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Catalysis Today 63 (2000) 159–164

CATALYSIS TODAY

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New aspects of syngas production and use

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Abstract

The syngas based routes are efficient, but still expensive. The presentation summarizes the state of art and analyzes the constraints of the technology, and the role of the catalyst. Recent studies have led to a better understanding of the mechanism. The coverage of carbidic carbon which is the precursor for forming whisker carbon is determined by the methane dissociation as well as the availability of surface oxygen. There is evidence that both reactions can be influenced by the composition of the catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Syngas; Steam reforming; Methane activation; Promoter

1. Trends in syngas application

The conversion of hydrocarbons to hydrogen and syngas will play an important role in the 21st century ranging from large gas to liquid plants and hydrogen plants for refineries to small units providing hydrogen for fuel cells.

The conversion of fossil fuels to transportation fuels aims at hydrocarbon mixtures with an overall H/C close to two [1]. This requires the addition of hydrogen to heavy crude by hydrotreating and hydrocracking with the additional scope also to remove sulphur, nitrogen, and metals. A big fraction of the hydrogen need has been supplied from catalytic reforming units, but it may be available to a smaller extent because of the constraints on the content of aromatics in diesel and gasoline. As a result, there is an increasing *need for hydrogen plants* capable of operating on a variety of hydrocarbon streams such as off gases, naphtha and natural gas. The use of a prereformer [2] ensures maximum flexibility.

Another trend is the *conversion of natural gas* into transportation fuels [3] such as methanol, DME, synthetic gasoline, and diesel. The direct conversion routes can hardly compete because of the high selectivity of syngas based routes [4,5]. The syngas routes are highly efficient, but capital intensive because they involve a big exchange of energy through the steam reformer and heat recovery units [5] as illustrated in Fig. 1.

The required properties of the syngas vary with the synthesis in question [3,6]. In the synthesis of MeOH, DME and in the High Temperature Fischer–Tropsch synthesis, CO_2 and CO are both reactants linked by the CO-shift reaction. This means that the syngas ideally has the same stoichiometry as the final product. This is expressed by the module $M = (H_2 - CO_2)/(CO + CO_2) = 2$.

In contrast, the shift reaction is not active in the Low Temperature Fischer–Tropsch synthesis for wax and diesel and CO_2 remains inert. This results in different requirements for the syngas composition [3,6]. The desirable composition is best characterised by $H_2/CO =$ ca. 2.

The *choice of technology* for manufacture of syngas depends on the scale of operation as illustrated in Fig. 2. For methanol, tubular reforming would be cheapest at capacity below 1000–1500 MTPD, whereas the autothermal reforming (ATR) is favoured at capacities about 6.000 MTPD. This is caused by

PII: S0920-5861(00)00455-7

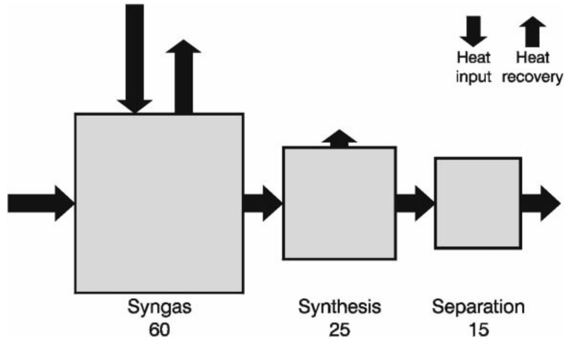


Fig. 1. Indirect conversion of natural gas (numbers indicate the relative investments).

Table 1
Syngas reactions

	$-\Delta H^0_{298}$ (kJ/mol)
Steam reforming	
$CH_4 + H_2O = CO + 3H_2$	−206
$C_nH_m + nH_2O = nCO + (n + \frac{1}{2}m)H_2$	−1175[a]
$CO + H_2 = CO_2 + H_2$	41
CO_2 reforming	
$CH_4 + CO_2 = CO + 2H_2$	−247
ATR	
$CH_4 + 1\frac{1}{2}O_2 = CO + 2H_2O$	520
$H_2O + CH_4 = CO + 3H_2$	−206
$CO + H_2O = CO + H_2$	41
CPO	
$CH_4 + \frac{1}{2}O_2 = CO + 2H_2$	38

[a] For nC_7H_{16}.

the economy of scale being different for the tubular reformer and the oxygen plant [3]. For the intermediate range representing the capacity of world scale methanol plants, a combination of tubular reforming and a secondary oxygen blown reformer is normally the optimum [6].

It may be argued that CO_2-*reforming* would be better than steam reforming to meet the required gas compositions (Table 1). However, CO_2-reforming (or "stoichiometric reforming") is rarely feasible [3,7]. At the economic pressure of the syngas plant (20–40 bar), stoichiometric reforming will result in non-complete conversion of methane due to thermodynamics and further the process economy depends strongly on the pressure and cost of the CO_2 available. However, the combined steam and CO_2 reforming may result in the right stoichiometry for MeOH synthesis.

$$\frac{3}{4}CH_4 + \frac{1}{4}CO_2 + \frac{1}{2}H_2O = CH_3OH \tag{1}$$

This may be feasible with natural gas containing CO_2 and with cheap CO_2 available. Reaction (1) forms the basis for a recent 3000 MTPD MeOH project.

For *large scale Fischer–Tropsch* units, ATR appears to be the cheapest solution fulfilling the requirements to a gas with H_2/CO close to two [6].

Catalytic partial oxidation (CPO) may represent the ideal solution. This "dream reaction" (Table 1) has

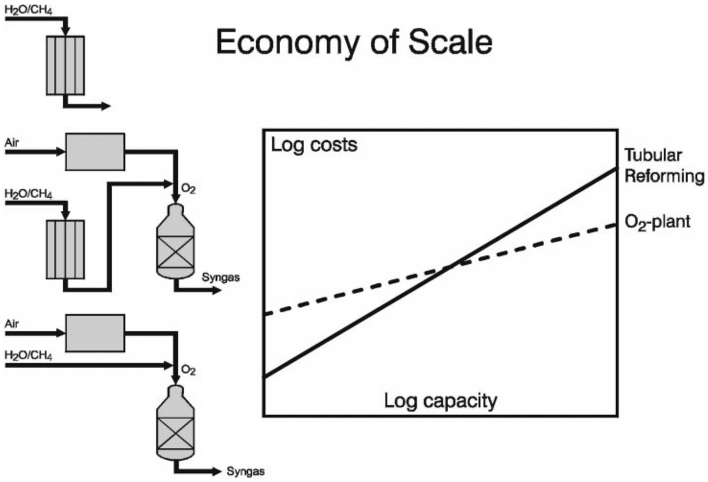


Fig. 2. Impact of scale of operation.

Table 2
ATR-selectivity for $CO + H_2$[a]

Product gas	vol.%
H_2	56.8
N_2	0.2
CO	29.0
CO_2	2.9
CH_4	1.0
H_2	10.1
	100

[a] Data from pilot test [8]: $H_2O/C = 0.21$, $O_2/C = 0.59$, $P = 24.5\,\text{bar}$, $T_{\text{exit}} = 1057°\text{C}$. CH_4 conversion = 96.9%, selectivity to CO = 90.8%. Equilibrium temperatures : reforming = 1063°C, shift = 1076°C.

the right $H_2/CO = 2$ and a very low heat of reaction comparable to that of the CO-shift reaction. In fact, the ATR has a high selectivity for the CPO-reaction as illustrated in Table 2 and hence CPO does hardly offer an economic advantage.

Up to 40% of the costs of a syngas plant based on ATR (CPO or POX) is related to the oxygen plant [6]. As a result, *routes based on air* eliminating the cryogenic air separation plant have been suggested.

The use of air in the process stream is possible only in once-through synthesis schemes to avoid a huge accumulation of nitrogen (the syngas will contain about 50 vol.% N_2). Attempts to use air instead of oxygen result in big gas volumes and consequently big feed/effluent heat exchangers [9] and compressors [5] as illustrated in Fig. 3. This is hardly feasible for large scale plants.

Cheaper technology for oxygen manufacture may be one route to reduce costs of syngas manufacture. One attempt is to eliminate the oxygen plant and to include a reactor concept with oxygen addition through a *membrane* [10]. With the high driving force across the membrane, there is no need for compression of air to the process pressure. However, as illustrated in Fig. 4 [6], there is still a need for big feed/effluent heat exchanger [19] in the process scheme for catalytic membrane reforming (CMR). The reported oxygen ion diffusivities [10] make a syngas unit possible, but still the feasibility is to be proven.

For small scale units providing *hydrogen for fuel cells*, the choice of technology may be dictated by parameters as simplicity and quick response to transients, not the least for automotive applications. Although steam reforming may be most energy efficient catalytic partial oxidation or ATR using air may be the preferred choice [11].

2. Catalysis of steam reforming

In spite of the growing role of oxygen or air blown syngas technologies, steam reforming will remain a key technology. Recent years have shown progress resulting in cheaper plants not the least because of better construction materials, better control of carbon limits and better catalysts with high flexibility to feedstocks [3]. This has allowed operation at higher exit temperatures and higher heat fluxes and the use of lower steam to carbon ratios. For hydrogen plants, it means less export of steam and hence lower investments. For

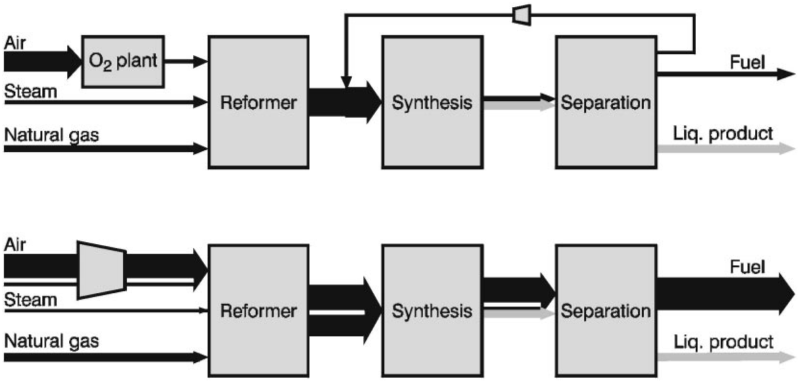


Fig. 3. Natural gas conversion to liquids. Oxygen and air-based schemes [5].

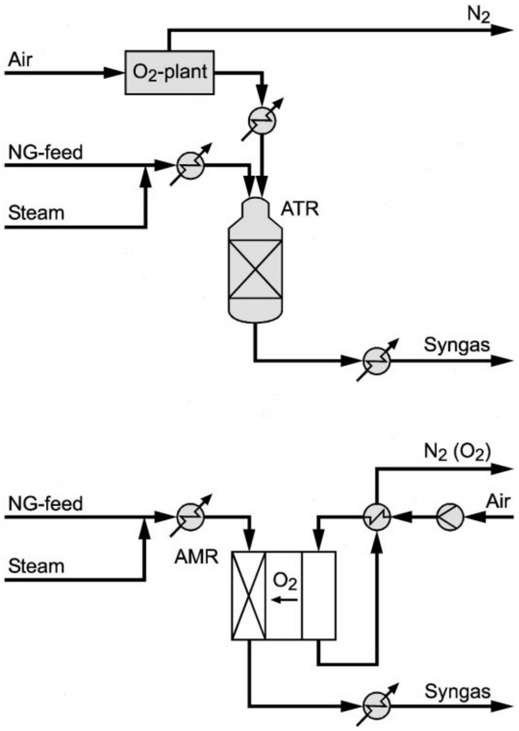


Fig. 4. Process schemes for ATR and CMR [6].

$$CH_4 + {}^* \xrightarrow{k_1} CH_x{}^*$$

$$CH_x{}^* \xrightarrow{k_2} C^* \longleftrightarrow [C, Ni]_{bulk} \rightarrow \text{whisker carbon}$$

$$CH_x{}^* + OH_y{}^* \xrightarrow{k_3} \text{gas}$$

$$C^* + OH_y{}^* \xrightarrow{k_4} \text{gas}$$

Fig. 5. Methane reforming. Simplified reaction sequence [13]. $*$ represents nickel site disregarding the ensemble size.

syngas plants, it means less production of surplus hydrogen and hence a smaller reformer.

This development has been supported by a better understanding of the reforming reactions [12]. The key problem is to avoid the formation of carbon [13]. Whether carbon-free operation is possible depends on the kinetic balance as illustrated in the simplified two-step mechanism [13] shown in Fig. 5. For a nickel catalyst carbon is normally formed by the whisker mechanism [14,15]. Adsorbed carbon atoms that do not react to gaseous molecules are dissolved in the nickel crystal and carbon whiskers nucleate from the nickel support interface of the crystal. Carbon formation is avoided when the concentration of carbon dissolved in the nickel crystal is smaller than that at equilibrium — in other words, when the steady state activity of carbon is smaller than one. In terms of the sequence in Fig. 2, the steady state activity is proportional with [C*] which can be expressed by [12,13]:

$$a_c^s \sim [C^*] \sim \frac{k_1 k_2}{k_3 k_4} \frac{1}{[OH_y{}^*]^2} \tag{2}$$

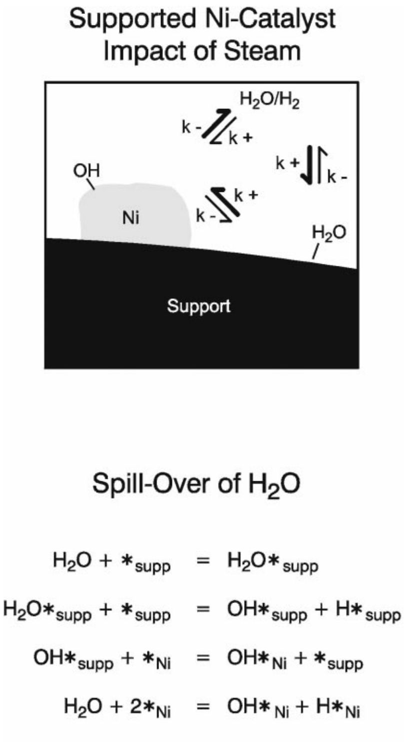
Hence, the steady state carbon activity can be decreased by:

- enhancing the adsorption of steam or CO_2;
- enhancing the rate of the surface reaction;
- decreasing the rate and degree of methane activation and dissociation.

The whisker mechanism may also be blocked by use of noble metal catalysts [16] because these metals do not dissolve carbon.

In an earlier approach, the idea was to reduce the steady state activity of carbon by *enhanced steam adsorption* [17]. This was achieved by the addition of alkali or the use of magnesia as support. The stronger steam adsorption was reflected by negative reaction orders with respect to steam and it was assumed that there was spill-over of steam from the support to the nickel surface as illustrated in Fig. 6. However, use of a micro-kinetic model [18] implies coverages of oxygen species to be low. The coverages of H_2O^* and OH^* on a non-promoted catalyst are estimated to 10^{-3} and 10^{-5}, respectively (conditions: $H_2O/CH_4 = 4$, $H_2O/H_2 = 10$, 1 bar, 450°C). At 30 bar, the coverages may be eight times larger. On a promoted catalyst, the coverages may be more than 10 times larger. This means that coverages of 10^{-1} and 10^{-3} may be typical for promoted catalysts at industrial conditions.

Micro-calorimetric studies [13] on steam adsorption on various supports showed that equilibrium coverages and heats of adsorption were lower on magnesia (with high “spill-over” effect) than on non-promoted supports (alumina, magnesium aluminium spinel). In contrast, H_2/D_2O exchange studies showed that the *rate* of dissociation of steam was most pronounced on



$$H_2O + *_{supp} = H_2O*_{supp}$$
$$H_2O*_{supp} + *_{supp} = OH*_{supp} + H*_{supp}$$
$$OH*_{supp} + *_{Ni} = OH*_{Ni} + *_{supp}$$
$$H_2O + 2*_{Ni} = OH*_{Ni} + H*_{Ni}$$

Fig. 6. Spill-over of steam.

magnesia. This emphasises that the spill-over is a dynamic phenomenon and that the improved resistance to carbon formation of magnesia-supported nickel catalysts is not caused by an increased adsorption equilibrium constant of steam on the support, but by a high *rate* of dissociation of water on magnesia. As a result, the amount of OH_y species present on the nickel is increased on magnesia-supported nickel, thereby enhancing the removal of CH_x and retarding the full dehydrogenation of CH_x to C^*.

The above means that the spill-over of steam as suggested in the literature [17] probably involves OH-species instead of molecular water. This is in agreement with other studies [19].

Recent work [12,20] indicates that the control of the degree of *methane dissociation* may play as important a role as enhanced steam adsorption.

The knowledge of methane adsorption on nickel has become more precise. By means of DFT-calculations [21], it is possible to quantify enthalpy and the activation barrier for the stepwise dissociation of methane on nickel as illustrated in Table 3. The overall energy barrier for complete dissociation of methane was measured to 59 [22] and 72 kJ/mol [23] on Ni(1 0 0) and Ni(1 1 1) at 500 K, respectively.

Table 3
Dissociation of methane on Ni(1 1 1) by means of DFT-calculations ($T = 0\,K$) [21]

	$-\Delta H$ (kJ/mol)	E (kJ/mol)
$CH_4 = CH_3{}^* + H^*$	−41	86
$CH_3{}^* = CH_2{}^* + H^*$	+3	71
$CH_2 = CH^* + H^*$	−43	71
$CH^* = C^* + H$	−53	86

The impact of *alkali* on methane activation was studied on well-defined nickel surfaces with preadsorbed potassium [13,24]. The methane sticking probabilities were found to decrease much more than could be explained by simple ensemble blocking effect. This could be expected from DFT-calculations showing that a strong dipole moment is induced in the transition state of the dissociating methane molecule when adding potassium. This is reflected by an increase of the energy barrier for dissociation of methane and hence the formation of adsorbed carbon atoms as shown in Table 4. Although the absolute values for the energy barrier are higher than the measured values and those shown in Table 3. The difference (ca. 20 kJ/mol) between alkali-doped and alkali-free nickel surfaces as well as the difference between the clean (1 0 0) and (1 1 1) surfaces (ca. 15 kJ/mol) is in reasonable agreement.

This increased energy barrier for methane dissociation may explain the promoting effect of alkali for inhibition of carbon formation. In addition, alkali promotion results in enhanced steam adsorption (reflected by negative kinetic order [17]) and hence less potential for carbon formation.

The inhibition of complete methane dissociation was also indicated by isotope exchange studies on

Table 4
Impact of alkali on the energy barrier for CH_4 adsorption on Nickel (kJ/mol) by means of DFT-calculation ($T = 0\,K$, $\theta_K = 0.125\,ML$) [24]

Ni(1 1 1)	Ni(1 1 1) + K	Ni(1 0 0)	Ni(1 0 0) + K
127	147	115	131

various catalysts [20] and promoting effects have been reported on a number of alloys [25], sulphur passivated nickel catalysts [26] or by decoration of the metal surface by oxides [12,27].

It is likely that in most cases the inhibition of carbon formation may be due to enhanced adsorption of steam coupled to spill-over of OH-species to the nickel surface as well to a reduced degree of dissociation of the methane molecule. These effects are still to be studied.

3. Conclusions

The future use of syngas and hydrogen will need more efficient hydrogen plants, cheaper large scale syngas plants for gas to liquid plants, and the small scale applications of syngas technologies for fuel cells whether for stationary or for automotive use. Although catalysis is only one of several key factors for these developments, it plays an important role for advanced reactor designs, feedstock flexibility, and control of carbon formation. The catalysis of reforming reactions has long been a field for mainly applied catalysis, but recent years have shown important input from fundamental studies.

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