Short communication

Catalytic carbon gasification: Understanding catalyst-carbon contact and rate jump behavior with air

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ABSTRACT

It is easier to optimize reactions when the mechanism is well understood. Nowadays, catalytic carbon gasification is an area of industrial importance. The mechanism based on C-bulk diffusion has been recently updated. The relevance of the Tammann temperature to get efficient carbon/catalyst nanoparticle contact is now better understood. However, the interaction between kinetics and thermodynamics still needs some clarification. Rate jump is a kinetic phenomenon observed in some cases in catalytic carbon gasification by air or oxygen following a minor increase in temperature (v.g. $\Delta T = 5\,°C$). This occurrence has been reported, but the phenomenon is not well understood. In this short review, we show that the rate jumps can be consistently explained by the "carbon-worm" mechanism due to a jump in the temperature of the moving nanocatalyst particles. The carbon bulk diffusion step is then much faster and the external film mass transfer becomes the rate-limiting step. The reaction order changes from zero to one. The nature and role of catalyst-carbon contact in catalytic carbon gasification is discussed.

1. Introduction

Reactions based of carbon/coke are an important area of research and of industrial development nowadays. A review of kinetics and mechanism studies of catalytic carbon gasification has been recently published [1]. However, the rate jump phenomenon observed in carbon gasification by air or O_2 has not been interpreted yet. Also, the catalyst-coke (or catalyst-graphite) contact requires clarification. Table 1 lists data on carbon/coke gasification by the most common gases used. The reaction mechanism of $H_2/CO_2/H_2O/O_2$-carbon reactions should be the similar (see our recent papers on the subject [1,10–12]) but the rate-determining step may change. For example, the surface reaction with H_2 is much slower, so the reaction is 1st order and the surface reaction C/H_2 is the rate-determining step. Experimental studies reporting rate jumps are listed in Table 2 [2–8].

2. Modeling carbon gasification

In the 1960's several researchers studied graphite/catalyst particle interaction in carbon gasification using in-situ microscopy [13–15]. Tamai and Tomita studied carbon gasification by H_2 in 1974. Both the tight contact graphite/carbon and the particle shape were well-documented [16], as shown in Fig. 1. The requirement of thigh contact between catalyst particle and carbon can be seen as indicative of the flux of carbon atoms: carbon dissolution, carbon atoms diffusion through the metal particle and emerging carbon atoms reaction with the gas on the opposite side of the nanoparticle. An important finding: the identification of armchair (1,1,0) orientation prevailing in the sidewalls of the channels (90% with Co and Fe; 96% with Ni). This indicates that the front of attack of the particles being perpendicular to the sidewalls, is zigzag oriented - (0,1,0) or (1,0,0) - both initially and during the "carbon-worm" penetration.

More information about catalytic carbon gasification was gathered in the next two decades. Extensive modeling of carbon/coal gasification was performed using non-porous and porous models, cylindrical and random pore diameters, particularly by Petersen (1957), Levenspiel et al. (1975), Turkdogan et al. (1968–1970), Bathia and Perlmutter (1980–89; 1996–2002), as recently reviewed [1].

Baker and co-workers, studied gasification of graphite using TEM [17–19]. Interpreting TEM images is frequently difficult: transparency is the basis for the visual observation. This is sometimes misleading. The resolution of the Brownian movement in 1904 was accepted quickly as the optical microscopy images were easily interpreted. The studies by Thomas and Walker [14] and Tomita and Tamai [16] used

Table 1
Main carbon gasification systems: thermodynamics and catalysts.

Reactant/ products	Thermodynamics	Catalysts
R: O_2 P: CO_2, CO	Exothermic, fast $*\Delta T \sim +160\,°C$	Alkali metal oxides and salts, alkaline earth oxides and salts, transition metals or oxides, noble metals
R: CO_2 P: CO	Endothermic, slow, high T	Alkali metals and alkaline earth salts, metals of the Pt and Fe groups
R:H_2O P: CO, H_2	Endothermic $*\Delta T \sim -50\,°C$	CaO, NaCl, KCl, Na_2CO_3, K_2CO_3, Co $(OH)_2$, Fe_2O_3, Fe_3O_4, Ni, NiO, CuO, ZnO, MnO_2, PbO_2, V_2O_5, BaO …
R: H_2 P: CH_4	High pressure	Alkali and alkaline earth metals salts and oxides, Fe, Co, Ni, noble metals of group VIII, sulfides of Mo and W; $(NH_4)_2MoO_4$; chlorides of Zn, Al, Sn

Note: The average difference ($*\Delta T$) between the onset mobility temperature observed in graphite and the Tammann temperature of the probable operating catalyst phase is indicated, as estimated by Baker [9].

Table 2
Examples of "rate jumps" in carbon gasification by air/O_2.

	Carbon	Gas	Catalyst	Temp/°C	Year	Ref.	Authors
1	Coal char	Air	Cu	200–400	1987	[2]	Moreno-Castilla et al.
2	Graphite	Air	Tl_2O_3	500	1987	[3]	McKee
3	Activated C	O_2	MoO_3	400–800	1990	[4]	Silva, Lobo
4	CMC	Air	Cu	200–300	1990	[5]	Devi, Richards
5	CMC	Air	Ni	200–400	2001	[6]	Devi, Kannan
6	Olive husk	O_2	(ashes)	> 450	2007	[7]	Senneca
7	CMC	Air	Ca, K	250–450	2010	[8]	Devi et al.
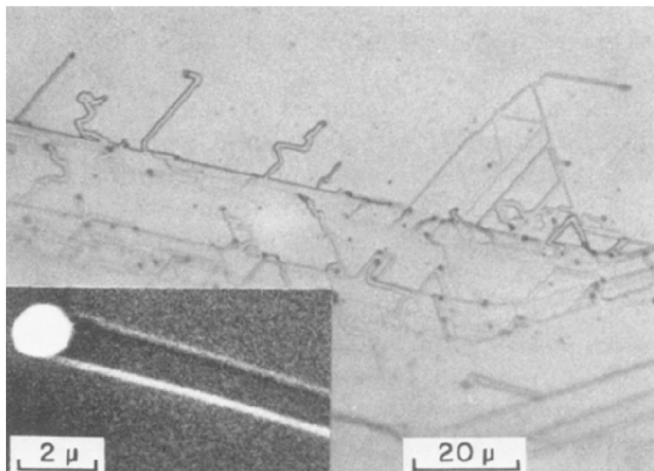
Fig. 1. "Channels formed by Ni particles in the hydrogenation at 1050° for 3 h", observed under an optical microscope by Tamai and Tomita in 1974. Reprinted with permission from [16]. Copyright (1974) American Chemical Society. "A SEM photograph is inserted to show the tip of the channel at a large magnification".

optical microscopy. In situ heating stage microscopy is again being used with success in carbon gasification to understand and optimize the process [20,21]. This is a promising approach.

3. Catalyst-carbon contact

The role of the carbon-catalyst nanoparticle contact as well as the nature of the phase present was discussed by several authors in some detail. Important information is whether the metal or carbide is the stable phase in a given system. However, mechanisms involving carbon atoms diffusion through the metal nanoparticles were avoided. Ding et al. [22,23] used Na_2CO_3 as additive on coal pyrolysis and gasification. Those papers are quite important in understanding the catalyst/carbon contact. However, the carbon gasification by CO_2 and H_2O are not exothermic and so this subject will not be further addressed on this paper.

Evidence of the mechanism operating can be gathered in a detailed isothermal kinetic study, evaluating: 1) Early kinetic behavior; 2) Steady-state rate period (kinetic linearity); 3) Reaction order; 4) Activation energy. That information lead to the proposal of the carbon bulk diffusion mechanism in view of the kinetic linearity observed and zero order at lower temperatures (C bulk diffusion controlling) [20]. Bulk diffusion of carbon atoms through solids is well known since the 1930's. The prevalence of interstitial diffusion of C through transition metals is to be expected. The covalent radius ratio solute/solvent is lower than 0.60 [21].

The discussion about which solid phase prevails and operates during reaction should include the possible existence of two different phases (at each side of the catalyst particle), one in equilibrium with the gas (O_2) and another in equilibrium with carbon [10,11]. Operando X-ray diffraction offers a good way to confirm the nature of the solid phases. XRD gave evidence in a recent study of rice husk gasification of the metallic Ni prevailing during reaction. But NiO was dominant at the end, when the gasifying husk was consumed [24]. During reaction a thin NiO layer ("invisible" by XRD) should prevail at the gas side of the nanoparticles. The difference in C diffusivities in Ni and NiO explains the much lower thickness of the oxide phase during reaction. Under steady-state diffusion the thickness of two meta-stable phases must be inversely proportional to the respective diffusivities [10]. The Tammann temperature in solid-solid contact was defined observing the behavior of sintering processes by Gustav Tammann in 1936, facilitating the shape adjustment and merging of particles. In the present case, it facilitates the carbon–catalyst contact and easier C atoms dissolution. Interstitial C atoms diffusion through the metal nanoparticle follows. In recent years, the so-called graphite etching, sometimes called "nanocutting", became important. It aims at the precise construction of minute integrated circuits on graphene nanoribbons [25–27]. Images and behavior similar to the ones observed by Tomita and Tamai in 1974 were reported. Sustained armchair or zigzag orientation of nanoparticles movement was confirmed despite the occasional changes of direction [16]. The mechanism of nanocutting is certainly a "carbon-worm" behavior in view of the detailed kinetic data recorded in many carbon gasification systems [1].

4. Understanding rate jumps

It was reported in the 1980's that there is a deviation of the temperature at which the particle movement starts (ΔT) when gasification of graphite is observed under in-situ TEM or SEM as remarked in Table 1 (*). In the case of gasification by O_2 (exothermic process), the particles start moving, apparently, 160 °C below the Tammann temperature. In our opinion, this indicates that the active contact (CASA) front becomes operative. The temperature of the particle rises to that level, despite the prevailing lower temperature of the operating cell.

In order to understand and model the rise of temperature of the particles, the following 3 factors must be considered: 1) The heat capacity of the particles; 2) The thermal conductivity of the solid; 3) The size of the particle.

Fig. 2 shows the geometry of a particle and catalyst-carbon contacts involved in graphite gasification observed by in-situ electron microscopy (in graphite gasification: Fig. 2A). In coke gasification (Fig. 2B) the catalyst particles are not seen but the carbon/catalyst contact should operate in a similar manner [10,11].

In the correlation observed by Baker et al. [9], the 160 °C temperature difference is understandable given the exothermic nature of the oxygen gasification reaction, the poor thermal conductivity of graphite in the crystallographic *c* direction and the small thermal