Review article

Kinetics and mechanism of catalytic carbon gasification

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HIGHLIGHTS

- The behavior of catalyst nanoparticles in catalytic carbon gasification is reviewed.
- Evidence of the carbon bulk diffusion mechanism operating is summarized.
- Linking kinetics with in-situ HRTEM and XRD studies allows a better understanding.

ARTICLE INFO

ABSTRACT

The evidence of the carbon bulk diffusion mechanism, operating in catalytic carbon gasification, is summarized. Linking visual and structural observations (transmission electron microscopy and X-ray diffraction) with comprehensive kinetic studies offers a good basis to understand the details of the phenomenological behavior. The role of the catalyst nanoparticles in catalytic coal/coke gasification and in graphene reactions is briefly reviewed. Knowledge of the solid-state phases operating *under steady-state reaction* and of the "sintering like" catalyst-carbon contact is essential to understand the most likely reaction sequence: 1st step - carbon dissolution; 2nd step - C bulk diffusion; 3rd step - surface reaction of emerging C atoms with the reactant gas. Kinetics and preliminary solid-state changes observed in graphite gasification and in coke/coal gasification leads to the conclusion that they follow the same mechanism. Using an analogy with *proton exchange* membranes in fuel cells: catalytic carbon gasification is promoted by *carbon exchange* moving nanoparticles. A better understanding of the mechanism may lead to improvements in industrial processes.

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1. Introduction

Carbon gasification is an important topic nowadays in view of the energy market, bioenergy trends and the bio-refinery concept, which is expanding due to recent political and economic developments. The use of carbon gasification in blast furnaces, Fisher-Tropsch units, combined cycle power plants, diesel soot abatement equipment and, recently, fuel cells based in carbon gasification, reinforce its importance.

In the last 30 years, several proposals for the mechanism have been advanced. Important reviews are available [1–8]. The two general mechanisms first proposed for catalytic carbon gasification were electron-transfer and oxygen transfer, the latter initially proposed for the O_2 reaction [9–11]. Both mechanisms fail to explain the kinetic behavior. From in-situ observations there are several indications that carbon bulk diffusion is the key step in the process. The mechanism of catalytic carbon gasification has been recently reviewed in that perspective [12]. There is enough kinetic evidence that the prevailing mechanism involves carbon bulk diffusion through the catalyst [13]. This fact has been ignored (or forgotten) for 30 or 40 years. The main carbon gasification systems are briefly listed in Table 1: gases used (reactants and product/s), thermodynamics, catalysts and temperature changes (ΔT) observed in catalyst particles [4].

In graphite gasification the bulk diffusion mechanism has been frequently assumed. In this case, the main clues are the image, the geometry and the movement of the catalyst particles observed by in-situ transmission electron microscopy (TEM), but no (or little) kinetics are taken into account, although it is the most important key to evidence the mechanism. Joining the information from the two areas of study, the operating mechanism is better understood.

In order to fully understand catalytic carbon gasification it is essential to distinguish the initiation phase from the steady-state gasification process – two sequential but different stages. During initiation, thermodynamics and 2nd Fick's law are essential to understand the changes: phase transitions and/or solid-state reactions. Next, under steady-state 1st Fick's law (carbon bulk diffusion), geometry and gas surface catalytic reaction are the essential elements to understand kinetics: *a sustained diffusion-reaction mechanism is operating*.

Recently two Italian groups have tried new experimental thermo gravimetric approaches. Badini et al. have shown that the so-called Ozawa method enables non-isothermal thermogravimetry analysis (TGA), i.e., TGA and TPO (temperature programmed oxidation) with a good estimation of the activation energies. This is a powerful technique, but will be misleading when solid-state phase changes take place in the temperature interval under study [14]. Senneca et al. compared 3 techniques: TGA, non-isothermal TGA and ALPR (aerodynamic levitator particle reactor) in non-catalytic gasification with excellent results [15]. These experimental approaches are very convenient for scale-up modeling kinetics but not for studies to understand the mechanism, the solid-state chemistry, and the role of the catalysts. Only isothermal studies can show the transition from initial solid-state reactions to successful steady-state gasification, as discussed below.

2. Reactivity of graphite vs. coal/char/coke

There are two types of studies on carbon gasification reactivity, mostly: (a) studies observing images of *graphite* gasification by TEM or scanning electron microscopy (SEM) - but no formal kinetics; (b) kinetic studies of *coke or activated carbon* gasification using thermo-gravimetry and chromatography – without in-situ images. The role of geometry in kinetics is frequently ignored. Most studies treat the two approaches as separate realities. However, both observe the same reaction and the same reality.

The internal graphite-based structure of hard and soft cokes and carbon blacks has been known since the 1950s [16]. In more recent graphitization studies of various coals, the authors performed studies based on X-ray diffraction (XRD) observations, on thermal diffusivity and on differential scanning calorimetry [17]. There is a strong kinetic evidence that the mechanism of catalytic gasification is the same for graphite, coal, char, coke and diesel soot [13]. Even diesel soot particles were found to be jagged rather than spherical, enabling the same mechanism of catalyst particles sliding on graphite planes, and attacking the graphitic structure in a direction perpendicular to the crystallographic c axis.

There is also evidence that non-catalytic gasification of low rank chars is catalyzed by impurities. Naidu et al. performed very recently a study of CO_2 gasification kinetics for low-rank Indian coals and biomass fuels. They observed extensive zero order kinetics (linearity, in fact) with lignite and biomass chars, known to have high alkali oxides [18]. When kinetic linearity is observed (*w* vs. *t*, that is, weight vs. time), in a catalytic reaction where a solid reactant is disappearing, we must conclude that a constant reaction front is operating [13]. The overall catalyst front is the sum of all the worm "carbon eating" nanoparticles forming an overall stable contact active surface area (CASA). We will discuss first coal gasification and then graphite gasification. Comparing the findings from both areas at point 15 below, we conclude that the same reaction occurs and the same mechanism applies.

3. Linearity in observed kinetics

We assume that the intrinsic kinetics in the case of catalytic carbon gasification is based on the "contact active surface area" (CASA) [12,13]. This easily explains linearity in the experimental *w* vs. *t* plots (Figs. 1 and 2) as well as the two alternative patterns of fast and slow moving catalyst particles according to size, observed under *in-situ* electron microscopy, when the CASA front is stable [12]. However, the CASA front being *stable* does not mean being exactly *constant*. That depends on the stable nanoparticle

Table 1
Main carbon gasification systems.

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 and oxides, noble metals
R: CO_2 **P**: CO	Endothermic, slow	Alkali metals and alkaline earth salts, metals of the Pt and Fe groups
R: H_2O **P**: CO, H_2	Endothermic $\Delta T \sim -50\,°C$	Transition metals
R: H_2 **P**: CH_4	High pressure, low temperature	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