Section 7

CARBON FORMATION ON
ALUMINA-SUPPORTED RUTHENIUM CATALYST

7.1   Introduction

Ruthenium is unique among the other Fischer-Tropsch (F-T)
catalysts, such as Fe and Co by not forming stable bulk carbides.[1-4]*
In Section 5 we present experimental evidence that during Fischer-Tropsch
synthesis of hydrocarbons the bulk Fe_2C (Hagg) phases plays an important
role. However, the accumulation of amorphous elemental carbon or
graphite reduces catalyst performance.[5] Similarly, in the case of Ru
catalysts a decrease in methanation activity has been observed and
ascribed to surface coverage with carbonaceous material.[6] Since surface
carbon adspecies may be intermediates in hydrocarbon formation, such as
in Ni catalyzed methanation, it is important to establish in the case
of Ru the type of surface carbon species formed and their reactivity
towards hydrogen.

7.2   Experimental

Using temperature programming techniques, we studied the hydro-
genation of carbon deposited on a Ru/Al_2O_3 catalyst. The carbon was
deposited by cracking ethylene at temperatures ranging from 470 to 715 K
or by disproportionation of CO at 330 to 623 K. About 25 ± 10 mg of
finely powdered catalyst was placed on a frit of a 1/4-inch-diameter

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*References for Section 7 are listed on page 7.7.

"Vycor" microreactor and reduced in situ for 14.5 hr at 668 K and 1 hr at 734 K in 1 atm of flowing hydrogen. For carbon deposition 0.5 cm^3 aliquots of ethylene or 2.85% CO in helium mixture were injected into a helium carrier stream passing over the catalyst. Subsequently, the catalyst bed was cooled to room temperature and the carrier gas changed to hydrogen before temperature programming. The temperature of the catalyst bed was measured by direct contact with a 0.003 in "Chromel-Alumel" thermocouple. The concentration of gas in the reactor effluent was measured by a calibrated quadrupole mass spectrometer.

The alumina-supported 1.5 wt% ruthenium catalyst was highly dispersed. The specific metal surface was calculated to be 200 m^2/g Ru, based on 53 μmol CO uptake at 300 K per gram catalyst and assuming that 1.0×10^{19} CO molecules adsorbed per square meter of reduced ruthenium surface.

7.3.1 Hydrogenation of Carbon Deposited via Cracking of C$_2$H$_4$

Amorphous carbon was deposited on the catalyst by exposure to ethylene at temperatures between 470 and 710 K. Most of the carbon was removed by reaction with hydrogen below 775 K. The temperature programmed surface reaction (TPSR) curves for reaction of hydrogen with the carbon deposits are shown in Figure 7-1 at a heating rate of 45 ± 10 K s^{-1}. In this figure we plot the rate of methane formation against the catalyst bed temperature. In the constant H$_2$ flow stream, the methane formation rate is proportional to the methane concentration in the reactor effluent, which is in turn proportional to the 15 AMU mass spectrometer ion current. The TPSR curve is represented by a strip chart recording of the mass spectrometer signal voltage. The results of the carbon deposition by C$_2$H$_4$ cracking and reaction with H$_2$ are summarized in Table 7-1, where T$_{dep}$ refers to the catalyst bed temperature during C$_2$H$_4$ exposure; T$_p$(15) and T$_p$(28), to the peak temperature

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location during the TPSR experiments with H_2 for AMU 15 (CH_3^+) and AMU 28 ($C_2H_4^+$); A (15) and A (28), to the integrated areas under the TPSR curves for CH_3^+ (Figure 7-1) and $C_2H_4^+$ in arbitrary units of ion current multiplied by time; and ϵ, to the ratio of the methane recovered by TPSR from a deposited carbon layer to methane produced during similar TPSR of chemisorbed CO. As the amounts of carbon (and temperature of deposition) increased from about 0.5 to 6 monolayers, the methane peak temperature shifted from 625 K to more than 725 K. Relatively small, constant amounts of C_2 hydrocarbons were produced during TPSR. They may have originated from C_2H_4 adsorbed onto the Al_2O_3 support.

7.3.2   TPD of CO on Clean and Oxidized Ru/Al$_2$O$_3$

The heterogeneous disproportionation of CO by ruthenium is much slower than CO desorption. A saturation surface layer of CO adsorbed at 300 K on the freshly reduced Ru/Al$_2$O$_3$ catalyst does not yield appreciable quantities of CO_2 during TPSR in He (1 K/s heating rate). The amount of CO_2 produced is about 5% of the amount of CO initially adsorbed on this catalyst. Figure 7-2 shows the CO and CO_2 TPSR curves for CO adsorbed at 300 K. Most of the CO adsorbed at 300 K desorbs with maximum rates observed between 450 K and 640 K.

The rate reaction of CO with oxygen chemisorbed on ruthenium is quite rapid and suggests that this reaction does not limit the rate of carbon deposition. Figure 7-3 shows the result of a TPSR experiment of coadsorbed CO and oxygen adspecies on Ru/Al$_2$O$_3$. Oxygen adatoms were deposited by N_2O exposure to saturation at 390 K before CO adsorption at 300 K. The amount of CO_2 produced was equivalent to the amount of oxygen previously adsorbed. At a heating rate of 45 ± 10 K min^{-1} the maximum reaction rate occurred at $T_p = 430$ K. At this low temperature it is unlikely that reaction of CO with surface oxygen was limiting the evolution of CO_2 during TPSR of chemisorbed CO. For a Langmuir-Hinshelwood

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mechanism, we estimate on the basis of these results an activation
energy of 25 ± 5 kcal mol^{-1} for CO_2 production. In the absence of
chemisorbed oxygen, the dissociation of CO must be limiting the production
of CO_2, i.e., $CO \rightarrow C(a) + O(a)$ followed by $CO + O(a) \rightarrow CO_2$.

7.3.3 Hydrogenation of Carbon Deposited by CO Decomposition

The rate of methane formation by reaction of carbon-containing
surface intermediates with hydrogen was examined by first exposing the
catalyst to CO pulses at various temperatures and then subjecting it to
TPSR in hydrogen (heating rate 45 ± 10 K min^{-1}). The results of three
experiments are shown in Figure 7-4. Curves A and B were obtained after
exposing the catalyst to CO/He pulses at 573 K and 623 K. Carbon dioxide
formation was detected during CO exposure, indicating that CO dis-
sociation and carbon deposition had taken place on the catalyst. After
the catalyst was cooled in He to room temperature, TPSR in H_2 demonstrated
the presence of a very reactive surface carbon species capable of forming
methane at 300 K (or below). Another methane peak was observed near
475 K. Adsorption of CO on the freshly reduced catalyst at 300 K and
TPSR in H_2 yielded curve C (Figure 7-4) with a peak reaction temperature
very close to the β peak of curves A and B. The data suggest that some
methane is produced at 300 K by very reactive carbon adspecies at low
surface coverage (< 0.1 monolayer). In addition the TPSR curves indicate
CH_4 formation at $T_p = 480 - 500$ K. This process appears to involve
chemisorbed CO or a surface intermediate derived from it.

7.3.4 Disproportionation of CO on Ru/Al$_2$O$_3$

Carbon accumulated on the Ru/Al_2O_3 catalyst when it was exposed
to a steady flow of 2.85 vol% CO in helium under isothermal conditions.
Figure 7-5 shows the TPSR curves for methane production after CO exposure
at room temperature after steady flow CO exposure for 340 sec at 576 K

and after steady flow CO exposure for 1190 sec at 572 K. Two TPSR peaks are seen for CO exposure at elevated temperature, one at $T_p = 480 \pm 3$ K and one at $T_p = 610 \pm 10$ K. The location of the second peak agrees with the TPSR peak (620 ± 10 K) for amorphous carbon deposited to an equivalent surface coverage by cracking ethylene (see Figure 7-1). The yield of amorphous carbon seen in Figures 7-5b and 7-5c represented only 0.5% of the total CO passed through the catalyst bed. These results are summarized in Table 7-2. The first peak in Figures 7-5b and 7-5c was located within a few degrees of the TPSR peak exhibited in Figure 7-4 (curve C).

Additional studies under isothermal conditions confirmed our TPSR results. In these measurements, the Ru/Al_2O_3 catalyst was exposed to a flow of CO/He (10 vol% CO in helium) at 1 atm and 573 K for a period of 10 to 30 min before exposure to pulses of H_2 at 573 K and product analysis of the exit gas. The results (Table 7-3) indicate a slow buildup of surface carbon capable of reacting with hydrogen to form methane.

7.4   Discussion

Our results demonstrate that carbon surface deposition occurs on Ru/Al_2O_3 by exposure to C_2H_4 or CO at elevated temperatures. However in contrast to nickel[7] and iron[8] the net rate of dissociative chemisorption of CO is very slow. The slow rate of CO dissociation on ruthenium could be due to (1) a high activation energy barrier, or (2) a rapid reverse reaction, i.e., the association of adsorbed carbon and oxygen atoms. Association may be faster than CO dissociation because of the weak binding energy of oxygen on ruthenium.[9,10,11] Recent work[12] on Ru(0001) has shown that the recombination of carbon and oxygen adspecies has an activation energy of 30 to 35 kcal mol^{-1}. With a heat of adsorption of oxygen on

Ru(0001),[11] -40 kcal/g atom oxygen, and assuming that the heat of adsorption for C (atomic) is 0 ± 10 kcal/g atom, as for nickel[13] and iron,[14] we find the transition state for CO dissociative adsorption lies 47 ± 12 kcal/mol above chemisorbed CO, and 18 ± 14 kcal/mol above gaseous CO. These results suggest that CO dissociation on Ru(0001) should be very slow up to 600 K.

Our TPSR results indicate that dissociation is occurring at special sites. The rate of such irreversible dissociation of CO at step or kink sites on Ru would decrease as these sites became populated with carbon adatoms, (the oxygen adatoms being consumed by reaction with another CO molecule). In the presence of hydrogen, such carbon adspecies could rapidly react to form methane. As a matter of fact the high reactivity of the carbon atoms, as demonstrated by methane production at 300 K on hydrogen exposure (following CO dissociation at 600 K) is in agreement with such a model. Recent work on nickel[16,17,18] has shown that surface carbon is an intermediate in methanation of CO synthesis of CH_4 by reaction of CO and H_2. We might expect that a similar mechanism prevails on Ru-based catalysts.

7.5   Conclusions

Based on the TPSR results for hydrogenation of carbon deposited by ethylene cracking we conclude that

- Multiple layers of carbon can be deposited on Ru/Al_2O_3 by ethylene exposure at elevated temperatures

- Methane is the predominant product, but significant amounts of C_2 hydrocarbons are formed during TPSR with H_2 following carbon deposition. The C_2 hydrocarbons desorb from the catalyst surface at somewhat lower temperatures (80 to 100 K) than methane.

The TPSR results for carbon deposition from CO exposure suggest that

o   CO disproportionation at 575 K on Ru/Al_2O_3 is slow,

o   Some of the carbon deposited is very reactive with hydrogen at 300 K, and probably represents carbon atoms chemisorbed at special high coordination sites.

o   Unlike nickel and iron, ruthenium cannot accomodate large amounts of chemisorbed carbon atoms, probably because of instability of the carbon adatoms on low index planes and the absence of a stable bulk carbide.

7.6   References

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Table 7-1

CARBON DEPOSITION ON Ru/Al_2O_3 BY EXPOSURE TO
ETHYLENE AT INCREASING TEMPERATURES

T_{dep} (K)	$T_p(15)^*$ (K)	A(15)	$T_p(28)^*$ (K)	A(28)	θ
468	619 ± 10	41	493 ± 20	40	0.5
562	625 ± 5	106	543 ± 10	25	1.3
660	659 ± 5	265	583 ± 10	28	3.2
706	713 ± 5	485	633 ± 10	22	5.9

*Heating rate = 45K min^{-1} except for 706K T_{dep} where the
heating rate was 55K min^{-1}.

Table 7-2

TPSR RESULTS FOR CARBON DEPOSITED ON Ru/Al_2O_3
BY CO EXPOSURE (AT 21 TORR CO)

Exposure Temperature (K)	Total CO Exposure (μmol)	CH_4 Produced from C(μmol)	Peak Temperature (K)
298	5 (saturation)	–	–
576	160	0.28	625
572	600	0.67	600

Table 7-3

CO DISSOCIATION AND FORMATION OF
SURFACE CARBON ON Ru/Al$_2$O$_3$[*] at 573 K

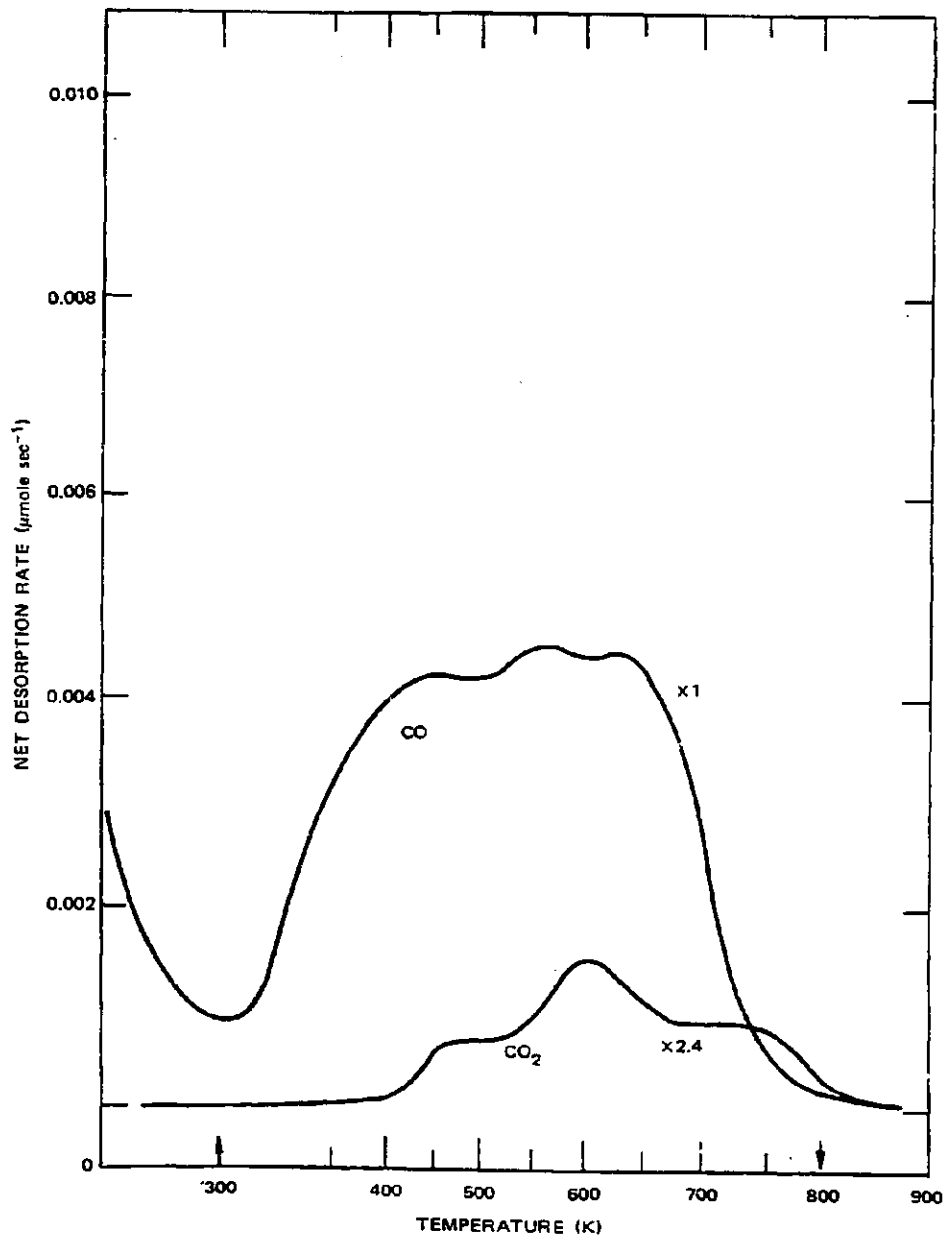| CO Exposure[†] (minutes)	Carbon Removed as CH$_4$ (mol x 10^6)	Fractional Coverage with Surface Carbon[‡] (%)
10	0.30	30
30	0.55	55

[*]Catalyst mass = 15 x 10^{-3} g (1.5 wt% Ru).

[†]10 vol% CO in He

[‡]Based on CO adsorption capacity of 66 x 10^{-6} mol/g catalyst.
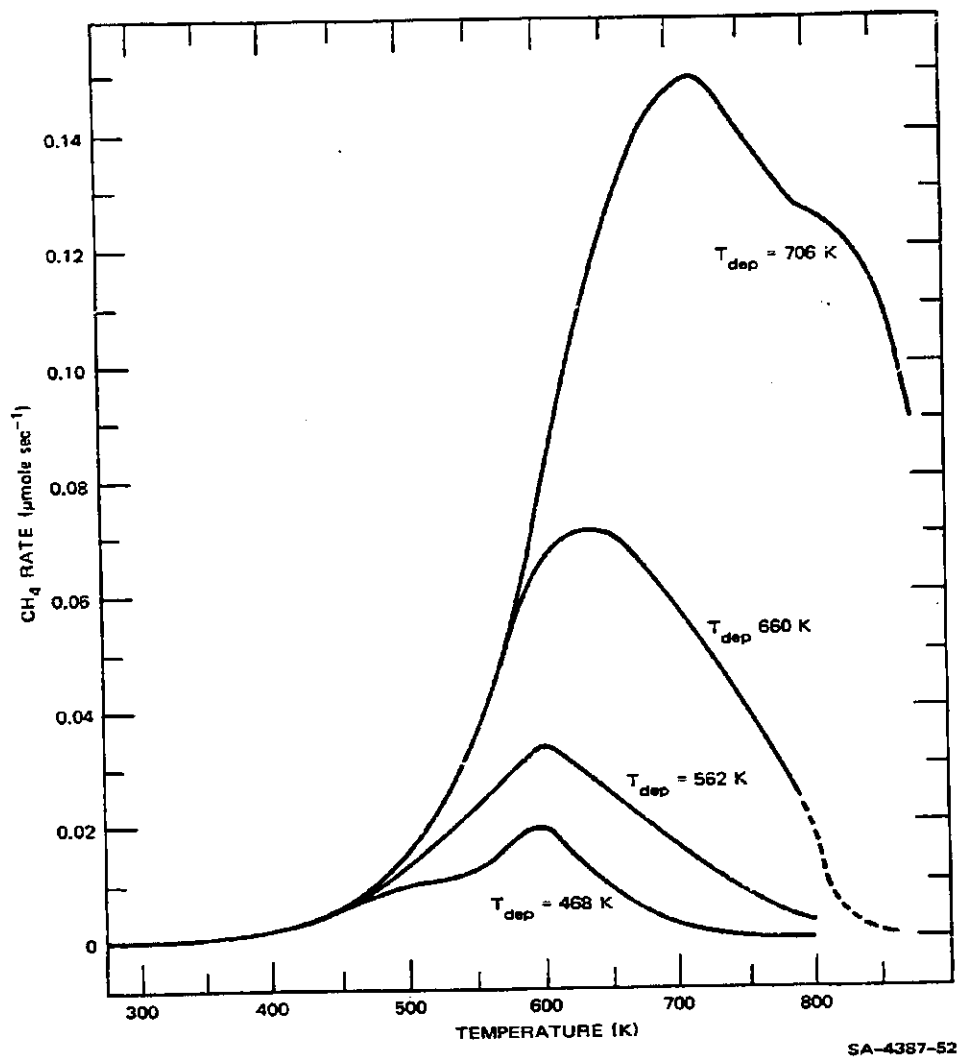
FIGURE 7-1   TPSR OF H_2 WITH CARBON DEPOSITED ON Ru/Al_2O_3 BY ETHYLENE EXPOSURE

FIGURE 7-2   TPSR FOLLOWING CO ADSORPTION AT 300K ON Ru/Al$_2$O$_3$ (1.5 WT%)
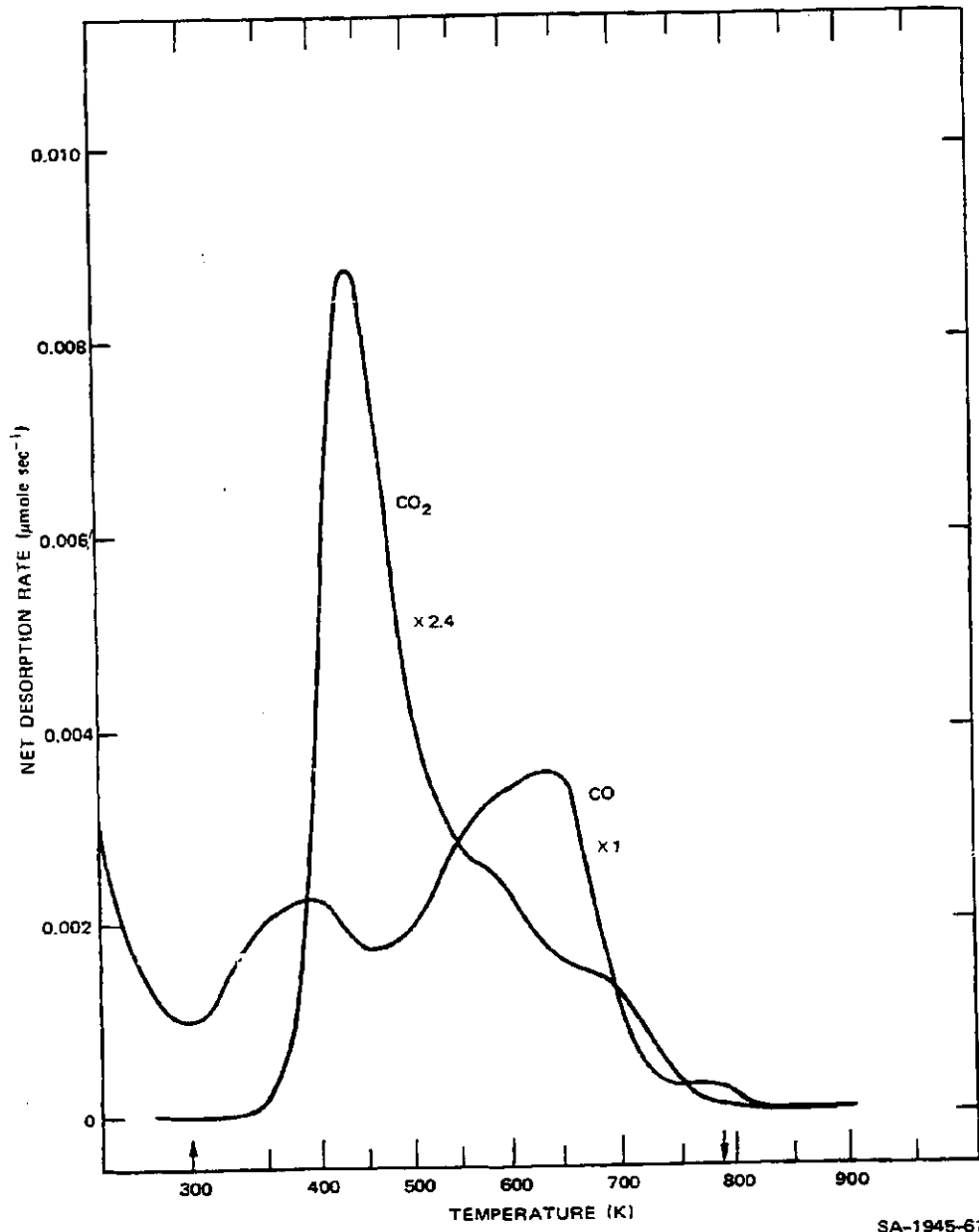
SA-1945-60

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FIGURE 7-3   TPSR FOLLOWING CO ADSORPTION AT 300K ON OXIDIZED
(1.2 MONOLAYERS) Ru/Al_2O_3 (1.5 WT%)

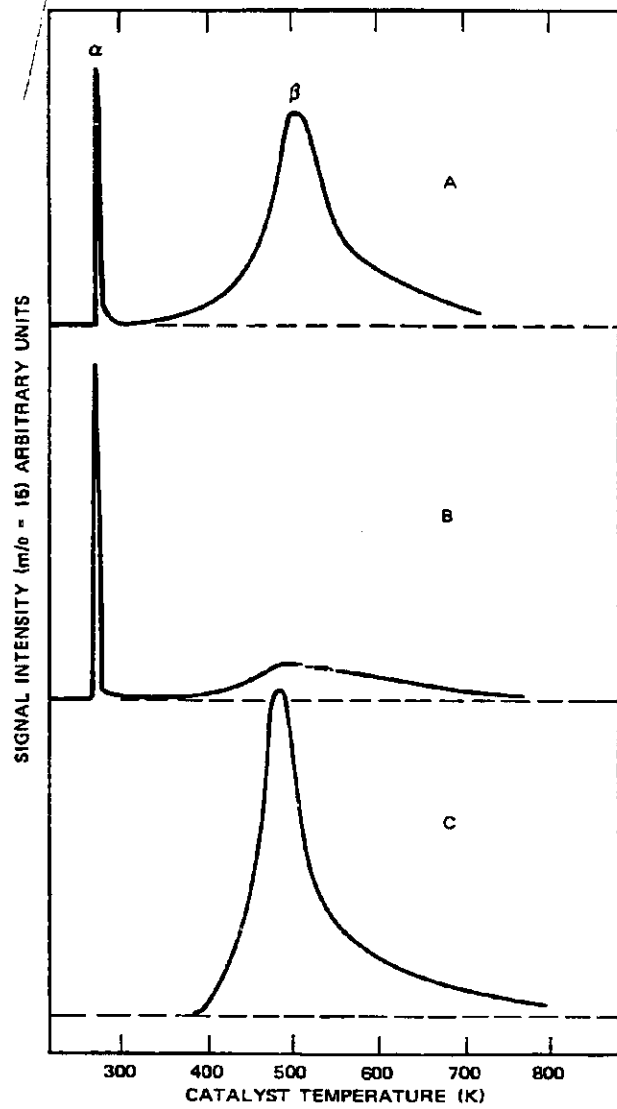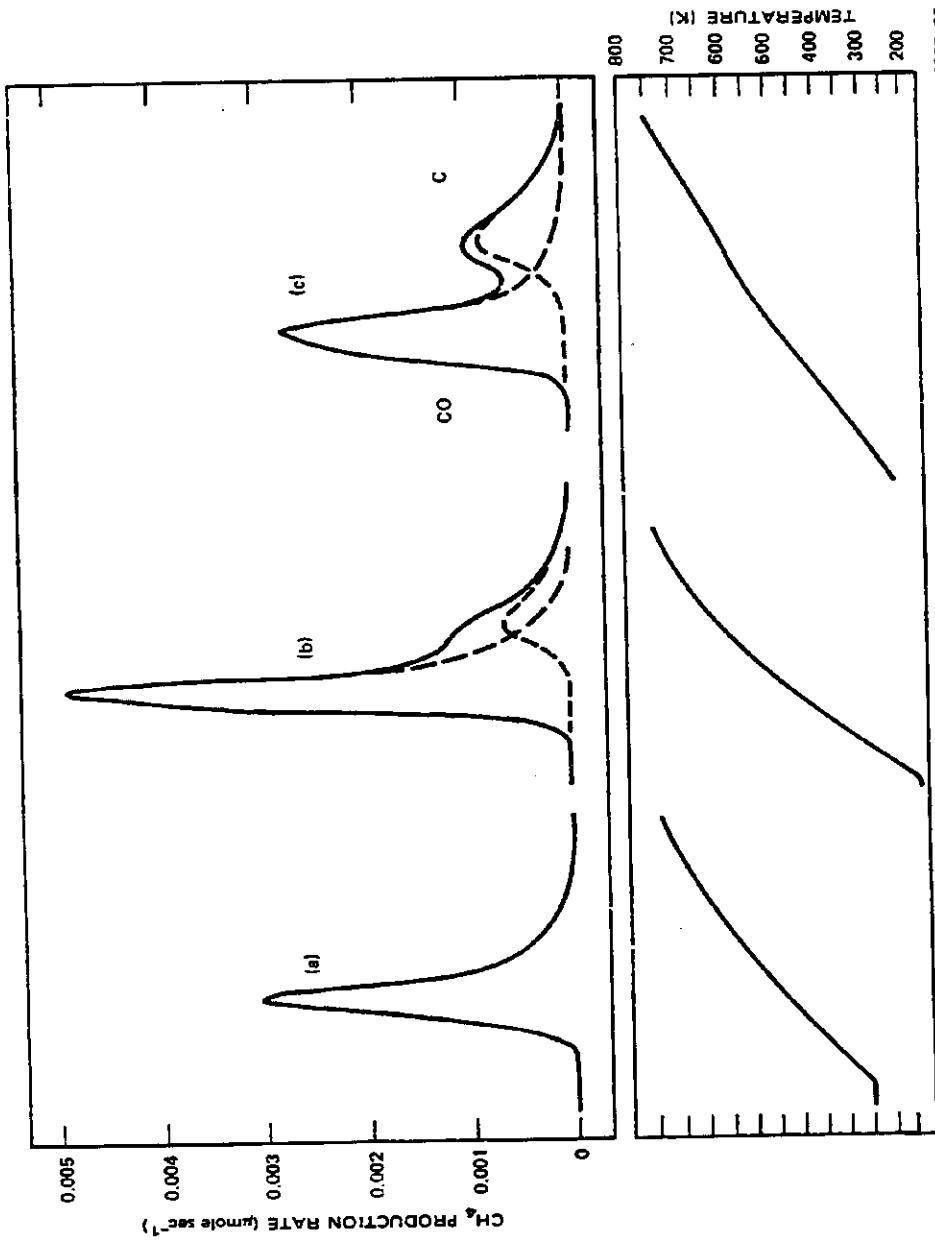FIGURE 7-4   TPSR OF HYDROGEN WITH SURFACE ADSPECIES FORMED
              BY EXPOSURE OF Ru/Al$_2$O$_3$ TO CO

              (A: 3.4 μmole CO at 553 K; B: 3.4 μmole CO at 623 K;
              C: 1.8 μmole CO at 298 K)

FIGURE 7-5   TPSR OF SURFACE CARBON DEPOSITED ON Ru/Al₂O₃ BY EXPOSURE

(a)   Saturation exposure at 298K
(b)   160 μmole exposure at 576K
(c)   600 μmole exposure at 572K

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