

Methanation over Transition Metal Catalysts

II. Carbon Deactivation of Co/Al₂O₃ in Sulfur-Free Studies

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Hydrogenation of CO catalyzed by Co/Al₂O₃ was studied in an all-quartz internal-recycle reactor between 200 and 400°C and from 0.1 to 20% CO in H₂ at atmospheric pressure. The surface and subsurface regions of the aged Co/Al₂O₃ catalysts were investigated using Auger electron spectroscopy (AES). Two pseudo steady states were observed. The upper pseudo steady state corresponds to a cobalt surface mainly containing active reaction intermediates; the lower pseudo steady state corresponds to deactivated cobalt which has large deposits of graphitic carbon on its surface, and for which the bulk CO is carburized to great depths as shown by AES. Methane is the primary reaction product; other hydrocarbons constitute less than 10% of the total products formed. The activation energy for methanation over Co/Al₂O₃ in the upper pseudo steady state is 28 ± 2 kcal/mole, whereas that in the lower pseudo steady state is 16 ± 2 kcal/mole. The change in the activation energy appears to be caused by changes in the electronic structure of CO due to bulk carburization.

INTRODUCTION

According to most recent estimates, the proven natural gas reserves in the United States would last for slightly more than 1 decade at the current rate of consumption; a similar future shortage of hydrocarbon liquids is projected. Hydrogenation of CO to form methane and higher hydrocarbons has received increasing attention during the past decade. At 1 atm CH₄ is the major product of CO hydrogenation catalyzed by Group VIII transition metals (1). The specific methanation activity of metals supported on η -Al₂O₃ at 275°C and a H₂/CO ratio of 3 was put in the following order (1):

Ru > Fe > Ni > Co

> Rh > Pd > Pt > Ir.

In contrast, Co has also been reported to be about an order of magnitude more active

than Ni for methanation (2, 3). The above studies are measures of initial activity; they do not address the question of activity behavior in commercial operation. Cobalt and Fe catalysts undergo marked deactivation during the first few days of typical commercial operation; carbon deposition is an important aspect of this deactivation (4). An improved understanding of the mechanism and kinetics of carbon deactivation is important to the development of catalysts with improved activity, selectivity, and life.

Active methanation catalysts such as Ni, Co, and Fe catalyze the deposition of carbon. Joyner and Roberts (5) have demonstrated, using XPS and UPS, that CO dissociates on a number of transition metals above 150°C. Araki and Poniec (6) have shown that carbon thus deposited on Ni is easily hydrogenated to CH₄. The process by which this surface carbon transforms into catalyst deactivating species has been studied only recently. Surface studies (7-11) have focused on Ni. Carbon deposition from benzene on Ni-Cu alloys proceeded at a constant rate in H₂-rich atmospheres,

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whereas in He the deposition rate decreased gradually (12). Presumably H₂ affected the rate of carbon deposition by removing surface carbon species blocking the sites active for benzene dissociation.

The structure of surface carbon intermediates is fundamental to the activity and selectivity of CO hydrogenation catalysis. Methanation and Fischer-Tropsch (F-T) synthesis necessarily involve the formation of metal-carbon bonds, but carbon-carbon bond formation is unique to F-T synthesis. The two extremes in the structure of surface carbon intermediates are: (i) isolated carbon atoms with only carbon-metal bonds, and (ii) carbon species with strong carbon-carbon bonds and weaker bonds with the surface metal atoms. In the extreme, the former can be considered to be a surface carbide and the latter to be a graphitic residue or free carbon. The important surface carbon intermediate in catalytic methanation is probably surface carbide (6, 10); the chain propagation in F-T synthesis may involve a different surface carbon intermediate (18).

Here, we report the intrinsic activity for CO hydrogenation over Co/Al₂O₃ under sulfur-free reaction conditions; the effect of reaction conditions on the carbon deactivation of Co/Al₂O₃ has been studied. To gain a better understanding of the carbon deactivation, the surface and subsurface regions of the aged catalysts were characterized using Auger electron Spectroscopy (AES).

EXPERIMENTAL

Apparatus

An all-quartz internal-recycle reactor was used; details are described elsewhere (13). This reactor has several advantages over a conventional tubular flow reactor: (i) it is gradientless allowing reaction rates to be measured directly over a broad range of feed composition and conversion; (ii) catalyst configurations which are free of external and internal transport limitations can be used over a large conversion range; (iii)

quartz construction provides a sulfur-free environment (14); and (iv) rates of carbon deactivation can be measured directly. The reactor was heated externally by a quartz heating mantle, and temperatures to 600°C could be controlled within $\pm 1^\circ\text{C}$. Tracer studies demonstrated that the reactor behaved as an ideal CSTR. A manifold system containing rotameters and flow controllers was used to measure and mix H₂, CO, and He to give the desired feed gas composition. The gases exiting the reactor were fed to an on-line gas chromatographic analysis system; all components could be determined. The instantaneous reaction rate could be determined as a function of on-stream time.

AES was used to examine the aged Co/Al₂O₃ catalysts. The Auger electron spectrometer was equipped with a cylindrical mirror analyzer (CMA), an ion gun for Ar⁺ bombardment of samples for depth profiling or sputter cleaning, and a quadrupole mass spectrometer for residual gas analysis (RGA). An antechamber, with ultrahigh vacuum integrity, was attached to the Auger electron spectrometer to allow treatment of the samples under a controlled gas environment to above atmospheric pressure and to 500°C; detailed design of the antechamber is presented elsewhere (15). The antechamber permitted studies of the effect of pretreatment and of reaction on the catalyst followed by subsequent surface analysis without exposure to the atmosphere.

Materials

High-purity (99.9%) fused α -Al₂O₃ plates were used as the catalyst support because they had negligible internal surface area; therefore, all the surface metal atoms were exposed to a uniform gas environment. The catalysts were prepared by two methods (16): (i) Co metal was evaporated onto the Al₂O₃ plates, and (ii) the plates were impregnated with cobalt ammonium nitrate solution (pH \approx 7.0). The evaporated film

was carefully passivated with 10 ppm O₂, and the impregnated samples were decomposed to oxide by heating slowly to 300°C before exposure to the atmosphere. This eliminated sulfur contamination of the catalysts otherwise observed during transfer to the reactor.

The evaporated Co film was approximately 3000 Å thick and was continuous as observed by SEM and AES. SEM studies showed that the α -Al₂O₃ surface was composed of large, well-formed cubic crystals and had a surface roughness factor of about 4 (16). The evaporated metal film contoured the α -Al₂O₃ surface well and should have had the same roughness factor. The surface area of Co film was thus taken to be four times the geometric surface area of the Al₂O₃ plate, and the methanation turnover numbers were computed on the basis of per surface Co atom. The impregnated Co/Al₂O₃ had a visibly noncontinuous film and was difficult to analyze using AES due to surface charging. To overcome this problem, multi-impregnated Co/Al₂O₃ plates were prepared by repeating five cycles of impregnation, with calcination after each cycle.

All the gases were ultrahigh purity (UHP) and were first passed over reduced Cu/Al₂O₃ to remove traces of O₂ and then over molecular sieves to remove traces of H₂O. Mixtures of CO in H₂ (UHP, Matheson primary grade) were passed over molecular sieves to remove H₂O and then over activated charcoal (~175°C) to decompose and remove metal carbonyls.

Analytical

Analysis was carried out with two gas chromatographs (GC) connected in parallel. One GC had a flame ionization detector for hydrocarbon analysis; C₁ to C₃ hydrocarbons were separated on a 1.2-m × 3-mm stainless-steel column packed with 60–80 mesh Carbosieve B. The other GC had a thermal conductivity detector for CO, CO₂, and CH₄ analysis, using a 2-m × 3-mm stainless-steel column packed with 60–80

mesh Carbosieve B. Analysis time for each of the GCs was less than 5 min.

Procedure

The Co/Al₂O₃ plate (which typically had 50–100 cm² metal surface area) was reduced with H₂ in the reactor at 400°C. The reactor was brought to the desired temperature, and the reaction was started by setting the desired CO/H₂ ratio. The concentration of various components in the reactor effluent was determined as a function of time. Kinetic measurements were made only in regions in which the methanation activity at the initial operating condition changed by less than 10% over a 5-hr period. To ensure that constant catalyst activity prevailed during the kinetic measurements, activity checks were made by periodically returning to the initial operating conditions.

Runs were terminated by stopping the flow of CO, reducing the reactor temperature to 175°C, and holding it for 1 hr with flowing H₂ to ensure that all the CO was purged from the reactor. The reactor was then cooled to room temperature in flowing H₂. This procedure was used to prevent the formation of metal carbonyls. The catalyst was removed from the reactor and stored in a glass bottle under He for AES analysis.

Aged Co/Al₂O₃, to be analyzed by AES, was mounted on the sample holder of the antechamber. The transfer procedure used here has been shown to introduce no substantial changes in the composition of the sample surface, other than the adsorption of O₂ or H₂O (15–17). The main chamber was pumped down to $\sim 5 \times 10^{-9}$ Torr. An initial AES scan was taken from 0 to 1500 eV to determine the surface composition of the sample, and peaks of interest were then measured more carefully. The sample was then heated to 400°C and held there while the surface was monitored using AES until it was evident that no further changes had occurred. Heating the sample under UHV conditions caused the H₂O and/or oxygen, adsorbed during sample transfer through

the atmosphere, to desorb; H_2O desorption was confirmed by RGA. Argon was next introduced into the vacuum chamber to $\sim 5 \times 10^{-5}$ Torr, and the sample surface was sputtered intermittently for short intervals with an Ar^+ beam. An AES scan was taken after each sputtering interval; the sample was sputtered until further sputtering caused no significant changes in the composition (16).

RESULTS

The results are divided into subsections describing the catalytic behavior of CO hydrogenation and the AES analysis. An initial period of high methanation activity and two pseudo-steady-state activity regions were observed. The kinetic behavior of $\text{Co}/\text{Al}_2\text{O}_3$ was investigated in both of these pseudo-steady-state regions. The results of AES studies are discussed after the reaction studies.

Initial Activity and Transient Behavior

Figure 1 shows the transient methanation activity of $\text{Co}/\text{Al}_2\text{O}_3$ at 277°C for a feed of 0.6% CO in H_2 . The rate drops sharply during the first 60 min to a pseudo-steady-state activity which is 30 to 40% of the initial value. The term pseudo steady state is used because the activity, although not constant, continues to decline, only slowly (first-order decay constant $0.01\text{--}0.02\text{ hr}^{-1}$). In this pseudo-steady-state region the activity decreases about 30% over a 24-hr period (Fig. 2); this region will hereafter be referred to as the *upper pseudo steady state*.

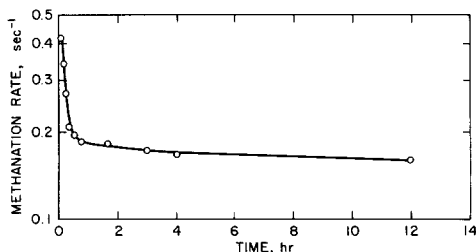


FIG. 1. Transient methanation activity (turnover number) of $\text{Co}/\text{Al}_2\text{O}_3$. Reaction conditions: 0.6% CO in H_2 at 277°C and 1 atm pressure.

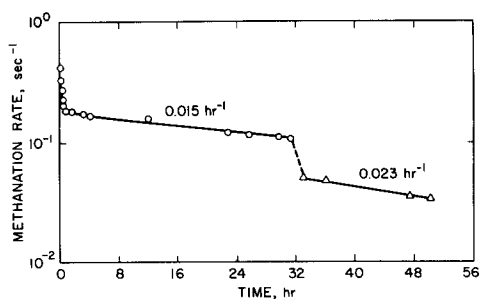


FIG. 2. Effect of CO concentration on transient methanation activity (turnover number) of $\text{Co}/\text{Al}_2\text{O}_3$. Reaction conditions: $T = 277^\circ\text{C}$; \circ —0.6% CO in H_2 ; \triangle —4.0% CO in H_2 .

After approximately 31 hr, the molar concentration of CO in the reactor was increased from 0.6 to 4.0% (Fig. 2); the broken line represents a rapid twofold drop in methanation activity. Subsequently, the activity reached a new pseudo-steady-state value characterized by a somewhat higher deactivation rate. At 277°C deactivation followed first-order decay behavior with a decay constant ($1/\tau$) of 0.015 hr^{-1} [Rate = $R_0 e^{-t/\tau}$] for 0.6% CO and a decay constant of 0.023 hr^{-1} for 4.0% CO. A sevenfold increase in the CO concentration resulted in only a small increase in the rate of deactivation.

At 400°C catalyst deactivation appears to be more complex. Figure 3 shows the transient methanation activity of a freshly reduced $\text{Co}/\text{Al}_2\text{O}_3$ catalyst at 400°C with 4.0% CO in H_2 . There is a rapid initial decay similar to that observed at 277°C . Between 1.5 and 5 hr, the methanation activity appears to be in a pseudo steady state with a decay constant of 0.068 hr^{-1} . However, deactivation accelerates after about 5 hr, and the activity drops almost 50-fold over the next 20 hr with a decay rate of about 0.20 hr^{-1} , as shown by Curve 1 in Fig. 4. Another pseudo steady state with a decay constant of 0.014 hr^{-1} is achieved after about 40 hr. Hereafter, this region will be referred to as the *lower pseudo steady state*.

The transient methanation activity from

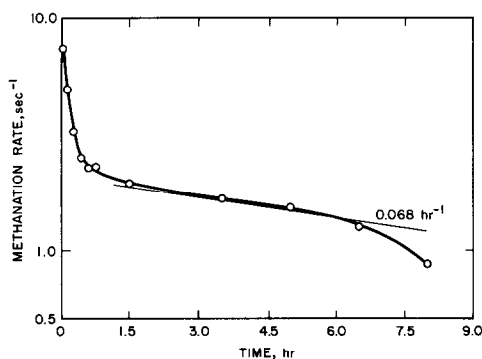


FIG. 3. Transient methanation activity of $\text{Co}/\text{Al}_2\text{O}_3$. Reaction conditions: 4.0% CO in H_2 at 400°C .

another experiment at 400°C with 0.5% CO in H_2 is shown by Curve 2 (Fig. 4). With 0.5% CO in the feed gas, the catalyst maintains a fairly constant activity for a much longer period of time than with 4% CO. After 30 hr, the concentration of CO was increased from 0.5 to 4.0% and methanation activity dropped rapidly in a manner similar to that of the earlier experiment which was started with 4.0% CO (Curve 1, Fig. 4). This clearly demonstrates that the effect of CO concentration on the deactivation rate is more pronounced at 400°C than at 277°C (Fig. 4 versus Fig. 2).

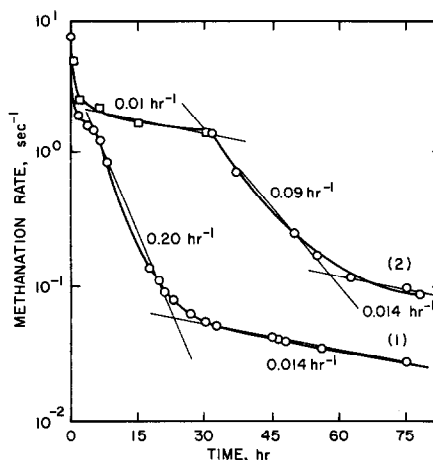


FIG. 4. Effect of CO concentration on deactivation of $\text{Co}/\text{Al}_2\text{O}_3$. Reaction conditions: (1) \circ —4.0% CO in H_2 at 400°C ; (2) \square —0.5% CO in H_2 at 400°C , \circ —4.0% CO in H_2 at 400°C .

Table 1 summarizes the time constants for activity decay as a function of temperature, CO concentration, and activity regime. In the upper pseudo steady state at low temperatures the decay constant is weakly dependent on CO concentration, whereas at high temperatures it is strongly dependent on CO concentration. At 400°C the dependence appears to be almost first order in CO concentration. In the same

TABLE I
Deactivation Rates for $\text{Co}/\text{Al}_2\text{O}_3$

Regime	Temp. ($^\circ\text{C}$)	$1/\tau^a$ (hr^{-1})		
		0.5% CO	0.6% CO	4.0% CO
Upper pseudo steady state	277	—	0.015	0.023
Upper pseudo steady state	400	0.010	—	0.068
Transition to lower pseudo steady state after 0.5% CO (Curve 2, Fig. 4)	400	—	—	0.09
Transition to lower pseudo steady state at continuous 4.0% CO (Curve 1, Fig. 4)	400	—	—	0.20
Lower pseudo steady state	400	—	—	0.014

^a Rate = $R_0 e^{-t/\tau}$.

regime at low CO concentrations the effect of temperature is more pronounced. The rate of deactivation in transition to the lower pseudo steady state is apparently dependent on the previous history in the upper pseudo steady state (Table 1). The rate of deactivation in the lower pseudo steady state is about the same as that in the upper pseudo steady state. These observations indicate the complexity of the deactivation process.

Activation Energy

Figure 5 shows the temperature dependence for methanation in the upper pseudo steady state over $\text{Co}/\text{Al}_2\text{O}_3$ prepared by different techniques. The activation energy is 28 ± 2 kcal/mole. Not only does Fig. 5 demonstrate the reproducibility of the activation energy measurements, but it also shows that methanation activity is about the same over $\text{Co}/\text{Al}_2\text{O}_3$ prepared by different techniques. Less than $\pm 20\%$ variation in turnover number may be caused by variations in the roughness factor resulting from the different preparation techniques.

In the lower pseudo steady state the activation energy for methanation over

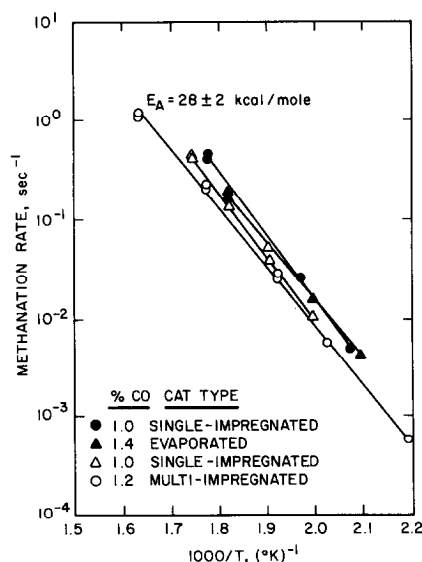


FIG. 5. Temperature dependence of methanation over $\text{Co}/\text{Al}_2\text{O}_3$ in the upper pseudo steady state. Each symbol represents a new run with $\text{Co}/\text{Al}_2\text{O}_3$ prepared by a different technique. The CO concentration was maintained at the value indicated during each run.

$\text{Co}/\text{Al}_2\text{O}_3$ is 16 ± 2 kcal/mole. The value is surprisingly reproducible in view of the large variation in activity for the lower pseudo steady state (Fig. 6). These differences in intrinsic activity are due to large

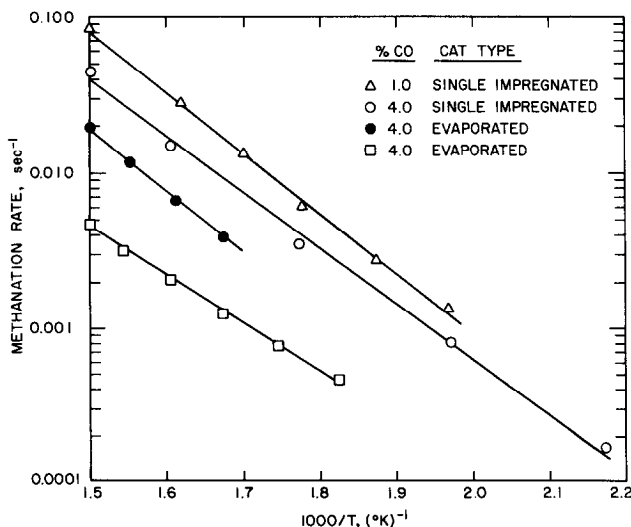


FIG. 6. Temperature dependence of methanation over $\text{Co}/\text{Al}_2\text{O}_3$ in the lower pseudo steady state. Each symbol represents a new run with $\text{Co}/\text{Al}_2\text{O}_3$ prepared by a different technique, and deactivated to varying extents. The CO concentration was maintained at the constant value indicated during each run.

variations in the prior history of the catalyst. For example, the data indicated by the lowest curve in Fig. 6 represent a catalyst which had been deactivated under continuous operation at 400°C and 4.0% CO for 212 hr; the data shown by the uppermost curve represent a catalyst operated at 1.0% CO for 80 hr. Obviously, the continued slow deactivation of Co/Al₂O₃ in the lower pseudo steady state reduces its intrinsic methanation activity, but the activation energy for methanation does not change with the extent of deactivation.

Product Distribution

Under the experimental conditions used, CH₄ was the main product. The reasons for this high selectivity toward CH₄ are: (1) the reaction was carried out at atmospheric pressure, (2) high H₂/CO ratios (9 to 99) were employed, and (3) reaction temperatures of 300 to 400°C were used. In the upper pseudo steady state, the only other hydrocarbons detected were C₂H₆ and C₃H₈; neither olefins nor oxygenated products were detected.

As Co/Al₂O₃ underwent deactivation, the product distribution changed little. The selectivity for higher hydrocarbons in the product shifted, however, from paraffins to olefins. In the lower pseudo steady state, C₂H₄ instead of C₂H₆, and C₃H₆ instead of

C₃H₈, were the major products. As the catalyst deactivated the $\Sigma C_2/C_1$ ratio changed by less than 2-fold. This change by less than a factor of 2 is negligible as compared to the 100-fold reduction in the catalytic activity.

At 400°C in the upper pseudo steady state the $\Sigma C_2/C_1$ ratio was ~ 0.006 and only C₂H₆ was detected (Fig. 7). As the catalyst rapidly deactivated in transition from the upper to the lower pseudo steady state, C₂H₄ began to appear without a concurrent reduction in the amount of C₂H₆ formed relative to that of CH₄; therefore, the ratio (C₂ + C₂^{*})/C₁ increased significantly. As the catalyst approached the lower pseudo steady state, the formation of C₂H₆ ceased without concurrent increase in the amount of C₂H₄ formed relative to that of CH₄, and the ratio (C₂ + C₂^{*})/C₁ decreased and stabilized at a value only twice that found in the upper pseudo steady state (Fig. 7). This change (2-fold increase) is very small compared with the 100-fold decrease in CO hydrogenation rate.

Regeneration of Deactivated Catalysts

Regeneration of deactivated catalysts was attempted in the reactor and in the antechamber attached to the Auger electron spectrometer. The results of the *in situ*

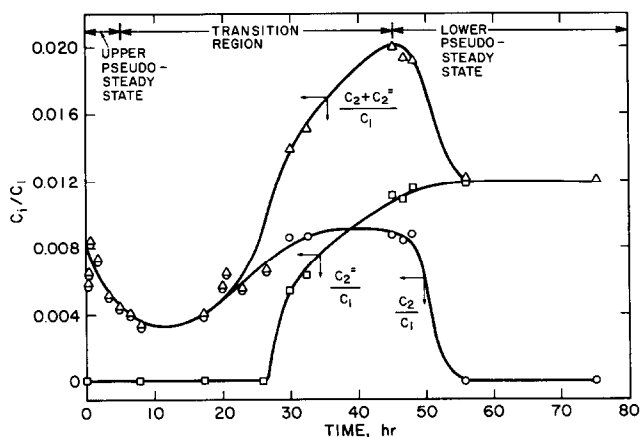


FIG. 7. Selectivity behavior of Co/Al₂O₃ in the formation of C₂ hydrocarbons. Reaction conditions: 4.0% CO in H₂ at 400°C.

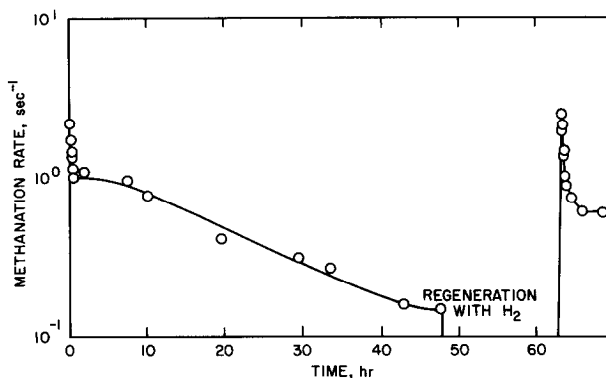


FIG. 8. Transient methanation activity and regeneration of $\text{Co}/\text{Al}_2\text{O}_3$ in the upper pseudo steady state. Reaction conditions: 0.8% CO in H_2 at 300°C ; regeneration was carried out with H_2 treatment at 400°C for 15 hr.

regeneration studies in the reactor are presented below.

Figure 8 shows the transient methanation activity of $\text{Co}/\text{Al}_2\text{O}_3$ at 300°C with 0.8% CO in UHP H_2 . After 48 hr of operation, CO was removed from the feed gas, and the temperature was increased to 400°C in flowing H_2 . The $\text{Co}/\text{Al}_2\text{O}_3$ was treated for 15 hr in flowing UHP H_2 at 400°C , and the temperature was then reduced to 300°C . Two hours later, 0.75% CO in UHP H_2 was fed to the reactor; the activity transient is shown in Fig. 8. The lost activity was completely restored, and the initial transient response for a fresh catalyst was reproduced. The initial activity after regeneration was about three- to fourfold higher than the activity in the upper pseudo steady state; identical behavior occurred for fresh $\text{Co}/\text{Al}_2\text{O}_3$.

Similar regeneration procedures were used for a catalyst which had been treated with 4.0% CO in H_2 at 400°C for 75 hr and had undergone severe deactivation to the lower pseudo steady state. After treatment in flowing H_2 at 400°C for 16 hr, 4.0% CO in H_2 was started; the transient activity is shown in Fig. 9. The methanation activity of $\text{Co}/\text{Al}_2\text{O}_3$, thus treated, was initially an order of magnitude higher than that observed just prior to regeneration. The activity decreased rapidly (in 1 hr) to the value observed before the regeneration proce-

cedure was used. This decrease in methanation activity was much more rapid than that observed for fresh $\text{Co}/\text{Al}_2\text{O}_3$. Initially high activity may have been the result of a few surface sites being regenerated by H_2 , but these sites were deactivated very rapidly. The majority of the activity was not regained, however.

AES Analysis of Aged $\text{Co}/\text{Al}_2\text{O}_3$

This section presents AES analysis of $\text{Co}/\text{Al}_2\text{O}_3$ plate catalysts used in the reactor and the results obtained on cobalt films treated in the AES antechamber.

Figure 10a shows the AES spectrum of a

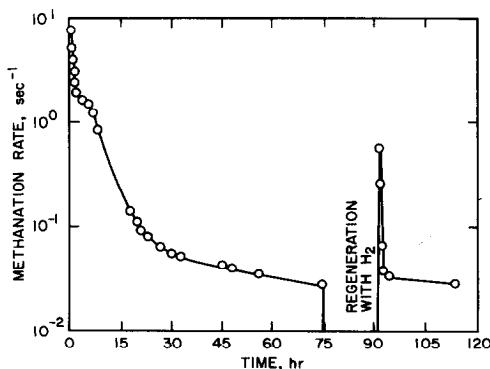


FIG. 9. Transient methanation activity and regeneration of $\text{Co}/\text{Al}_2\text{O}_3$ in the lower pseudo steady state. Reaction conditions: 4% CO in H_2 at 400°C ; regeneration was carried out with H_2 treatment at 400°C for 16 hr.

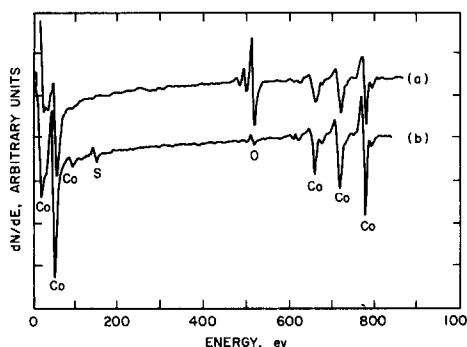


FIG. 10. AES spectra of fresh $\text{Co}/\text{Al}_2\text{O}_3$ prepared by evaporation technique; (a) before any treatment; (b) after heating in the main chamber of the Auger electron spectrometer at 400°C for 25 min.

Co film prepared by evaporation of Co powder onto an $\alpha\text{-Al}_2\text{O}_3$ plate. Other than oxygen there were no contaminants. The film was heated in the main vacuum chamber of the Auger electron spectrometer at 400°C for 25 min. Residual gas analysis (RGA) in the AES chamber showed that water was desorbed as a result of heating the sample. During this heating there was a marked decrease in the oxygen signal intensity indicating that the oxygen was associated with water adsorbed on the film. Analysis of the valence level Co peaks (<100 eV) prior to heating showed that the Co surface atoms were in a metallic state and not in an oxidized state, confirming that the oxygen was associated with adsorbed water.

After 25 min of heating at 400°C , most of the oxygen had disappeared, and there was a small sulfur peak (Fig. 10b). This sulfur represents less than one-tenth of a monolayer and may have been adsorbed during catalyst transfer through the atmosphere, which contained ~ 30 ppb H_2S . The amount of sulfur adsorbed during transfer through the atmosphere was small, and the catalysts used in the reaction studies can be considered to be essentially clean; for catalysts prepared by the same technique the initial activity was reproduced by $\pm 10\%$.

Figure 11 shows the AES spectrum of a $\text{Co}/\text{Al}_2\text{O}_3$ sample which had been removed

from the reactor while it was still in the upper pseudo steady state. A metallic Co surface is indicated; the oxygen signal is mainly due to the Al_2O_3 . Essentially no carbon was present on the catalyst surface. At this molar ratio of CO to H_2 ($\sim 10^{-3}$) carburization of the Co did not occur, and the surface carbon which may have been present during reaction was probably hydrogenated to methane during reactor shut-down. Araki and Ponc (6) and McCarty *et al.* (10) have shown that surface carbon is an active intermediate which is readily hydrogenated to methane.

Figure 12 shows the AES spectrum of $\text{Co}/\text{Al}_2\text{O}_3$ which had been deactivated in the reactor to the lower pseudo steady state; its methanation activity had decreased 100-fold from that in the upper pseudo steady state. The catalyst surface is covered mainly with graphitic carbon; only very small peaks of cobalt are present (Fig. 12). There is essentially no oxygen on the surface indicating that there is no incorporation of oxygen into the Co surface during methanation and that no oxygen was adsorbed on the carbon-covered $\text{Co}/\text{Al}_2\text{O}_3$ during transfer. The surface of the catalyst was then sputtered with Ar^+ , and the composition depth profiles were obtained. The carbon signal decreased with increased sputtering, and the cobalt signal increased (Fig. 13). Clearly, methanation does not

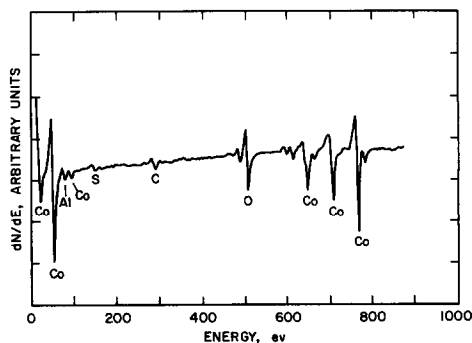


FIG. 11. AES spectrum of $\text{Co}/\text{Al}_2\text{O}_3$ prepared by multi-impregnation technique and aged in upper pseudo steady state only. Reaction conditions: 0.10% CO in H_2 at 400°C for 24 hr.

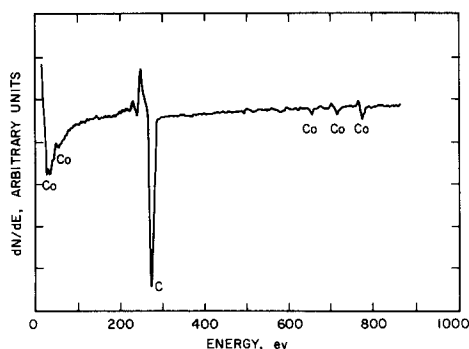


FIG. 12. AES spectrum of $\text{Co}/\text{Al}_2\text{O}_3$ prepared by evaporation technique and aged to lower pseudo steady state. Reaction conditions: 4.0% CO in H_2 at 400°C for 200 hr.

cause oxygen incorporation into Co , and the deactivation is caused by carbon deposits on the catalyst surface and by bulk carburization of the Co . For other catalysts deactivated to a similar extent, regeneration attempts using H_2 treatment at 400°C at 1 atm in the antechamber and at $\sim 3 \times 10^{-5}$ Torr in the main AES chamber resulted in no carbon removal even though Co peaks were visible. However, antechamber treatment with 1 atm of O_2 at 325°C for 10 min

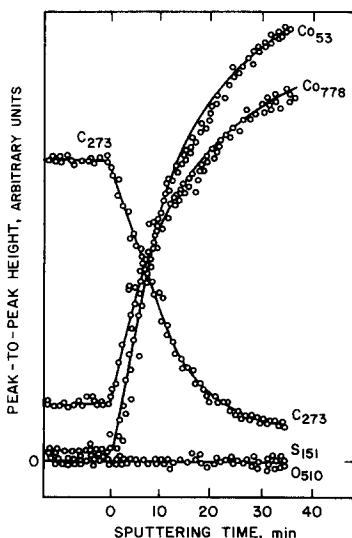


FIG. 13. Composition-depth profiles of aged $\text{Co}/\text{Al}_2\text{O}_3$ (same as Fig. 12). Sputtering conditions: 5×10^{-5} Torr Ar ; beam voltage, 2 kV; filament current, 10 mA.

resulted in complete carbon removal when Co peaks were visible.

In another experiment, operated at more severe conditions, the catalyst had undergone a 200-fold reduction in methanation activity from that in the upper pseudo steady state. The catalyst surface was completely covered with graphitic carbon, and no cobalt peaks were visible (Fig. 14). The surface was sputtered with Ar^+ for 35 min (Fig. 15). Even after sputtering for 35 min (approximately 100 \AA), no Co peaks were visible. Again, as in the previous experiment, no sulfur or oxygen was found upon depth profiling. The catalyst surface was then treated in flowing O_2 at 1 atm in the antechamber at 325°C for 45 min. The AES spectrum of the surface after O_2 treatment was identical to that shown in Fig. 14. The carbon on the surface was not removed by the 45-min O_2 treatment at 325°C , in contrast to the deactivated Co sample which had small Co peaks visible and which underwent total carbon removal with 10-min O_2 treatment under the same conditions.

Figure 16a shows the AES spectrum of a Co film (thickness $\sim 2000 \text{ \AA}$) evaporated onto a SiO_2 plate. Both graphitic carbon and sulfur are present on the Co surface. This film was heated at 340°C for 10 min in the presence of H_2 ($P_{\text{H}_2} \cong 1 \times 10^{-5}$ Torr) in the main chamber of the Auger electron spectrometer. Figure 16b shows the AES spectrum of the Co surface after H_2 treat-

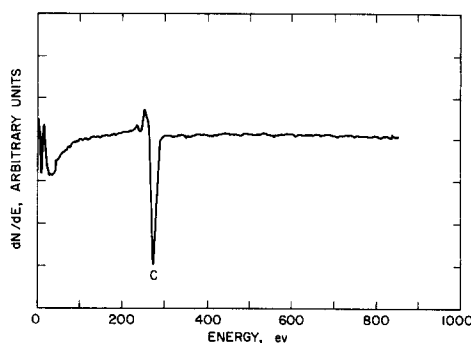


FIG. 14. AES spectrum of aged $\text{Co}/\text{Al}_2\text{O}_3$ prepared by evaporation technique. Reaction conditions: 10% CO in H_2 at 400°C for 120 hr.

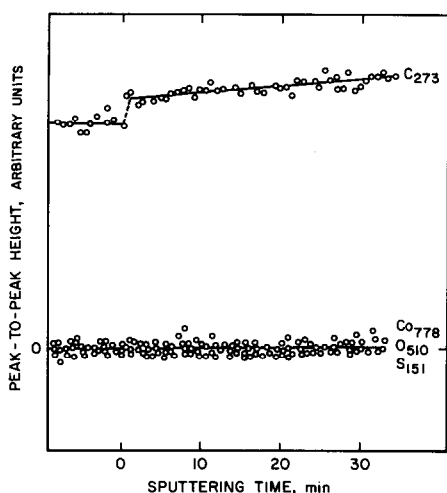


FIG. 15. Composition-depth profiles of aged $\text{Co}/\text{Al}_2\text{O}_3$ (same as Fig. 14). Sputtering conditions: 5×10^{-5} Torr Ar; beam voltage, 2 kV; filament current, 10 mA.

ment; the carbon was hydrogenated off, presumably to methane. Any effect of metal-support interactions can be neglected here because the Co film was continuous and $\sim 2000 \text{ \AA}$ thick. Similar behavior would be expected for $\text{Co}/\text{Al}_2\text{O}_3$. It is inferred that carbon can be hydrogenated off a Co surface when the surface is only partially covered with carbon, even when a small fraction of the surface is covered with sulfur. The carbon cannot be easily removed, on the other hand, from a cobalt surface which has multilayer graphitic carbon deposits on the surface and large quantities of carbon incorporated into the bulk. When the surface is totally covered with carbon, even oxidation cannot remove the carbon.

DISCUSSION

Initial Activity

The initial rate of methanation at temperatures from 277 to 400°C is high, and it drops sharply over the first 40 to 60 min, independent of temperature. The upper pseudo steady state is reached at the end of this period, and has an activity which is only 30–40% of the initial methanation ac-

tivity. This initial rapid drop in activity could be due to the fact that the catalyst was not well reduced at the time of CO introduction. Incompletely reduced oxides of nickel and cobalt have been shown to be about an order of magnitude more active for methanation than the well-reduced metals (2, 14, 20). AES studies showed that pretreatment with H_2 at 400°C for 1 hr produced well-reduced metallic cobalt. The H_2 reduction period in the reactor was varied from 30 min to several hours with no effect on the initial transient behavior. It thus appears that the highest activity occurs on a freshly reduced metal surface with all the surface Co atoms present in the metallic form and accessible to catalyze the reaction. The surface of the catalyst was apparently rapidly covered with reactants, side products, and/or reaction intermediates, resulting in a reduction in the activity for CO hydrogenation, perhaps due to increasing CO concentration as discussed below.

If reaction between one of the adsorbed reactants and an adsorbed intermediate is the rate-controlling step in methanation, a large fraction of surface covered either with adsorbed reactant or with adsorbed intermediate would inhibit the rate of reaction. The rate of methanation over $\text{Co}/\text{Al}_2\text{O}_3$ has a negative dependence on the CO concentration (1, 19) supporting the above asser-

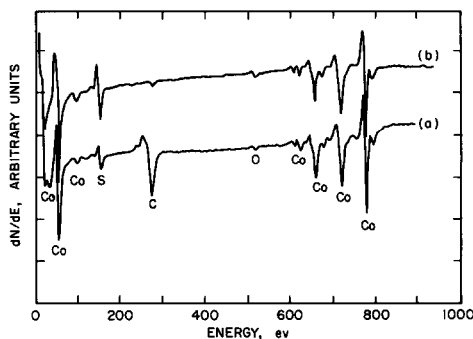


FIG. 16. AES spectra of Co/SiO_2 prepared by evaporation technique; (a) before any treatment; (b) treated with H_2 in main chamber of the Auger electron spectrometer for 10 min at 340°C ($P_{\text{H}_2} = 10^{-5}$ Torr).

tion concerning adsorbed CO. In these studies the reactor, initially containing only H₂, is subjected to a step input of CO in H₂. This causes the CO concentration of the CSTR to increase from an initial value of zero to a steady-state value in three to four residence times (45–90 min). The 1-hr period for the rapid drop in rate of methanation correlates well with the three to four residence times requirement for the CO concentration to reach steady state. Thus, the observed transient in the initial activity is undoubtedly due to the coupled effect of CSTR response and negative dependence of methanation rate on CO concentration. AES studies of Co/Al₂O₃ aged in the upper pseudo steady state confirmed that the Co surface did not contain deposited carbon species that are not readily hydrogenated.

Catalyst Deactivation

A slow, continual deactivation of Co/Al₂O₃ in the upper pseudo steady state occurred at both 300 and 400°C (Table 1). The deactivation rate accelerated after a few hours at 400°C; no such acceleration in the deactivation rate was observed even after 60 hr at 300°C (Figs. 2 and 4). Carbon deactivation could occur by: (1) carburization of bulk Co, and (2) formation of graphite deposits on the Co surface. Above 150°C, CO adsorbs on Co and undergoes dissociation forming surface carbon species (5). These surface carbon atoms can undergo one of several reactions including: (i) reaction with hydrogen to form CH₄, (ii) reaction with Co resulting in bulk carburization, and (iii) transformation to graphite on the Co surface. The concentration of this surface carbon is governed by: (i) reaction temperature, (ii) CO concentration, (iii) adsorption–desorption dynamics of CO, and (iv) H₂ concentration.

It seems reasonable that carbon diffusion into the Co bulk is the rate-controlling step in catalyst carburization. It is speculated that the slow and continuous deactivation observed at temperatures below 300°C is caused by a slow graphitization process on

the Co surface. Graphitization on Ni is very slow at temperatures below 300°C during methanation, and temperatures higher than 325°C are needed for rates of graphitization to be appreciable (10). The rate of bulk carburization appears to be very slow at 300°C since carbon diffusion into the Co bulk is required for bulk carburization. Graphitization on the Co surface would not be expected to affect the catalytic properties of Co/Al₂O₃, other than through the reduction in active surface by the blockage of active sites. The strong carbon–carbon bonding in graphite suggests only a weak metal–carbon interaction. For the same reasons graphitic carbon on the Co surface probably does not participate in bulk Co carburization; only isolated (single) carbon atoms are expected to be involved in bulk Co carburization. This is supported by the observation that the activation energy for methanation over Co/Al₂O₃ is independent of the extent of deactivation in the upper pseudo steady state. Hence, the slow deactivation of Co/Al₂O₃ at 300°C appears to result from geometrical blockage of the catalyst surface by graphite. The Co/Al₂O₃ deactivated at 300°C is regenerable by H₂ treatment at 400°C (Fig. 8) suggesting that graphitic carbon in intimate contact with the Co was hydrogenated. Our AES studies showed that carbon could be hydrogenated off a Co surface when it was only partially covered with graphitic carbon (Fig. 16), whereas carbon could not be removed from a Co surface having multilayer graphitic deposits (Figs. 14 and 15).

At temperatures below 300°C the rate of deactivation is only weakly dependent on Co concentration (Table 1 and Fig. 2), whereas at 400°C the rate of deactivation is strongly dependent on CO concentration, and the catalyst undergoes rapid, bulk carburization at CO concentrations greater than 1% (Fig. 4). This can be explained as follows. At higher temperatures the rates of carbon hydrogenation to methane and of graphitization on the surface increase, reducing the nongraphitic carbon concentra-

tion. The rate of bulk carburization should increase with temperature, presumably due to an increase in the rate of diffusion of carbon into the bulk. For Fe the activation energy for carbon diffusion in the bulk is 20 to 32 kcal/mole (21); the activation energy for graphitization of carbon-saturated Fe is 68 to 98 kcal/mole (22). However, if the concentration of nongraphitic carbon on the surface is low at higher temperature, bulk carburization will be very slow. Therefore, higher CO concentrations resulting in an increased surface carbon concentration should result in more rapid bulk carburization and rapid deactivation (Table 1).

It has been reported that carbon dissolved in Fe and Ni can contribute to graphitic growth (8, 22). If Co behaves similarly, its carburization should increase the rate of graphitization. Thus at 400°C, when Co undergoes rapid carburization, it also undergoes an accelerated rate of graphite formation.

After the activity is reduced to the lower pseudo steady state due to bulk carburization and formation of multilayer graphitic deposits, the rate of deactivation markedly decreases. We infer that the continued activity reduction is due to continued growth of the multilayer graphitic deposits approaching a virtually encapsulated Co surface. A Co surface fully encapsulated with graphite (no Co peaks visible in an AES spectrum) was inert to carbon oxidation, whereas a graphite-covered surface with visible Co peaks underwent complete carbon oxidation in a short time under the same conditions. For Ni the rate of oxidation of graphitic carbon was 10³-fold faster on a partially graphite-covered surface than on a surface fully encapsulated with graphitic carbon (12).

A Co surface containing a fractional monolayer of graphitic carbon was fully regenerated by H₂ at 400°C as is also shown by AES (Fig. 16). However, Co surfaces containing multilayer graphitic deposits were not regenerable by 400°C H₂ treat-

ment, and AES studies showed no increase in the Co peak intensity after such treatment.

Methanation Rate

The methanation turnover number in the upper pseudo steady state of Co/Al₂O₃ at 400°C and 1% CO is 15 ± 5 sec⁻¹, as extrapolated from the activation energy data at lower temperatures (Fig. 5); this is about an order of magnitude higher than that for Ni/Al₂O₃ obtained in the same reactor system under similar reaction conditions (14). Palmer and Vroom (2) found that Co foil was about an order of magnitude more active for methanation than Ni foil under similar reaction conditions. Luengo *et al.* (3) also reported similar results for methanation over Ni/Al₂O₃ and Co/Al₂O₃. Vannice (1) has reported a methanation turnover number of ~0.02 sec⁻¹ for Co/Al₂O₃ at 275°C, which is six- to eightfold lower than our measurements at 275°C in the upper pseudo steady state. This may be due to the lower H₂/CO ratio of 3.0 used by Vannice (1) as compared to the ratio of 99 used in the present study, since the methanation rate increases with increasing H₂O/CO ratio (1, 19).

The methanation turnover number for Co/Al₂O₃ in the lower pseudo steady state is ~0.1 sec⁻¹ at 400°C, which is about two orders of magnitude lower than the value observed in the upper pseudo steady state. In contrast to the large change in catalytic methanation activity from the upper to the lower pseudo steady state, the selectivity to formation of higher hydrocarbons changes very little. This implies that there is no change in the mechanism or in the rate-limiting step of the reaction in transition from the upper to the lower pseudo steady state. We infer that C₁ and C₂⁺ (hydrocarbons other than C₁) form via the same intermediate, otherwise the C₂⁺/C₁ selectivity would have been expected to change more dramatically. The shift in selectivity of paraffins to olefins is undoubtedly due to a reduction in the hydrogenation activity of

the catalyst upon deactivation. Therefore, the C_2H_4 formed as a primary product, which is hydrogenated to C_2H_6 in the upper pseudo steady state, is not hydrogenated in the lower pseudo steady state. The observation of olefinic hydrocarbons only in the lower pseudo steady state supports their being the primary product of the CO hydrogenation reaction to C_2^+ , consistent with the observations of Biloen *et al.* (23). The transient behavior of the ($C_2 + C_2^{2-}$) species formed during deactivation (Fig. 7) is possibly due to small changes in the relative concentration of species on the surface.

Activation Energy

The activation energy for methanation over Co/Al_2O_3 in the upper pseudo steady state is 28 ± 2 kcal/mole, in agreement with the value of 27 ± 4.4 kcal/mole reported by Vannice (1).

The activation energy for methanation over Co/Al_2O_3 in the lower pseudo steady state is 16 ± 2 kcal/mole. Such a large change in the activation energy resulting from catalyst deactivation has not been reported for any other reaction system to the best of our knowledge. This decrease in activation energy was not caused by the diffusion of reactants through the graphitic carbon deposits built up on the catalyst surface. Such diffusional effects are unlikely to explain a uniform activation energy of 16 ± 2 kcal/mole over a temperature range of $200^\circ C$. If there were an important diffusional resistance in the diffusion of reactants through the graphite deposits, it would be equivalent to diffusion through an ash layer for which the activation energy would be ~ 2 kcal/mole. Thus, there is clear evidence that the observed decrease in activation energy for methanation is not due to physical effects but is due to chemical effects. We infer that the reduction in activation energy is due to electronic effects induced by carburization of the Co bulk. These electronic effects are also manifested in the kinetic behavior: the methanation rate has a negative order depen-

dence on CO concentration in the upper pseudo steady state, whereas it has a positive order dependence on CO concentration in the lower pseudo steady state. Kinetic behavior similar to that observed in the lower pseudo steady state was also observed for sulfur-poisoned Co/Al_2O_3 . The kinetic behavior is treated in more detail elsewhere (19).

Overview

It is demonstrated here that the catalytic activity and the activation energy for methanation obtained on the novel catalyst system used in this study are in agreement with the results reported by others for commercial, supported-Co catalysts. This work has clearly shown that CO hydrogenation over Co involves two pseudo-steady-state regions: an upper pseudo steady state in which the activity is that of metallic Co, and a lower pseudo steady state in which the activity is that of a deactivated, carburized Co. The lower pseudo steady state has not previously been characterized; in this region the activity is about 10^2 -fold lower than that in the upper pseudo steady state. This severe deactivation is caused by bulk carburization of the Co and the growth of multilayer graphitic deposits. The kinetic behavior is different and the activation energy is lower in the lower pseudo steady state than in the upper pseudo steady state. These kinetic changes are caused by electronic effects due to bulk carburization. However, the reaction mechanism and the rate-controlling step appear not to change upon bulk carburization. A catalyst deactivated to the lower pseudo steady state is not readily regenerated. Although rates of deactivation measured at 1 atm will not match those under higher-pressure commercial conditions, it appears that higher-pressure behavior can be simulated by working at higher H_2/CO ratios (24). Furthermore, it is expected that the mechanism and nature of carbon deactivation will be the same as under commercial conditions.

The occurrence of two pseudo steady

states in a catalytic reaction system has not been previously reported, and there are no quantitative data available on the activity and selectivity of a catalyst operating under such conditions. The work has shown that a careful and complete mapping of the activity and selectivity behavior (including partial-pressure and temperature dependencies) in and between such multiple pseudo steady states can provide more insight into the catalytic chemistry of the reaction system than if only one pseudo steady state is studied.

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