A Comparison of Nickel- and Platinum-catalysed Methanation, using Transient-kinetic Methods

C.-H. Yang, Y. Soong and P. Biloen*

Chemical and Petroleum Engineering Department, University of Pittsburgh, Pittsburgh, PA 15261, U.S.A.

Transient-kinetic experiments reveal that the surface intermediates on platinum exhibit lifetimes and abundances which are two orders of magnitude lower than on nickel.

On abruptly changing the flow of ^{12}CO–H_2 over nickel or platinum to a flow of ^{13}CO–H_2 the system responds by changing its production from $^{12}CH_4$ to $^{13}CH_4$. Figure 1 and Figure 2 show the responses over nickel and platinum respectively. A noteworthy feature is that with nickel the production of $^{12}CH_4$ in the ^{13}CO–H_2 atmosphere continues for some 100 s, whereas with platinum it ceases immediately.

With regard to the analysis of transient responses we note that the continued production of $^{12}CH_4$ in the ^{13}CO–H_2 atmosphere (Figure 1) is derived from ^{12}C-containing surface intermediates.[1,2] The integrated production corresponds to the total number of intermediates, and it is represented by the area bounded by the curves for the ^{12}CO and the $^{12}CH_4$ transients. A further analysis[3] reveals that this area represents only those surface intermediates which do not convert back into ^{12}CO, i.e., the intermediates located 'downstream' of the first unidirectional step in the reaction pathway. On the assumption that there is one predominantly abundant surface

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 (mol CH$_4$ g^{-1} s^{-1})[a]	1.7×10^{-7}	1.4×10^{-8}
Dispersion ($N_{surface}/N_{bulk}$)[c]	0.052	0.24
TOF (Rates/$N_{surface}$ g^{-1})	3.2×10^{-4}	5.8×10^{-4}
τ(s)	91	$\leqslant 2^d$
θ($N_{intermediates}/N_{surface}$)	3×10^{-2}	$\leqslant 1 \times 10^{-3}$ [d]

[a] Reaction conditions: $H_2/CO = 3$; 1 bar total pressure; $T = 225$ °C; $F(H_2 + CO) = 2.4$ nl h^{-1}; catalyst 0.61 g (Ni–SiO$_2$) or 0.91 g (Pt–TiO$_2$). [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 stocheiometry CO$_{ad}$/Ni(Pt) = 1. Refs. 3 and 4. [d] The upper limit for τ and θ derives, in the case of platinum, entirely from the accuracy of the area measurement: $\tau = 0 \pm 2$ s at 95% confidence interval (cf. Figure 2).
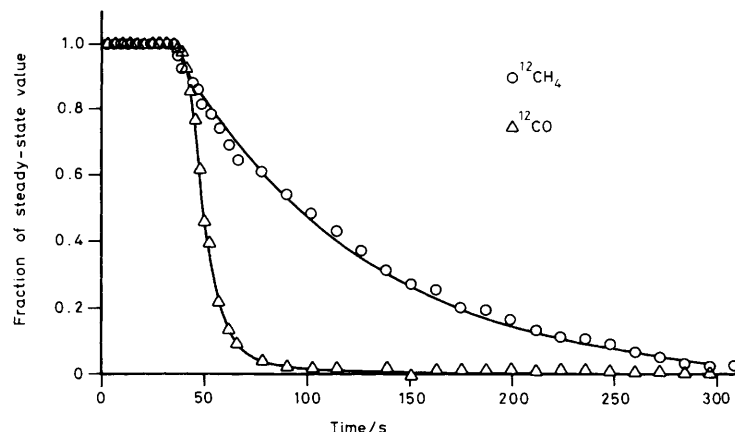
Figure 1. $^{12}CH_4$ response when switching from $^{12}CO-H_2$ to $^{13}CO-H_2$ over nickel. The production of $^{12}CH_4$ in the $^{13}CO-H_2$ atmosphere is derived from ^{12}C-containing surface intermediates and continues for approximately 100 s.
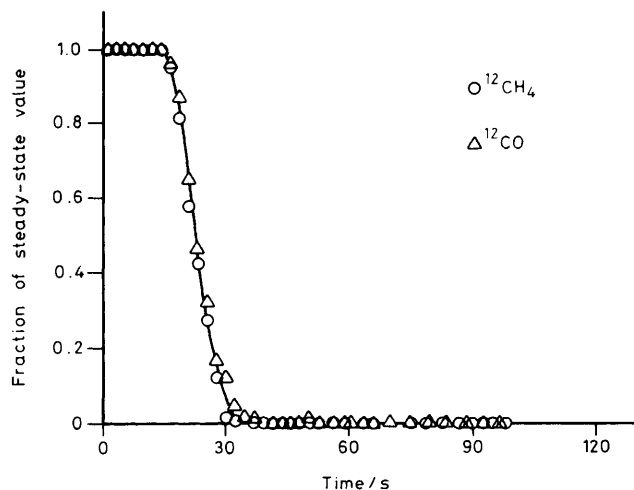
Figure 2. $^{12}CH_4$ response when switching from $^{12}CO-H_2$ to $^{13}CO-H_2$ over platinum. In the $^{13}CO-H_2$ atmosphere the production of $^{12}CH_4$ ceases immediately.

intermediate, the time constant (*i.e.* time required to attain e^{-1} of original value) of the $^{12}CH_4$ decay curve reflects the lifetime, τ, of that 'downstream' intermediate.[3] The very fact that we can observe coverages (θ) and lifetimes [$k^{-1} = \tau$ (s)] in these experiments is due to their transient-kinetic nature. We can make these observations at, essentially, steady state

($\theta_{12} + \theta_{13}$ = constant; τ = constant) since the displacement of ^{12}CO is by a species with identical chemical behaviour, *i.e.*, ^{13}CO. The decay of $^{12}CH_4$ is being mirror-imaged by an increase in $^{13}CH_4$ (not shown in Figures 1 and 2), and the total $^{12}CH_4 + {}^{13}CH_4$ production is constant.

Inspection of Figure 1 confirms earlier observations[1,2] that with nickel the lifetime of the 'downstream' intermediates is of the order of 100 s. With platinum (Figure 2) the lifetime is below the detection limit, *i.e.*, < 2 s. Table 1 shows further comparison of the two metals. At a *comparable* turnover frequency (TOF), approximated by[2,3] equation (1), the

$$TOF = \theta/\tau \tag{1}$$

surface intermediates on platinum are much less abundant ($\theta_{Pt} \ll \theta_{Ni}$) and much more reactive ($\tau_{Pt} \ll \tau_{Ni}$). A mechanistic interpretation of this finding will be given later.[4]

References

1 J. Happel, J. Suzuki, P. Kokayeff, and V. Fthenakis, *J. Catal.*, 1980, **65**, 59.
2 P. Biloen, J. N. Helle, F. G. A. van den Berg, and W. M. H. Sachtler, *J. Catal.*, 1983, **81**, 450.
3 C.-H. Yang, Y. Soong, and P. Biloen, Proceedings of the 8th International Congress on Catalysis, Berlin, 1984, Vol. II, p. 3.
4 C.-H. Yang, Y. Soong, and P. Biloen, *J. Catal.*, submitted.