TRANSIENT-KINETIC STUDY OF NICKEL-CATALYZED METHANATION: PERFORMANCE REPORT

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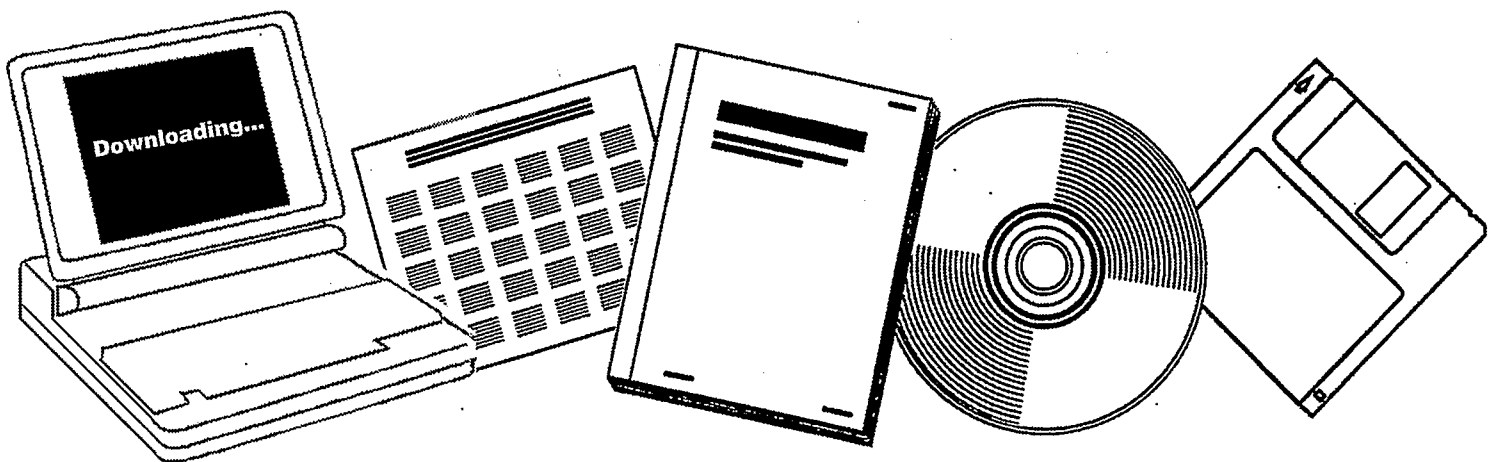
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A TRANSIENT-KINETIC STUDY OF NICKEL-CATALYZED METHANATION

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Performance Report

Budget period: 09-1-83 until 03-01-86

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FOR U.S. DOE

A. Summary of Rounded Off and Published Work

The work summarized below has been performed under the current grant, "The Carbidic Adlayer as Rate-Controlling Factor in CO/H_2 Catalysis," and has been published [10-14].

The notion of a "carbidic" mechanism for methanation (and Fischer Tropsch hydrocarbon synthesis) has been challenged by isotopic transient-kinetic experiments. "Carbidic mechanism" is being utilized in the prevailing context for a global scheme [5]:

$$CO(g) \xrightarrow[-H_2O]{+H} CH_x\text{-ad} \begin{array}{c} \nearrow CH_4(g) \\ \searrow C_nH_{2n(+2)}(g) \end{array}$$
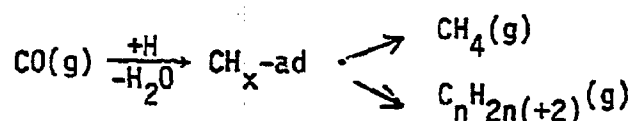
characterized by an inventory of non-oxygen containing ("carbidic") intermediates CH_x-ad, serving as the precursors for methane and higher hydrocarbons. Platinum is known to be a methanation catalysts at the one hand, and being incapable of dissociating CO efficiently at the other hand [15]. It therefore is unplausible that methanation over platinum proceeds via a "carbidic" mechanism. Nickel dissociates CO efficiently and has been identified with the "carbidic" mechanism. Accordingly, an isotopic transient-kinetic comparison of platinum and nickel was performed [13].

Fig. 1a and b give representative transient responses of Ni and Pt. In the pertaining experiments the feed at the inlet of a plug-flow reactor was switched abruptly from $^{12}CO/H_2$ to $^{13}CO/_{12}$. With on-line mass spectrometry the transient decay of $^{12}CH_4$ and the transient ingrowth of $^{13}CH_4$ was monitored at the reactor outlet. The transient response of platinum and nickel is clearly different. When changing from $^{12}CO/H_2$ to $^{13}CO/H_2$, the production of $^{12}CH_4$ over platinum ceases immediately, whereas over nickel it continues for some
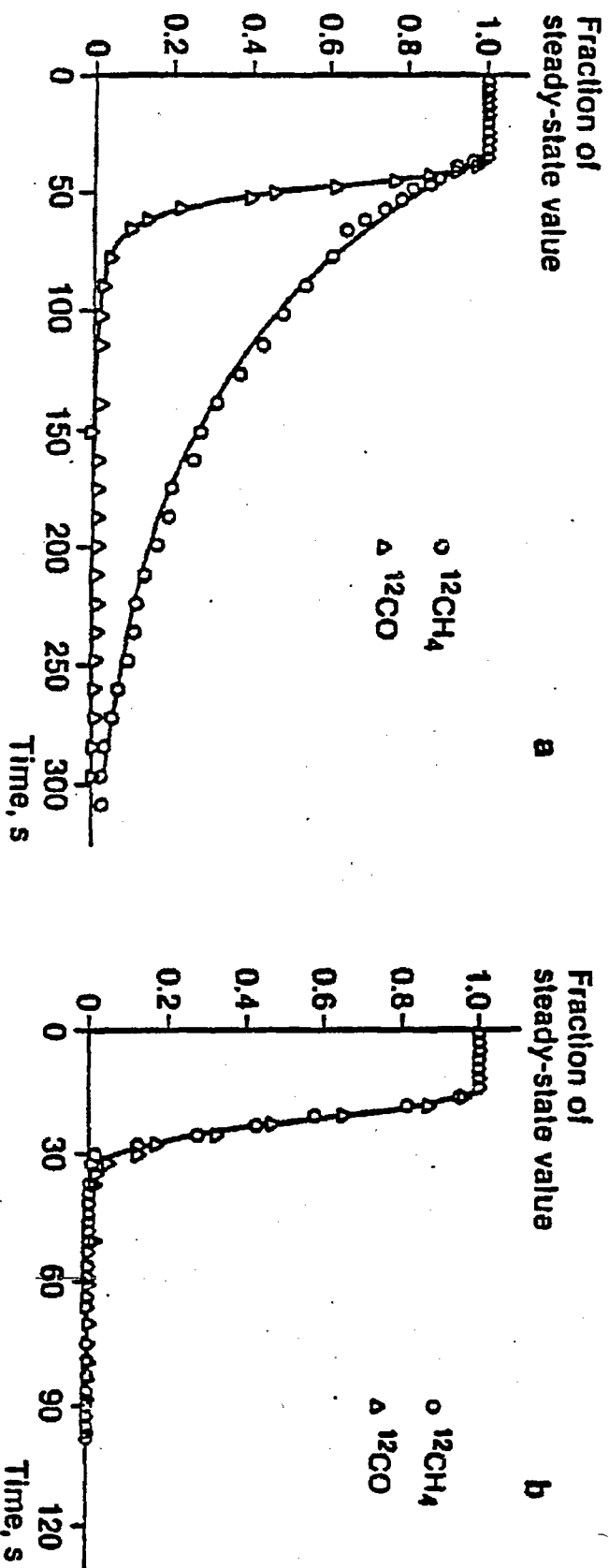
FIG. 1. (a) $^{12}CH_4$ response when switching from $^{13}CO/H_2$ to $^{12}CO/H_2$ over *nickel*. The production of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere continues for approximately 100 s. (b) $^{12}CH_4$ response when switching from $^{13}CO/H_2$ to $^{12}CO/H_2$ over *platinum*. In $^{13}CO/H_2$ atmosphere the production of $^{12}CH_4$ ceases immediately. From (13).

Fraction of
steady-state value

○ $^{12}CH_4$
△ ^{12}CO

a

Time, s

Fraction of
steady-state value

○ $^{12}CH_4$
△ ^{12}CO

b

Time, s

2

100 s (Fig. 1a and b). Noteworthy is that reaction conditions have been selected which lead to turn-over-frequencies (TOF's) which are very similar for Ni and Pt.

The data have been analyzed starting from the response of a single unidirectional elementary step:

$$CO(g) \xrightarrow{R} N_c, \tau_c \xrightarrow{R} CH_4(g)$$
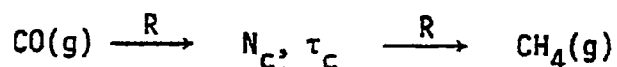
In response to a switch from ^{12}CO to ^{13}CO the abundancy of ^{12}C-containing surface intermediates (abundancy N_{12}, average lifetime τ) will decay:

$$R = \frac{N}{\tau} \tag{1}$$

$$\frac{dN_{12}}{d\tau} = -\frac{N_{12}}{\tau} \tag{2}$$

For the lifetime, τ, of the intermediates it is immaterial whether they are being surrounded by ^{12}C- or ^{13}C-containing surface intermediates. The quantity τ in (2), therefore, is independent of N_{12}, and (2) integrates into:

$$N_{12} = N\ell^{-\frac{t}{\tau}} \tag{3}$$

with $N = N_{12} + N_{13}$ being the total coverage of C-containing intermediates at steady state. The decay of N_{12} is being observed as a decay of the rate of $^{12}CH_4$ production at the reactor outlet, R_{12}:
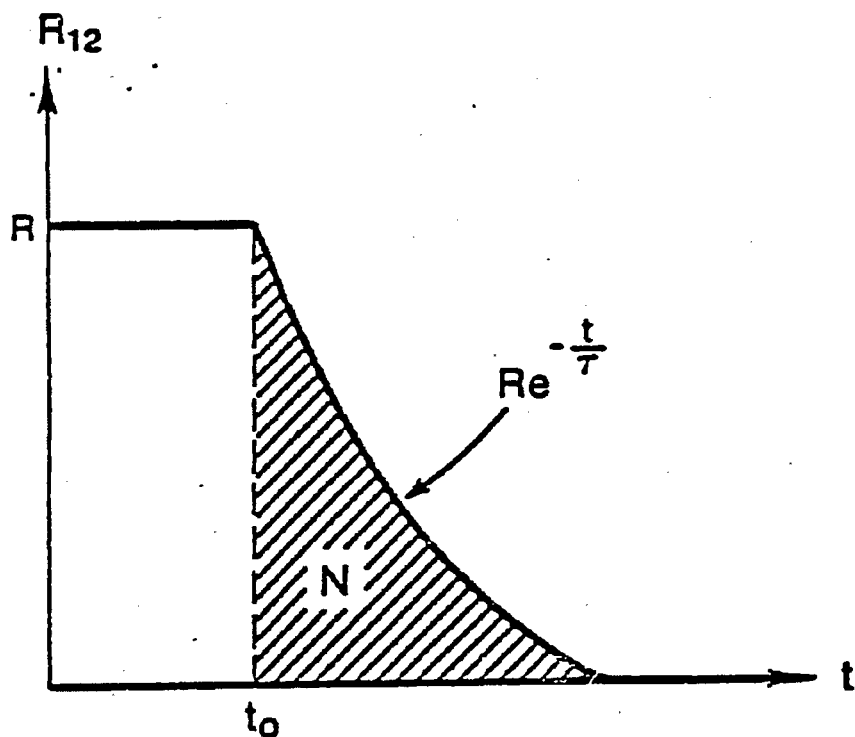
$$R_{12} = R\ell^{-\frac{t}{\tau}} \tag{4}$$

FIG.2 . Production of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere derives from ^{12}C-containing surface intermediates. The decay constant reflects the lifetime (τ), the integrated production gives the abundancy (N) of the surface intermediates from (13).
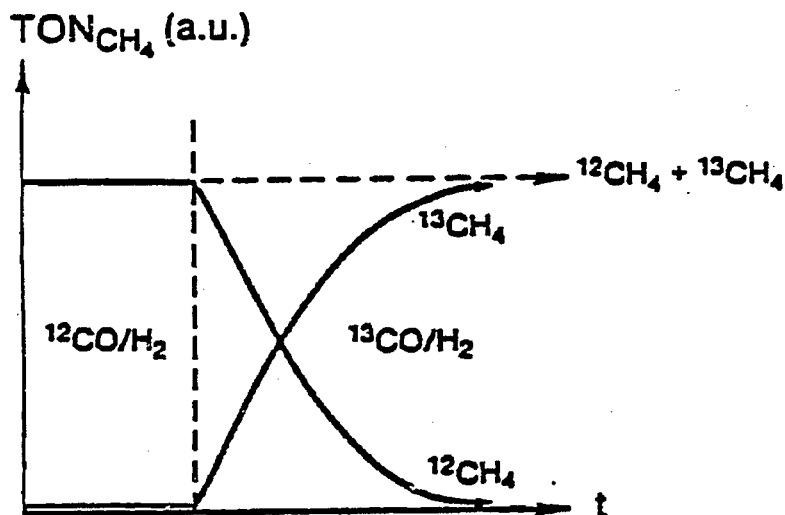

FIG.3 . Replacing ^{12}CO by ^{13}CO allows for the observation of the full transient-kinetic information without disturbing steady-state catalysis; neither the total CH_4 production nor τ is being affected from (13).

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with $R = R_{12} + R_{13}$ being the methanation rate at steady state: Figs. 2 and 3. From a comparison of Fig. 1a and Fig. 1b it follows that the lifetime of platinum-bonded intermediates is some two orders lower than that of nickel-bonded intermediates.

By dividing in the relation $R = \frac{N}{\tau}$ the left- and right-hand side by N_s, the number of surface-exposed atoms, one obtains:

$$TOF = \frac{\theta}{\tau} \tag{5}$$

With $TOF_{Pt} = TOF_{Ni}$ and $\tau_{Pt} \ll \tau_{Ni}$ one obtains:

$$\theta_{Pt} \ll \theta_{Ni} \tag{6}$$

The two orders difference in magnitude of τ and θ at comparable TOF support the notion of a different reaction mechanism being operative over platinum, which is being discussed further in [13].

In separate work, not covered by the current grant, the notion of a carbidic mechanism for the higher hydrocarbon (FT) synthesis has been challenged. Fig. 4 summarizes a pertinent result. The incorporation of ^{12}C in hydrocarbons continues after replacement of $^{12}CO_{ad}$ by $^{13}CO_{ad}$ (see also below). Accordingly, CH_x-ad rather than CO-ad precursors feature in the steady-state(!) production of hydrocarbons.

In preliminary transient-kinetic experiments [8] we observed coverages in carbidic intermediates which were generally very low ($0.01 \leq \theta \leq 0.1$). Accordingly, we formulated the hypothesis that at "normal" (high pressure) steady-state catalysis the majority of the surface was being blocked by irreactive byproducts. Post-reaction examination of nickel surfaces with AES
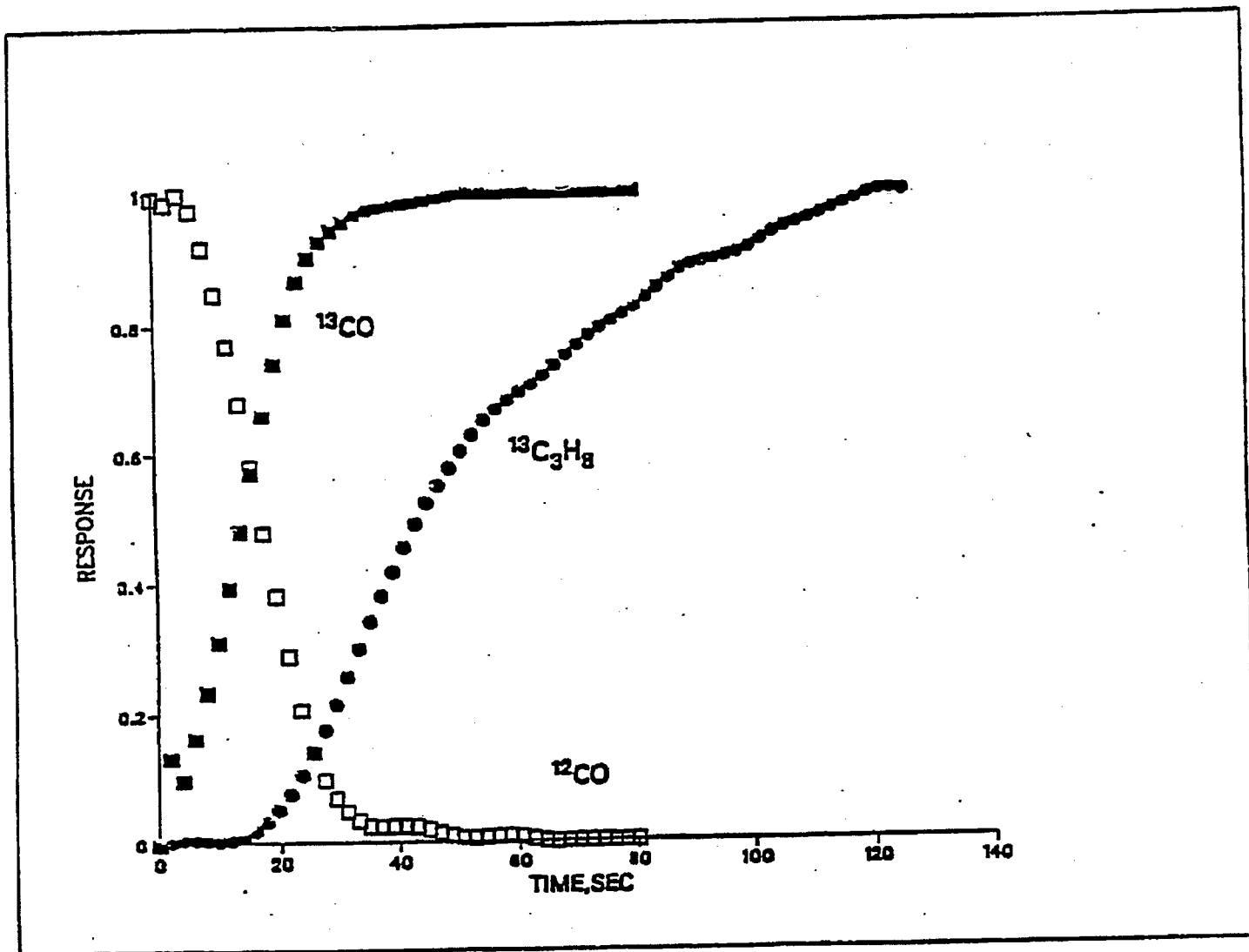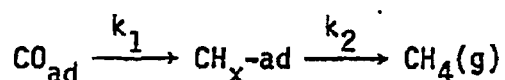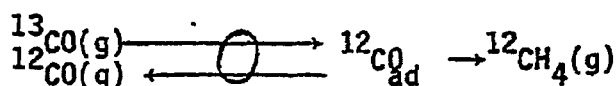
Fig. 4. The incorporation of ^{12}C in C_3H_8 continues after removal of all $^{12}CO_{ad}$ from the surface.

however led Goodman et al. [16-18] to a different conclusion, i.e., low coverages in CH_x-ad deriving from a low rate constant of production (k_1) compared to the rate constant of consumption (k_2):

$$CO_{ad} \xrightarrow{k_1} CH_x\text{-ad} \xrightarrow{k_2} CH_4(g)$$

Similar conclusions were reached by Gardner and Bartholomew [27] and by Underwood and Bennett [28]. A focal point of the work under the current grant, accordingly, was to challenge our hypothesis. This was done by counting in-situ the number of surface-exposed (unblocked) metal atoms via $^{12}CO/^{13}CO$ exchange [10].

The ^{12}CO stream was traced with a 5% amount of Ar: $^{12}CO(Ar)$. When switching a steady-state reaction conditions from $^{12}CO(Ar)/H_2$ to $^{13}CO(He)/H_2$ there is a noticeable delay between the disappearance of ^{12}CO and Ar at the reaction outlet: Ar decays first (Figure 5). The effect arises from the reactor containing an inventory of adsorbed CO which is not being paralleled by an inventory of adsorbed Ar. Entering ^{13}CO displaces $^{12}CO_{ad}$ in a very rapid exchange process:

$$\begin{array}{c} ^{13}CO(g) \\ ^{12}CO(g) \end{array} \rightleftharpoons \bigcirc \longrightarrow \; ^{12}CO_{ad} \rightarrow \; ^{12}CH_4(g)$$

The (chromatographic, frontal elution) delay in Fig. 5 does not derive from the rate of exchange, but rather obeys [10]:
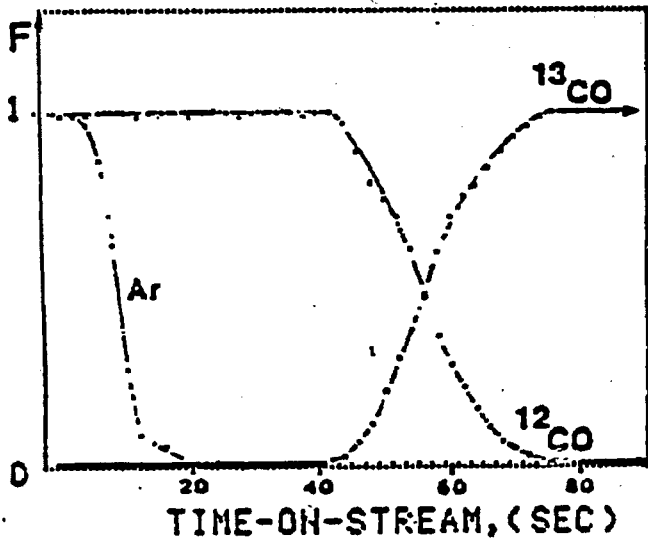
$$\Delta t = \frac{V}{F} \tag{7}$$

Figure 5: Although ^{12}CO and Ar are being switched off simultaneously at the reactor inlet, ^{12}CO arrives delayed at the reactor outlet. This chromatographic effect is due to ^{13}CO-induced desorption of $^{12}CO_{ad}$. We use this effect routinely to measure coverages in CO_{ad} during the reaction (at higher SV conditions) from (10).
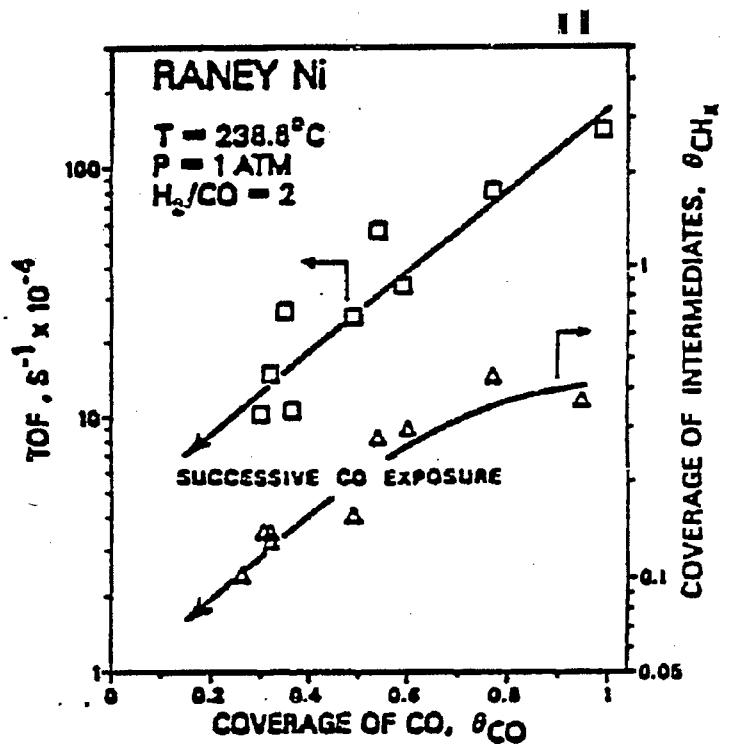
Figure 7: Successive carbon depositions (short exposures to CO at 300°C) lead to a proportional decrease of CO_{ad}, $CH_{x,ad}$ and TOF, indicative of a surface blocking process which does not change the intrinsic properties of the unblocked surface (i.e., k=c) from (10).
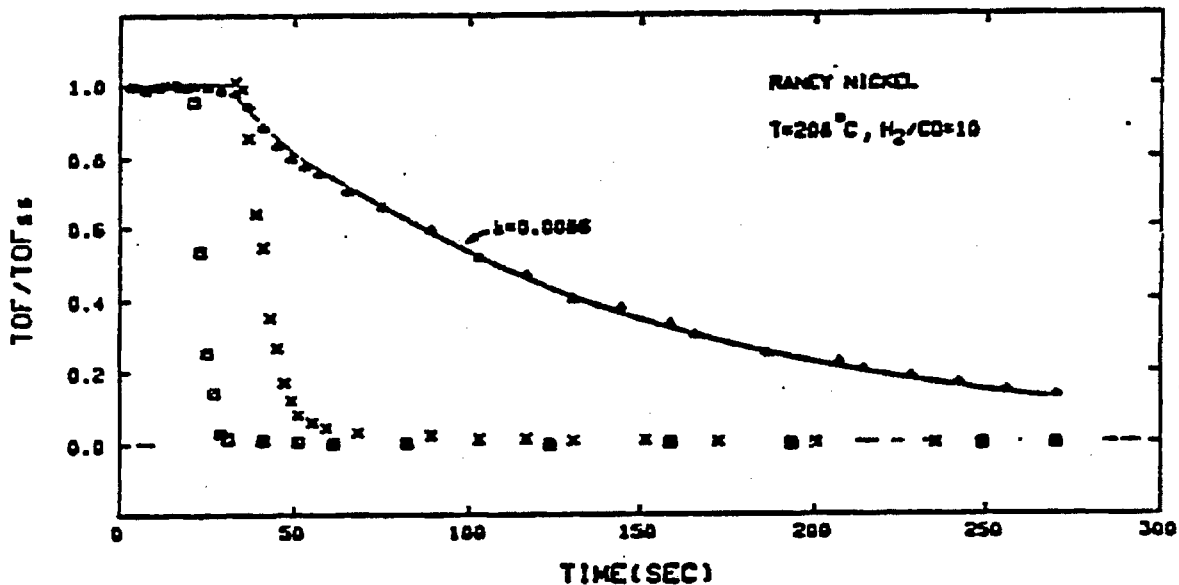

Figure 6: Transient response in Ar (□), ^{12}CO (×) and $^{12}CH_4$(▲), accompanying a $^{12}CO(Ar)/H_2$ to $^{13}CO/H_2$ switch. The $^{12}CH_4$ response is close to purely exponential from (10).

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in which V the magnitude of the reservoir of CO_{ad} (ml stp) and F the inlet flow rate (ml stp/s). As justified more fully in [10] it follows (Fig. 6) that in-situ observation of the chromatographic delay, Δt, gives a measure for the amount of CO_{ad} present at the surface during steady-state catalysis.

In separate experiments it was established that deliberate surface blocking (short successive exposures to pure CO at 300°C) leads to a proportional decrease of the TOF and the amount of CO_{ad} present during steady-state catalysis: Fig. 7. It therefore follows that, at reaction conditions, CO does not adsorb on top of surface blocking C_{ad}. Accordingly, a high value of CO_{ad} provides evidence of a largely unblocked surface.

Ample evidence was obtained [10] that on virtually unblocked surfaces (θ_{CO} high) coverages in carbidic intermediates can be very low, especially at lower temperatures (190°C $\leq$ T $\leq$ 240°C). We therefore had to discard our starting hypothesis: low intermediate coverages are not merely the result of an irreactive carbidic adlayer, blocking unselectively the majority of the catalyst surface [10].

Having established that unselective surface blocking is not rate controlling within the first few hours of exposure to CO/H_2, measurements were extended to significantly longer times-on-stream. The work focused on Raney Nickel, with the result summarized in what follows.

A Raney nickel catalyst, when exposed to hydrogen-lean syngas, initially declines at a rate of approximately 0.2%/h. In an approximately 120h period the decline rate levels off at a value of approximately 0.03%/h. Based on the existing literature [17,19-21] an "adlayer deterioration" hypothesis was formulated:

• concurrent with reactive carbidic intermediates site-blocking "carbon" is being produced. This is responsible for the initially high decline rate (0.2%/h). The site-blocking "carbon" is being removed from the surface in a slow hydrogenation reaction, resulting in an average residence time at the surface of the order of 120 h. Accordingly, it takes approximately 120h to reach steady state, i.e., a balance between the "carbon" production and removal. The residual decline of 0.03%/h is due to irreversible deterioration of "carbon" into irremovable "graphite".

The hypothesis subsequently was challenged by conducting transient-kinetic experiments in a repetitive mode during the entire line-out period. The results disproved the above-formulated hypothesis, as shown below.

Aging is found to be reflected in the transient behavior: the transients develop a "tail": Fig. 8. These transients are found to be described by:

$$F_{13_{CH_4}} = C_1 e^{-(t/\tau_1)} + C_2 e^{(-t/\tau_2)} \tag{8}$$

Such a behavior is characteristic for CH_4 originating via two _parallel_ pathways. This could be confirmed by frequency-response experiments, fully described in [12].

Whereas the time constants of the two parallel pathways are essentially independent of aging:

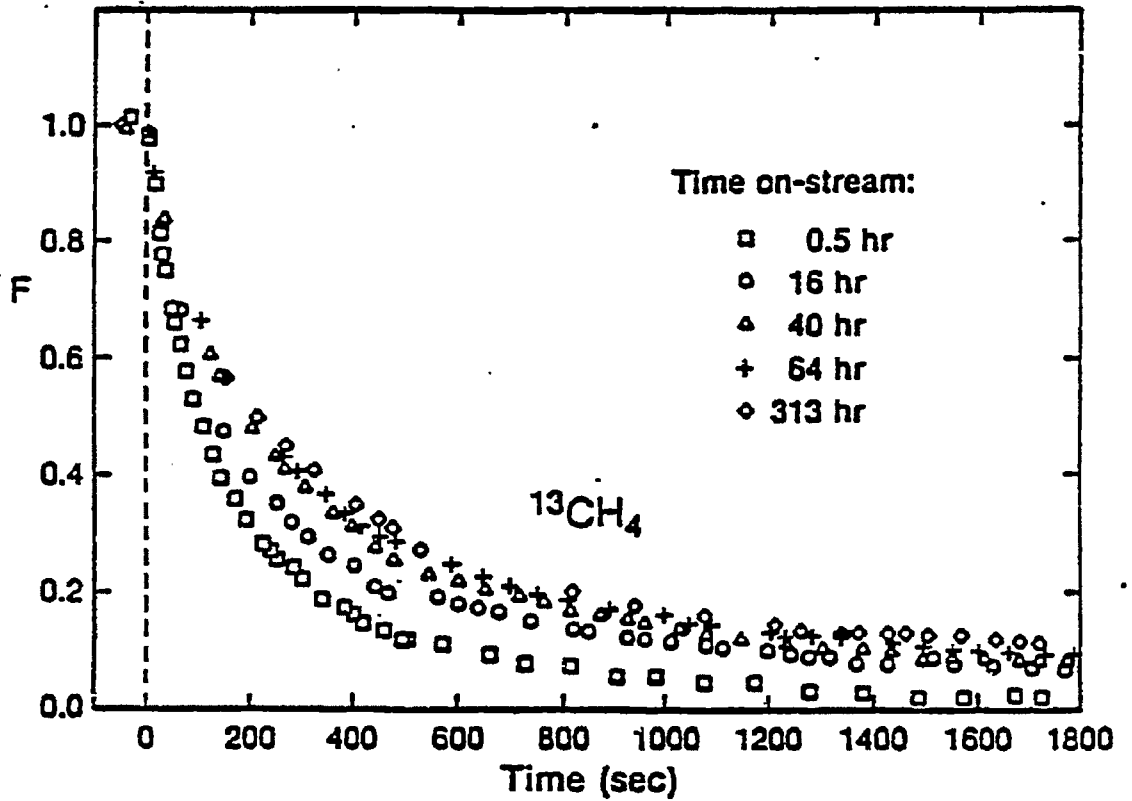$$\tau_1 = 120 \pm 20 \text{ s}$$

$$\tau_2 = 850 \pm 200 \text{ s}$$

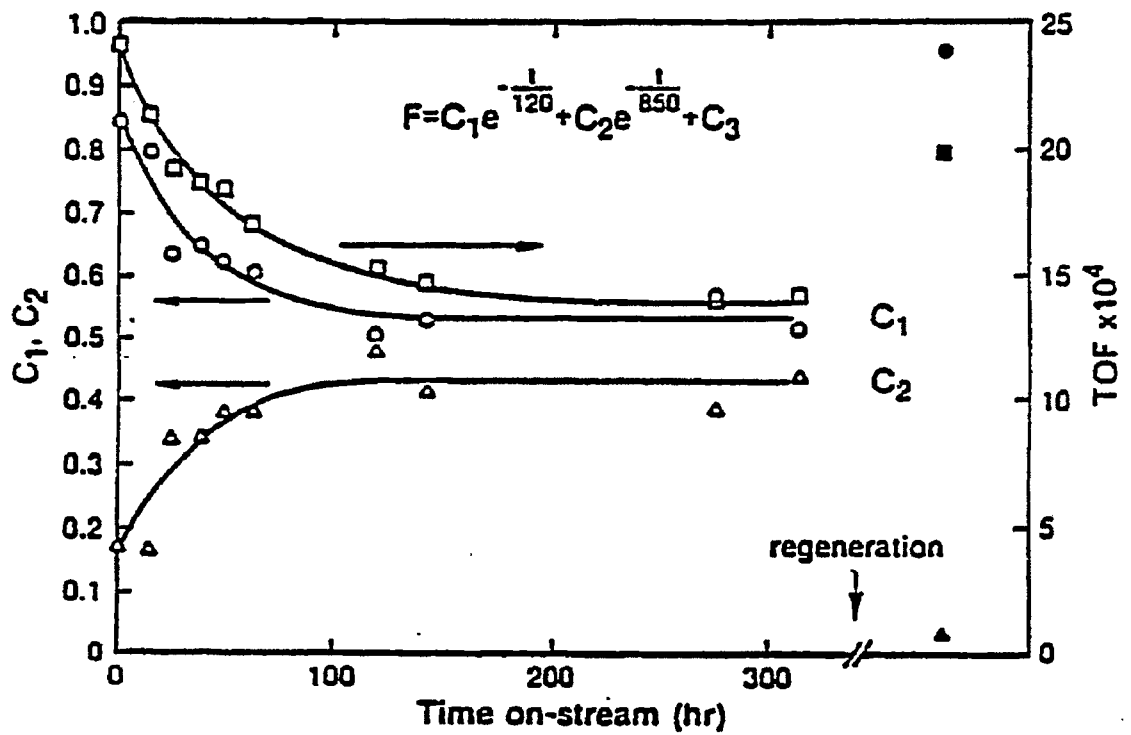FIG.8 . As a result of the aging a tail develops from (12).

$$F = C_1 e^{-\frac{t}{120}} + C_2 e^{-\frac{t}{850}} + C_3$$

Figure 9 . Transient behavior (C_1, C_2) lines out *concurrent* with the steady-state TOF from (11).

the relative contribution of the two pathways is observed to change upon aging: the coefficients C_1 and C_2 in (8) are slowly changing in time (Fig. 9).

What emerges is a situation of a "slow" pathway $(\tau_2 = 850$ s) taking over from a "fast" pathway $(\tau_1 = 120$ s) over a period of 120 h. The total surface coverage, corresponding to pathway 1 and 2 combined, slightly <u>increases</u> over the first 120h period. This, combined with the observation that surface species with a surface residence time of only 850 s do <u>not</u> require 120h to reach steady-state coverage, leads to the conclusion that aging in this particular case is in essence <u>not</u> a process of site blocking but rather a slow "deterioration" of the nickel itself, causing pronounced kinetic heterogeneity [12].

B. Summary of Currently Unfinished Work

As work in the first period of the current grant yielded more and more indications that unselective site blocking is not a major activity-determining factor we changed our focus towards the intrinsic kinetic properties of the nickel-catalyzed methanation pathway. As isotopic transients have the unique capability of furnishing value for θ_{CH_x}, θ_{CO} and θ_H, we set out to determine the behavior of these quantities, with P_{CO}, P_{H_2}, T and the nature of the nickel catalyst being the independent variables. A sample of representative results is presented below.

The amount of CO_{ad} present during steady-state catalysis was determined from the amount of $^{12}CO_{ad}$ removed in $H_2/^{13}CO$ atmosphere (cf. Fig. 5). Pertinent results are being summarized in Figs. 10 - 12. It appears that up to T = 250°C, CO is present at close-to-saturation coverage, conform earlier IR evidence [4,22,23].

The total amount of "H_{ad}" (i.e., H bonded to metal and H bonded to carbon) was estimated likewise, i.e., from the amount of H_2 and HD removed in D_2/CO atmosphere. Inconsistent results orginate. Fig. 13 (i.e., ml H_2 vs. P_{H_2}) suggests imcomplete coverage, whereas Fig. 14 (i.e., ml H_2 vs. P_{CO}) suggests saturation coverage. In addition, the value obtained for "H_{ad}" exceeds that for CG_{ad}. Coexistence of large amounts of CO_{ad} and "H_{ad}" also has been observed recently by Bell et al. [24].

The amount of carbidic intermediates, CH_x-ad, was estimated from the production of $^{13}CH_4$ in $^{12}CO/H_2$ atmosphere. The amount of CH_x-ad varies significantly and reversibly with P_{H_2} and P_{CO}: Figs. 15,16. Noteworthy is that θ_{CH_x} increases with increasing P_{H_2}, a trend opposite to that observed with post-reaction AES analysis by Goodman et al. [18].

The decay of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere is, for "fresh" catalysts, close to exponential: $F = \exp[-t/\tau]$. Figs. 17-19 describe the variation of τ with P_{H_2}, P_{CO} and T. Fig. 17 is suggestive of a __hydrogenation__ reaction determining the relaxation time.

By conducting back-to-back $D_2/^{12}CO \rightarrow D_2/^{13}CO$ and $H_2/^{12}CO \rightarrow H_2/^{13}CO$ transients we could compare (k, θ) of CD_x intermediates with (k, θ) of CH_x intermediates: Fig. 20. Noteworthy is that at the conditions prevailing in Fig. 20 there is a significant inverse "kinetic" H/D effect: R_{CD_4}/R_{CH_4} ~ 1.3. Surprisingly, the "kinetic" H/D effect turns out to be a θ effect rather than a k effect. This is seemingly inconsistent with a hydrogenation reaction determining the relaxation time ($k = \tau^{-1}$, see above).

The aforementioned results all pertain to 60% w Ni/SiO$_2$. Highlights of results obtained for Raney Nickel and nickel powder are given below.

Fig.21 presents data on the decay of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere ($k = \tau^{-1}$). It appears that the reactivity of the carbidic intermediates varies with the nature of the nickel catalyst.

Fig. 22 presents data on the integrated production of $^{12}CH_4$ in $^{13}CO/H_2$ atmosphere (i.e., on the coverage in intermediates). Again, a significant variation of θ is being observed.

Fig. 23 presents data on the variation in coverage with the ratio H$_2$/CO. The nickel powder behaves seemingly abnormal. However, in doing so it conforms to the trend reported by Goodman et al. [18].
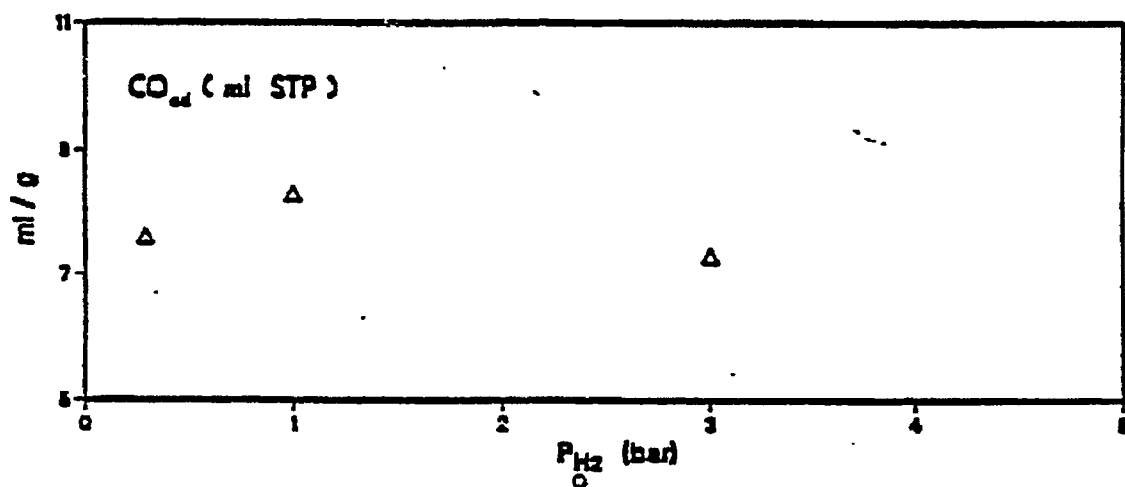
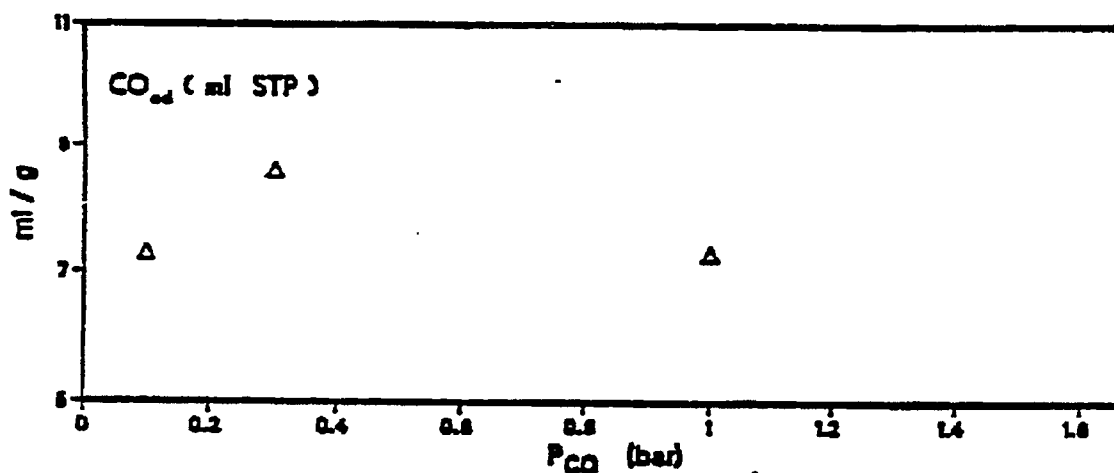Fig. 10. CO_{ad} vs. P_{H_2}. $T = 220\ °C$, $P_{CO} = 0.1$ bar, Catalyst : 60% Ni-SiO$_2$

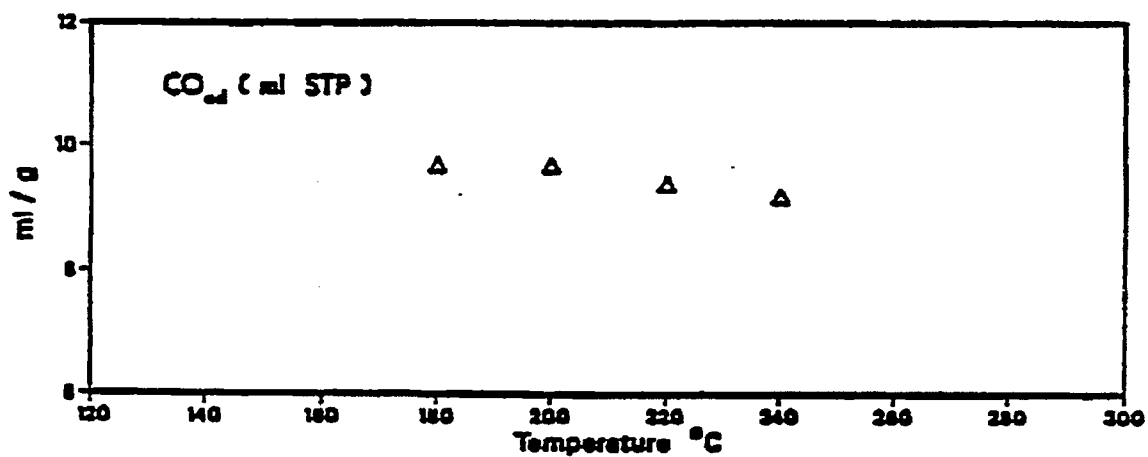Fig. 11. CO_{ad} vs. P_{CO}. $T = 220\ °C$, $P_{H_2} = 3$ bar, Catalyst : 60% Ni-SiO$_2$

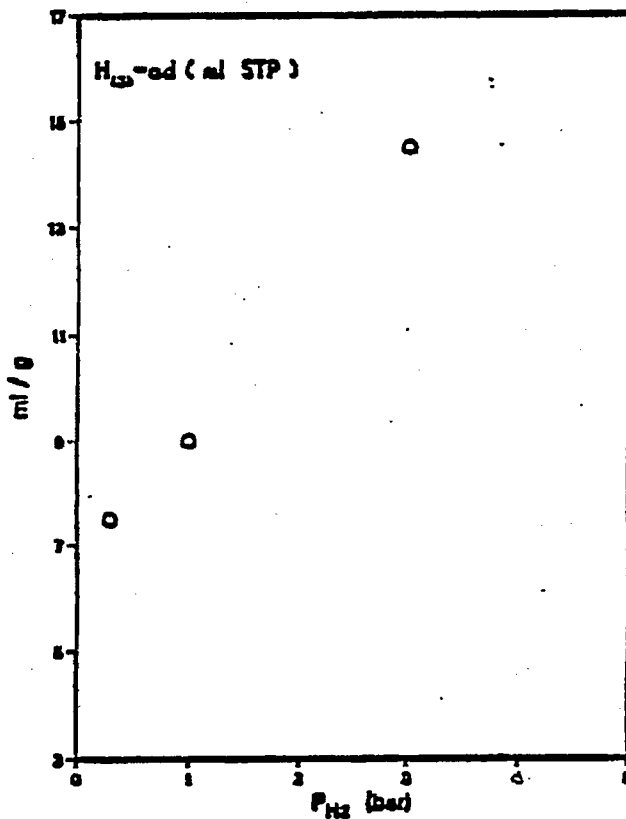Fig. 12. CO_{ad} vs. T. $P_{H_2} = 1$ bar, $P_{CO} = 0.3$ bar, Catalyst : 60% Ni-SiO$_2$

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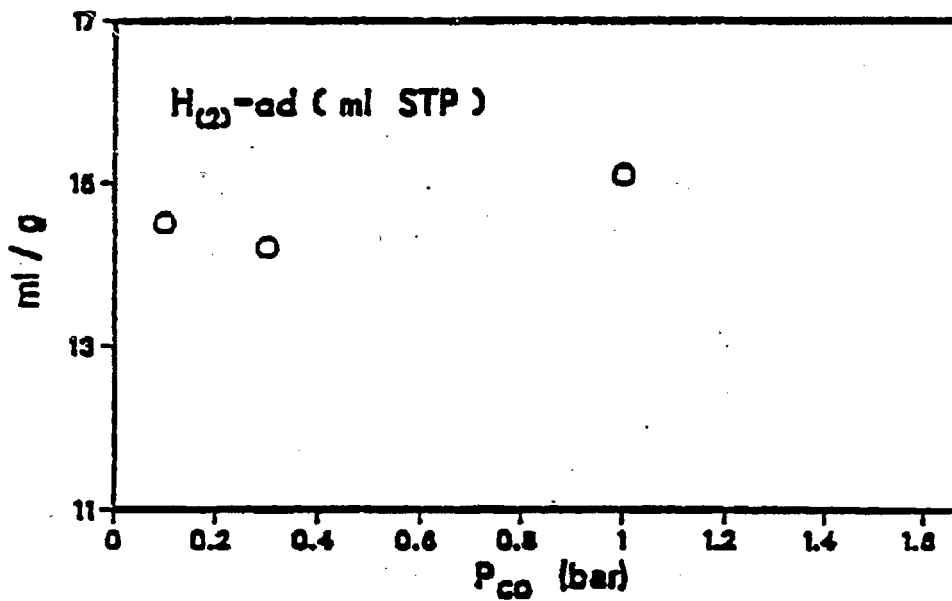Fig. 13. Amount of adsorbed hydrogen versus P_{H_2}. P_{CO}= 0.1 bar, T = 220 °C, Catalyst : 60% Ni-SiO$_2$.

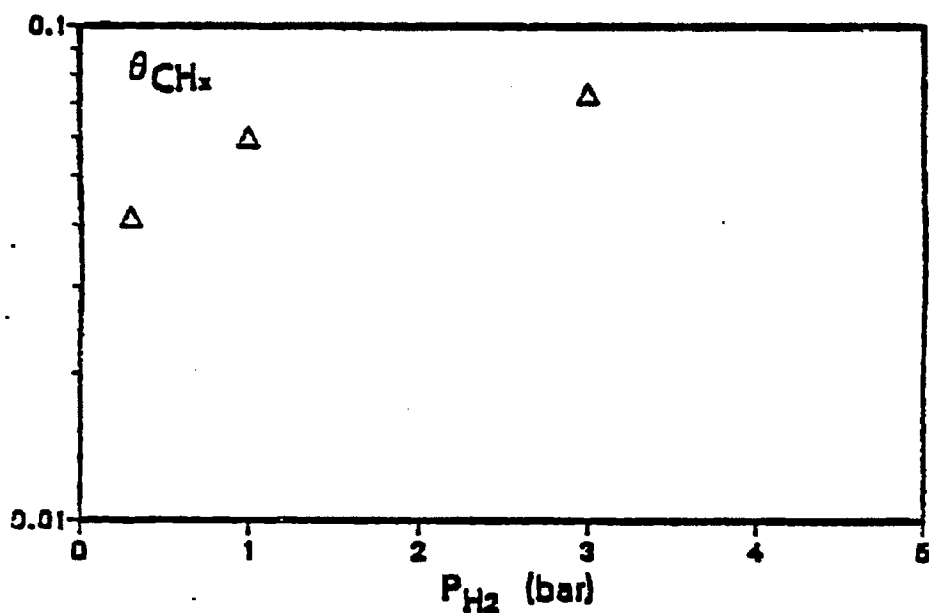Fig. 14. Amount of adsorbed hydrogen versus P_{CO}. P_{H_2} = 3 bar, T = 220 °C, Catalyst : 60% Ni-SiO$_2$.

Fig. 15. Coverage in carbidic intermediates, CH_x , versus P_{H_2} . P_{CO} = 0.1 bar, T = 220 $^{\circ}$C, Catalyst : 60% Ni-SiO$_2$.
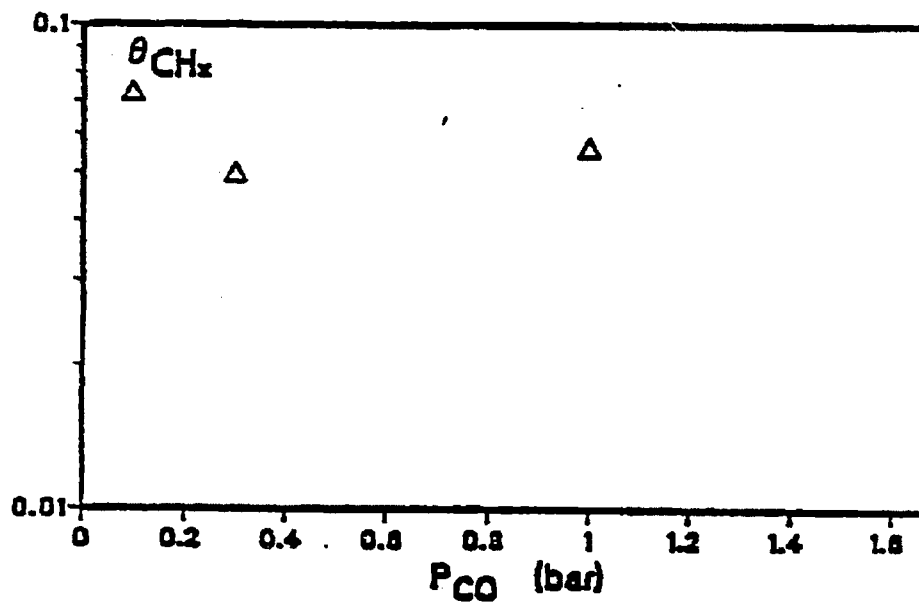

Fig. 16. Coverage in carbidic intermediates, CH_x , versus P_{CO} . P_{H_2} = 3 bar, T = 220 $^{\circ}$C, Catalyst : 60% Ni-SiO$_2$.
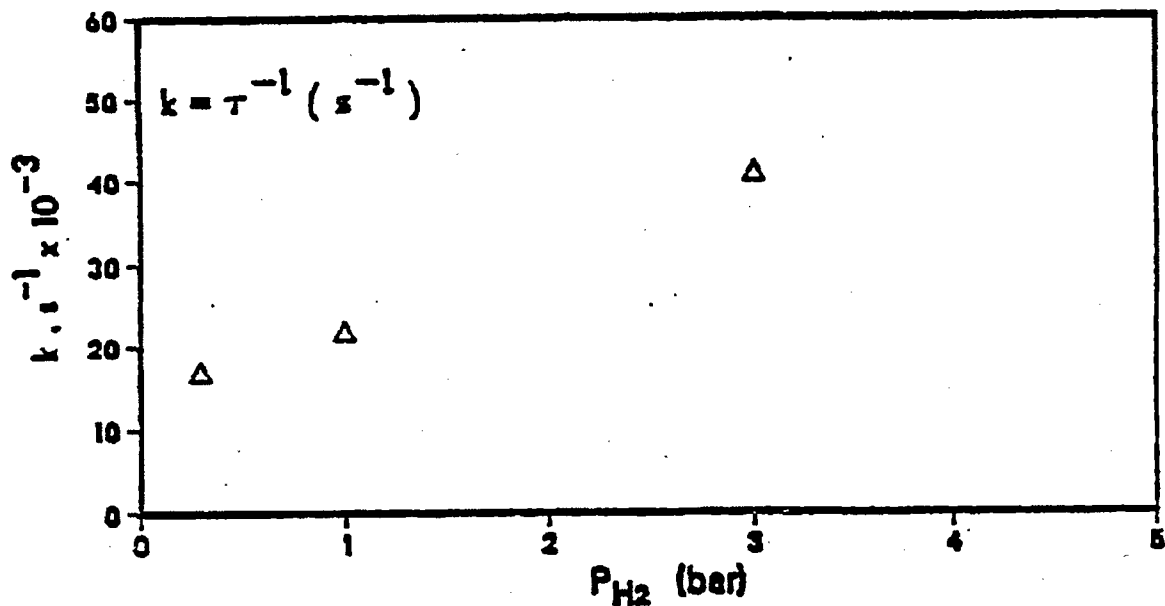
Fig. 17. The reactivity of carbidic intermediates increases with increasing P_{H_2}. P_{CO} = 0.1 bar, T = 220 ^{o}C, Catalyst : 60% Ni-SiO$_2$.
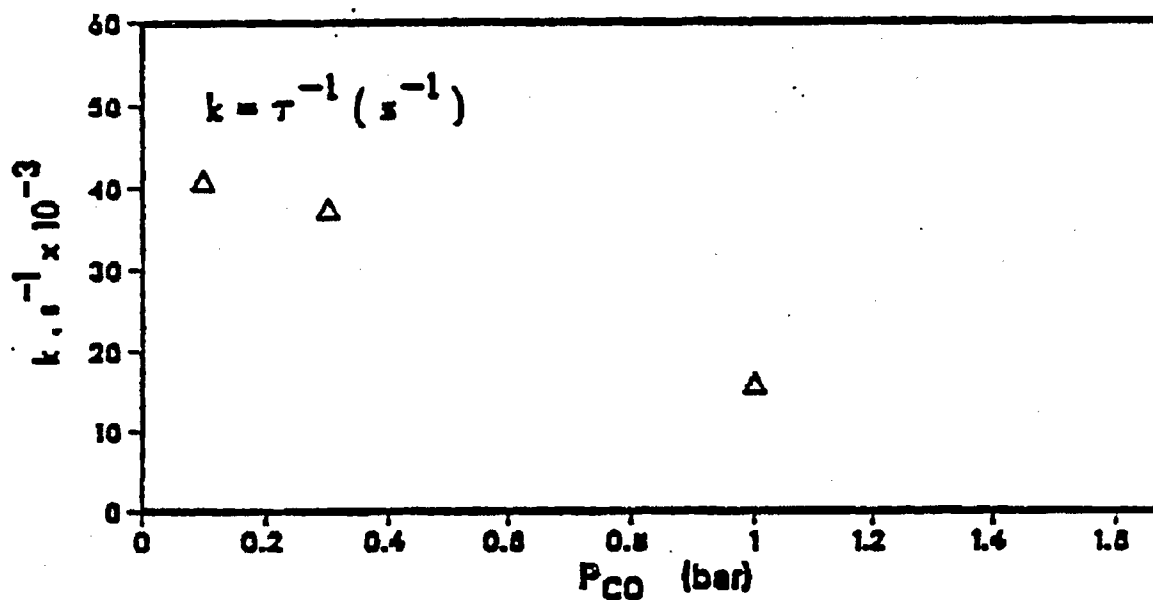

Fig. 18. The reactivity of carbidic intermediates decreases with increasing P_{CO}. P_{H_2} = 3 bar, T = 220 ^{o}C, Catalyst : 60% Ni-SiO$_2$.
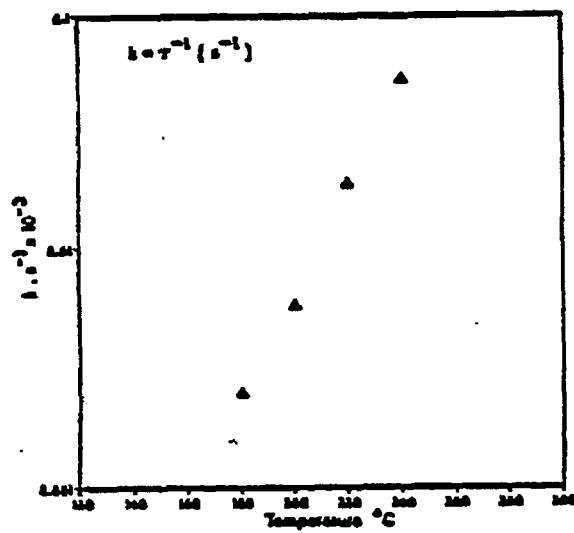
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Fig. 19. The reactivity of carbidic intermediates increases with increasing temperature. $P_{H_2} = 1$ bar, $P_{CO} = 0.3$ bar, Catalyst : 60% Ni-SiO$_2$.
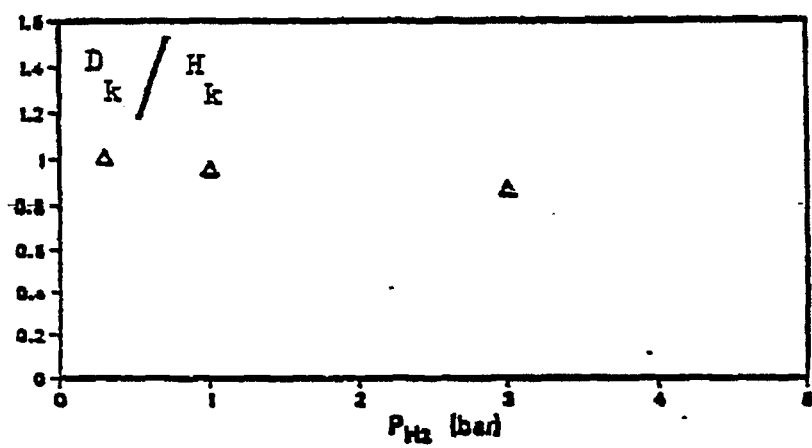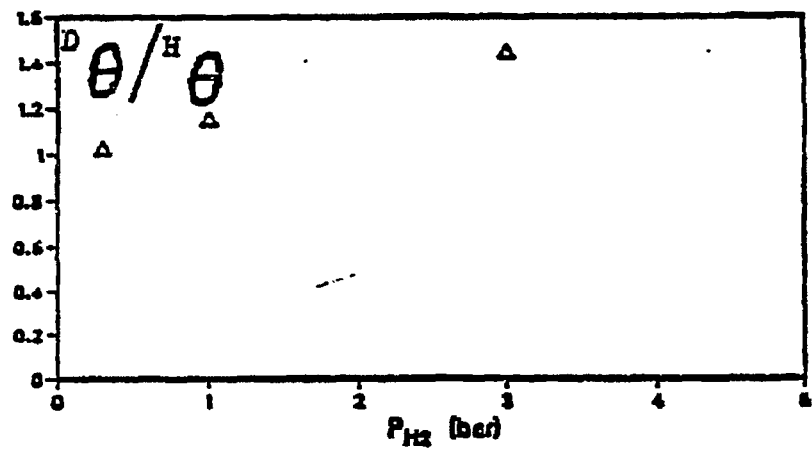

Fig. 20. The inverse kinetic isotope effect ($R_{CD_4}/R_{CH_4} = 1.3$) is a θ rather than k effect, T = 220 ^{o}C, $P_{CO} = 0.1$ bar, Catalyst : 60% Ni-SiO$_2$.
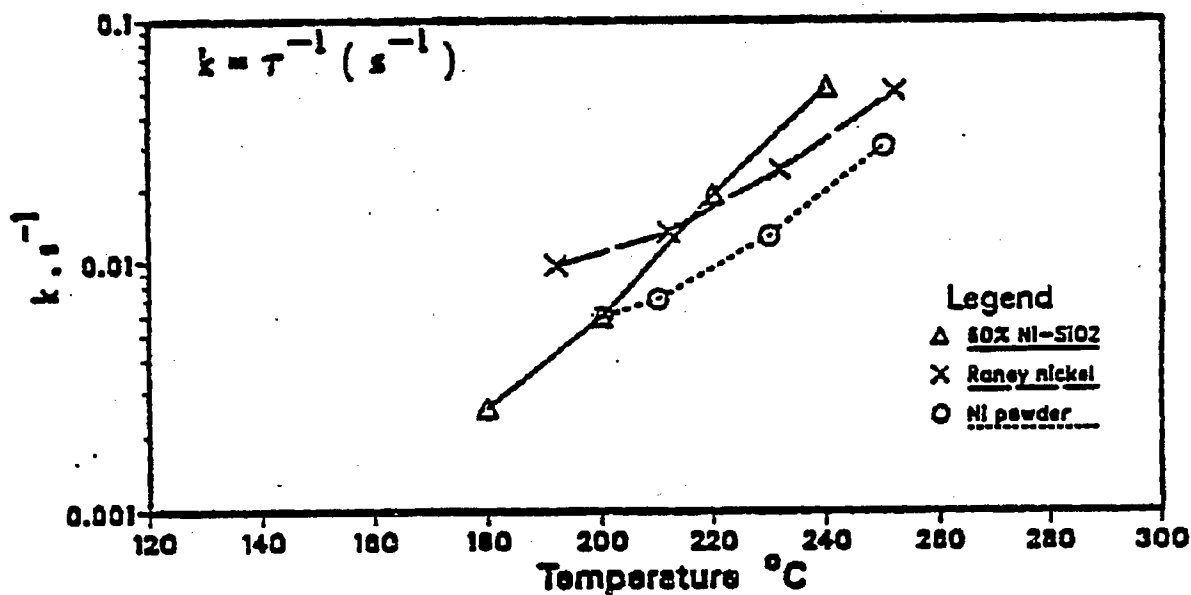
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Fig. 21. Reactivities of carbidic intermediates depend on the detailed nature of the catalyst. For Raney nickel and Ni powder P_{H_2} = 0.75 bar, P_{CO} = 0.25 bar. For 60% Ni-SiO$_2$ P_{CO}= 0.3 bar, P_{H_2} = 1 bar.
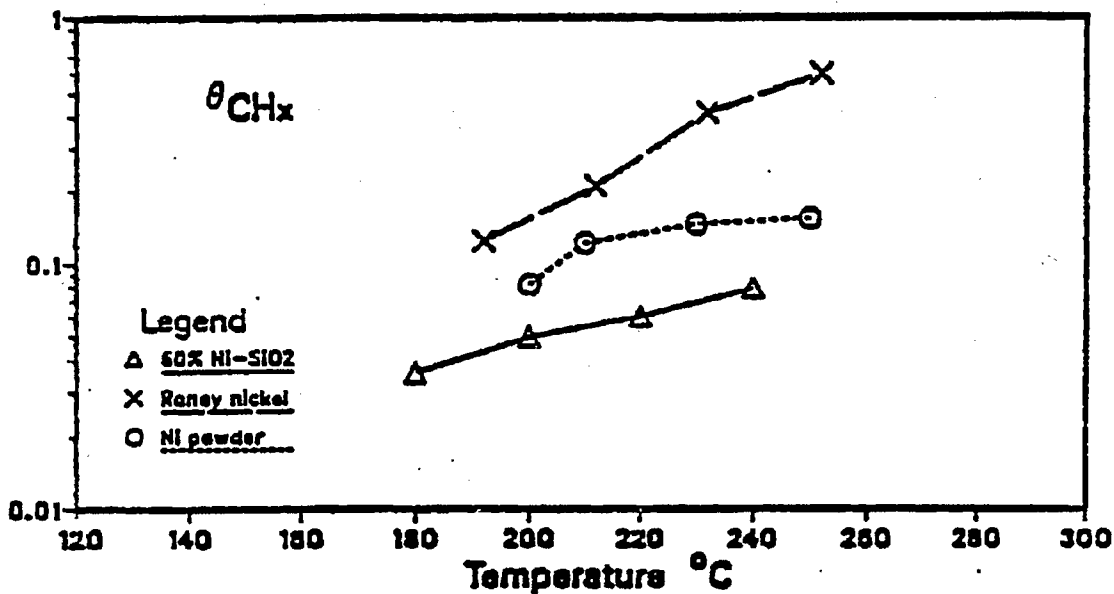

Fig. 22. Coverages in carbidic intermediates depend on the detailed nature of the catalyst. For Raney nickel and Ni powder P_{H_2}= 0.9 bar, P_{CO}= 0.09 bar. For 60% Ni-SiO$_2$ P_{CO} = 0.1 bar, P_{H_2} = 1 bar.

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