In situ perpetual regeneration of a Ni–faujasite methanation catalyst

N.I. Jaeger, G. Schulz-Ekloff and Jiri Kapicka [1]

Institut für Angewandte und Physikalische Chemie, Universität Bremen, D-2800 Bremen 33, Germany
[1] The J. Heyrovsky Institute of Physical Chemistry and Electrochemistry,
18223 Prague 8, Czechoslovakia

Received 28 November 1991; accepted 11 May 1992

A prolonged lifetime of a Ni–faujasite methanation catalyst and a stable rate of methanation can be achieved by operating the fluidized catalyst bed under unsteady state conditions. A higher rate of methanation is accompanied by a shift in selectivity compared to a steady state operation due to an enhanced disproportionation of CO.

Keywords: Unsteady state catalysis; methanation; Ni–faujasite catalyst

1. Introduction

The methanation of nearly stoichiometric syngas is studied with respect to the production of synthetic natural gas from coal [1] or the transport of heat via gases with high chemical energy content [2]. The methanation at the temperatures that are necessary for the generation of electric power via live steam, i.e. > 700°C, results in relatively rapid catalyst deactivation by coke deposition for thermodynamic and kinetic reasons [3,4]. The extent of coking can be reduced drastically by employing a relatively slight stoichiometric excess of hydrogen because of the favorable thermodynamics [4].

In the following, the activities and selectivities of a nickel faujasite catalyst are studied using fluidized-bed reactors with H_2 and CO fed either in a premixed form or separately. The latter design provides local gradients of the H_2/CO ratio or temporal fluctuations in the degree of coking of the catalyst pellet, respectively, and could influence the global activity and selectivity of the catalyst bed.

Nickel-loaded faujasites are used as model catalysts, since the strong acidic sites of the zeolite support favour coke deposition in the methanation reaction and, thus, enable the study of the coking at relatively low temperatures [5,6].

2. Experimental

2.1. PREPARATION AND CHARACTERIZATION OF THE CATALYST

The sodium faujasite X (Si/Al = 1.2; average crystal size 7 μm) was prepared by hydrothermal crystallization [7]. The nickel-loaded catalyst was obtained by ion-exchange (degree of exchange 19.9% corresponding to 3.9 wt% Ni) in an aqueous solution of nickel acetate (0.018 M) performed at room temperature for 8 h. After filtration, the catalyst was washed with water and dried at 80°C. The crystallinity of the samples is controlled by X-ray diffraction and N_2 physisorption.

The nickel-loaded catalyst was dehydrated in situ under an Ar stream by temperature-programmed heating (3 K min^{-1}) to 693 K and was maintained at this temperature for 16 h. Then the catalyst was reduced in situ by the CO/H_2 reaction mixture at 623 K for 16 h in the first run of the reaction. After the regeneration of the catalyst and its reduction by hydrogen at 623 K, nickel crystallite sizes were determined by TEM (Philips EM 420) and found to have a broad range of dispersion (from 20 Å to 100 Å in diameter) and to be located both inside and outside the zeolite crystals.

The regeneration of the catalyst, i.e. the removal of coke, was carried out by temperature-programmed hydrogenation (TPH) and temperature-programmed oxidation (TPO) up to 723 K. The products of coke gasification (CH_4, CO_2) were determined by IR absorption analysis.

The platinum-loaded catalyst, which was used as an activating phase for hydrogen spillover, was prepared by platinum tetra-ammine ion exchange (degree of exchange 10.5% corresponding to 6.2 wt% Pt), subsequent calcination in air and final reduction by H_2. The catalyst contained mostly Pt crystallites of 1–2 nm in diameter.

2.2. APPARATUS

The comparative study of the CO hydrogenation was carried out in two versions of a continuous flow differential glass reactor with a fluidized bed. In one of the glass reactors (I) the fluidized catalyst bed was fed with the pre-mixed reaction components. The other glass reactor (II) was designed to allow separate feeding of the fluidized catalyst bed with hydrogen and CO (fig. 1). A fluidized bed in the reactors was established by means of an external vibrator. The experiments were carried out in the temperature region from 573 to 673 K at atmospheric pressure. The GHSV ranged from 8000 to 10000 h^{-1}. The H_2/CO ratio was 7/3. The catalyst bed consisted of 0.2 g of nickel-loaded faujasite X. The catalyst had been pressed, then crushed and sieved for a particle size of 0.28–0.45 mm.

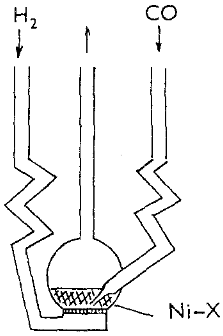

Fig. 1. Glass reactor II with separate inlets for hydrogen and CO.

The conversion was always kept to a value below 3%. The composition of the reaction mixture was controlled by the flow rates of both CO and H_2. Traces of carbonyls from the CO tank were decomposed in a glass preheater (kept at 673 K) positioned in front of the reactor. The composition of the outlet mixture was analyzed continuously by IR absorption analyzers for CH_4 and CO_2 (URAS) or discontinuously by GC using a capillary column for higher hydrocarbons. All changes in the operating conditions were carried out under streaming argon.

3. Results

The curves in fig. 2 illustrate the time on-stream dependence of the rate of methane formation $R(CH_4)$ for the two reactor types described above, which contained the catalyst prereduced by H_2. In both cases, the reaction started immediately after feeding the reaction mixture into the reactors. In the case of

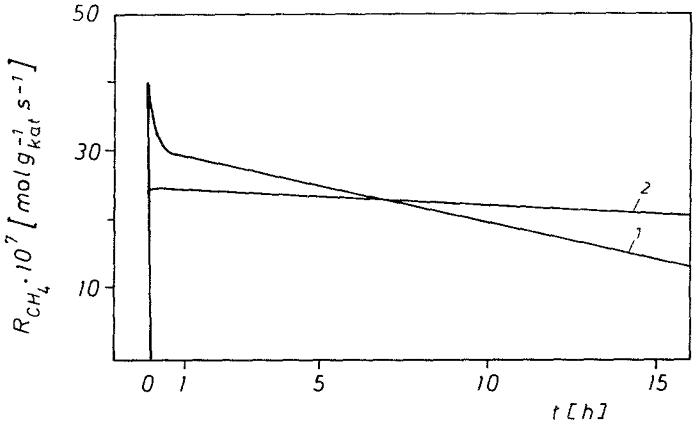

Fig. 2. Time dependence of $R(CH_4)$. $T = 623$ K, GHSV = 8000 h^{-1} (STP), mass of catalyst 0.2 g, $H_2/CO = 7/3$. (1) Glass reactor (type I) with one inlet of premixed CO and H_2, (2) glass reactor (type II) with separate inlets of CO and H_2.

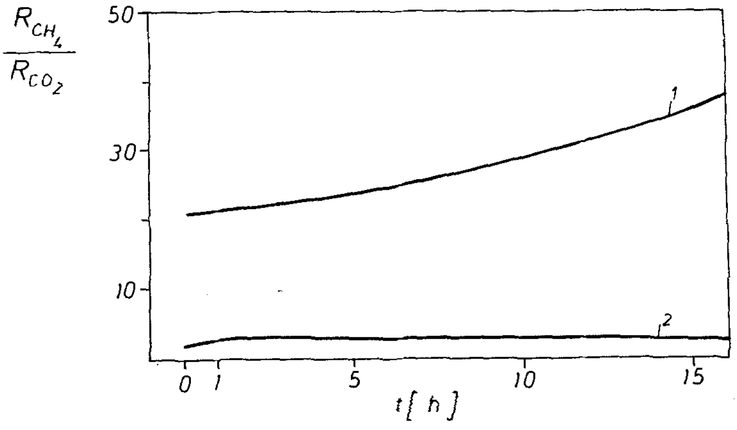

Fig. 3. Time dependence of the selectivity ($R(CH_4)/R(CO_2)$). $T = 623$ K, $H_2/CO = 7/3$, GHSV = 8000–10000 h^{-1}. (1) Glass reactor I, (2) glass reactor II.

type I glass reactor with one inlet for the premixed reaction mixture, the rate of methane formation exhibited an overshoot (fig. 2, curve 1) followed by a rapid decrease during the following 30 min. After 16 h on-stream the rate of the methane formation decreased to about 35% of the maximum value as a result of coke formation [8].

In the glass reactor with separate feed of CO and H_2 (type II) the time dependence of the reaction rate was smooth and exhibited no overshoot (fig. 2, curve 2). Although the initial stationary value of the reaction rate in glass reactor II was about 35% lower than the maximum value for glass reactor I, the final value of the reaction rate after 16 h on-stream in glass reactor II was about 30% higher than that in glass reactor I, and was still at 84% of its starting value. Thus, in the reactor with the separate feed of CO and hydrogen, the rate of the deactivation was five times slower than in the reactor which was fed with the premixed reaction components. Under the reaction conditions used, the GC analysis revealed that practically the only hydrocarbon product of the CO hydrogenation was methane. In a side reaction CO_2 is formed from the disproportionation of CO.

In fig. 3 the selectivity of CO hydrogenation expressed by the ratio of the rates of CH_4 and CO_2 formation is depicted for the two reactors. The $R(CH_4)/R(CO_2)$ ratio changed significantly in dependence on the reactor type. Since the reaction was operated in the kinetic regime with respect to the CH_4 formation the methane concentration could be changed in dependence on the flow rate F at a constant rate of the methane formation ($R(CH_4) = C(CH_4)F$). The selectivity in the different reactors could then be compared at the same average concentration of methane (approximately 2%) which was adjusted by changing the flow rate. The time dependences of the reaction rate were, however, qualitatively different as shown in fig. 2.

In glass reactor I, the selectivity exhibits a monotonous increase (fig. 3, curve 1). The much lower selectivity in glass reactor II (curve 2) results from the much higher rate of CO disproportionation $R(CH_2)$, which was found to be eight times higher after one and 13 times higher after 16 hours on-stream, compared to glass reactor I.

The experiments were reproduced repeatedly with a standard variation of $\pm 10\%$. The different character of the time dependence of the reaction rate for the two types of reactor remained unchanged.

4. Discussion

The comparative study of the methanation reaction over a NiX catalyst was carried out under differential reaction conditions. In both reactor types, the conversion reached a maximum value of $\approx 3\%$ and the operating conditions guaranteed that the observed differences in the activity and selectivity can be attributed to the reaction kinetics and not to effects of heat and mass transfer limitations. Further, it follows from the thermodynamic data [9] that, under the reaction conditions used, the reaction proceeded far from equilibrium.

The CO hydrogenation was started on the active metal surface of the prereduced catalyst. On the active surface the dissociation of both CO and H_2 proceeds as the first step in the methanation reaction. At a reaction temperature of 350°C and for the ratio of $H_2/CO = 3/1$, the rate of the formation of adsorbed carbon is larger than that of the carbon hydrogenation [10], leading to the accumulation of adsorbed carbon followed by its transformation to more stable forms [11]. This process can be expected to be even more dominant in the presence of the CO-rich gas mixture ($H_2/CO = 7/3$) used in the experiments.

The surface carbon has a strong influence on the decrease in the rate of both the chemisorption and the dissociation of CO and hydrogen due to geometric and electronic effects [12]. The dissociative adsorption of CO is directly related to the number of pairs of unoccupied four-fold sites [13]. Therefore, after starting the reaction, the initial rate of methane formation drops rapidly in glass reactor I. The subsequent course of the CO hydrogenation is accompanied by a steady state rate of carbon deposition [14], causing slow deactivation.

In glass reactor II the reaction components hydrogen and CO were mixed directly in the catalyst bed. Although the mixing of the catalyst and of the gas phase was very intense, local differences in the reaction mixture composition can be expected, i.e. some portion of the catalyst pellets can be exposed either to an excess of hydrogen near the bottom of the reactor or to an excess of CO at the entrance of the CO feeding tube. The sequence of reaction steps proceeding on an individual catalyst pellet can then be described as follows: CO hydrogenation accompanied by carbon deposition proceeds in the CO-rich zone. The residence time of a catalyst pellet for the fluidized bed in this zone is short so that the carbon formed on the catalyst surface could not be transformed to stable forms. The pellet is subsequently exposed to the H_2-rich zone at the bottom of the reactor, where regeneration of the pellet by the hydrogenation of the adsorbed carbon can be expected leading again to a high activity for CO and hydrogen chemisorption. This mechanism provides for a periodic deactivation and regeneration of individual pellets, and curve 2 in fig. 2 represents the average reaction rate over both the deactivated and the activated pellets. The initial rapid decrease in the rate of CH_4 formation is missing in this case. Direct evidence for the effect of the separate feed by characterizing the deposited carbon could not be obtained in our experiments. While the total amount of carbon deposits on the metal surface and within the zeolite could be determined by temperature-programmed hydrogenation and oxidation [8], it was not possible to distinguish various forms of carbon contributing to the observed spectra.

Activity and selectivity of a catalyst can be influenced by operating the reaction under consideration under unsteady state conditions.

This can be achieved by external composition forcing [15], i.e. by periodical switching of the feed composition at the inlet of the reactor. Reactor II is also operated under unsteady state conditions, which, in this case, are achieved by establishing reactor zones with different compositions of the gas phase. Separate catalyst pellets of the fluidized bed are periodically exposed to different feed compositions leading to a continuous in situ regeneration of the catalyst and hence to the observed prolongation of the lifetime.

Carbon dioxide could be formed either by the disproportionation of CO (Boudouard reaction) above 623 K [16] or by the water gas shift reaction [9]. The activation energy of the former reaction and the turnover number for the formation of atomic carbon on Ni at coverages less than a monolayer were found to be comparable to the methanation of CO [17]. The rate of this reaction depends on the CO partial pressure and on the availability of four-fold sites on the metal surface [13]. Therefore, the reaction rate should decrease with time on-stream due to the deactivation of the nickel surface.

Due to the low conversions, the concentration of water was low and the contribution of the water gas shift reaction to the CO_2 formation can be neglected, especially, since the nickel is not a very efficient catalyst. It can be summarized that the relatively high rates of methane formation and CO disproportionation observed for reactor II can both be explained by internal composition gradients due to separate feeding of the reaction components and periodic exposition of the catalyst pellets in CO-rich deactivating as well as H_2-rich regenerating zones of the fluidized bed reactor.

Acknowledgement

Financial support from the DFG (AZ 436 CSR-113-11-0) is gratefully acknowledged.

References

[1] F.W. Moeller, H. Roberts and B. Brite, Hydrocarbon Processing 53 (1974) 69.
[2] H. Hanus, B. Hoehlein and A. Skov, Chem. Ing. Techn. 52 (1980) 504.
[3] G.Gruber, in: *Methanation of Synthesis Gas*, Advances in Chemistry Series, Vol. 146, ed. L. Seglin (Am. Chem. Soc., Washington, 1975) p. 31.
[4] D. Danziger, D. Popovic, G. Schulz-Ekloff and E. Wendland, Chem. Ing. Techn. 58 (1986) 46.
[5] D.J. Elliot and J.H. Lunsford, J. Catal. 57 (1979) 11.
[6] H. Schrübbers, G. Schulz-Ekloff and G. Wildeboer, in: *Metal Microstructures in Zeolites*, Stud. Surf. Sci. Catal., Vol. 12, eds. P.A. Jacobs, N.I. Jaeger, P. Jiru and G. Schulz-Ekloff (Elsevier, Amsterdam, 1982) p. 261.
[7] H. Kacirek and H. Lechert, J. Phys. Chem. 79 (1975) 1589.
[8] J. Kapicka, N.I. Jaeger and G. Schulz-Ekloff, Appl. Catal. (1992), in press.
[9] G.A. Mills and F.W. Steffgen, Catal. Rev. 8 (1973) 159.
[10] C.H. Bartholomew, Catal. Rev. Sci. Eng. 24 (1982) 67.
[11] J.G. McCarthy and H. Wise, J. Catal. 57 (1979) 406.
[12] C.H. Bartholomew, in: *Catalyst Deactivation*, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1987) p. 81.
[13] J. Oudar, in: *Chemical Industries*, Vol. 20, eds. J. Oudar and H. Wise (Dekker, New York, 1985) p. 81.
[14] D.C. Gardner, C.H. Bartholomew, Ind. Eng. Chem. Prod. Res. Dev. 20 (1981) 80.
[15] P.L. Silveston and R.R. Hudgins, Chem. Eng. Sci. 41 (1986) 923.
[16] R.T.K. Baker and P.S. Harris, in: *Chemistry and Physics of Carbon*, Vol. 14, ed. P.L. Walker Jr. (Dekker, New York, 1979) p. 83.
[17] D.W. Goodmann, R.D. Kelley, T.E. Madey and J.M White, J. Catal. 64 (1980) 479.