

Catalytic Combustion of Carbon

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Abstract

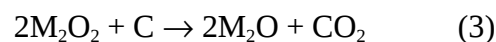
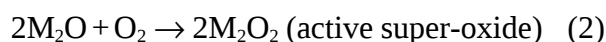
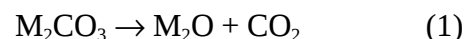
Present day energy needs of mankind are strongly dependent on the combustion of fossil fuels and other carbonaceous materials. The combustion reaction is accompanied by simultaneous production of gaseous pollutants like CO, NO_x and SO₂. In the catalytic combustion, the advantages are two fold: i. The combustion efficiency will be higher and this results in the higher energy realization and ii. The operating temperatures being much lower the emission level of the pollutants also will be greatly reduced. In this study, thermogravimetric analysis (TGA) has been used in following the non-isothermal kinetics of the combustion using two different models. . In the present study an attempt has been made to evaluate from the thermogravimetry, the kinetic parameters for carbon combustion in oxygen and their dependence on the catalyst present in the system. Four different supported systems have been used for the oxidation. Similarly, four different pure carbon materials, differing in their surface areas and crystallinity, have been investigated. For evaluating the catalytic activity, two rate equations have been applied for the isothermal oxidation kinetics of the carbon samples. The catalytic activity on the oxidation of carbon has been observed in the form of lower ignition temperature and a decrease in the energy of activation. The possible role of oxygen spill-over is discussed.

Introduction

More than three fourth of the world's energy needs is derived from the fossil fuels, namely, oil and gas. With the re-emphasis on coal, as an important source of energy, numerous studies have been initiated and focused on the improvement in coal gasification and increasing the efficiency in coal combustion through catalytic processes [1]. Catalytic combustion has certain advantages over conventional flame combustion. The main advantage in using coal is its vast reserves in contrast to depleting oil sources. The main problem is in handling which gives rise to a lot of environmental problems. The major problems in utilising the fossil fuels are the thermal and gas pollution (generation of CO, NO_x and SO₂). The concentration levels of the gas pollutants can be drastically reduced by increasing the efficiency of the combustion. Both noble metal catalysts (platinum group of metals) [2], and metal oxide catalysts (mainly of alkali and alkaline earth metals)[3] have been studied in coal combustion. It is known that catalyst plays a major role in the reactivity of chars [4]. They (chars)

can be visualized as supported catalyst systems in which the coal component can be considered to be support and the inorganic impurities functioning as a catalyst [5]. The kinetics of this solid-gas interfacial reaction depends on a variety of experimental parameters like gas diffusion in the pores of the sample, the surface area, the nature of inorganic component and the reactivity of oxygen. It has been shown that the degree of dispersion of the inorganic species has a definite role in the catalytic combustion [6].

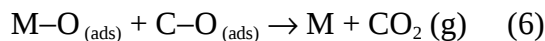
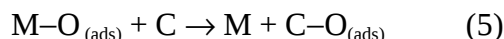
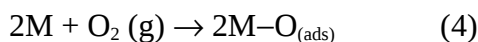
In the case of metal oxides, an active super-oxide of the metal (Na₂O₂, CaO₂, etc.) is formed *in situ* during combustion, which being unstable, especially, at higher temperatures of combustion, supply oxygen in a highly active form (probably as atomic oxygen) to the carbon in the coal for oxidation. The proposed mechanism is as follows [7]:



When the noble metal acts as a catalyst, the redox mechanism, wherein the metal oxide $\rightarrow$ metal $\rightarrow$ metal

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oxide has been proposed [8].



In the above mechanism the dissociative adsorption of oxygen on the metal is invoked. This precursor is the source of active oxygen supply. In spite of the difference in mechanistic paths, a feature, which is common to both the mechanisms, is the migration of oxygen in the active form from the catalyst to that of the carbon sites in coal. The spill-over of oxygen has been shown to be the cause for the catalytic effect [9]. The catalytic effect is expected to be revealed in the form of lowered temperature of ignition and lesser energy of oxidation. However there are reports showing that the catalytic combustion has been observed even without affecting the value of energy of activation [5]. Nevertheless, the decrease in the ignition temperature is universally accepted as an indication for the setting in of the catalytic pathway for the reaction process. The rate process (both catalytic and non-catalytic) is found to obey the Arrhenius equation:

$$k = A \times e^{-E_a/RT} \quad (7)$$

There are two major views put forward, when the catalytic combustion obeys the Arrhenius law. Normal expectation of a decrease in E_a during catalysis and the other school of thinking is that the E_a remains constant and the increased rate is explained on the basis of increase in the value of the pre-exponential factor or Arrhenius factor, "A" in the equation (7). This means that the number of active sites increased during the combustion. Because of this the rate of the reaction increases without the activation energy being altered.

Two different rate equations have been employed for the evaluation of the kinetic parameters. Coats – Redfern equation (8)

$$\ln[g(\alpha)/T^2] = \ln[AR/\phi E_a][1 - (2RT/E_a)] - E_a/RT \quad (8)$$

where A is the frequency factor, ϕ is the heating rate, E_a is the energy of activation and α is the degree of conversion [10]. This equation is applicable for a reducing sphere model. To describe the kinetics of weight loss in carbon, due to oxidation, yet another equation has also been employed (Equation (9)) [11].

$$-(1/m_i - m_f)(dm/dt) = A \times e^{-(E_a/RT)} \times [(m - m_f)/(m_i - m_f)] \quad (9)$$

where m_i and m_f are the initial and final weight of carbon respectively, and m is the weight at any time. The equation (9) assumes the following: i) the rate constant 'k' obeys the Arrhenius law and ii) the reaction is first order. The activation energy calculated by any one of the two equations (8) or (9) should be understood to be an apparent procedural activation energy, because it is dependent on the heating rate.

Experimental

Carbon

Four carbon samples, namely, two having low surface area, < 15 m²/g (Sevacarb and crystalline graphite) and the other two (Ketjen Black and Filtrasorb 400) having large surface area, ~ 1000 m²/g. The carbon samples and the catalyst supports (TiO₂ and SiO₂ with purity > 99 %) were used as received without any further treatment for the combustion study.

Catalysts

The catalysts were prepared by wet impregnation. For the platinum catalyst a solution of H₂PtCl₆ and for other supported catalysts the corresponding nitrate salt solution as precursor were used. For platinum catalyst the metal loaded was 5 % w/w and for all the others the metal content was 10 % w/w.

The catalyst used were TiO₂, Pt/TiO₂, Pt/SiO₂, Fe₂O₃/TiO₂ and Cu-Fe-O/TiO₂. The catalysts samples were dried in air at 120°C for 6 h and calcined at 500°C for 12 h. Carbon containing catalyst sample was prepared by physically grinding the corresponding carbon and the catalyst together in the ratio 20:1 for 0.5 h.

Thermogravimetric study

Thermograms of carbon combustion were obtained in a Perkin Elmer Thermogram analyser (Model Delta Series TGA 7). The thermograms were recorded at a gas flow rate of 25 mL/min and a heating rate of 20°/min. High purity oxygen extra dry air, supplied by Asiatic Oxygen Ltd., were used for the analysis. About 4-5 mg of catalyst premixed carbon sample was taken for each run and combusted until no further weight loss was observed.

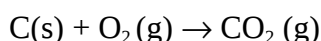
Results and Discussion

Analysis, of the catalyst, by X-ray diffractogram revealed the presence of anatase of TiO_2 support and the corresponding metal oxides. In the supported platinum system, in addition to PtO_2 , the peaks corresponding to metallic platinum also could be seen. The surface area, of all the catalyst systems, has been found to be around $10 \text{ m}^2/\text{g}$. In Table 1 the surface area of the carbon samples is given.

Table 1
Surface area of different carbon samples

S. No	Sample	Surface Area (m^2/g)
1	Graphite (crystalline) C_1	11.5
2	Seavacarb C_2	7.5
3	Ketjen Black C_3	1018.0
4	Filtrisorb-400 C_4	963.0

The samples of pure carbon, carbon mixed with metal/metal oxide loaded on TiO_2 have been oxidised either in dry air or pure oxygen and the weight change with respect to temperature has been recorded. The weight loss observed is due to the fact that the solid carbon gets oxidised to give gaseous product, as per the simplified reaction given below,



The formation of CO in the present study is ruled out as reported by Baumgarten and Schuck [12]. The gas diffusion probably has not been encountered in view of the very fine particles and small amount of carbon samples taken for each run.

The results of TGA are presented in Table 2. From

the data presented, the following points can be inferred.

- All the samples (with/without catalyst) are unstable and undergo oxidation at temperatures $> 700 \text{ K}$ (427°C)
- In the presence of pure oxygen the onset of oxidation occurs always at a lower temperature compared to that in the air
- The carbon samples having higher surface area show the least resistance to oxidation
- Excepting for the run in the presence of Pt/TiO_2 , all the other supported catalysts including pure TiO_2 shift the oxidation to higher temperatures
- All the carbons in the presence of Pt/TiO_2 show a considerably reduced temperature of oxidation

The oxygen activity being higher in pure oxygen than in air, the instability and faster oxidation of carbon in the oxygen atmosphere is understandable. All the kinetic parameters have been calculated for combustion in pure oxygen only. In Table 3 kinetic parameters as per equation (8) are given for the three carbons in the presence and absence of catalyst Pt/TiO_2 . For all the three samples, both the energy of activation and preexponential factor, indicate non-comprehensible values. When reaction is taking place at a lower temperature, normally one would expect a decrease in the value of activation energy: but this is not observed in our case. Thus it is clear that reaction model assumed for the Coats-Redfern equation is not suitable. This is because in this model shrinkage of the reaction sphere is assumed to which will not be valid for the catalytic process. In the catalytic process, the catalyst site is not part of the reaction sphere but it is present at an adjacent site to supply oxygen in the active form for a faster combustion. Moreover the number of reactive/active sites in a solid/gas inter-phase is expected to increase with increase in tem-

Table 2
Results of the thermogravimetric analysis: effect of catalyst on the temperature of ignition.
(Accuracy of T_i is $\pm 5 \text{ K}$ & T_m is $\pm 1 \text{ K}$)

S. No	Carbon sample	Dry air				Pure Oxygen			
		Pure C		C+Pt/ TiO_2		Pure C		C+Pt/ TiO_2	
		T_i/K	T_m/K	T_i/K	T_m/K	T_i/K	T_m/K	T_i/K	T_m/K
1	C_1	896	1080	873	1049	873	1050	827	1008
2	C_2	853	983	833	953	818	883	799	816
3	C_3	740	877	733	845	725	839	693	808
4	C_4	895	931	885	1071	865	919	793	884

perature; but in the present case the pre-exponential factor 'A' which is a measure of the number of active sites, is observed to increase with decrease in temperature. Hence, one can safely rule out the validity

of the equation (8). In all probability this may be applicable to a situation where the catalyst component of the system is part of each and every sphere (particle) so as to satisfy the shrinking sphere model.

Table 3

Kinetic parameters for carbon combustion in oxygen as per equation (8) [Coats- Redfern equation]

Sample	Pure C		C+Pt/TiO ₂	
	Energy of Activation, E _a (kJ/mol)	Frequency factor, A (min ⁻¹)	Energy of Activation, E _a (kJ/mol)	Frequency factor, A (min ⁻¹)
C ₁	164 ± 20	3.9 ± 2.7×10 ⁷	195 ± 45	4.5 ± 6.8×10 ⁹
C ₂	162 ± 20	4.0 ± 3.0×10 ⁹	202 ± 45	3.4 ± 7.2×10 ¹¹
C ₃	143 ± 25	7.2 ± 3.1×10 ⁸	154 ± 40	8.5 ± 5.3×10 ⁸
C ₄	155 ± 25	5.2 ± 3.4×10 ⁸	160 ± 50	6.2 ± 7.2×10 ⁸

The equation (9) assumes a different approach, where the gas/solid inter-phase is not affected by the rate process and hence, one can easily visualize that the presence of inorganic component (non-combustible) can alter inter-phase parameters, which will be manifested in the reaction tempera-

tures, (ignition temperature, T_i and peak maximum temperature, T_m respectively) and rate of the reaction (energy of activation, E_a and pre-exponential factor, A) The results are tabulated in Table 4. One can clearly see the catalytic effect of Pt/TiO₂ on the combustion.

Table 4

Kinetic parameters for carbon combustion in oxygen from non-isothermal TGA (using equation 9)

Carbon sample	Pure C		C+Pt/TiO ₂		C+Pt/SiO ₂	
	E _a , (kJ/mol)	A, (min ⁻¹)	E _a , (kJ/mol)	A, (min ⁻¹)	E _a , (kJ/mol)	A, (min ⁻¹)
C ₁	206 ± 15	8.7 ± 2.1×10 ⁹	166 ± 12	8.2 ± 1.8×10 ⁷	172 ± 15	1.7 ± 1.9×10 ⁸
C ₂	220 ± 15	2.1 ± 2.3×10 ¹²	Not measurable	Not measurable	153 ± 10	1.8 ± 1.4×10 ⁸
C ₃	150 ± 15	2.0 ± 1.9×10 ⁹	136 ± 15	1.6 ± 2.0×10 ⁸	145 ± 10	3.8 ± 1.3×10 ⁸
C ₄	170 ± 15	5.2 ± 2.0×10 ⁸	105 ± 12	1.2 ± 1.7×10 ⁵	110 ± 8	3.1 ± 1.3×10 ⁵

In the presence of Pt/TiO₂ catalyst not only the reaction starts at a much lower temperature, but also it is completed much faster. This indicates that the platinum on titania surface activates the oxygen. In the literature also there are reports [13] about activation of oxygen by oxide supported platinum catalysts.

The catalytic role of supported platinum system in the combustion of the carbon (all the 4 samples) can be associated with the activation of oxygen on the metal sites and its migration in the active form

(probably in atomic form) to the carbon center to initiate the reaction at a much lower temperature. Same observation has been seen in Pt/SiO₂ system also. This phenomenon is usually termed as spill-over. The oxygen is dissociatively adsorbed on platinum site and then transported to the carbon site for initiation of the oxidation as shown in equations (4-6). This has been well documented in the literature. The generation and transportation of such active species will be limited in other oxide catalysts.

For the other oxides employed in this investigation one does not find any catalytic effect. In Table 5 the ignition and peak temperatures for the combustion are tabulated. For all the samples studied, there is always a shift to the higher temperatures in the presence of the inorganic oxide. The probable *in situ* for-

mation of carbonate species or the metal oxide used being stable species having greater affinity for oxygen, under the experimental conditions, may be the reason for the non-occurrence of catalytic effect in the supported oxide catalysts like TiO_2 , $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and $\text{Cu-Fe-O}/\text{TiO}_2$.

Table 5

Effect of metal oxides on combustion temperature of carbons.
(Accuracy of T_i is ± 5 K & T_m is ± 1 K)

Catalyst Carbon	No catalyst		TiO_2		Fe_2O_3		$\text{Cu-Fe-O}/\text{TiO}_2$	
	T_i/K	T_m/K	T_i/K	T_m/K	T_i/K	T_m/K	T_i/K	T_m/K
C_1	873	1050	933	1096	936	980	918	990
C_2	818	883	908	931	922	989	920	995
C_3	725	839	731	933	808	895	812	892
C_4	865	919	878	1018	965	1012	955	986

Conclusions

It has been shown that supported noble metal catalysts contribute favourably for the carbon combustion. The presence of *in situ* catalyst, present originally in the carbon, and the one mixed externally can have different reaction models, which will lead to different kinetic parameters. From the knowledge gained with the external catalysts one can extend the same usefully with gas phase combustors. With slight modification of the gas combustion chamber, one may achieve continuous flame with reduced noise due to turbulent flow of fuel/air mixture.

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