CARBON GASIFICATION (II)
Pt-CATALYZED HYDROGENATION OF CARBON

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Abstract—The hydrogenolysis up to 90% carbon conversion of graphitized carbon black on platinum-catalyst in a flow reactor, at 873-1073K under 101 KPa hydrogen pressure, has shown that the reaction rates (g carbon reacted (initial surface area)$^{-1}$ (time)$^{-1}$) reached the maximum in the half way of 90% conversion. The change of Pt particle size over this range of the conversion was also measured by H_2 chemisorption, X-ray line broadening and TEM. Pt particle size calculated from H_2 chemisorption was too large due to the decrease of H_2 uptake on the Pt surface. In the early stage of conversion, Pt particle sizes measured by XRD and TEM did not change significantly. The mechanism of Pt catalyzed carbon gasification is discussed in the light of these observation.

INTRODUCTION

While the catalytic gasification of carbon has been actively investigated in the past decade, the carbon hydrogenolysis has been the least studied area because of the very low reactivity of hydrogen toward carbon [1,2]. Recently, however, the advent of new experimental techniques and the availability of highly purified and crystalline carbons have made it possible to understand the course of reaction in detail. Using CAEM in Pt catalyzed hydrogenation of graphite, Baker et. al. [3] observed that a unique catalytic particle redispersion took place during the reaction. Along with these workers, Keep et. al. [4] also found the formation of channels being oriented predominately parallel to $(11\bar{2}0)$ direction and that the larger the catalyst particle the faster became the rate of catalytic attack for channels of similar depth: i.e., channel propagation rate is proportional to the square of catalytic particle size in catalyzed hydrogenation of graphite. Holstein et al. [5] proposed that the rate determining step in platinum catalyzed hydrogenolysis of carbon was the breakage of carbon-carbon bonds by platinum resulting in the removal of a carbon atom from the carbon lattice. Although it is well known that the catalysts break carbon-carbon bonds of hydrocarbons adsorbed on the surface during hydrogenolysis [6,7] this direct breakage of the carbon-carbon bonds by the catalyst has not been considered for solid carbon during catalyzed gasification of carbon at temperatures (700 to 1300 K) comparable to or higher than those encountered for catalyzed hydrogenolysis.

Carbon is not only the substrate but also the support for the catalyst particles in the gasification reaction. As the reaction proceeds, the carbon support is consumed and it is expected that the total surface area and the nature of the active carbon sites are changed. Accordingly, metal particles become more concentrated and which, in turn, affect the metal dispersion: i.e., not like on a well defined, and not changing reaction surface reproducible measurements are, in this case, not easily made. A more reliable kinetic rate expression for the carbon gasification reaction is, therefore, required to compare with other experimental results.

In this paper we present the result of studies on the carbon hydrogenolysis over the entire life of the carbon in the conversion process i.e., for the entire period of conversion of the initial carbon. In addition, the determination of the changes in both the total surface area and the Pt particle size with the conversion are described. For the determination of Pt particle size, H_2 chemisorption, X-ray line broadening and TEM methods were employed and the results were compared.

EXPERIMENTAL

The catalyst used for the experiments was 1% Pt/Spheron carbon as previously described [5]. Hydrogen was purified by diffusion through a palladium membrane before use or a Matheson hydrogen generator was used. Helium (99.995%, Matheson) was used as it was received.

In order to remove the surface oxide complexes present on the carbon surface and to provide a reproducible state for kinetic measurements, samples were pretreated either by flowing He at atmospheric pressure or in vacuum (8×10^{-4} Pa.) for 2 hrs. at 1225 K. All the kinetic experiments were carried out as previously described [5].

Interrupted kinetic experiments for the determination of the BET surface area and the average platinum particle size as measured by hydrogen chemisorption, as a function of the fraction of carbon gasified during the C-H_2 reaction, were carried out in a standard volumetric gas adsorption apparatus [8].

X-ray diffraction measurements were performed using a Norelco diffractometer with CuK α radiation. Analysis of the line broadening for the Pt (111) and Pt (200) peaks was done according to the procedure of Klug and Alexander[9].

Samples for TEM were mechanically well ground and dispersed ultrasonically in ethanol. A few drops of the suspension were spread over self-perforated microgrids coated with an evaporated carbon film. TEM measurement were conducted using a Hitachi electron microscope at NASA Ames Research Center, capable of better than 0.5 nm resolution. All catalyst samples were examined at a magnification of 180,000 x.

RESULTS

Reaction rate as a function of carbon conversion

Reaction rate profiles, expressed as the weight C gasified (initial surface area)$^{-1}$ (time)$^{-1}$ vs. carbon conversion, f, are shown in fig. 1. Carbon conversion was used for the values in abscissa instead of time, to account the fact that the overall reaction time varies considerably with the temperature.

Initially, the rates were about a factor of three times higher than the extrapolation of the curves to zero conversion indicated, but this initial activity (not shown in the figures) was only transient and a minimum when the rate was measured at $f < 0.01$

The rate then increased sharply, reaching a maximum around a fractional carbon conversion of about 0.2, and decreased at the stage of higher fractional carbon conversions.

Rates of the Pt-catalyzed C-H_2 reaction observed both in the continuous and in the interrupted kinetic ex-

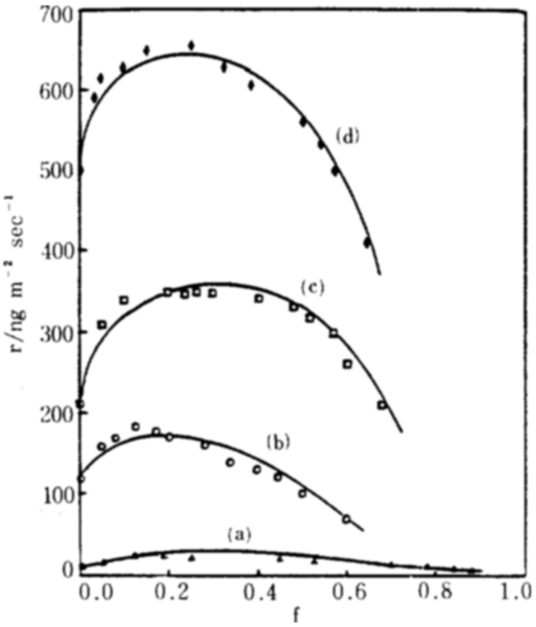


Fig. 1. Platinum-catalyzed hydrogenolysis of carbon : Rate r of gasification of carbon as a function of the fraction of carbon gasified f

Temperature △ 923 K ☐ 1023 K
○ 973 K ◇ 1073 K

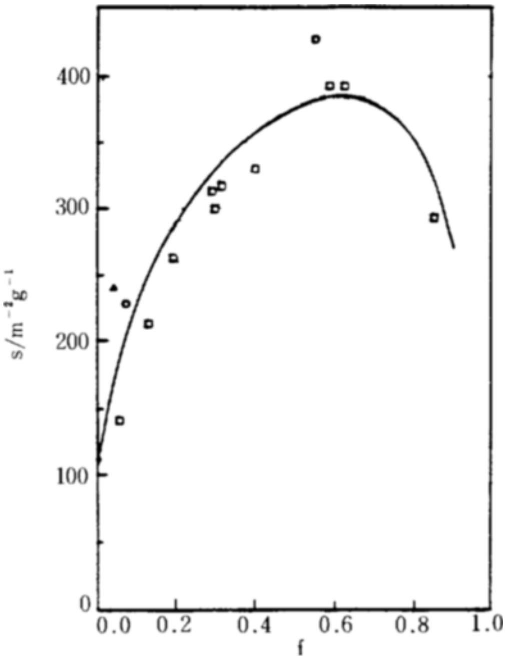


Fig. 2. Platinum-catalyzed hydrogenolysis of carbon : BET surface area per gram of carbon remaining, s, as a function of the fraction of carbon gasified f

Temperature ◆ Before reaction ○ 973 K
△ 923 K ☐ 1023 K

periments were identical with the exception of the first few minutes after the adsorption measurements, where the rate was higher for the interrupted experiments.

At the very early stage of the reaction the reproducibility of the data was poor and the rate measurements were unreliable. This period of the reaction, hence has been regarded as the initial period. However, a careful examination of these phenomena can throw considerable light on the mechanism of carbon gasification.

Total specific surface area

BET results are shown in Fig. 2. Prior to gasification the sample has a specific surface area of 115 m^2/g. It is increased to 220 m^2/g at $f = 0.1$ and its increase continued thereafter with a slightly lower rate. Shelef [11] reported, when gasification of the graphite flakes were occuring only at particle edges, that the surface area increase due to reduction in particle size would be negligible. The large increase in surface area following gasification, therefore, could be explained in terms of vigorous roughening and etching of the basal planes due to channel formation.

Pt particle size change with reaction

The results for the change of Pt particle size measured by H_2 chemisorption at various stage of carbon conversion are listed in Table 1 and depicted in Fig. 3. The effect of pretreatment method on the size of Pt particle was negligible. As the reaction proceeded, the size of Pt particle increased very sharply at lower conversion and then increased slightly independent of reaction temperature. Particle size increased from 4 nm initially to 100 nm at about $f = 0.6$. What factors were playing dominant roles in the change of particle size? First possibility is a particle sintering. Ehrburger et. al., [12] and Bett et. al., [13] showed that the carbon supported Pt particles had a low tendency to sinter in He atmosphere. In particular, Baker's in situ CAEM experiment results [14] showed that Pt particles on a carbon support increased in size by a factor of only 3 under 20 KPa H_2 atmosphere for 1 hr from 470 to 1075 K.

Table 1. Particle Size Changes as a Function of Carbon Conversion.

Temperature (K)	f	$d^a_{H_2}$(nm)	$d^b_{X\text{-}ray}$(nm)
	0.0	4.92	
923	0.0068	6.46	
	0.0121	9.16	
	0.0293	8.66	
	0.0654	8.74	
	0.1116	8.90	
973	0.0695	9.83	
	0.1271	10.72	
	0.5532	20.08	14.2
	0.6025	55.52	
1023	0.0132	10.26	
	0.0438	10.97	
	0.0643	10.97	
	0.5881	25.51	
	0.6490	26.96	
	0.6670	24.20	18.8
	0.7250	44.94	
1043	0.6961	33.71	
1073	0.447	17.48	
	0.965	104.86	25.9

a Calculation based on cubic structure

b Average value of two peaks

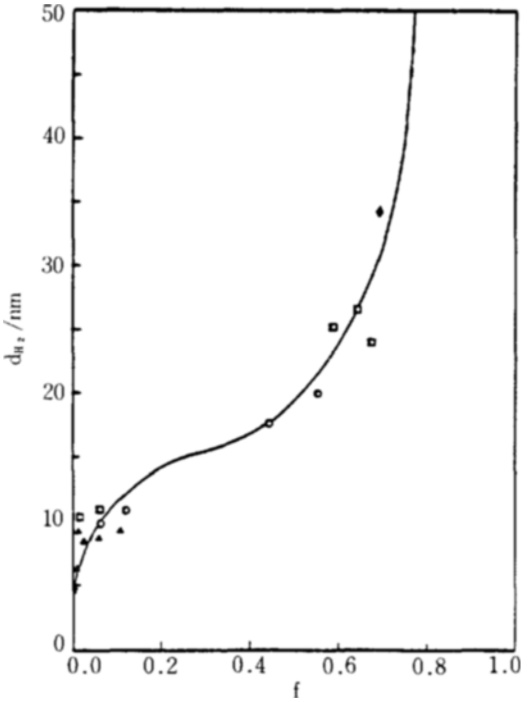


Fig. 3. Platinum-catalyzed hydrogenolysis of carbon : Average platinum particle size (determined by hydrogen chemisorption) d_{H_2} as a function of the fraction of carbon gasified f.

Temperature : ◆ Before reaction ☐ 1023 K
△ 923 K ◇ 1073 K
○ 973 K

The heterogenized carbon surface had many active sites where Pt particles might nucleate during preparation, and it was not removed in the mild H_2 treatment. There is another claim that strong metal-support interactions may exist which retard H_2 chemisorption for unknown reasons [15]. These interactions may occur in Pt/C system although strong metal-carbon interactions have not been reported for this system.

Pt particle sizes were calculated from Pt(111) and Pt(200) peaks using Scherrer equation for cubic crystals. In each case the line width was corrected for instrumental broadening using a polycrystalline silicon standard. These values are listed in Table 1 for the comparison with the chemisorption data. These values do not agree well with chemisorption results. Although the particle size calculated from X-ray line broadening is generally smaller than that from the chemisorption results, the size difference is too large.

Table 2. Effect of O_2 Treatment of the Pt Dispersion.

Temperature(K)	f^a	No treatment	After treatment
	0.0	D = 0.192	D = 0.247
1023	0.0643	D = 0.086	D = 0.115
	0.6490	D = 0.035	D = 0.057
	0.7250	D = 0.009	D = 0.027
1043	0.6961	D = 0.028	D = 0.054

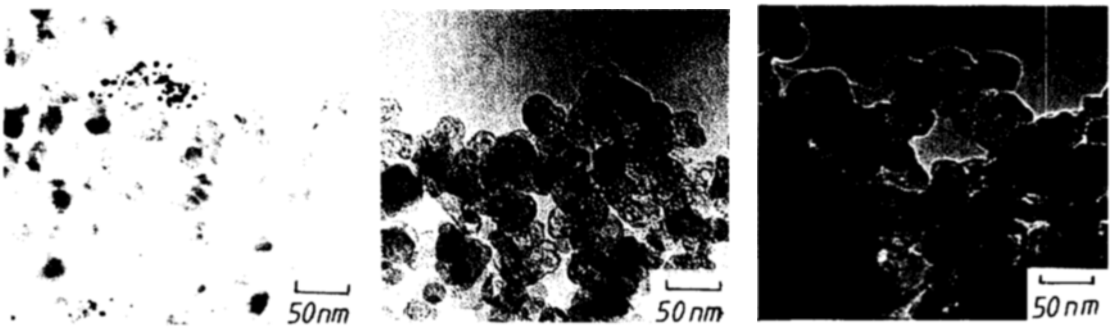
[a] Fraction of carbon conversion

We exposed samples which had been used for H_2 chemisorption to 25 KPa oxygen for 20-120 min. according to the procedure of Boudart et. al.,[10]. Reduction of samples was done in flowing hydrogen for four hours following evacuation at 650 K until no water could be detected by gas chromatograph. After cooling to room temperature in vacuum, we examined H_2 chemisorption isotherms. A part of those results are listed in Table 2. Remarkably enough the amounts of chemisorbed H_2 increased to more than twice the previously obtained values. This phenomena indicates either that some of the platinum particles were polycrystalline or that the entire surface of the platinum was not available for the adsorption of hydrogen, possibly due to site blockage by carbon or the decreased ability of the platinum to adsorb hydrogen because of the carbon-platinum interaction. It was also possible that the Pt particles penetrated into the carbon layer, but because Pt intercalated graphite compounds were not prepared at the same condition as in this study, we would not consider here.

We took TEM pictures of several samples characterized by H_2 chemisorption in order to confirm these results by direct observation (Fig. 4). It was evident that TEM results well agreed with X-ray line broadening, but not with H_2 chemisorption. There were negligible changes in particle size during the initial stages of reaction, independent of temperature over a 100 K range. After 50-60% conversion some of the particles became larger, but the largest one was less than 50 nm and we could observe many 5-7 nm particles coexisting with larger ones. While the TEM picture does not give information on the reaction environment or possible changes during quenching, the data obtained in this study qualitatively support the hypothesis that carbon complex deposits on the Pt surface in the reaction.

DISCUSSION

Following conclusions could be readily drawn based on results of the kinetics study and of Pt particle size measurements. Firstly, the hydrogenolysis is catalyzed until all the carbon is gasified (since the uncatalyzed reaction, around 2000 times slower[5], is undetected at the experimental temperature.). Secondly, the rate is not constant, but changes as the carbon is gasified. Thirdly,



(a) (b) (c)

Fig. 4. Platinum catalyzed hydrogenolysis of crbon: transmission electron micrographs of the Pt/C
a) after pre-treatment.
b) after reaction at 923 K for 0.7 h
c) after reaction at 1023 K for 0.9 h

the average size of platinum particle determined by hydrogen chemisorption increased continuously throughout the course of the reaction and was almost insensitive to the reaction temperature (Fig. 3). Finally, there was no correlation between the reaction rate and the average size of platinum particle determind by hydrogen chemisorption.

The changes in rate of carbon hydrogenolysis with fractional carbon conversion can be rationalized based on the following reasoning.

The decrease in rate at fractional carbon conversions higher than around 0.5 is due to increase in size of platinum particles. In the proposed rate determining step[5], the breakage of carbon-carbon bonds by the platinum requires contact between the platinum and the carbon. When the platinum particle size becomes the order of the carbon particle size (30 nm), the amount of carbon-platinum contact decreases, resulting in a decrease in the rate. At low fractional carbon conversions, the size of platinum particle is much smaller than the size of carbon particle. A CAEM study of the platinum catalyzed hydrogenolysis of graphite[3] has shown that the rate of channel formation (particle propagation) parallel to the graphite basal plane increased almost linearly when size of platinum particles comprises between 30 and 80 nm in diameter. Since the rate of carbon gasification by an individual particle is also nearly proportional to its cross-sectional area, and the total number of particles present is inversely proportional to the cube of particle size, these CAEM results would suggest that the observed rate of gasification is independent of particle size when the platinum particles are much smaller than the carbon particles. In the present study, a polycrystalline carbon was used. The initial increase in the rate might result from increased contact between the platinum and the prismatic planes of the carbon during the initial stages of the reaction. The discrepancy in platinum particle sizes measured by chemisorption of hydrogen and by X-ray line broadening (Table 1) increased as the reaction progressed. After hydrogen chemisorption measurements, some used samples were exposed to a static mild oxygen atmosphere and they showed restoring ability for hydrogen chemisorption (Table 2). CAEM studies of the catalyzed hydrogenolysis of graphite by platinum[3] and by nickel[4] have indicated that both particle agglomeration and break-up could occur, but no indication has been presented whether particle agglomeration resulted in single crystalline or polycrystalline particles.

The carbon used in this study, Spheron 6, has a large fraction of the surface consisting of prismatic planes capable of being wet by platinum. This platinum may stack in between layers like a thin monolayer that is unable to adsorb hydrogen. Nickel which has wet graphite during the C-H_2 reaction has been shown by CAEM to recoagulate into small particles by heating in an oxidizing atmosphere such as water[4]. The observed restoring ability of platinum for hydrogen chemisorption on mild oxygen treatment may be due to recoagulation of platinum into small particles which again adsorb hydrogen.

Site blocking by the active carbon complex prevents hydrogen adsorption from platinum surface, and this could contribute to the large Pt particle size measurement by H_2 chemisorption. These carbon complex might be easily removed by oxygen at mild condition as we have shown. Periodic interruption of the reaction for the surface measurement didn't cause any drastic changes in rate. Transient reaction rates were also observed for the iron catalyzed Fischer-Tropsch reaction where carbon complex formation was considered as the rate determining step [16,17]. These are another indirect indication of the possibility of active carbon complex deposition on the platinum surface during the reaction.

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