

CATALYSIS OF PETROLEUM COKE GASIFICATION
BY CALCIUM HYDROXIDE AND CARBONATE

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ABSTRACT

Catalysis of petroleum coke gasification in pure CO_2 by $\text{Ca}(\text{OH})_2$ or CaCO_3 has been investigated with a thermobalance. The reactivity of the original coke is very low. $\text{Ca}(\text{OH})_2$ kneaded with the carbon in water enhances the reactivity drastically, and thus realizes complete gasification at 900°C within 25 min. CaCO_3 shows almost the same catalytic activity as $\text{Ca}(\text{OH})_2$ except for the initial stage of gasification. The X-ray diffraction measurements and X-ray photoelectron spectroscopy of partly gasified samples reveal that the calcium promotes remarkably the formation of non-crystalline carbon, in other words, surface oxygen complexes, during gasification. The temperature programmed desorption shows that there are strong interactions between calcium and carbon, which contributes to the creation of reactive sites.

1. INTRODUCTION

Petroleum coke as a byproduct in coking processes of residual oils is used partly as an energy source [1]. Since it is composed of graphitized carbon, however, the gasification reactivity is low compared with coal. It may be interesting from a practical point of view if the reactivity is enhanced by catalyst addition and consequently petroleum coke can be employed as a feedstock for the production of hydrogen and syngas. However, no successful approach has been reported so far.

In earlier publications we have found that inexpensive $\text{Ca}(\text{OH})_2$ and CaCO_3 are the most promising gasification catalysts [2-4], as long as water slurry of $\text{Ca}(\text{OH})_2$ or CaCO_3 is mixed with low rank coals with large amounts of oxygen functional groups as ion exchangeable sites. Whereas, recent dynamic studies on the catalysis of carbon gasification by Ca have shown that the catalyst can create surface oxygen complexes, that is, reactive sites, even on well-ordered graphite [5,6].

It may be expected from these observations that graphitized carbon in petroleum coke is also activated during gasification by the calcium from $\text{Ca}(\text{OH})_2$ or CaCO_3 . Therefore the present work focuses on making clear catalyst effectiveness of these compounds for the gasification of petroleum coke and on elucidating the catalysis by the calcium.

2. EXPERIMENTAL

Petroleum coke of size fraction 75-150 μm was used. The proximate and ultimate analyses are shown in Table 1. The ash and oxygen contents were very low. The X-ray diffraction (XRD) analysis revealed the presence of graphitized carbon, but the degree of graphitization was not so developed, as shown by the XRD parameters of interplanar spacing (d_{002}) and average crystalline height (L_c) in Table 1. Powdery $\text{Ca}(\text{OH})_2$ or CaCO_3 was loaded onto the carbon by simply kneading them in water, Ca loading in the dried sample being 3 wt% as metal. The $\text{Ca}(\text{OH})_2$ -loaded carbon was used unless otherwise described.

About 20 mg of the sample was heated quickly up to 800 - 1000°C in a stream of pure CO_2 , and the weight loss during the isothermal gasification was monitored with a thermobalance [3,4]. The XRD, X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD) of partly gasified samples were carried out to characterize the catalyst state and reactive sites. In the TPD runs, the sample after gasification at 850°C followed by cooling to room temperature was heated in He up to 1000°C , and CO and CO_2 released were determined with a gaschromatograph.

3. RESULTS AND DISCUSSION

Rate Enhancement by Calcium Catalyst

The profiles for the CO₂ gasification of petroleum coke are shown in Figure 1, where conversion is calculated on a basis of fixed carbon after devolatilization. The reactivity of the original coke was quite low at 800-900°C, and fixed carbon conversion at 900°C was < 20 wt% after 2 h. On the other hand, Ca(OH)₂ enhanced the reactivity dramatically; the conversion at 800°C reached 65 wt% after 2 h, and at 900°C the carbon was gasified completely within 25 min. Our previous studies have shown that the Ca cations in saturated Ca(OH)₂ solution can readily be ion-exchanged with COOH groups when mixed with low rank coals at room temperature [7], and the exchanged Ca is very active for the steam gasification [2,3,7]. No exchange reactions would take place significantly in the present work, however, since there are almost no oxygen functional groups as exchangeable sites in petroleum coke, as is expected by very low content of oxygen (Table 1). It should therefore be noted that Ca(OH)₂ loaded on the carbon by simple kneading shows the high catalytic activity for the gasification.

The specific rate of carbon, defined as the gasification rate per unit weight of remaining carbon, is plotted as a function of conversion in Figure 2. The rate of the Ca(OH)₂-loaded coke at 800°C was independent of the conversion, and it was comparable to the rate at 1000°C without catalyst. This observation means that the use of Ca(OH)₂ can lower the temperature by 200°C. The rate of the Ca-catalyzed gasification at 850 or 900°C changed as fixed carbon conversion increased, and seemed to have minimum at the conversion of around 50 wt%. Since such the change would be determined by the balance between catalyst agglomeration and enrichment due to the consumption of carbon [8], the decreased rate observed in the conversion range of less than 50 wt% suggests that the agglomeration of Ca catalyst may be dominant at the initial stage of reaction. At 900°C the initial rate of the catalyzed gasification was 90 times as large as that of the uncatalyzed one.

As is seen in Figure 2, CaCO₃ also promoted the gasification remarkably. The initial rate at 850°C was lower than that with Ca(OH)₂, but it increased gradually with increasing conversion, and both rates were almost the same at the latter part of reaction. The use of CaCO₃ as alternative to Ca(OH)₂ is interesting from a practical point of view, since limestone and seashell wastes as received can be used as catalyst sources.

Catalyst State and Reactive Sites

Strong, sharp diffraction lines of Ca(OH)₂ were observed on the Ca(OH)₂-loaded coke. When the coke was devolatilized in pure N₂, these lines disappeared and CaO peaks with very weak intensities appeared. These observations show that Ca(OH)₂ loaded is transformed mostly to non-crystalline species, which suggests catalyst redistribution on devolatilization, possibly the formation of finely dispersed Ca species. The surface of petroleum coke might be mildly oxidized in the kneading process, and the preoxidation and/or mechanochemical effects during kneading, if any, might affect the dispersion of Ca catalyst.

Figure 3 shows the XRD patterns after gasification of petroleum coke with and without Ca(OH)₂ to 50 wt% conversion. Ca(OH)₂ was transformed mainly to CaCO₃ and partly to CaS during gasification. Since CaO was stable in the devolatilization step preceding carbon gasification, as mentioned above, CaCO₃ was formed by the reaction of CaO with CO₂. The presence of CaS may mean the catalyst deactivation by the sulfur evolved, which may be one reason for the decrease in specific rate with conversion at the initial stage of reaction (Figure 2). Figure 3 also revealed lower diffraction intensities of C(002) lines than those from the corresponding original carbon. Higher *d*₀₀₂ and lower *I*_C were observed in the Ca-bearing sample. These observations point out the formation of non-crystalline carbon in the presence of the catalyst.

When the XPS spectra of these gasified samples were measured, the C 1s peak of the Ca-bearing carbon was broad compared with the

original carbon, and the intensities of the spectra at 286-288 eV, attributable to ether and carbonyl bonds, were higher in the presence of the catalyst. Further, the atomic ratio of O/C, determined by the O and C 1s spectra, with Ca was about 5 times as that without Ca. It is evident from the XPS observations that surface oxygen complexes are formed on the carbon to a larger extent during the Ca-catalyzed gasification.

In order to characterize surface oxygen complexes, the TPD runs of gasified samples were carried out, and the results are summarized in Table 2. No significant amount of CO₂ was detectable without Ca catalyst, and CO alone was released with the largest rate at around 950°C, where the CO₂ gasification of the original coke proceeded at an appreciable reaction rate.

On the other hand, CO₂ desorbed in the presence of Ca catalyst. The desorption started at about 550°C, showed a maximal rate at 700°C, and completed at around 750°C. Since the catalyst was present in the form of CaCO₃ after gasification (Figure 3), it is no doubt that CO₂ desorption comes mainly from the decomposition of CaCO₃. However, the peak temperature of CO₂ desorption was much lower than the decomposition temperature of CaCO₃ bulk, and the TPD pattern was broad. Further, as is seen in Table 2, CO desorption occurred significantly at 700°C where CO₂ desorbed at the largest rate. These observations point out strong interactions between CaCO₃ and carbon surface. The CO evolved at 700°C may originate partly from the formation of CaCO₃-C intermediate and subsequent CO desorption [9,10]. The promotion of CaCO₃ decomposition by carbon has been confirmed by the high temperature XRD technique [2]. The total amount of CO₂ released was larger than Ca loading onto petroleum coke, which suggests that surface complexes such as lactone and acid anhydride formed during the Ca-catalyzed gasification may be decomposed into CO₂ [11,12].

Most of CO desorbed in the wide temperature range of 750-1000°C, where the calcium showed high catalytic activity. The total amount of CO released with Ca catalyst was two times as that without Ca (Table 2). Consequently, the presence of the catalyst lead to about four-fold oxygen uptake on carbon. This is in good agreement with the oxygen increase determined by XPS measurements. Since the sample after gasification of the CaCO₃-loaded coke showed almost the same TPD profiles as in the case of Ca(OH)₂, CaCO₃ also enhanced the number of reactive sites. It is probable that the increased sites are responsible for large reactivity of petroleum coke in the presence of Ca(OH)₂ and CaCO₃.

4. CONCLUSION

Ca(OH)₂ or CaCO₃ showed high catalytic activity for the CO₂ gasification of petroleum coke at 800-900°C when loaded by simple kneading. The calcium promoted the formation of surface oxygen complexes on the carbon during gasification.

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Table 1 Analysis of petroleum coke used

Ash (wt%, dry)	V.M.	C	H	N	S	O	d_{002} (nm)	L_c
				(wt%, daf)				
0.3	11.2	89.4	4.0	2.5	2.1	2.0	0.348	2.5

Table 2 Desorption of CO₂ and CO from the samples gasified at 850°C

Catalyst	Peak temperature (°C)		Total amount released (mmol/g)	
	CO ₂	CO	CO ₂	CO
None	n.d. ^a	950	n.d. ^a	7
Ca(OH) ₂	≈700	700 ^b , 900-1000	8	14

^aNot detectable. ^bShoulder peak.

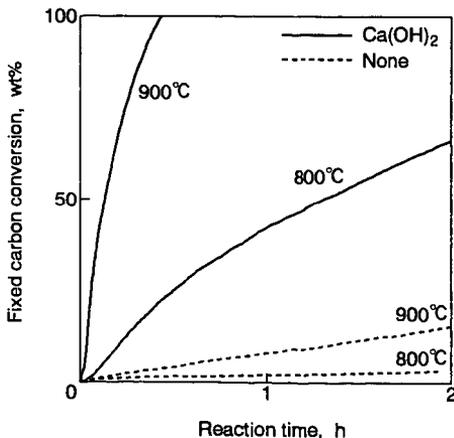


Figure 1. Profiles for the gasification of petroleum coke with CO₂.

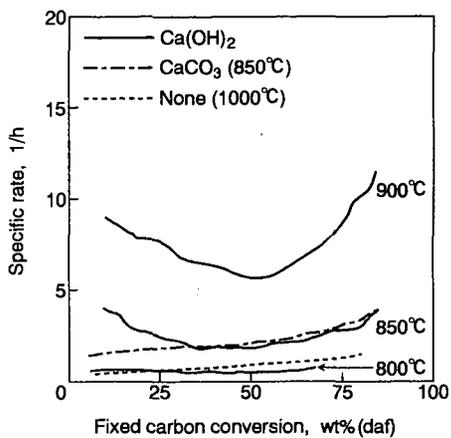


Figure 2. Relationship between specific rate and fixed carbon conversion.

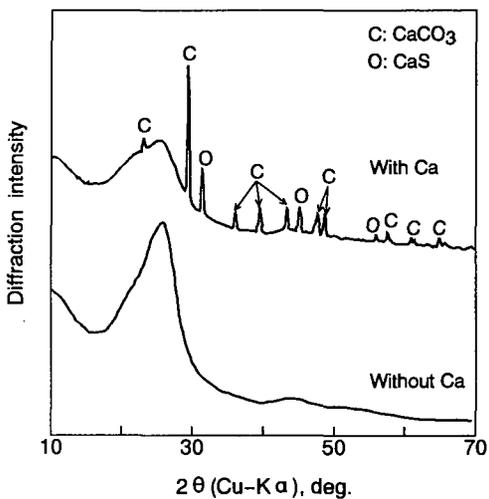


Figure 3. X-ray diffraction patterns of gasified samples with and without Ca catalyst.