Substitute Natural Gas. Methanation Revisited

Jens R. Rostrup -Nielsen and Jens Sehested
Haldor Topsøe A/S, Dk-2800 Kgs Lyngby, Denmark
jrn@topsoe.dk

Introduction

Manufacture of Substitute Natural Gas (SNG) was studied during the energy crisis in the 1970'ties, but few plants were built. Today SNG is becoming important to ensure stable energy supply. High temperature methanation is advantageous[1]. The catalytic challenges are outlined.

The methanation heat is high and amounts to 20% of the heating value of the syngas ($H_2/CO = 3$). Consequently, the heat recovery is a key element of an industrial process. In thermodynamic terms, this means to maximize the exergy, in practice to recover the reaction heat at high temperature as superheated steam.

The key to solve the problem of a high temperature rise is a catalyst capable of working at a low temperature ($250\text{-}300^{\circ}C$) after having been exposed to the high temperatures ($600\text{-}700^{\circ}C$) as illustrated in Fig. 1 [2].

The operation of high temperature methanation involves catalyst sintering at high temperatures and exposure to high partial pressures of carbon monoxides at low temperatures.

High CO partial pressure

High partial pressure of carbon monoxide leads to low temperature phenomena [3,4] that need to be eliminated in industrial operation.
The formation of nickel carbonyl is favoured by low temperature and CO-partial pressure to the forth power .
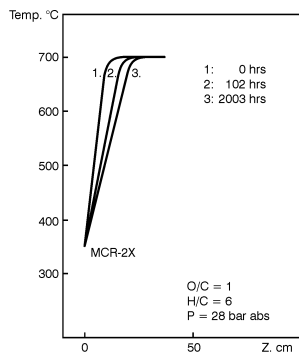

Fig. 1. TREMP-process. Temperature profiles in first methanation reactor [2].

The formation of nickel carbonyl leads to excessive growth of the nickel crystals and deposition of a nickel mirror at high temperatures as a result of decomposition of the carbonyl [3]. This mirror may also be an indication of formation of nickel carbonyl in the equipment prior to (up -stream) the methanation reactor. In practice, carbonyl formation is not a problem above $300^{\circ}C$.

The hydrogenation of the adsorbed carbon species into methane may be accompanied by a slow formation of less reactive hydrocarbon chains similar to the Fischer-Tropsch synthesis. This may lead to a blockage of the active nickel surface resulting in a movement of the temperature profile in the reactor [3,4]. It was observed that the catalyst could be regenerated in hydrogen.

This phenomenon (ß-deactivation) corresponds to the formation of ß-carbon observed by Wise et al. [5]. In practice, the ß-deactivation is counteracted by the selection of operating parameters (CO-partial pressure, inlet temperature, sulphur removal etc).

High Temperature Phenomena

DFT -calculations and in -situ studies in electron microscope (HREM) [6] showed that step-sites are favoured for the nucleation of carbon. The principle of equilibrated gas shows an upper carbon limit temperature, above which there is a thermodynamic potential for carbon depending on the size of the nickel crystals (i.e. the diameter of the carbon fibre) [3].

Control of the sintering is critical for high temperature methanation. It requires a stable support and means to interfere with the growth of the nickel crystals. Recent studies using in -situ high resolution electron microscopy (HREM) [7] has given new insight to the understanding of sintering of nickel catalysts. Analysis of spent catalyst from pilot plants indicates that sintering proceeds via the atom migration sintering mechanism [8]. The sintering studies indicated that the methanation reaction is structure sensitive [8] and that step sites may play an important role [9] in contrast to earlier conclusions by Goodman et al.[10].

Process Development

Sintering of methanation catalyst may be reduced by advancements within catalyst technology. The developments at Topsøe have led to a catalyst showing a high degree of stability. This formed the basis for a high temperature methanation process (TREMP®) [1,2], which was studied extensively in the ADAM/EVA project around 1980 [3,11]. The high temperatures for methantion may also be used in pre -conversion to improve the efficiency of coal gas based fuel cells and for energy transport systems.

References

1. Udengaard, N.R., Olsen, A., Wix-Nielsen, C. Pittsburgh Coal Conf. 2006
2. Harms, H., Höhlein, B., Skov, A. *Chem.Ing. Tech.* 52 (1980) 504.
3. Rostrup-Nielsen, J.R., Pedersen, K. and Skov, A. *ACS Preprints*, Fuel Chem. Div. 25 (2) (1980) 89.
4. Gierlich, H.H., Fremmery, M., Skov, A., Rostrup-Nielsen, J.R. *Stud.Surf.Sci.Catal.*
6. 59 (1980)
5. McCarty, J.G., Wise, H., *J. Catal.* 57, 406 (1979).
6. Rostrup-Nielsen, J.R., Nørskov, J.K., and Sehested, J. *Adv.Catal.* 47, 65 (2002)
7. Sehested, J., *Catal.Today* 111, 103 (2006).
8. Anderson, M.P., Blidgaard, T., Kustov, A., Larsen, K.E., Greeley, J., Johannessen, T., Christensen, C.H., and Nørskov, J.K. *J.Catal.* 239, 501 (2006)
9. Rostrup-Nielsen, J.R., Pedersen, K., Sehested, J. *Appl.Catal.* (submitted)
10. Kelley, R.D.,Goodman, D.W. in "Chemical Physics of Solid Surface and Heterogeneous Catalysis (D.A. King, D.P. Woodruff eds). Vol. 4, chapt. 10, p. 427, Elsevier, Amsterdam, 1982.
11. Harms, H., Höhlein, B., Jørn, E., Skov, A. *Oil Gas J.* 78 (15) 120 (1980).