

A Study of Carbon Formation on Noble-Metal Steam Reforming Catalysts

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Introduction

Steam reforming of methane or naphtha is currently a most practical large-volume source of hydrogen; however, future sources may include middle and high petroleum distillates and coal liquification products. Processing heavy hydrocarbon feedstocks is more difficult due to the greater tendency for carbon fouling and the possibility of sulfur poisoning of the reforming catalyst. At SRI International, we conducted an experimental research program (supported in part by the U.S. Department of Energy) to examine the source and reaction pathways that lead to carbon deposition in reforming catalyst beds.

The formation of catalyst carbon (i.e., carbon contacting catalytically active surfaces as opposed to homogeneous condensation and pyrolysis) was thought to be a primary step leading to coke formation. We examined the conditions that favor formation of catalyst carbons and the reactivity and stability of such carbons. Carbon formed by exposure of model hydrocarbons, such as ethylene and acetylene, to nickel and noble-metal catalysts, was studied because under coking conditions ethylene may compose on a mole basis as much as one-third of the hydrocarbons present in those regions of the catalyst bed where carbon deposition occurs. In the course of these studies a temperature programming technique was developed to quantitatively determine carbon deposits by their characteristic reactivity with hydrogen and dilute steam in helium. Results for alumina-supported nickel catalysts have been previously reported.¹ In this paper we present the results for noble-metal catalysts.

Experimental Methods

The reactivity of carbon deposits on reforming catalysts was studied with a quartz micro-reactor system using the temperature programmed surface reaction (TPSR) technique.^{1,2} During TPSR, the rate of gasification of the carbon deposit (as determined by continuous measurement of the effluent gas composition) was recorded as a function of time. The data are represented by the gasification rate versus bed temperature as in conventional thermal analysis. TPSR analysis was performed following decomposition under various conditions of exposure temperature, exposure duration and exposure gas (CO , C_2H_4 , or C_2H_2) for both 1 atm H_2 and 0.03 atm H_2O in He as the gasifying reactant.

Results

TPSR of Carbon Deposited on $\text{Rh}/\text{Al}_2\text{O}_3$ by C_2H_2 Exposure

TPSR experiments were performed for carbon deposited by C_2H_2 exposure on a 5 wt% $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst by C_2H_2 exposure at various temperatures. Like nickel, the rhodium catalyst exhibited a number of carbon states during TPSR (H_2), depending upon the temperature of C_2H_2 exposure (Fig. 1). Both catalysts form similar carbon states at elevated temperature. However, several low temperature carbon states on rhodium were observed following C_2H_2 exposure at 573 K. A comparison with the TPSR (H_2) results for the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts suggests the presence of filament carbon state at $810 \text{ K} \pm 10 \text{ K}$ following C_2H_2 exposure at 573 K and 773 K (which would correspond to the filament carbon state^{1,4,5} on $\text{Ni}/\text{Al}_2\text{O}_3$). For C_2H_2 exposure at 573 K, the carbon states at 645 K and 460 K probably represent surface (monolayer) carbon states.

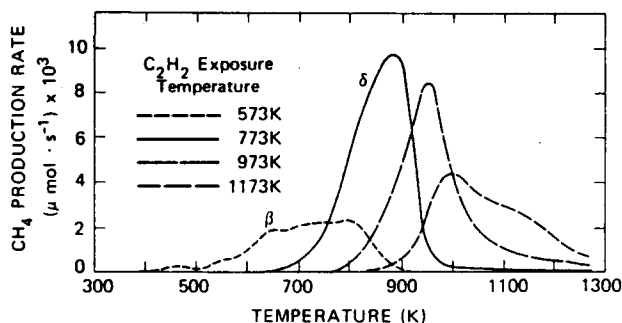


Figure 1. TPSR with H_2 of carbon deposited on 5 wt% $\text{Rh}/\text{Al}_2\text{O}_3$ by exposure to C_2H_2 (Exposure time, 100 s).

TPSR with H_2 of Carbon Deposited on 5 wt% $\text{Pt}/\text{Al}_2\text{O}_3$

Carbon deposits on $\text{Pt}/\text{Al}_2\text{O}_3$ produced by exposure to C_2H_4 exhibited significantly lower reactivity during TPSR with H_2 (Fig. 2). For $\text{Pt}/\text{Al}_2\text{O}_3$, like $\text{Rh}/\text{Al}_2\text{O}_3$, exposure to C_2H_4 at low temperature (523 K) produced two carbon states with peak temperatures at 610 K and 730 K during TPSR with H_2 . These carbon states are comparable in magnitude to the surface carbon states for Ni, but appear at $\sim 100 \text{ K}$ higher temperature. Between 773 K and 1173 K, C_2H_4 exposure produces bulk quantities of carbon composed primarily of a carbon state with a peak temperature which shifts from 985 K to

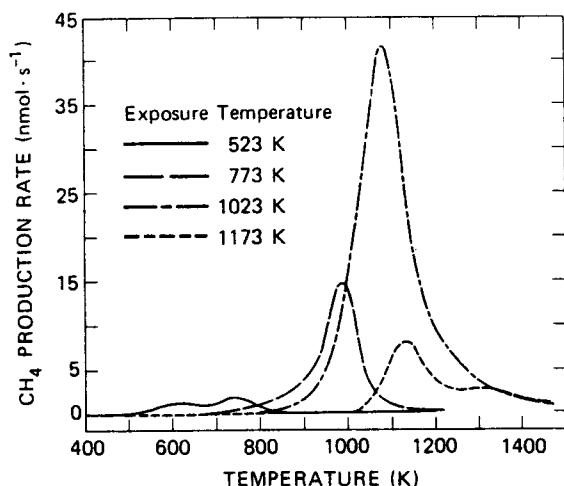


Figure 2. TPSR with H_2 of carbon deposited on 5 wt% Pt/Al_2O_3 by exposure to C_2H_4 . Partial pressure $C_2H_4 = 1.1 \times 10^{-3}$ atm. Exposure time and flow rate = 100 s at $0.5 \text{ cm}^3 \cdot \text{s}^{-1}$.

1125 K. These results are similar to results for the δ' , δ carbon states on Ni/Al_2O_3 , although the peak temperatures are 200 and 135 K higher, respectively.

TPSR with H_2 of Carbon Deposited on Ru/Al_2O_3

In a limited number of experiments with carbon deposition on Ru/Al_2O_3 following exposure to C_2H_4 , filament carbon was observed with reactivity very similar to that of Ni/Al_2O_3 .

Critical Steam-to-Carbon Ratios

In a series of experiments the critical (H_2O/C) ratios were measured with C_2H_4 as the hydrocarbon for the following catalysts: pure Rh, 50% Rh + 50% Ni, pure Ni, 50% Ir + 50% Ni, and pure Ir (Fig. 3). These results do not show great differences for the H_2O/C ratio with C_2H_4 between various catalysts. All show a declining H_2O/C ratio with increasing temperature, that is, $H_2O/C = 25$ at 773 K, $H_2O/C = 8$ at 873 K, and $H_2O/C = 2$ at 973 K. Between 973 K and 1073 K some scatter in the data was noted, but most catalysts had H_2O/C ratios less than 3 in this temperature range.

Discussion

At least seven carbon states have been deposited on Ni/Al_2O_3 catalysts and identified by their characteristic TPSR responses.^{1,3} The distribution of carbon in the various states during carbon formation depended primarily on the temperature during deposition.

All the catalysts studied exhibited small (up to monolayer) carbon states following low temperature exposure to C_2H_4 . These chemisorbed carbon states are likely reforming intermediates. Chemisorbed carbon is formed by the absorption and rapid dissociation of C_2H_4 and is removed as CO by reaction with surface oxygen, which is produced in turn by dissociative adsorption of H_2O or CO.

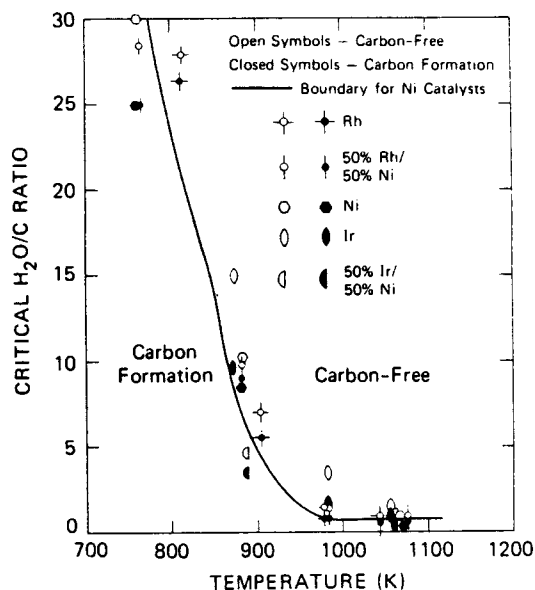


Figure 3. Critical steam-to-carbon ratio versus temperature for noble metal and noble metal alloy catalysts.

Gasification of dense catalyst carbon shells or tubes may be similar to catalytic gasification of a graphite substrate by small nickel particles. Direct controlled atmosphere electron microscopy (CAEM) of nickel catalyzed hydrogasification of crystalline graphite has provided many interesting observations about the nature of the gasification process.^{6,7} The nickel crystallites soften and change shape as they start to gasify graphite at temperatures well below the melting point of nickel (~ 1000 K). The interaction of graphite lowers the surface energy of the nickel crystallites with diameters of ~ 100 nm; and at 1075 K the nickel dissolved into the graphite substrate. This may explain why long filaments can be gasified by metal crystallites; the "wetting" action of the carbon keeps the metal in contact with the filament even as gasification proceeds. With metal-carbon contact assured, gasification proceeds as long as the reactant gas has diffusional access to the crystallite. Another important CAEM observation is that some nickel crystals deactivate at elevated temperature 1175 K and become immobile.⁶ This phenomena was attributed to dissolution of carbon into the nickel crystallites and its eventual precipitation as encapsulating graphite platelets, similar to observations on well-defined nickel, platinum, and iron surfaces.

The rates of nickel-catalyzed gasification of graphite are in reasonable accord with our TPSR results for the filamentous carbon state. For the δ carbon state, our E_a was $182 \pm 20 \text{ kJ} \cdot \text{mol}^{-1}$ in good agreement with the results of published value $220 \pm 40 \text{ kJ} \cdot \text{mol}^{-1}$. Hydrogasification of graphite by platinum and iridium have also been investigated with CAEM conditions and the results show that other noble metals are less active H_2 gasification catalysts than nickel. Rates comparable to nickel at 1035 K require 190 and 95 K greater temperature, respectively.

Conclusion

The results of the TPSR studies support the conclusion that the reversible deactivation of metal catalysts during hydrocarbon synthesis at low temperature (550 K) is due to formation of a carbonaceous film. Coking at moderate temperature (800 K) during hydrocarbon reforming is due to rapid formation of filamentous carbon which at very high temperature (1100 K) produces thick encapsulating layers of carbon.

References

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