Reduction of Carbon Dioxide Using Coal at Low Temperature

Fuminori Akiyama
Institute for Chemical Reaction Science, Tohoku University, Sendai 980

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Carbon dioxide was reduced to carbon monoxide at a temperature as low as 300 ℃ with a mixture of coal and alkali metal carbonate which was preheated at high temperature around 600-800 ℃. Reaction rate of carbon monoxide formation in this reaction at 800 ℃ increased by prolonged heating. These phenomena were more evident in the reaction of Cs_2CO_3 than in that of K_2CO_3, no such phenomena being observed in the reactions of $BaCO_3$ and $CaCO_3$.

Reduction of carbon dioxide(CO_2) has been investigated in view of utilization of carbon resources. Electrochemical, photochemical, and chemical methods were used for reduction of CO_2. Although various methods for reducing CO_2 using hydrogen as reducing agent have been world-widely investigated, the problem is relatively high cost for production of hydrogen. Therefore, reduction of CO_2 using coals, which are widespread on earth, is presumably a preferable method in economic view point. Although gasification of coal using CO_2 has been reported to give carbon monoxide(CO), literatures reported that the reactions took place at higher temperatures than 700℃.[1-8] Even in the reactions using precious transition metal salts reaction took place at higher temperatures than 500 ℃.[9] In the present paper it will be reported that CO_2 can be reduced using coals at a temperature as low as 300℃ in appropriate reaction conditions.

Although most of gasification reactions of coals using CO_2 were performed by flowing CO_2 gas, present paper adopted batch method since coal sublimes in the reaction conditions of present paper(vide infra). A 52 ml stainless steel(sus 316) autoclave was charged with 0.737 g of coal and 0.00307 mol of metal carbonate. This mixture was placed in the bottom of the autoclave and was mixed well using spatula[10], and was dried at 140 ℃ in vacuo for 2 h, followed by replacing inside of the autoclave with CO_2 gas of high purity several times and adjusting to 1.5 Mpa of CO_2 at room temperature. The autoclave was heated in a furnace at an appropriate temperature. After an appropriate reaction time the autoclave was cooled down to room temperature and gas of the inside of the autoclave was analyzed using G. L. C. Three sorts of coals having following elemental analysis data, which were purchased from Argonne National Laboratory, were used as reducing agent of CO_2. Pocahontas No.3(C, 91.1; H, 4.44; O, 2.5; S, 0.66; Ash, 4.8); Illinois No.6(C, 77.7; H, 5.00; O, 13.5; S, 4.83; Ash, 15.5); Beulah-Zap(C, 72.9; H, 4.83; O, 20.3; S, 0.80; Ash, 9.7).

Reaction of CO_2 with coal in the presence of various metal carbonates at 300 ℃ gave neither CO nor methane. However, when a reaction of CO_2 with coal in the presence of cesium carbonate or potassium carbonate was performed at higher temperatures than 600 ℃ for 2 h and the mixture was cooled down to room temperature, followed by replacement of resulting gas with fresh CO_2 and the resulting new mixture was heated at 300 ℃ for 2 h,[11] CO was formed as is shown in Table 1 (This procedure is demonstrated such as 600 → 300). This table indicates that the following tendencies: (1) Although Cs_2CO_3 exerts its effect in almost similar extent on the reactions of three coals, K_2CO_3 exerts strongest effect on the reaction of Beulah-Zap(lignite) of three coals; (2)CO forms in larger amount in the reactions of Cs_2CO_3 than in those of K_2CO_3; (3) The higher the preheating temperature is, the higher the yield at 300 ℃ is . Similar reaction procedure using alkaline earth metal carbonate such as $CaCO_3$ or $BaCO_3$ does not give CO at all at 300 ℃. Preheating of the mixture in nitrogen atmosphere brings about a weaker effect on CO formation at 300 ℃ than preheating in CO_2 atmosphere (see data in parentheses).

Table 1. Yield of carbon monoxide in the reaction of CO_2 with coals in the presence of cesium carbonate or potassium carbonate at 300 ℃ after preheating at high temperature

Coal	Temperature (℃)	Yield of CO(μmol) Cs_2CO_3[a]	K_2CO_3[b]
Pocahontas	700 →300[c]	388(224)[e]	31
	600 →300	107	—[d]
Illinois No.6	700 →300	329	54
	600 →300	135	12
Beulah-Zap	800 →300	607	218
	700 →300	377(199)[e]	130
	600 →300	138	16

[a]Yields in the reaction using Cs_2CO_3. [b]Yields in the reaction using K_2CO_3. [c]Meaning of arrow: see Text. [d]Not determined. [e]Yield in the reaction (CO_2 atmosphere, 300 ℃, 2 h) after preheating in nitrogen atmosphere at 700 ℃ for 2 h.

Although in literatures of CO_2 gasification of coals, in which only small amount of metal carbonate was used, above-stated phenomena were not observed, large amount of alkali metal carbonate brought about such phenomena as is clarified in Table 2. Although yield of CO in the reaction at 700 ℃ does not so much depend on the amount of Cs_2CO_3 used , yield of CO at

Table 2. Effect of amount of cesium carbonate on the yield of carbon monoxide in the reaction of CO_2 with Beulah-Zap at 300 ℃ for 2 h after preheating at 700 ℃ for 2 h

Cs_2CO_3(mol)	Yield of CO (μmol) 700℃[a]	700 ℃ → 300 ℃
0.00307	4050	377
0.00154	4110	283
0.000307	4830	101

[a]Yield in the reaction at 700 ℃.

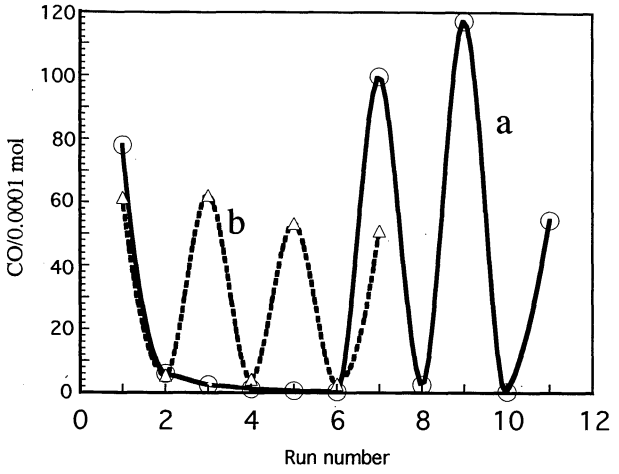

Figure 1. Yields of carbon monoxide in the repeated reactions of CO_2 with Beulah-Zap in the presence of cesium carbonate. a (○) : repeated reactions at 800 ℃for 2 h and 300 ℃ for 2 h; b (△) : repeated reactions of 800 ℃ for 3 min and 300 ℃ for 2 h. Upper symbols : reactions at 800 ℃; Lower symbols: reactions at 300 ℃.

300 ℃ after preheating at 700 ℃ strongly depends on the amount of Cs_2CO_3 used.

When the reactions of CO_2 with coal in the presence of Cs_2CO_3 were repeated between 800 ℃ for 2 h and 300 ℃ for 2 h by the same procedures as those in Table 1, yield of CO in the repeated reactions at 800 ℃ increased gradually as is shown in Figure 1-a.[12] In the fourth reaction at 800 ℃ for 2 h, decrease of reaction rate owing to consumption of coal exceeds the gradual increase of the reaction rate. When the reactions at 800 ℃ in Figure 1-a were performed for 3 min in place of 2 h, increase of the yield of CO was not observed as is shown in Figure 1-b. When the reactions at 800 ℃ were performed for 15 min, a lesser gradual increase of yield of CO than in Figure 1-a was observed (Figure not shown). Therefore, prolonged heating is considered to bring about increase of reaction rate of CO formation. When the repeated reactions in Figure 1 were performed using K_2CO_3 at 800℃ for 2 h, a lesser gradual increase of the yield of CO than in Figure 1-a was observed (Figure not shown).

In the end of repeated reactions shown in Figure 1-a, all of residual powder, which was placed at first in the bottom of the autoclave, was observed to transfer on to the wall of the autoclave. This means that coal sublimes. Scission of coal structure by heating of coal in the presence of Cs_2CO_3 or K_2CO_3 at 800 ℃ presumably brings about sublimation of coal. This scission reaction is presumably also responsible for formation of CO at 300 ℃ or increase of the rate of CO formation by prolonged heating at 800 ℃.

The fact that CO forms at 300℃ after preheating of a mixture of coal, CO_2, and Cs_2CO_3 or K_2CO_3 at 700-800℃ means that CO can be formed at lower temperature than 700℃ in a reactor, which was once heated at 700-800℃ and was kept warm after switching off heating, during gradual cooling down. This fact leads to saving of energy.

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References and Notes

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10 When a mixture of a coal (especially in the case of Beulah-Zap) was mixed in a mortar, adhesion of the mixture to a mortal owing to strong hygroscopicity of the mixture made transfer of the mixture to the autoclave difficult.
11 Prolonged heating of the resulting new mixture brings about slight decrease of yield of CO, yield at 300 ℃ for 16 h being less than 10 % relative to the yield in the reaction at 300 ℃ for 2 h.
12 In the first reaction at 800℃ not only CO but methane forms. After first reaction at 800℃, reactions at 300℃ were repeated several times to ascertain how many times CO formation occurs.