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THE CATALYTIC STEAM GASIFICATION OF COAL USING SODIUM HYDRIDOTETRACARBONYLFERRATE

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The catalytic steam gasification of Miike coal using hydridotetracarbonylferrates was investigated. Sodium hydridotetracarbonylferrate was found to be a much more effective catalyst than well known sodium carbonate catalyst especially at lower temperature (650∿700°C).

Catalytic steam gasification of coal to synthesis gas and methane is of current interest. Although catalytic activities of iron compounds are low, alkali metal compounds such as potassium and sodium carbonates have high catalytic activities for steam gasification.[1] Recently combination of transition metal compound with alkali or alkali earth metal compounds such as Ni-K and Ni-Ca systems can be used as effective catalysts for the steam gasification of coal.[2]

This communication deals with the Fe-Na catalyzed steam gasification of coal using sodium hydridotetracarbonylferrate as a catalyst precursor. The sodium ferrate showed excellent catalytic activities at lower temperature. Iron compounds, inexpensive and readily available, appear to have advantages as catalysts for coal conversion.

The sodium ferrate was prepared from pentacarbonyliron and sodium hydroxide in ethanol solution[3] and impregnated into a coal sample (100∿200 mesh) in a usual manner. A typical reaction procedure was as follows. A sample (50 mg) in a stainless steel boat was horizontally placed in a quartz reactor tube (32 cm×1.8 cmΦ) and heated at 650∿800°C for 15 min by using an infrared reflection furnace under a flow of argon (20 ml/min)-steam (130 mg/min) mixture. A heating rate was set at 50 °C/s. Gaseous products were collected into a gas burette together with the carrier gas and analyzed by gas chromatography. The coal used here was a Japanese high volatile Miike coal (ash, 8.2% dry base; C, 83.9% H, 5.4% daf base).

The typical results of the reaction are listed in Table 1. Hydrogen, carbon monoxide, and carbon dioxode were the main products from the steam gasification of a char produced from the coal. C_1∿C_4 hydrocarbons (5∿10 wt%) and tar were also obtained but as pyrolysis products. Coal devolatilization took place during heating up to give the hydrocarbon gases, tar, and char.

Very small amount of chars from Miike coal were gasified without added catalyst at 700∿800°C. In a separate experiment (50 mg coal) under an argon atmosphere, char from Miike coal was estimated 54∿55 % (daf), corresponding to ∿2.3 mmol carbon. The presence of sodium carbonate as a catalyst promoted the complete gasification of the char into the gases at 800°C (Run 3). The carbonate exhibited the moderate catalytic activity at 700°C, but a considerable amount of the residue was remained unchanged

Table 1 The catalytic steam gasification of Miike coal.[a)]

Run	Catalyst[b)]	Reaction Temp.(°C)	Product[c)] H_2	Product[c)] CO	Product[c)] CO_2	Residue (wt%)
1	———	800	1.49	0.24	0.37	45.6
2	———	700	0.38	0.04	0.08	56.0
3	Na_2CO_3	800	5.48	0.59	2.15	11.1[d)]
4	Na_2CO_3	700	1.88	0.11	0.94	41.0[d)]
5	$Na[HFe(CO)_4]$	700	5.16	0.12	2.09	17.4[d)]
6	$Na[HFe(CO)_4]$	650	3.14	0.05	1.57	38.1[d)]
7[e)]	$Na[HFe(CO)_4]$	700	4.72	0.15	2.25	22.9[d)]
8	$[(CH_3)_4N][HFe(CO)_4]$	800	2.45	0.21	0.83	45.3[d)]
9	$[(CH_3)_4N][HFe(CO)_4]$	700	1.56	0.09	0.57	48.8[d)]

a) Reaction time, 15 min ; Heating rate, 50 °C/s
Sample size, 50 mg coal (100∿200 mesh) including catalyst
b) Na_2CO_3, 2.1 wt% as Na
$Na[HFe(CO)_4]$ and $[(CH_3)_4N][HFe(CO)_4]$, 4.2 wt% as Fe and 1.7 wt% as Na
c) mmol/50 mg of coal (daf)
d) Residue including remainder of the catalyst
e) 1.6 wt% as Fe and 0.65 wt% as Na

(Run 4). The coal impregnated with sodium ferrate (4.2∿1.6 wt% as Fe and 1.7∿0.65 wt% as Na) was completely converted into the gases at 700°C (Runs 5 and 7). The ferrate also was effective even at 650°C (Run 6). These results clearly demonstrate that the sodium ferrate is much more effective than the sodium carbonate for water gas reaction of Miike coal. Hydridotetracarbonylferrate having tetramethylammonium ion as a counter cation, however, showed only moderate effects on this conversion (Runs 8 and 9), suggesting that excellent catalytic activities of the sodium ferrate come from a binary system, Fe-Na. The results obtained here show that the readily available binary catalyst (Fe-Na system) having an synergistic effect can be used as an excellent catalyst for the steam gasification of coal even at 650°C. To our knowledge, this is the first example that an iron compound highly promotes the gasification of coal.

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