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Innovation and science in the process industry
Steam reforming and hydrogenolysis

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Abstract

Innovations in the industrial applications of the steam reforming process have been inspired by scientific research influenced by the work of John Sinfelt. Steam reforming, hydrogenolysis and carbon formation on nickel catalysts, modified by sulphur adsorption and copper alloying, and compared. The rates of steam reforming and hydrogenolysis are closely correlated indicating common rate controlling steps. They depend in a similar way on sulphur and copper modifications indicating similar ensemble requirements. The ensemble requirement of carbon formation is much larger. It is therefore possible to suppress carbon formation by sulphur adsorption and to a smaller extend by copper alloying. However, copper also influences the electronic structure of the nickel sites resulting in promotion of carbon formation when the copper concentration in small. Recent experimental and theoretical results for NiAu surface alloys are mentioned. They have formed the basis for the development of a new carbon resistant catalyst. The importance of exploratory scientific research for industrial catalysis developments is emphasized. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Steam reforming; Hydrogenolysis; Carbon formation; Nickel catalysts; Surface modifications; Sulphur; Copper; Gold

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1. Introduction

The process industry faces challenges requiring innovative efforts. These are mainly related to environmental objectives [1] dictating requirements to the products, the use of processes being environmentally benign.

One major challenge to the process industry is the utilisation of remote natural gas [1–3]. The present focus on the conversion of natural gas into liquids may appear ‘dèjá-vu’ with reference to the efforts a few decades ago under the oil crises. Apart from a few examples, very little happened because of a questionable feasibility [2] but the situation may have changed today. Firstly, the environmental requirements may add a premium value to the sulphur-free synfuels and secondly, it has become a requirement that associated gas is not being flared.

Cheaper technology for the manufacture of syngas [1,2] is a key for improving the process economy of gas–liquid plants. Syngas-based routes to petrochemicals and synfuels are characterised by high carbon efficiency, which can hardly be met by direct conversion routes [1]. This paper will focus on a few scientific aspects of the steam reforming process, which resulted in a basis for process innovation. It will be illustrated how this part of the work was influenced by John Sinfelt’s studies on hydrogenolysis.

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Sinfelt [8]

$$C_2H_6 + 2\,{*} \leftrightarrow {*}_2\,C_2H_x + \frac{6-x}{2}\,H_2$$

$$*C_2H_x + H_2 \rightarrow \ldots$$

Boudart [9]

$$2\text{✳} + H_2 \leftrightarrow 2\text{✳}H$$

$$* + C_2H_6 + y\text{✳} \rightarrow *\,C_2H_x + y\text{✳}H + \frac{6-x-y}{2}\,H_2$$

$$*C_2H_x + H_2 \rightarrow \ldots$$

Fig. 1. Reaction sequences [8,9] for ethane hydrogenolysis;*: Ni site; ✳: Ni site different from *.

2. Steam reforming and hydrogenolysis

2.1. Catalyst activity

In our work around 1970 [4,5], we applied the steam reforming of ethane (1a-b) as a probe reaction and compared it with the hydrogenolysis of ethane

$$C_2H_6 + 2H_2O = 2CO + 5H_2 \qquad (-\Delta H^{o}_{298} = -348\,\mathrm{kJ/mol}) \qquad (1a)$$

$$CO + H_2O = CO_2 + H_2 \qquad (-\Delta H^{o}_{298} = 41\,\mathrm{kJ/mol}) \qquad (1b)$$

$$C_2H_6 + H_2 = 2CH_4 \quad (-\Delta H^{o}_{298} = 65\,\mathrm{kJ/mol}) \qquad (2)$$

The term reforming is misleading but a more logical term, oxygenolysis [6], corresponding to pyrolysis and hydrogenolysis of hydrocarbons using heat and hydrogen, respectively, to split the hydrocarbon has not been adapted.

In establishing a reaction sequence for the ethane reforming use was made of Sinfelt's work on hydrogenolysis [7,8] applying the two-step approach suggested by Boudart [9], as shown in Fig. 1. In principle, the reaction sequence for reforming was established by simply adding a step for reacting adsorbed carbon atoms with adsorbed oxygen atoms, as illustrated in Fig. 2.

$$H_2 + 2\text{✳} \leftrightarrow 2\text{✳}H$$

$$* + C_2H_6 + y\text{✳} \rightarrow *C_2H_x + y\text{✳}H + \frac{6-x-y}{2}\,H_2$$

$$*C_2H_x + H_2 \rightarrow 2{*}CH_z + \left(\frac{x}{2} + 1 - z\right)H_2$$

$$s + H_2O \leftrightarrow s\,H_2O$$

$$sH_2O + * \rightarrow *O + H_2 + s$$

Fig. 2. Reaction sequence for steam reforming of ethane [4,5]. s = support site. (Recent data [11,12] indicate that OH species rather than O species are involved).

The classical sequence for hydrogenolysis in Fig. 1 assumes a single rate-determining step. However, as was proposed by Boudart [9], the dissociative adsorption of ethane is most probably irreversible at the temperatures applied in steam reforming (500°C). Moreover, the surface reaction might also be considered irreversible since no influence on the rate from carbon monoxide nor carbon dioxide was observed [4]. This leads to a two-step sequence, as shown in Fig. 2.

The activities for the two reactions were compared for a series of nickel catalysts [4]. The rates were referred to the active surface area as specific rates or turnover frequencies, as also emphasised by Sinfelt et al. [10]. Results are shown in Fig. 3. A strong, direct correlation over several orders of magnitude of activity is hinting that the two reactions may be strongly related. It is surprising that the decrease in activity caused by promotion of the catalyst with alkali fits the correlation because of the different reaction conditions with and without steam present. This observation was very important to exclude a number of theories

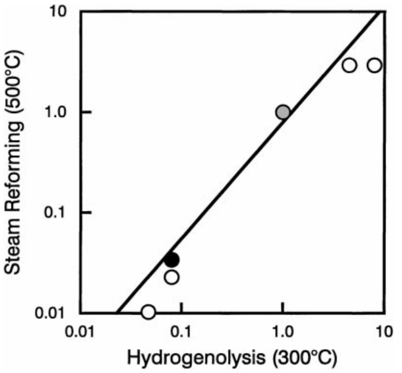

Fig. 3. Relative and specific rates of Ni-catalysts [4,5]. Steam reforming of ethane (500°C; 1 bar abs.; $H_2O/C_2H_6 = 8$; $H_2O/H_2 = 10$). Hydrogenolysis of ethane (300°C; 1 bar abs.; C_2H_6 $H_2N_2 = 5/20/75$).

on the function of alkali as promoter to avoid carbon formation in steam reforming [11,12] but the observation has not yet been fully understood. Steam reforming like hydrogenolysis shows a strong 'specificity' [7] among Group VIII metals, rhodium and ruthenium being one order of magnitude more active than nickel and platinum. It was also shown that the turnover frequencies for steam reforming of methane correlated directly with that of steam reforming of ethane [4,5].

2.2. Carbon formation and ensemble control

The problem in steam reforming is to design for carbon-free operation [6]. On a nickel catalyst carbon is formed as carbon fibres (whiskers) growing with a nickel crystal at the top. The carbon fibres will destroy the catalyst and result in disturbance of flow and poor heat transfer. The risk for carbon formation is higher when higher hydrocarbons are present in the feed. When using noble metals, the whisker growth mechanism is blocked simply because carbon is not dissolved.

A simplified reaction sequence for reforming of methane is shown in Fig. 4 [11]. Carbon-free operation is achieved when the concentration of carbon dissolved in the nickel crystal is smaller than that at carbon equilibrium. In other words, when the steady-state activity of carbon is less than one. This can be achieved by [11,12]: enhancing the adsorption of steam; enhancing the rate of the surface reaction; and by decreasing the rate and degree of methane activation and dissociation. It is well known that alkali and magnesia enhance the adsorption of steam [6].

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

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

$$*CH_x + *O \xrightarrow{k_3} \text{gas}$$

$$*C + *O \xrightarrow{k_4} \text{gas}$$

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

Fig. 4. Simplified mechanism for steam reforming of methane [11]. a_c^s = steady state activity for carbon whisker carbon for $a_c^s > 1$. $(k_1 = k_1' \cdot p_{CH_4})$.

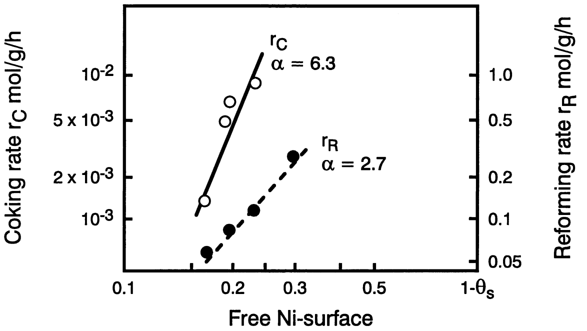

Fig. 5. TGA on sulphur passivated nickel catalyst [13]. 950°C; 1 bar abs.; feed (vol%): $H_2 = 27$; $H_4 = 5$; $H_2O = 7$; $CH_4 = 61$.

The dissociation of methane may be influenced by ensemble control. This was demonstrated over partly sulphur poisoned nickel catalysts [13]. The rate of carbon formation decreases more than the rate of reforming for increasing sulphur coverage, as illustrated in Fig. 5. At high coverages there were still ensembles available for the dissociation of methane but not for dissolution of the carbon atoms into the nickel crystal and, hence, not for nucleation of whisker carbon. This effect was utilised in the industry [14].

Similar ensemble effects were studied by alloying nickel with copper [15,16], again inspired by the early work of Sinfelt [17] illustrating ensemble effects on these alloys. However, in contrast to sulphur passivation it was not possible to achieve the required high surface coverages of copper atoms to eliminate the carbon formation.

The rate of carbon formation for more than 10 at.% Cu was more strongly decreased by alloying with Cu than the rate of steam reforming, the latter following closely the capacity for strongly adsorbed hydrogen [15]. This is illustrated in Fig. 6, which was made after the same principle as the Sinfelt plot [17] of dependency of the specific rate of dehydrogenation and hydrogenolysis on the Cu/Ni ratio of the alloy catalyst. Fig. 6 indicates that different ensembles are required for carbon formation and the surface reaction to gas, respectively:

$$CH_4 + ^* \rightarrow {}^*CH_x \rightarrow {}^*_mC \rightarrow [C, Ni] \rightarrow \text{whisker C} \quad (3a)$$

$$^*_nCH_x + {}^*OH_y \rightarrow \text{gas} \quad (3b)$$

$$m > n$$

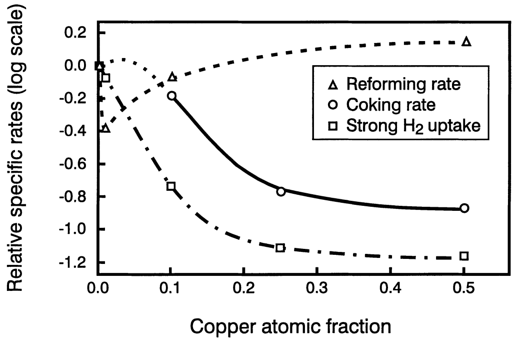

Fig. 6. Methane dissociation at 500°C and steam reforming at 550°C on NiCu/SiO_2 catalysts (based on data from [15]).

However, the effect of sulphur is much larger than that of copper. By extrapolation of the data in Fig. 5 the rate of carbon formation is decreased by a factor 2×10^{-4} at $\theta_S = 0.8$ (referred to free nickel surface area) whereas the maximum effect of copper is about 6×10^{-2} (at 50 at.% Cu) (Fig. 6).

2.3. Propane hydrogenolysis

A series of tests were carried out [18] on hydrogenolysis of propane on a Ni/$MgAl_2O_4$ catalyst to study the impact of ensemble control by sulphur passivation and Cu-alloying on the two reaction routes:

$$\text{Route1} \quad C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6 \tag{4a}$$

$$\text{Route2} \quad C_3H_8 + 2H_2 \rightarrow 3CH_4 \tag{4b}$$

The idea was to explore whether it would be possible to stabilise C_2-species on the nickel surface by ensemble control. Fig. 7 shows results on catalysts with various sulphur coverages. r_1 passes through a maximum with increasing temperature, whereas r_2 shows normal behaviour. The maximum can be explained by secondary hydrogenolysis becoming dominant at higher temperatures. This observation supports the reaction mechanism (Fig. 2) for steam reforming assuming that the hydrocarbon is cracked to C_1-species on the nickel surface [4]. The activation energies for route 1 (low temperatures) and route 2 were determined to be 50–55 and 60–75 kcal/mol, respectively, independent of sulphur coverage ($\theta_s = 0$–0.7).

The r_1 and r_2 decrease with sulphur coverages with a $(1-\theta_s)^n$ dependency showing n-values in the range of 2–3 for both reactions in the temperature range of 335–410°C. This indicates that C_2-species cannot be stabilised by sulphur passivation. Initially the selectivity $r_1/(r_1+r_2)$ increases by adding sulphur but decreases again at high sulphur coverages [18].

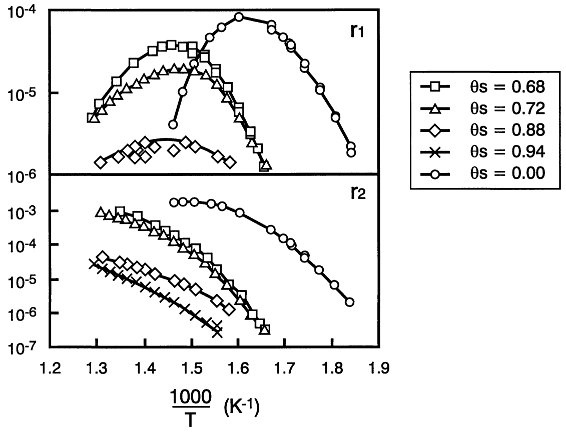

Fig. 7. Hydrogenolysis of propane [18]. Various sulphur-coverages of presulphided Ni/$MgAl_2O_4$ catalysts.

Similar tests on propane hydrogenolysis were carried out [18] on a series of NiCu/SiO_2 catalysts (identical to those previously used [15]). Again, r_1 passes through a maximum as shown in Fig. 8. The activation energies for route 1 (low temperature) and route 2 were determined to be 46–53 and 58–68 kcal/mol, respectively, independent of copper content and in very good agreement with the results of Dalmon and Martin [19]. When plotting rates as a function of free nickel area (expressed by the hydrogen capacity (θ_H) [15]),

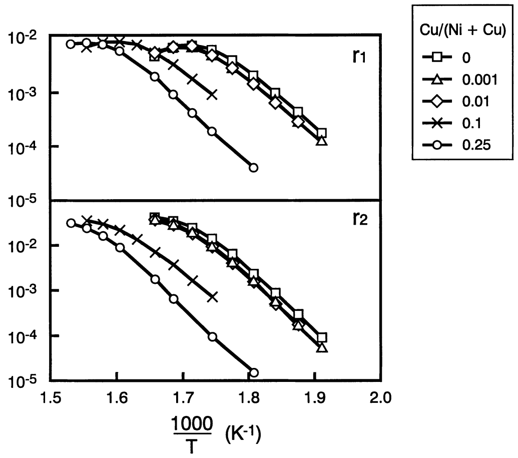

Fig. 8. Hydrogenolysis of propane [18] on NiCu/SiO_2 catalysts.

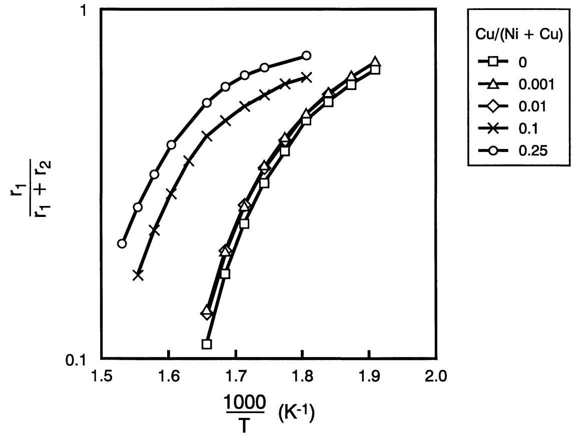

Fig. 9. Hydrogenolysis of propane [18] on NiCu/SiO$_2$ catalysts.Selectivity for C_2H_6: $r_1/(r_1+r_2)$.

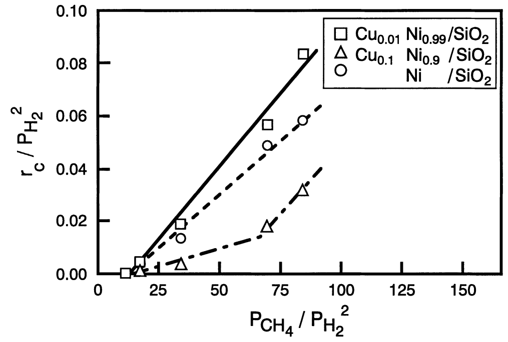

Fig. 10. Methane dissociation on NiCu/SiO$_2$ catalysts [16].

n-values of 2–2.6 and 2.7–3.5 were found for route 1 and route 2, respectively, indicating a slight ensemble control. This is reflected by an increase in selectivity for ethane, as shown in Fig. 9, indicating stabilisation of C_2-species. The dependence of the selectivity on the Cu content in Fig. 9 is also in very good agreement with the results of Dalmon and Martin [19]. This agreement is quite surprising considering the vastly different hydrogen chemisorption behaviours of the catalysts in the two studies [18].

3. Recent trends: prediction from density functional calculation

Later studies showed [16] that very small additions of copper (i.e. 1 at.%) even promotes dissociation rates, as illustrated in Fig. 10. This was confirmed by recent density functional theory (DFT) calculations [20] showing that the activation barrier for methane is decreased for nickel sites having copper neighbours. It illustrates that selectivity changes in bi-metallic catalysis are not just a question of ensemble control and changes in d-band structure.

As Sinfelt described [21,22] (being one of the first), it is possible to create bi-metal clusters also when the two metals are not miscible. One recent example is the Ni–Au system [20,23]. Ni and Au do not mix in the bulk but may form stable alloys in the outermost layer. DFT calculations predict that gold neighbours increase the activation barrier for the methane dissociation on nickel and, hence, that Au inhibits methane dissociation. This was confirmed by molecular beam scattering experiments on well defined Ni(111) surfaces. The DFT calculations also suggested that the stability of adsorbed carbon on the Ni(111) surface is drastically reduced in the vicinity of an Au-atom resulting in a lower carbon coverage. In terms of the simplified mechanism for carbon formation (Fig. 4), this means a lower steady-state activity for carbon and, hence, reduced risk of whisker carbon. This prediction was verified by TGA-experiments [12,20].

4. The need for explorative research

The examples show how a better scientific understanding may provide a basis for innovation. It is important that industrial research efforts have this in mind. This has characterised the work of John Sinfelt [24]. The science of catalysis involves many disciplines and there is a risk when loosing the overall view that it could develop into on the one hand side the ‘noble art of characterisation’ and on the other the ‘noble art of computer modelling’ [25]. These are important elements but as illustrated by Sinfelt’s work it is important to study the catalytic reaction, in particular by using probe reactions on a number of catalysts to explore the ‘specificity’ of catalysts. It is important that the fundamental research is linked to catalyst and process development [25,26]. It is important that a large fraction of the research is explorative, driven by curiosity and courage. This must be maintained at difficult times for industrial research and with university research being dependent on short-term grants promoting focus on fashionable fields. Without the strength and courage to look for new horizons it may become difficult to follow the track of John Sinfelt.

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