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Increasing of carbon monoxide methanation rate by forced feed composition cycling

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Abstract

The methanation of carbon monoxide on the commercial Ni/SiO_2 catalyst was studied experimentally under transient reaction conditions. Two types of concentration changes of the reactor feed were used: (i) step-changes for the investigation of elementary system dynamics, and (ii) forced feed composition cycling for examination of the effect of the periodic feed modulation on the time-average reaction rate. The experiments were performed in a laboratory flow microreactor in the temperature range between 458 and 538 K. It has been found that forced feed composition cycling significantly increases the reaction rate for any composition of reactor feed including composition leading to the highest steady-state rate. The enhancement of the methanation rate is caused by massive deposition of carbonaceous intermediates on the catalyst surface. Those deposits are unreactive under steady-state conditions due to the blocking of active sites for adsorption of hydrogen by CO but highly reactive during feed concentration cycling for alternating between CO-rich and CO-lean feeds.

1. Introduction

The possibility of improvement of catalyst performance by cycling of system variables has attracted the attention of many research teams in past decades. The phenomena resulting from (usually periodic) changes of feed composition, reactor temperature or flow rates have been widely discussed, e.g. Feimer et al. [1], Thulie et al. [2], Lynch [3], Nowobilski and Takoudis [4], Klusáček et al. [5], Cutlip [6], Koubek et al. [7], Jain et al. [8], Chiao et al. [9]. Application of periodic operation to heterogeneous catalytic systems was reviewed by Silveston [10].

It is now generally accepted that steady-state activity of the catalyst can be significantly exceeded through unsteady-state operation. Generally there are many parameters influencing the steady state of the catalytic system —e.g. composition of feed, reactor temperature, total pressure and total flow rate. However, the dominant method used in experimental work is to change the feed composition as this is the easiest to accomplish. The positive influence of the modulation of the feed composition on the catalytic activity was reported e.g. for CO oxidation (Cutlip [6], Abdul-Kareem et al. [11], Barshad and Gulari [12]), ammonia synthesis (Wilson and Rinker [13], Jain et al. [8,14–16], Rambeau and Amariglio [17,18]), sulphur dioxide oxidation (Unni et al. [19], Briggs et al. [20]), elimination reactions of amines (Koubek et al. [7]), and ethylacetate synthesis (Dettmer and Renken [21]). In this contribution the enhancement of catalytic reaction rate by feed composition cycling

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will be presented for the methanation of carbon monoxide on a commercial Ni/SiO_2 catalyst.

2. Experimental

Experiments were performed in a tubular flow microreactor (volume about 1 cm^3) in the temperature range 458–538 K under atmospheric pressure. The commercial, 29 wt.-% Ni/SiO_2 catalyst G-33 (Girdler Südchemie, Germany) was crushed into 0.16–0.25 mm particles and activated for 2 hours in a flow of hydrogen at temperature 623 K. The reaction temperature was measured by a thin thermocouple (iron-constantan) inserted into the catalyst bed. Typical catalyst load was 50–100 mg. Prior to measurements, the catalyst was treated in argon at 623 K for 30 minutes to remove hydrogen and water from the preceding activation procedure. The reaction components, CO, H_2, and argon were introduced into the reactor after purification and their flow was controlled by means of mass flow controllers.

Two different types of modulation of reactor feed composition were used in this work: (i) double step-changes $H_2 \rightarrow CO/H_2 \rightarrow H_2$, and (ii) periodic cycling of feed composition between pure hydrogen and a mixture of CO and hydrogen. Switching of reaction mixture was accomplished by a system of programmable six-way valves. The composition of the reaction mixture leaving the reactor was continuously followed using a Balzers QMS 420 quadrupole mass spectrometer at rates 1–50 scans/s.

3. Results and discussion

3.1. Step changes of feed composition $H_2 \rightarrow CO/H_2 \rightarrow H_2$

The transient system response to the above double step-change is shown in Fig. 1 for the temperature 458 K. Switches occurred at about 25 and 180 s, respectively. After the switch from pure hydrogen to the mixture of CO/H_2 (11/89 mol-%), hydrogen partial pressure quickly fell, and after a short induction period when the surface was partly covered by CO, the concentration of carbon monoxide increased. The production of methane gradually increased and attained monotonically the steady-state value. The concentration of water passed through a sharp maximum followed by a slow decline to the steady-state level. From comparison of areas under the methane and water responses in Fig. 1 it is apparent that water production exceeds significantly the stoichiometric ratio (1:1). This is evidence that the catalyst surface withholds some reaction intermediates not containing oxygen. The significantly higher initial production rate (slope of transient response) of water in comparison with methane shows that carbon monoxide splits on the catalyst surface and is hydrogenated to water much faster than its rate of hydrogenation to methane. After the switch to pure hydrogen at about 180 s, methane and water were immediately produced at a significantly higher rate of methane production. It is obvious that switching between CO-rich and CO-lean feeds creates a very fast time-average rate of hydrogenation of surface carbonaceous deposits.

The effect of reactor temperature on the transient response after the switch of feed composition from pure hydrogen to the mixture of CO/H_2 (5/

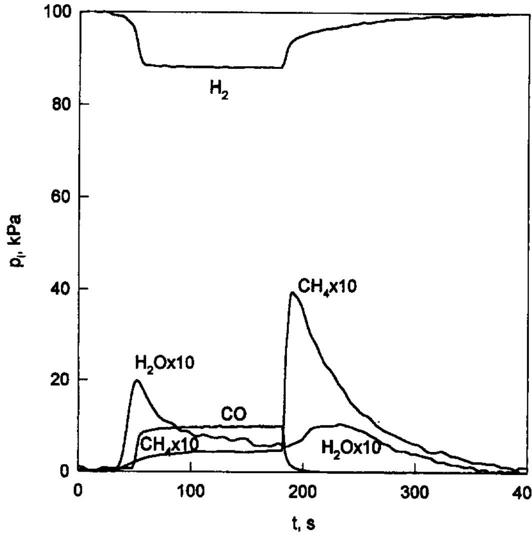

Fig. 1. Transient system response to the double step change of feed composition $H_2 \rightarrow CO/H_2 \rightarrow H_2$. $T = 458$ K.

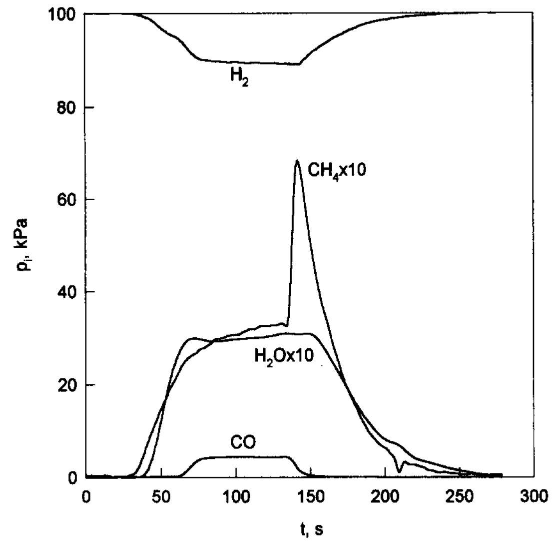

Fig. 2. Transient system response to the double step change of feed composition $H_2 \rightarrow CO/H_2 \rightarrow H_2$. $T = 498$ K.

95 mol-%) and back to pure hydrogen is illustrated in Fig. 2. The reaction temperature was increased to 498 K in this experiment. Under these experimental conditions, methane and water were produced at comparable rates after the first switch (at about 25 s). It is speculated that rates of methane and water formation are probably controlled by the same process, i.e., the C–O bond splitting. Immediately after the backward switch (at about 135 s) to pure hydrogen, a monotonic decrease in the water production was observed while the formation of methane passed through a pronounced maximum.

It has been found in our other work (Klusáček and Stuchlý [22]) that after the purging of the reactor by argon (1 minute) before the switch from the CO/H_2 mixture back to hydrogen, the methane production rate was markedly higher than if no purge was applied. The observed increase of the methanation rate after removal of CO from the gaseous phase is caused very likely by the poor ability of hydrogen to compete with CO for active surface sites.

The amount of methane evolved after the switch to pure hydrogen with preceding short purge by argon are shown in Table 1 for temperature range between 458 and 545 K. The adsorption (monolayer) capacity of catalyst has been determined (Klusáček and Stuchlý [22]) as 109 μmol/g. The evolved amount of methane of about 2000 μmol/g indicates the massive multilayer deposition of carbonaceous species during the contact of catalyst with the reaction mixture containing CO in high concentration. When the reactor is purged by argon and the feed is successively switched to pure hydrogen, the multilayer deposits are hydrogenated to methane and water. The surface storage of carbonaceous intermediates is quickly depleted and the production rates of methane and water decline. A switch back to the CO-rich feed composition must follow to restore the high production rate of the catalytic system.

Experiments using step-changes of feed composition $H_2 \rightarrow CO/H_2 \rightarrow H_2$ furnished information on the unsteady-state behavior of CO methanation important for understanding the system behavior under forced feed concentration cycling when reactor feed is periodically switched between CO-rich and CO-lean mixtures.

3.2. *Forced feed concentration cycling*

The record of outlet reactor concentrations for periodic cycling of feed composition is shown in Fig. 3. Cycle period was 20 s and feed was switched between pure hydrogen and mixture CO/H_2 (10/90 mol-%). Cycle split was 0.5, i.e., the composition of feed was changed after each 10 s. The reactor was maintained at temperature 478 K, the space velocity was 200 min^{-1}. Fig. 3 shows the unsteady behavior of catalytic system after achievement of a cycle-invariant pattern, i.e. when consecutive cycles were identical. Typically about 20 cycles were needed to fulfil this criterion.

Immediately after a change of feed to pure hydrogen (time = 5 s in Fig. 3), the rate of methane formation quickly increased and attained a maximum value after about another 5 s. The pro-

Table 1
Temperature dependence of evolved amounts of methane after switch from CO/H_2 (10/90 mol-%) to pure hydrogen

Temperature, K	458	478	498	525	545
Amount of methane, μmol/g	2123	2050	2119	1720	1504

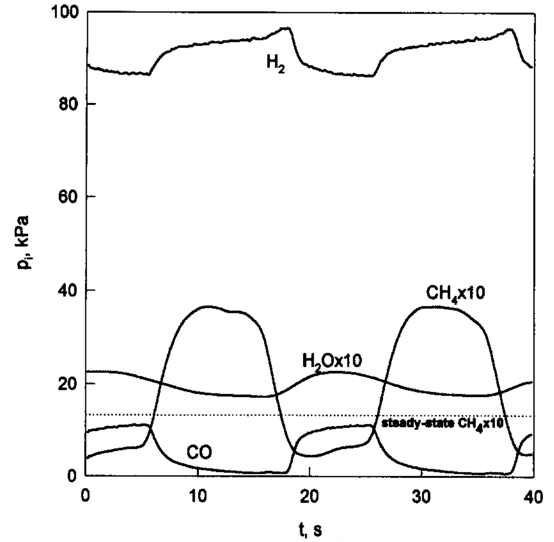

Fig. 3. Outlet reactor concentrations for cycling of feed between pure hydrogen and the CO/H_2 mixture. Cycle period 20 s, cycle split 0.5, $T=478$ K.

duction rate of methane began to decline due to the decrease of concentration of carbonaceous compounds stored on the catalyst surface. There is almost no carbon monoxide in the gas phase and catalyst surface is 'cleaned' by hydrogen. At 15 s, the feed was switched to the mixture of CO and hydrogen. The surface of catalyst is quickly covered by carbon deposits which inhibit the hydrogenation of carbon deposits through blocking the surface to hydrogen. Hydrogen is not able to compete for free centres with carbon monoxide, i.e. to remove (hydrogenate) CO by a substitution mechanism. This results in a fast decrease in the methane production rate. The delay of carbon monoxide is caused by fast and massive deposition of CO on the surface cleaned by hydrogen in the first part of the cycle. Almost all CO is stored on the surface and concentration of carbon monoxide at the reactor outlet is thus very low. The increase of water formation during the CO-rich half cycle corresponds to similar observations during step experiments showing that carbon monoxide splits and is quickly hydrogenated to water even when conditions for hydrogenation of non-oxygenated carbon deposits to methane are not favourable.

Steady-state production rate of methane is shown as line 5 in Fig. 3. From a comparison of areas below the steady-state line and unsteady-state methane profile, it is evident that periodic cycling of feed composition results in a significant enhancement of the methane production rate.

The important parameter of cycling is the cycle period, which strongly influences the system dynamics and consequently the results of cycling. The effect of cycle period on the performance of catalytic methanation rate is shown in Fig. 4. The reactor temperature was retained at 478 K, the space velocity was 120 s^{-1}, the time-average pressure of CO was 3.7 kPa and cycle split was 0.5 in all experiments. The time-average rate of methanation was always higher than the corresponding steady-state value for the same time-average feed composition. The highest improvement was achieved for periods about 40 s. For very short periods, the catalyst surface dynamics cannot follow the fast switching of reactor input and the system behaves as in the steady state with output concentrations equal to the steady-state ones. Under these conditions, mixing effects also play an important role and the input concentration wave is smoothed. The improvement of the methanation rate is also attained for long cycle periods. This indicates a relatively slow methanation rate and supports the idea of high storage of carbonaceous deposits on the catalyst surface.

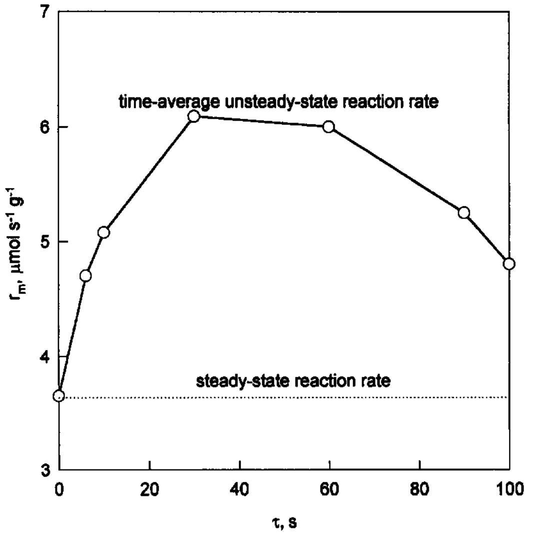

Fig. 4. Time-average methanation rate for different cycle periods τ. $T=478$ K.

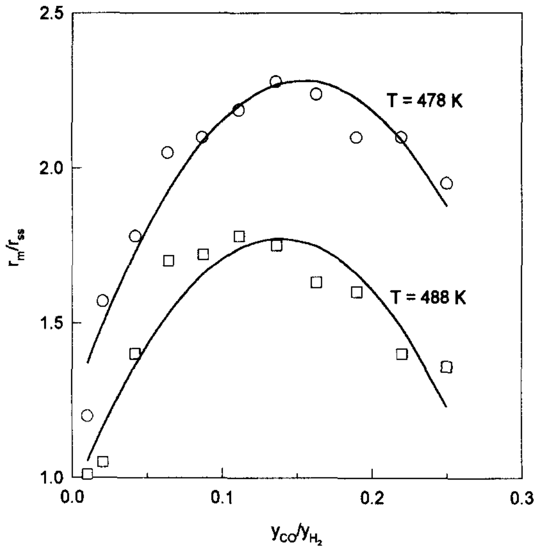

Fig. 5. The ratio of time-average methanation rate, r_m, and steady state value, r_{ss}, for different mean inlet reactor composition. Cycle period 30 s, cycle split 0.5.

For evaluation of the general enhancement of reaction rate by forced cycling, a comparison of the time-average rate with the steady state counterpart has to be made over a broad interval of feed compositions. The cycling may lead to higher average rates for some compositions but it can still produce worse results for others. The influence of the mean inlet molar ratio of carbon monoxide to hydrogen on the time-average methanation rate is shown in Fig. 5. The ratio of time-average rate r_m and corresponding steady-state value r_{ss} is always higher than one. This means that forced cycling led to higher methanation rates for any composition of reaction mixture. The rate enhancement was more pronounced at lower reaction temperature when the time-average rate under cycled feed conditions exceeded the steady-state value more than two-fold. Maxima of time-average reaction rates were achieved for the same mean composition of reactor feed as maxima for steady-state operation. It also indicates that unsteady-state and steady-state methanation of CO are controlled by the same process–surface reaction.

4. Conclusion

It has been experimentally verified that forced cycling of reactor feed composition increases the reaction rate of CO methanation on the Ni/SiO_2 catalyst. Time-average reaction rate under cycled conditions was higher than steady-state value for any composition of reaction mixture including the composition leading to highest steady-state methanation rate. It has been found that the basic prerequisite of the rate enhancement is the storage of carbonaceous reaction intermediates. Those species are deposited on the catalyst surface in the amount exceeding by several-fold the monolayer adsorption capacity of catalyst. Carbonaceous deposits can be formed only under the presence of CO in the gas phase. On the other hand, they can be hydrogenated only if CO is missing in the gas phase —otherwise CO blocks all sites needed for adsorption of hydrogen. These contradictory requirements can be achieved only under unsteady-state reaction conditions, for instance under periodic cycling between CO-rich and CO-lean reaction mixtures.

The presented contribution provides the explanation of experimentally observed enhancement of methanation rate under periodic cycling. This explanation is based on analysis of dynamic experiments when simple step-changes of feed composition were employed.

Acknowledgements

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References

[1] J.L. Feimer, A.K. Jain, R.R. Hudgins and P.L. Silveston, Chem. Eng. Sci., 37 (1982) 1797.
[2] J. Thulie, L. Chiao and R.G. Rinker, Chem. Eng. Commun., 48 (1986) 191.
[3] D.T. Lynch, Chem. Eng. Sci., 39 (1984) 1325.
[4] P.J. Nowobilski and C.G. Takoudis, Chem. Eng. Commun., 40 (1986) 249.
[5] K. Klusáček, P.L. Silveston and R.R. Hudgins, Coll. Czech. Chem. Commun., 49 (1987) 273.
[6] M.B. Cutlip, AIChE J., 25 (1979) 502.

[7] J. Koubek, J. Pašek and V. Růžička, in T. Seiyama and K. Tanabe (Editors), Proc. 7th Int. Congr. Catal., Tokyo, (Stud. Surf. Sci. Catal., Vol. 7B), 1980, p. 853.
[8] A.K. Jain, R.R. Hudgins and P.L. Silveston, Can. J. Chem. Eng., 61 (1983) 824.
[9] L. Chiao, F.K. Zack, J. Thullie and R.G. Rinker, Chem. Eng. Commun., 49 (1987) 273.
[10] P.L. Silveston, Sadhana, 10 (1987) 217.
[11] Abdul-Kareem, P.L. Silveston and R.R. Hudgins, Chem. Eng. Sci., 35 (1980) 2077.
[12] Y. Barshad and E. Gulari, AIChE J., 31 (1985) 649.
[13] D.H. Wilson and R.G. Rinker, Chem. Eng. Sci., 37 (1982) 343.
[14] A.K. Jain, R.R. Hudgins and P.L. Silveston, ACS Symp. Ser., 196 (1982) 97.
[15] A.K. Jain, R.R. Hudgins and P.L. Silveston, Can. J. Chem. Eng., 60 (1982) 809.
[16] A.K. Jain, R.R. Hudgins and P.L. Silveston, Can. J. Chem. Eng., 63 (1985) 166.
[17] G. Rambeau and H. Amariglio, Appl. Catal., 1 (1981) 291.
[18] G. Rambeau and H. Amariglio, Appl. Catal., 3 (1982) 273.
[19] M.P. Unni, R.R. Hudgins and P.L. Silveston, Can. J. Chem. Eng., 31 (1973) 623.
[20] J.P. Briggs, R.R. Hudgins and P.L. Silveston, Chem. Eng. Sci., 32 (1977) 1087.
[21] M. Dettmer and A. Renken, Ger. Chem. Eng., 6 (1983) 356.
[22] V. Stuchlý and K. Klusáček, J. Catal., 139 (1993) 62.