

Catalytic Gasification of Carbons of Different Optical Textures

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Abstract. Carbons were prepared with a wide variation in size of optical texture (domains to mosaics) from several industrial pitches of different chemical composition. Salts of alkali and transitional metals were added to the pitches. Gasification of resultant pure and doped carbons to oxygen and carbon dioxide was studied using a microbalance. Kinetic data are assessed in terms of rates of gasification and optical texture. Topographical changes created by 10% burn-off of doped carbons are monitored.

Introduction

The literature of carbon gasification is concerned with the kinetics of gasification using oxygen, steam, nitrous oxide, sulphur dioxide, carbon dioxide and hydrogen (1-3). The role of carbon structure and its influence on gasification reactions has received less attention (4, 5). Previous studies (6, 7) show that the reactivity to carbon dioxide of graphitizable carbons from petroleum pitch increases as the size of optical texture of the carbon decreases.

Solid carbon does not exist in a pure form. It contains also hydrogen, oxygen, other heteroatoms and mineral impurities which may significantly affect gasification rates (3). Carbons exhibit wide variations in structure and these may affect the catalytic process. Measurements of spontaneous ignition temperatures (SIT) have been used to monitor the relative efficacies of catalysts in a given carbon (8). Marsh *et al.* (9) related the relative effectiveness of catalysts during gasification to structure (optical texture) within carbons. Movement of catalyst particles over or through graphitic material is a characteristic of such catalytic gasification (10). With non-graphitic carbons, catalytic gasification produces a topography of fissuring or pitting dependent mainly on the size of the optical texture of graphitizable carbons (3, 9, 11). Overall, the literature does not contain studies dedicated to catalytic gasification of carbons of different structures using different catalysts at comparable concentrations.

Objectives. 1. To study carbon reactivity in terms of optical texture.
2. To relate relative efficacies of different catalysts in equal concentrations in carbons to their optical textures.

Materials Used. 1. Carbons prepared from four industrial pitches with a wide variation in optical texture, and carbon from Ashland A240 petroleum pitch.

2. To the five selected pitches the following catalysts were added (in solution) and the system carbonized:

Sodium carbonate
Iron acetylacetonate
Nickel acetylacetonate

0.01 atomic weight percentage of metal (as the salt) was added to each pitch prior to carbonization.

Experimental. The catalyst additions were made using solutions of iron or nickel acetylacetonate dispersed in acetone, or of sodium carbonate dissolved in water, added to the molten pitch at 423 K and stirred for 0.5 h. The water or acetone evaporated and the resulting pitch system was ground and heat-treated to 1173 K at 4 K min⁻¹, 0.5 h soak, in a Carbolite horizontal tube-furnace under nitrogen. Optical textures of polished surfaces of pure and doped carbons were assessed using polarized light microscopy. Measurements of reactivities to 5% oxygen in nitrogen and carbon dioxide were made using a microbalance in which 20 mg of carbon (250-500 μm) was reacted with the gas flowing at 50 cm min⁻¹. SIT values were studied by heating the sample at 18 K min⁻¹ until it ignited spontaneously. Topography of gasification of fractured carbon surfaces was assessed using scanning electron microscopy (SEM).

Results. Size of optical texture of the carbons decreased with metal addition, being greatest for the larger-sized optical texture. Optical texture index (OTI) of doped carbon followed a decrease in SIT produced by metal addition. Kinetic data are given in Table 1 with catalysed:uncatalysed rates shown in Table 2. Topography created by 10% burn-

Table 1

Kinetic Data of Pure and Doped Carbons

Carbon from Pitch			Na-doped		Fe-doped		Ni-doped	
OTI	k_{O_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{CO_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{O_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{CO_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{O_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{CO_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{O_2} 900 K $\times 10^{-6} \text{ s}^{-1}$	k_{CO_2} 900 K $\times 10^{-6} \text{ s}^{-1}$
3	110	3.5	215	8	130	4.5	110	6
5	85	2.5	220	9	110	3.5	85	5
11	40	1.5	180	7	90	2.5	40	5
14	35	0.5	240	7	110	3	40	4
24	15	0.5	115	9	110	12	55	6

Table 2

Ratios of Catalysed:Uncatalysed Rates for Pure and Doped Carbons

Na-doped			Fe-doped			Ni-doped		
OTI	k_{O_2}	k_{CO_2}	OTI	k_{O_2}	k_{CO_2}	OTI	k_{O_2}	k_{CO_2}
2	2	2	2	1	1	3	1	2
5	3	4	5	1.5	1.5	2	1	2
8	4	5	4	2	1.5	2	1	3.5
14	7	14	12	3	6	12	1	8
16	8	18	20	8	24	13	4	12

off in oxygen in doped carbons showed fissuring in large (dominantly domains) and pitting in small (dominantly mosaics) optical textures.

Discussion. The optical textures of the pitch-catalyst systems are reduced compared with the pure carbons. Ni is most effective and Na least effective reducing size of optical texture, with the greatest decrease for larger OTI carbons. Na, Fe or Ni decrease SIT values for carbons of all sizes of optical texture, with Na most effective at reducing SIT least effective. Largest decrease in SIT were observed in the higher OTI carbons.

Additions of Na, Fe or Ni increase values of k_{O_2} and k_{CO_2} at 900 K (Table 1); $Na > Fe > Ni$. In pure carbons, highest k_{O_2} and k_{CO_2} values are observed in the small OTI carbons, but Table 1 indicates that on addition of catalytic matter, more scatter is produced. Increase in reactivity, expressed as catalysed:uncatalysed rate (Table 2) shows how the rate of reactivity is dominantly increased in the larger-sized optical texture carbons, Na is most effective, Ni least effective. This is related to the catalyst efficacy for decreasing SIT - Na reduced SIT values more than Ni.

The topographical features of the gasified Na-carbons indicate how the Na has a channelling mode of catalysis in the larger optical texture (domain) of carbon which changes to a pitting mode of catalysis in the smaller (mosaic) optical texture carbon.

Conclusions. 1. Size of optical texture decreases with addition of metal catalysts: $Ni > Fe > Na$.

The largest decrease in optical texture size occurs in carbons of greatest initial size of optical texture.

2. For constant additions of catalytic mineral matter, all carbons show the largest catalytic gasification to Na, followed by Fe and Ni. All additions increase k_{O_2} and k_{CO_2} values at 900 K and decrease SIT values, Na being most effective.
3. The largest ratio of catalysed:uncatalysed rates are produced in carbons of largest optical textures.
4. Topography of gasified fracture surfaces indicate a channelling mode in large sized (domain) optical textures, and pitting mode in small sized (mosaic) optical textures.

References

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