CHEMISTRY LETTERS, pp. 151-154, 1983.

EFFICIENT CATALYTIC GASIFICATION OF CELLULOSE FOR PRODUCTION OF HYDROGEN AND CARBON MONOXIDE

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Synthesis gas of hydrogen and carbon monoxide mixture in about 1:1 ratio was efficiently produced by thermal catalytic gasification of cellulose with steam in the presence of KOH and Ni compounds at 800 °C.

Thermochemical conversion of cellulosic materials including wood, lignin, agricultural wastes and urban refuses to fuels and chemicals has been gaining attention as fossil fuels, particularly oil and gas, which presently provide most of our energy needs, are rapidly being depleted. With regard to pyrolysis, it is generally accepted that at around 300 °C gaseous products rich in CO_2 with substantial amounts of residuals and tarlike fragments are produced, whereas over 700 °C H_2, CO, CH_4 and CO_2 mainly form as well as oxygenated compounds.[1-5] Catalytic effects on thermochemical conversion of cellulosic materials, however, have been poorly understood with some exceptions. Kawai and co-workers[6] recently investigated the catalytic gasification of cellulose on Pt, Pt-TiO_2 and Ru/SiO_2 and reported that H_2, CO and CH_4 were produced at 300 °C. They also suggested that alkali metal ions took part in breaking of the cellulose skelton. The present paper presents marked effects of KOH and Ni compounds on the gasification of cellulose, in which synthesis gas of H_2 and CO mixture was efficiently produced.

Cellulose used in each run of reaction was approximately 300 mg, Toyo filter paper (5A) of dimensions 1mm x 5 mm x 0.2 mm thick, and elemental composition C, 42.25 wt%, H, 5.97 wt% and O, 51.78 wt%.[7] Chemicals, all used without further treatment or activation, were obtained from the sources indicated: KOH (chemical pure grade, Wako Pure Chem. Ind., Ltd.), Raney Ni (50% Ni, Wako Pure Chem. Ind., Ltd.), Ni and NiO (reagent grade, Wako Pure Chem. Ind., Ltd.) and Ni_2O_3 (reagent grade, powder, Nakarai Chemicals Ltd.). Doping of KOH was made by immersing cellulose into

an aqueous solution of KOH and by vaporization to dryness at 120 °C for 3 hours. Powderly Ni compounds were spread onto cellulose by simply mixing. Doped amounts of KOH and Ni compounds were 1.75 wt% and 14.5 wt% (as Ni metal) respectively unless otherwise stated. The reaction was performed in a glass closed recirculation system (411 ml) having a quartz reactor. Steam (ca. 20 mmHg) was supplied from a vessel connected to the system. Gaseous products were periodically analyzed by a gas chromatograph (HITACHI 063) equipped with an active carbon column at 100 °C. The amount of char was obtained by weighing the residuals in the reactor after washing them with a 2:1 (v/v) mixture of methanol and acetone. The amount of tar was calculated by the difference between the initial weight of cellulose and those of gas and char after 180 min of reaction.

Table shows the effects of KOH and/or four kind of Ni compounds on catalytic gasification of cellulose with steam at 800 °C. In case (A) where no catalyst was added, a considerable amount of unknown gaseous products (C_2^+) formed (17.0 %) in addition to H_2, CO, CH_4 and CO_2. This composition profile was entirely different from that obtained by Kawai et al.[6] who reported the preferential formation of CO and CO_2 at 300 °C. In the case of KOH addition (B), the carbon conversion increased markedly (46.1 %), while the yield of tar remained the same as (A). It is of interest that the amount of H_2+ CO (in a 1:1 ratio) was 90 % of gaseous products. The addition of Raney Ni (C) slightly enhanced the conversion, however, tar yield reduced, indicating that Ni may contirbute to secondary gasification of tar. The results of doubly promoted effects of KOH and Ni compounds were shown in (D)-(H). In all cases, the carbon conversion was improved as would be expected and the amount of H_2+ CO (in ca. 1:1 ratio) exceeded 93 % of gaseous products, irrespective of the kind of Ni compounds.

By comparison of (B), (D) and (E), we see that little effect of Ni was shown in the absence of steam (E), that is, the composition profile of (E) was almoat identical to that of (B). The role of KOH may be attributable to its ability to cleave the cellulose skelton as suggested by Kawai et al.[6] Tran and Rai[8], who studied kinetically the K_2CO_3 catalyzed pyrolysis of bark, also concluded that catalysts such as K_2CO_3 weaken the C-C bond of cellulose.

Since a somewhat equimolar mixture of H_2 and CO was obtained in more than 90 % of gaseous products, cellulose having ($C_6H_{12}O_5$) units can be efficiently gasified by the addition of KOH and Ni compounds. Cellulosic materials such as wood or agricultural wastes, containing substantial amounts of salts of alkali metal and moisture,

may be considered as desirable feedstocks for the gasification process of present type.

In conclusion, these results indicate that a synthesis gas of H_2 and CO mixture (in ca. 1:1 ratio), suitable for the raw materials of Fischer-Tropsch synthesis or C_1 chemistry, was efficiently produced by catalytic gasification of cellulose in the presence of KOH and Ni compounds.

TABLE

The effects of KOH and Ni compounds on thermal catalytic gasification of cellulose at 800 °C

	Catalyst*	Composition (wt%) of products in 3 h								Conversion*** (%)
		Gas	gaseous products (vol%)**					Tar	Char	
			H_2	CO	CH_4	CO_2	C_2^+			
(A)	Cellulose itself	19.6	(19.4	34.7	11.6	17.3	17.0)	26.1	54.3	18.1
(B)	KOH	49.3	(46.5	43.8	3.5	4.2	2.0)	24.3	26.4	46.1
(C)	Raney Ni	27.5	(56.7	38.4	1.6	3.3	0)	9.8	62.7	24.8
(D)	KOH-Raney Ni	69.4	(46.4	46.6	2.6	4.4	0)	8.2	22.4	64.7
(E)	KOH-Raney Ni+	59.2	(47.0	46.5	1.9	4.6	0)	19.2	21.6	54.7
(F)	KOH-Ni	74.2	(47.0	48.8	0.4	3.8	0)	8.8	17.0	68.7
(G)	KOH-NiO	86.4	(43.7	51.9	1.0	3.4	0)	0.4	13.2	81.3
(H)	KOH-Ni_2O_3	83.5	(44.9	52.3	0	2.8	0)	7.7	8.8	76.2

* The amounts of doped KOH and Ni compounds are: (A) cellulose-300 mg, (C), (D) and (E) Raney Ni-7.25 wt% as Ni metal. The amounts of KOH, Ni, NiO and Ni_2O_3 were given in the text.

** The composition of gaseous products was obtained by a G.C. analysis after 3 h of reaction.

*** The conversion is defined as carbon percentage of cellulose converted to CO, CH_4 and CO_2 at 3 h of reaction.

\+ In this case (E), no steam was added.

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(Received October 5, 1982)