

## Catalytic Gasification of Coals Using Rare Earth Compounds

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Catalytic gasification of coal with CO<sub>2</sub> or steam using rare earth compounds was investigated. Nitrates of lanthanum, cerium and samarium were found to be effective catalysts for the coal gasification.

Catalytic gasification of coal has been received much attention, and among the catalysts surveyed, compounds of alkali metals, alkali earth metals and transition metals of Group VIII are found to be effective.<sup>1,2)</sup> Recently, McKee investigated the behavior of rare earth oxides as catalysts for the oxidation of graphite in air and found that only CeO<sub>2</sub> showed significant activity for the oxidation.<sup>3)</sup>

This communication deals with the CO<sub>2</sub> or steam gasification of coals with rare earth compounds. To our knowledge, this is the first example that rare earth compounds promote the gasification of coal.

Coals used here were Yallourn coal (C;68.2%, H;4.5%, d.a.f.base, ash;1.1%, dry base), Sufco coal (C;76.2%, H;5.1%, ash;8.6%) and New Lithgow coal (C;82.0%, H;4.9%, ash;10.8%). The rare earth nitrates were impregnated into coal samples (100-200 mesh) from aqueous solutions followed by evacuation. The reaction was carried out in a thermobalance (Shimadzu, TGC-31). A weighed sample (ca. 45 mg) was placed in a platinum net basket. The sample was first heated from room temperature to 200 °C at a rate of 20 °C/min and then either CO<sub>2</sub> or steam-argon flow was introduced to the reactor tube. The temperature was then raised to the desired level at a heating rate of 100 °C/min. The flow rate of steam-argon was set at 20 ml/min (PH<sub>2</sub>O=530 mmHg) and of CO<sub>2</sub> was set at 20 ml/min.

Table 1 shows the typical results of the gasification of Yallourn coal. Rare earth nitrates increased the gasification rate in both CO<sub>2</sub> and steam. The coal loaded with nitrate of lanthanum, cerium or samarium exhibited higher gasification rate than that loaded with the same amount of sodium nitrate at 30% burn-off. Nitrates of neodimium, europium and gadolinium also promoted the gasification, but their catalytic activities were not remarkable. The initial gasification rate of rare earth loaded coal was high but the rate decreased with increasing burn-off and above burn-off of 30% the rate remained constant. On the other hand, the rate

Table 1. CO<sub>2</sub> and H<sub>2</sub>O gasification of Yallourn coal<sup>a)</sup>

Catalyst <sup>b)</sup>	Rate <sup>c)</sup> /10 <sup>-1</sup> min <sup>-1</sup>		Burn-off <sup>d)</sup> (%)	
	CO <sub>2</sub> <sup>e)</sup>	H <sub>2</sub> O <sup>f)</sup>	CO <sub>2</sub> <sup>e)</sup>	H <sub>2</sub> O <sup>f)</sup>
none	0.14	0.06	36.7	23.7
La(NO <sub>3</sub> ) <sub>3</sub>	0.49	0.58	75.2	72.3
Ce(NO <sub>3</sub> ) <sub>3</sub>	0.60	0.57	84.8	77.9
Nd(NO <sub>3</sub> ) <sub>3</sub>	0.26	0.19	52.6	47.5
Sm(NO <sub>3</sub> ) <sub>3</sub>	0.52	0.42	75.8	66.5
Eu(NO <sub>3</sub> ) <sub>3</sub>	0.28	0.21	54.8	49.7
Gd(NO <sub>3</sub> ) <sub>3</sub>	0.23	0.19	50.8	46.4
NaNO <sub>3</sub>	0.38	0.36	84.5	79.6

a) Sample size ; 45 mg coal including catalyst, Heating rate ; 100 °C/min

b) 0.30 mmol/g-coal c) Rate at 30% burn-off d) Burn-off of the coal at 30 min

e) Reaction temperature ; 800 °C f) Reaction temperature ; 700 °C

of sodium nitrate loaded coal increased above burn-off of 30%. The steam gasification behavior was similar to that of the CO<sub>2</sub> gasification. Due to the gasification behavior described above, burn-off of the coal loaded with rare earth nitrates at 30 min was lower than that with sodium nitrate.

Product gases by the steam gasification of cerium nitrate loaded Yallourn coal were analysed and ratios of CO<sub>2</sub>/CO were estimated 12.5 and 33.7 at burn-off of 30% and 60%, respectively. These values were larger than ratios obtained with sodium nitrate loaded coal. This suggests that the water gas shift reaction was promoted in the presence of cerium nitrate. Cerium nitrate also promoted the gasification of Sufco and New Lithgow coals which contain a large amount of mineral matters. However the catalytic activity decreased rapidly with increasing the burn-off. Yallourn coal was demineralized and cerium nitrate was loaded. Gasification rate of this coal also decreased with increasing the burn-off. This indicates that the decrease in the catalytic activities does not solely come from the reaction of the catalyst with the mineral matters in the coal.

#### References

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