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# A Comparison of Nickel- and Platinum-Catalyzed Methanation, Utilizing Transient-Kinetic Methods

Both nickel and platinum are capable of catalyzing the hydrogenation of CO to $CH_4$. However, the by-products are quite different, i.e., $C_2$+ hydrocarbons (Ni) (*1*) versus methanol (Pt) (*2*). Moreover, when compared to the rate of the methanation reaction, the rate of CO dissociation over clean nickel is fast and the rate over clean platinum is slow (*3*). For these two metals, and more generally for the group (Ni, Co, Ru, Fe) when compared with the group (Pt, Pd, Ir), different methanation mechanisms could therefore be operative. Accordingly, it has been proposed that over nickel the C–O bond is being ruptured *before* (*1, 4*) and over platinum *after* (*5*) the addition of hydrogen.

In this Note we report transient-kinetic observations which might bear relevance on the question whether or not methanation over nickel and platinum proceeds via different sequences of elementary steps. In the pertaining experiments we switch abruptly the feed at the inlet of a plug-flow reactor from $^{12}CO/H_2$ to $^{13}CO/H_2$. With on-line mass spectrometry we monitor at the reactor outlet the (transient) decay of $^{12}CH_4$ and the concurrent ingrowth of $^{13}CH_4$.

Figures 3a and b give representative responses of Ni and Pt, recorded at high space velocity (2000 1/1/h) and low conversion (2%). In order to analyze these data we consider the response of a single unidirectional step (Fig. 1). In response to a switch from $^{12}CO$ to $^{13}CO$ the abundancy of $^{12}C$-containing surface intermediates (abundancy $N_{12}$, average lifetime $\tau$) will decay:

$$\frac{dN_{12}}{dt} = -\frac{N_{12}}{\tau}. \qquad (1)$$

For the lifetime, $\tau$, of the intermediates it is immaterial whether they are being surrounded by $^{12}C$- or $^{13}C$-containing surface intermediates. The quantity $\tau$ in (1), therefore, is independent of $N_{12}$, and (1) integrates into

$$N_{12} = Ne^{-t/\tau} \qquad (2)$$

with $N = N_{12} + N_{13}$ being the total coverage of C-containing intermediates at steady state. The decay in $N_{12}$ is being observed as a decay of the rate of $^{12}CH_4$ production, $R_{12}$,

$$R_{12} = Re^{-t/\tau} \qquad (3)$$

with $R = R_{12} + R_{13}$ the methanation rate at steady state. Integration of the total amount of $^{12}CH_4$ produced in $^{13}CO/H_2$ atmosphere (i.e., the hatched area in Fig. 1, and the

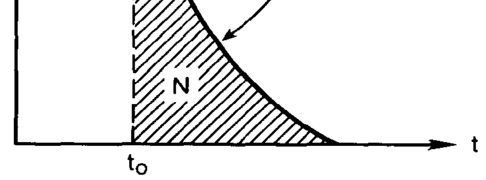

FIG. 1. Production of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere derives from $^{12}C$-containing surface intermediates. The decay constant reflects the lifetime ($\tau$), the integrated production gives the abundancy ($N$) of the surface intermediates.

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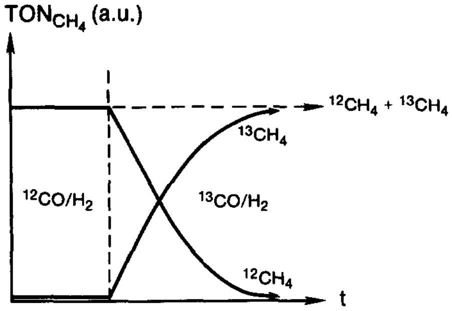

FIG. 2. Replacing $^{12}CO$ by $^{13}CO$ allows for the observation of the full transient-kinetic information without disturbing steady-state catalysis; neither the total $CH_4$ production nor $\tau$ is being affected.

area bounded by the $^{12}CO$ and $^{12}CH_4$ transients in Figs. 3a, b) gives $N$. For a single unidirectional step the decay constant of the exponential decay of $^{12}CH_4$ gives $\tau$. For a series of several unidirectional steps the decay is a complex function of several $\tau$'s (*6*). However, integration of the area under the decay curve still gives $N$. $N$ now is to be identified with the total of intermediates involved in all steps together (*7*). Further, to the invariant nature of $\tau$ we notice that steady state is being maintained throughout the experiment (Fig. 2).

The main finding of the present study is that, *at comparable TOF, N* and $\tau$ over platinum are several orders of magnitude below $N$ and $\tau$ over nickel. When changing from $^{12}CO/H_2$ to $^{13}CO/H_2$ the production of $^{12}CH_4$ over platinum immediately ceases (Fig. 3b), the quantities $N$ and $\tau$ being below the detection limit.

The data collected in Table 1 enables a further comparison. $^{12}CO/^{13}CO$ exchange has been utilized to measure for both nickel and platinum the number of surface-exposed atoms, $N_s$ (*8, 9*). This number has been utilized to calculate values for the dispersion, the TOF (Rate/$N_s$), and the fractional coverage in surface intermediates $\theta$ ($N/N_s$). The $\tau$, $\theta$ values for platinum are upper limits, derived from the precision of the area measurement:

$$\tau = 0 \pm 2 \text{ s} \qquad (95\% \text{ confidence interval}).$$

Within the single-unidirectional step analysis we have the relation (*8*)

$$\mathrm{TOF} = \frac{\theta}{\tau}. \tag{4}$$

We therefore conclude that platinum and nickel, when compared at similar reaction conditions *and* TOF, function via differently behaving surface intermediates; in the case of platinum the surface intermediates are much less abundant ($\theta_{Pt} \ll \theta_{Ni}$) and much more reactive ($\tau_{Pt} \ll \tau_{Ni}$).

Before attempting a mechanistic interpretation we have to consider one additional characteristic of (isotope) transients. Upon exposing a $^{12}C$-intermediates-cov-

TABLE 1

Methanation over Ni and Pt; Data on Catalysts, Rates, and Transient Responses

| | 60 w% Ni–$SiO_2$ | 2 w% Pt–$TiO_2$[b] |
|---|---|---|
| Rates (moles $CH_4$/g/s)[a] | $1.7 \times 10^{-7}$ | $1.4 \times 10^{-8}$ |
| Dispersion ($N_{surface}/N_{bulk}$)[c] | 0.052 | 0.24 |
| TOF (Rates/($N_{surface}$/g)) | $3.2 \times 10^{-4}$ | $5.8 \times 10^{-4}$ |
| $\tau$ (s) | 91 | $\leq 2$[d] |
| $\theta$ ($N_{intermediates}/N_{surface}$) | $3 \times 10^{-2}$ | $\leq 1 \times 10^{-3}$[d] |

[a] Reaction conditions: $H_2/CO = 3$, 1 bar total pressure, $T = 225°C$.

[b] Reduced at 225°C, i.e., *not* suffering from $TiO_2$-induced suppression of CO chemisorption.

[c] As measured from *in situ* $^{12}CO/^{13}CO$ exchange at 100°C, assuming a stoichiometry $CO_{ad}/Ni(Pt) = 1/1$ (*8*).

[d] The upper limit for $\tau$ and $\theta$ derives, in case of platinum, entirely from the accuracy of the area measurement: $\tau = 0 \pm 2$ s at 95% confidence interval (cf. Fig. 3b).

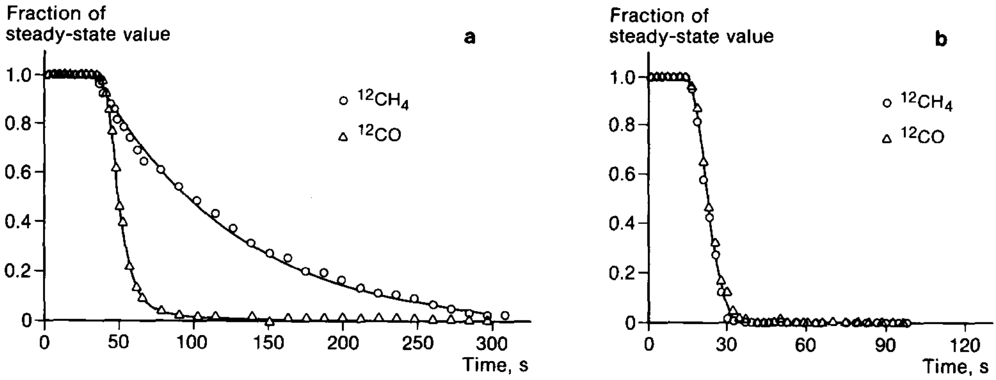

FIG. 3. (a) $^{12}CH_4$ response when switching from $^{12}CO/H_2$ to $^{13}CO/H_2$ over *nickel*. The production of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere continues for approximately 100 s. (b) $^{12}CH_4$ response when switching from $^{12}CO/H_2$ to $^{13}CO/H_2$ over *platinum*. In $^{13}CO/H_2$ atmosphere the production of $^{12}CH_4$ ceases immediately.

ered surface to $^{13}CO(g)$ only part of the $^{12}C$-containing intermediates will leave the surface as $^{12}CH_4(g)$. The remainder will convert back and leave the surface as $^{12}CO(g)$ (Fig. 4). Two features pertaining to methanation are noteworthy. First, at the prevailing low temperature and conversion, the overall reaction is essentially unidirectional ($R_+/R_- > 10^4$). Second, CO exchange is observed to be fast (*8*), i.e., $r_{-1} \gg r_i$ with $r_i$ being the first essentially unidirectional step in the pathway (Fig. 4). It emerges from Fig. 4 that under these conditions the quantity $\theta$ quoted in the table and measured from the $CH_4$ transient reflects the coverage in all surface intermediates located at the right-hand side ("downstream") of the first unidirectional step, *i*, in the reaction pathway.

A mechanistic *interpretation* of our results originates when we make two assumptions:

1. Both on nickel and platinum the first unidirectional step pertains to C–O bond rupture.

2. The difference in reactivity, $\tau$, of the "downstream" intermediates derives from a difference in their composition, with the more reactive intermediates being richer in hydrogen.

On the strength of these two assumptions we infer from our results that the intermediates involved in the C–O bond rupture step have different compositions formally:

$$\rightleftarrows CH_xO \xrightarrow[-H_2O]{r_i} CH_x \rightleftarrows \ldots\ldots\ldots\ldots \text{(Ni)}$$

$$\rightleftarrows CH_yO \xrightarrow[-H_2O]{r_i} CH_y \rightleftarrows \ldots\ldots\ldots\ldots \text{(Pt)}$$

with

$$x < y.$$

An interpretation consistent with earlier propositions (*1*, *4*, *5*) arises when taking $x$ equal to zero.

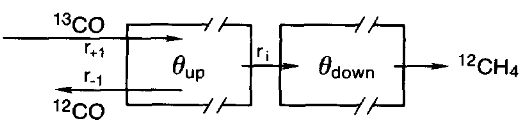

FIG. 4. In $^{13}CO/H_2$ atmosphere the $^{12}C$-containing intermediates leave the surface as $^{12}CH_4$ *and* $^{12}CO$. For $r_{-1} \gg r_i$ the $^{12}CH_4$ transient exclusively senses $\theta$ and $\tau$ of the *downstream* intermediates.

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