel by oxidation reaction over the LiLaNiO/γ-Al_2O_3 catalyst.

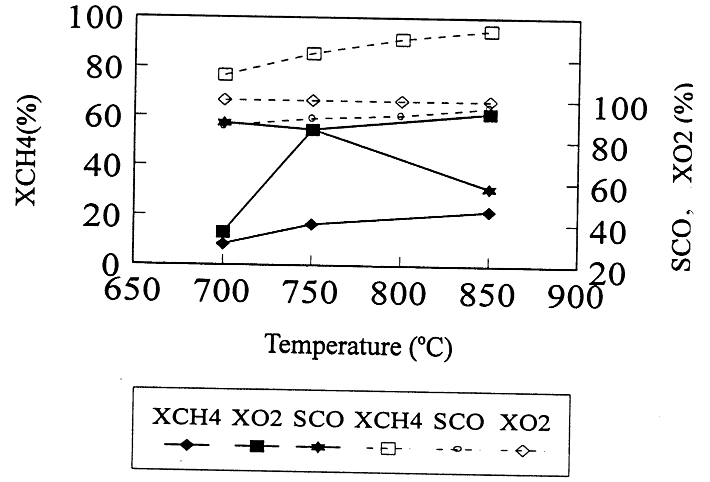

Fig. 3. Influence of initial conditions on the reaction performance of LiLaNiO/γ-Al_2O_3

Solid line: 700°C initiated for 60 min, $CH_4/O_2/He$ = 4/2/94, W/F_{total} = $5x10^{-5}$ g min/mL, then $CH_4/O_2/He$ = 4/2/0, W/F_{CH4} = 1.25 x 10^{-3} g min/mL

Dashed line: 700°C initiated, $CH_4/O_2/He$ = 4/2/0, W/F_{CH4} = 1.25 x 10^{-3} g min/mL

*: XCH_4 is CH_4 conversion (%) and SCO is CO selectivity (%)

Influence of initial conditions on the reaction performance of the LiLaNiO/γ-Al_2O_3

As the LiLaNiO/γ-Al_2O_3 catalyst was reduced *in situ* in H_2 (20 mL/min) at 850°C for 1 h, the oxidized nickel of the catalyst, *i.e.* $NiAl_2O_4$ [4] was transformed to reduced nickel [7]. After that, the catalyst was cooled to 700°C in a flow of N_2 and then used the CH_4 /O_2/He reaction. This course was named as initial conditions. When the feed contained only CH_4 and O_2 (Fig. 3, dashed line, initial conditions I), CH_4 conversion and CO selectivity with high value increased with increasing temperature (700-850°C), and oxygen conversion was always kept at 100%. However, at a CH_4/O_2/He ratio of 4/2/94, the catalyst performed for 60 min, then at CH_4/O_2/He=2/1/0 (Fig. 3, solid line, initial conditions II). Both CH_4 and O_2 conversions increased with increasing temperature, but the methane conversion in the initial conditions II was much lower than that in the initial conditions I. And the CO selectivity in the initial conditions II was decreased with raising temperature, while that in the initial conditions I was increased with increasing temperature. These indicate that the active sites in the kinetic controlling regime are different from that not in the kinetic controlling regime such as initial conditions I. The active sites in the latter are the reduced nickel [7] that causes high conversion and selectivity. While in the kinetic control regime, the active sites may be reduced nickel and the oxidized state of the reduced nickel that may be a group of Ni-O and Ni-O_2 (the nature of such a new state is unclear). The dissociative adsorption of CH_4 on the reduced nickel produces surface carbon and surface hydrogen. Surface carbon reacts with the oxidized state of nickel to produce CO. CO_2 is obtained from either the deep oxidation of CO or the reaction of surface carbon with molecular oxygen. It should be noted that this is speculation and would be investigated.

Influence of temperature on the reaction performance of the LiLaNiO/γ-Al_2O_3

Figure 4 shows CH_4 and O_2 conversions, and CO selectivity as a function of temperature. O_2 conversion increased more than CH_4 conversion with raising temperature (O_2 conversion did not reach 30%, even the reaction temperature was 850°C). This means that O_2 is activated easier than CH_4. It was interesting that the CO selectivity first increased (from 700 to 770°C), then decreased (from 770 to 850°C), while as the reaction temperature decreased, the CO selectivity first increased (850-750°C), then decreased (750-600°C). This is obviously different from our previous paper [4]. In the kinetic controlling regime, because suitable oxygen adsorbs on the catalyst surface, and oxygen is activated easier than methane (although methane and oxygen activate easily at such temperatures, Fig. 4), the relative ratio of reduced nickel to the oxidized state concentration may not increase with raising temperature. The CO selectivity depends on the relative concentration of two nickel states, so the CO selectivity may not increase with increasing temperature; it even decreases with raising temperature so as in Fig.3 (solid line). Au *et al.* [9,10] proposed that the direct production of CO is determined by the ratio of Ni^o/Ni^{2+} on the catalyst surface, which is expected to increase with increasing reaction temperature. This hypothesis obviously cannot interpret our results presented in Figs 3 and 4.

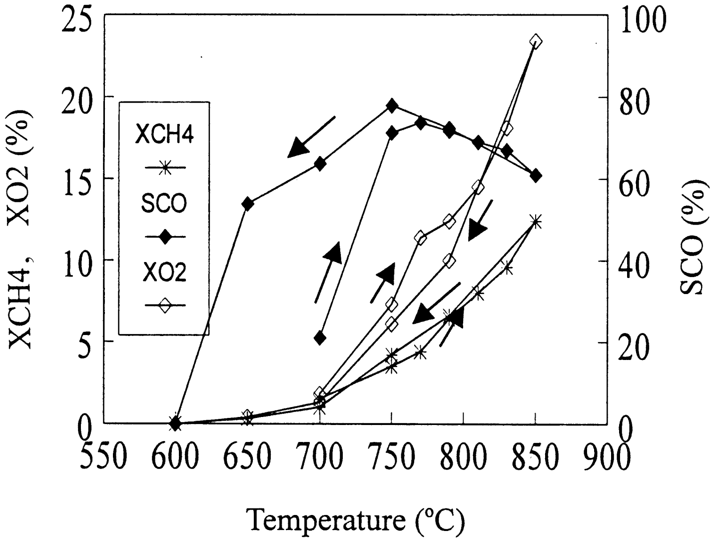

Fig. 4. Variation of methane and oxygen conversions and CO selectivity as a function of reaction temperature, first increasing and then decreasing stepwise (700°C initiated, $CH_4/O_2/He$ = 4/2/94, W/F_{total} = 5x 10^{-5} g min/mL)
*: XCH_4 is CH_4 conversion (%) and SCO is CO selectivity (%)

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