

The dynamics of methanation of carbon monoxide on nickel catalysts

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THE DYNAMICS OF METHANATION OF CARBON MONOXIDE ON NICKEL CATALYSTS

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ABSTRACT

Earlier we studied methanation kinetics on a 5% Ni/SiO₂-catalyst. The extensive data were described well with a mechanism involving dissociative adsorption of H₂ and CO and stepwise hydrogenation of C_a and O_a. Hydrogen isotope effects were also described with fair accuracy.

Since then kinetic data were obtained on two further catalysts, 52% Ni/SiO₂ and 4% Ni/Al₂O₃. The mechanism described also these data. However, using a feed containing ¹³C¹⁶O and ¹²C¹⁸O no isotope scrambling was found. The assumption of equilibrated dissociative CO adsorption was invalidated. The original mechanism was extended by a s.s. approximation for CO dissociation. The rate data were well described but scrambling was not eliminated.

A new mechanism was designed, involving hydrogen-assisted dissociation of adsorbed CO with formation of C_a. With fast H₂O-elimination this step is unidirectional. A new rate equation describes kinetics and isotope effects very well and excludes isotope scrambling.

Two types of transient rate observations were performed, one on switching ¹²CO to ¹³CO, the other with a switch from CO to He. The new mechanism also describes these data. Information on residence times \bar{t} and surface occupation CH_x on the nickel surface were obtained. Combining these with the s.s. rate information yields two independent estimates of the fraction F_s of S_{Nj} which is active. Both agree closely and yield values between 8 and 25%, depending on catalyst type. At the same time additional confirmation of the essential correctness of the new mechanism is obtained.

Finally a larger range of catalysts, supported on silica, alumina and titania is tested. As found before, larger crystallites are more active. Alumina and titania supports yield higher activity. The higher activity was found to be equally due to higher F_s and higher r_s, the activity per active site.

INTRODUCTION

Even though economic large scale application of hydrocarbon synthesis from coal-based synthesis gas lies in a remote future, both methanation and Fischer Tropsch synthesis have been subjects of numerous studies in the past decade, not least as studies in fundamental catalysis. In the past seven years much effort has been directed in our laboratory at measurement and understanding of the rate behaviour of methanation of carbon monoxide/hydrogen mixtures on nickel catalysts. At the moment of completion of this study the present paper compactly presents the essential methods, results and conclusions. In a series of papers full details of the investigation will be presented shortly to this journal.

Earlier we found, that the methanation activity per unit nickel surface area

increases almost linearly with average crystallites size [1,2], levelling off for sizes of about 4 nm [3]. Near the end of the present paper we will come back to these findings and identify two contributing effects.

On one silica supported nickel catalyst, NZ 5, we did an extensive kinetic study [4], with specific rates covering five orders of magnitude. Since the recent literature provides massive evidence for assuming an active oxygenfree carbon species [5-11] as an essential reaction intermediate, we chose a reaction mechanism in which adsorbed carbon atoms are produced by dissociation of adsorbed carbon monoxide, as suggested by others [7,9,12] which is then converted to methane by stepwise addition of hydrogen atoms. Assuming addition of the second hydrogen atom to be rate determining, we could derive a rate equation, which after some simplifications, justified by a computer fit to the rate data, had the simple form

$$r = (Z_1 p_{CO}^{\frac{1}{2}}) / [1 + Z_2 (p_{CO}/p_H)^{\frac{1}{2}}]^2 \quad (1)$$

This equation, in which Z_1 and Z_2 are combinations of equilibrium and rate constants for reaction steps in the mechanism and thus temperature dependent parameters, describes the rate data surprisingly well. We further measured the hydrogen isotope rate effect and this also was described reasonably by the assumed mechanism [13]. We thus thought to have provided strong evidence for the essential correctness of the assumed mechanism. We should further recall that from the entropy contributions contained in Z_1 and Z_2 the conclusion was derived that only a small part F_s of the nickel surface did all the work.

In the present study the investigation is extended essentially in three directions: (a) extension of the steady state kinetic data to two further catalysts and a somewhat wider range of conditions, (b) measurement of isotopic exchange ("scrambling") when feeding a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ with hydrogen, (c) transient kinetic experiments upon a sudden switch of gas composition in methanation, [9,14-16]. We will see that the first block of data cannot be accommodated entirely by the earlier mechanism and rate equation. These shortcomings might still be corrected by relatively minor adjustments. We further found that the findings in the second block completely invalidate the assumed mechanism. A new mechanism and rate equation will solve the difficulty.

The transient kinetic data finally will prove especially valuable. They provide strong support for the new mechanism. They further provide, together with the steady state rate data, two independent means for estimation of the active fraction F_s .

EXPERIMENTAL

Catalysts

In these studies, 12 supported nickel catalysts were used: 7 on silica, e.g., NZ5 (number is approximate nickel content in unreduced state), 4 on alumina, e.g., NA4 and one on titania, NT4. Their preparation will be described elsewhere. The

catalyst was activated by 4 h reduction at 723 K in flowing hydrogen. Nickel surface area, degree of reduction and nickel crystallite size were determined as described elsewhere [1-3,15].

Steady state flow apparatus

This apparatus allows any combination of reactant partial pressures up to a total pressure of 120 kPa and reactor temperatures from 450 to 840 K. For a description, see ref. [4]. Conversions are limited to below 10%.

Apparatus for isotope exchange and transient kinetics

The main part of the equipment is identical to the s.s. flow apparatus, a train comprising gas stores, purification, mass flow controllers, mixer, reactor, analysis section. Only in this case provision is made for dosage of six different gases. Analysis is not only by gas chromatography but also by mass spectroscopy (Leybold/Heraeus Quadrupac Q 200 with multichannel peak processor). Moreover a special valve arrangement allows, when the apparatus is running at steady state, an instantaneous switch from one feed composition to another while flow rate and total pressure remain constant. This arrangement is used in the transient kinetic experiments. To improve time resolution the reactor section is specially designed.

Gases

Unlabelled hydrogen and carbon monoxide are commercial high purity gases. Purification has been described [4]. The same holds for Ar and He, used in the transient experiments. $^{13}\text{C}^{16}\text{O}$ was purchased from Merck Sharp and Dohme, Canada in 90% purity; $^{12}\text{C}^{18}\text{O}$ was obtained from Rohstoff Einfuhr GmbH, Düsseldorf, purity 99%.

Procedures

Steady state kinetics. Procedures have been described [4].

Isotopic exchange. These are normal s.s. experiments, in which the CO component in the feed is composed of a 1:1 mixture of the two labelled gases mentioned above. MS analysis for "scrambled" species, masses 28 and 31. Formation rate is expressed as fraction of methanation rate.

Transient experiment 1. The reactor is fed a mixture of ^{12}CO , H_2 , He and a trace of Ar and run at steady state. It is then switched abruptly to a similar mixture in which ^{12}CO is replaced by ^{13}CO , Ar by He. The Ar serves as a marker gas, a non-adsorbing CO, " CO_0 ", which yields information on the physical hold-up of the reaction system. The effluent is monitored by MS for Ar, ^{12}CO and $^{12}\text{CH}_4$. All analysis data are plotted against time as a fraction of their respective s.s. value - all three curves start at unity.

Transient experiment 2. In this experiment the initial feed is the same as in Transient 1. Now the switch is from $^{12}\text{CO} + \text{Ar}(\text{tr})$ to He. As before the effluent

is analysed for $\text{CO}_0(\text{Ar})$, CO and CH_4 . Again all data are plotted as a fraction of their respective s.s. values. CO_0 and CO show a sharp decline, CH_4 shows a steep upswing to a maximum, followed by a gradual decline.

RESULTS AND DISCUSSION

Steady state kinetics

As already mentioned, comprehensive kinetic data were obtained for two further catalysts, NZ 54 and NA 4. All data are described reasonably well by equation (1) but systematic deviations, already noticed for extreme conditions on NZ 5, are clearly apparent now. Specifically the rate equation does not allow but should allow negative reaction order in hydrogen and reaction orders in CO smaller than $-\frac{1}{2}$ and larger than $+\frac{1}{2}$.

To cater for these requirements the reaction mechanism was marginally adjusted: an adsorbed state of undissociated CO was taken into account, for the CO dissociation the equilibrium assumption was dropped and replaced by a steady state approximation. A rate equation (2) was derived which - obviously - reduced to equation (1) for a large range of the experimental conditions and which improved the fit to the experimental data somewhat. The final death sentence of equations (1) and (2) was provided by the isotope exchange experiments.

Isotopic exchange

The original mechanism assumed equilibrated dissociative adsorption of CO. If this were true, then substantial isotopic scrambling should occur if the methanation is fed with an equimolar mixture of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. Surprisingly we found no significant scrambling under normal methanation conditions. Thus most certainly mechanism (1) and rate equation (1) are invalidated. But also mechanism (2) with the s.s. assumption for CO-dissociation proved inadequate. With this description $r_{\text{scrambling}}/r_{\text{methanation}}$ should be at least 5 and we found 0.2 at most. Clearly more drastic changes of mechanism are required. An entirely new mechanism, still involving C_a -intermediates, was designed.

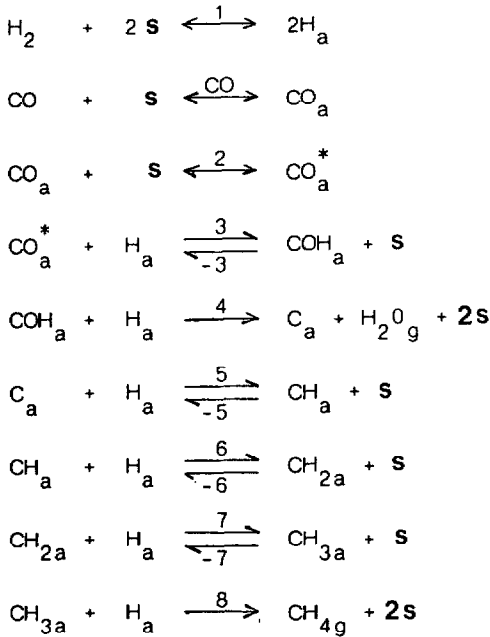
A new mechanism

In the design of a new mechanism we are facing a list of boundary conditions:

- * It should involve hydrogenation of C_a
- * CO dissociation, to produce C_a must be irreversible
- * The resulting rate equation must describe the data. In view of the success of equation (1) the new equation should reduce to equation (1) over a large range of conditions
- * The new rate equation must allow negative reaction order in p_{H} and orders in p_{CO} outside the limits $-\frac{1}{2}$ and $+\frac{1}{2}$
- * Also the hydrogen isotope effect must be described.

The following mechanism (Mechanism 3) proved to satisfy the requirements.

M E C H A N I S M 3



Two forms of adsorbed CO are assumed, a singly and a doubly bonded one. Both are required to satisfy the reaction order requirements for CO and in fact they do not appear unreasonable. Provided elimination of water is fast enough it is not unreasonable to consider reaction 4 as an unidirectional one.

For reactions 1, CO and 2 undisturbed equilibrium was assumed. The computer fit proved that this also holds for reaction 3. For reactions 5, 6 and 7 the stationary state assumption was applied. The ultimate computer fit indicated that over most of the field reaction 6 can be considered as the final (rds) step. Obviously the resulting rate equation is much more complicated than the simple equation (1). However, it can be shown that over a substantial part of the field of reaction conditions the equation can be approximated by equation (1).

Rate equation 3 reads

$$r = \frac{F_s K_1 K_3 k_4 p_H}{A(1+K_1^{\frac{1}{2}} p_H^{\frac{1}{2}} + K_{CO} p_{CO})} \cdot \frac{B}{(1+B)^2} \quad (3)$$

in which: $A = P_1 p_H^{-1} + P_2 p_H^{-\frac{1}{2}} + P_3 + P_4 p_H^{\frac{1}{2}}$ P_{1-4} are combinations of rate and equilibrium constants

$$B = \frac{1}{2} \left[\sqrt{1 + \frac{4AK_2 K_{CO} p_{CO}}{(1+K_1^{\frac{1}{2}} p_H^{\frac{1}{2}} + K_{CO} p_{CO})^2}} - 1 \right]$$

In the following total reactive carbon species $C_a + CH_a + CH_{2a} + CH_{3a}$ will be called CH_x . Over most of the range C_a is the dominant intermediate.

This equation proved to describe the extensive rate data very well. The requirements enumerated before are all satisfied. It is of interest for later use that this theoretical set-up also allows calculation of $\bar{\tau}/F_s$, in which $\bar{\tau}$ is the average residence time of active CH_x - intermediates on the nickel surface and F_s is the fraction of the nickel surface, which actively contributes to the observed methanation rate. We calculate from $(\bar{\tau}/F_s) = B/(B+1) \cdot r_{ss}$. We defined B earlier.

Transient experiments, type 1

From the fall-off curves of the ^{12}C -fraction in CO and CH_4 we can easily derive two important quantities: $\bar{\tau}_{CH_x}$ and $\bar{\tau}_{CO}$ such as these prevail on the surface under steady state conditions:

$$\bar{\tau}_{CH_x} = \int_0^{\infty} \left(\frac{r_{tr}}{r_{ss}} \right)_{CH_4} dt - \int_0^{\infty} \left(\frac{r_{tr}}{r_{ss}} \right)_{CO} dt \quad \bar{\tau}_{CO} = \int_0^{\infty} \left(\frac{r_{tr}}{r_{ss}} \right)_{CO} dt - \int_0^{\infty} \left(\frac{r_{tr}}{r_{ss}} \right)_{CO_0} dt$$

These in turn may be used to calculate the surface coverage with these intermediates:

$$\theta_{CH_x} = \bar{\tau}_{CH_x} \cdot r_{CH_4} \quad \theta_{CO} = \bar{\tau}_{CO} \cdot r_{CO}$$

where r_{CO} is the feed rate of CO and r_{CH_4} the methanation rate. Since these rates are referred to the total nickel surface this also applies to the derived values for the surface coverages.

For Ni/SiO₂-catalyst NZ 5 values for θ_{CH_x} were determined as a function of the partial pressures p_H and p_{CO} . It was found that θ_{CH_x} was very little dependent on reactant partial pressures, which suggests that the active surface is almost fully covered with CH_x . On the other hand the value of θ_{CH_x} is far below unity, for NZ 5 about 0.08. This already indicates that the active fraction F_s must be far from unity.

We can quantify F_s now by comparing the values for $\bar{\tau}/F_s$, calculated earlier from the steady state data, with the values for $\bar{\tau}$ derived from Transient 1. Plotting the logarithm of both quantities as a function of p_{CO} and p_H we obtain sets of parallel curves. The vertical distance between the curves is equal to $-\ln F_s$. The parallel course of the $\ln(\bar{\tau}/F_s)$ and $\ln \bar{\tau}$ curves provides further confirmation of the essential correctness of Mechanism 3.

Transient experiments, type 2

In this case we withhold CO from the feed and we observe a steep upswing in the methanation rate. This is not surprising: in the foregoing we obtained indications that the acting part of the nickel surface is almost saturated with CH_x -intermediates,

TABLE 1
Two estimates of F_s for 3 catalysts

Catalyst	% Ni	\bar{D}_{Ni} nm	$F_s(1)$ %	$F_s(2)$ %
NZ 5	4.9	1.5	9 ± 1	8 ± 1
NZ 54	52.5	5.1	16 ± 2	15 ± 1
NA 4	3.9	2.5	22 ± 3	26 ± 2

which is far from optimum, since there is not much room for adsorbed hydrogen. As will be demonstrated in another paper the height of the maximum in the CH_4 -curve in a transient-2 plot is given by:

$$(r_{max}/r_{ss}) = (4 \theta_{CH_x,ss} (1 - \theta_{CH_x,ss}))^{-1}$$

This equation is independent of the location of r.d.s., 6, 7 or 8.

With the aid of this equation we can now calculate $\theta_{CH_x,ss}$ from the height of the maximum. However the θ -values we now obtain refer not to the total nickel surface but to the active part. These were again determined as a function of reactant partial pressures. The curves are remarkably similar to the ones for θ_{CH_x} which we determined earlier, only the θ -values are now much larger. The ratio provides us with a new, independent estimate of F_s . In Table 1 the F_s -values for three catalysts by two methods are shown. We recall that an earlier estimate of F_s for NZ 5 [4] was less than 1% but the method then applied, relying on estimates of entropy contributions holds greater uncertainty.

Activity and catalyst structure

As mentioned before, we can approximate the methanation rate, i.e., the activity, by the expression

$$r_{exp} = F_s \cdot r_s = F_s \cdot k_6 \cdot f(p_H) \cdot \theta_{CH_x} \cdot (1 - \theta_{CH_x})$$

For the 12 catalysts used in the present investigation earlier findings for Ni/SiO₂ [1-3] were confirmed: larger crystallites are more active per unit surface area. We can now split this effect in two influences, the active fraction F_s and the specific rate r_s . We find that higher activity is about equally due to higher F_s and higher r_s . A new element is the finding that catalysts supported on alumina and titania are, for equal crystallite size, somewhat more active than those supported on silica. It is possible that this is still a crystallite size effect. We have reason to believe that the crystallite size distribution for the silica supported catalysts is much narrower than for the other two supports. If this is so the higher activity of the alumina and titania supported catalysts may be due to the fraction large crystallites they contain.

Remains the question why larger crystallites have both larger F_s and higher r_s . Obviously larger crystallites have a higher proportion of their surface in flat facets. We might assume that edges and corners are too strongly bonding and therefore self-poisoning. In a sense then we are faced with another example of Balandins volcano-shaped curve. There might yet be another interpretation; in recent years it has been often suggested that the catalytic act requires a certain ensemble size. It might be that the ensemble required for methanation is a flat nickel plane and requires a certain size. In the crystallite size distribution of catalysts with larger average crystallite size these ensembles may be more abundant.

CONCLUSIONS

We may now summarise a number of conclusions from this investigation.

1. Notwithstanding the apparent success of a mechanistic description involving dissociation of CO_a to C_a and O_a the non-scrambling of CO isotopes, together with the kinetic behaviour of the methanation reaction invalidates this mechanism.
2. As an alternative a mechanism involving hydrogen-assisted CO dissociation proves successful in quantitatively describing all known phenomena. In essence this mechanism was already proposed by Van Ho and Harriot in 1980, but in the present mechanism the essential step, forming C_a and H_2O is split in our mechanism in no less than four successive reactions [8].
3. The methanation activity we observe is located in part of the surface of the nickel F_s . In catalysts where F_s is greater this part is also more active.

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