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CATALYTIC GASIFICATION OF WOOD FOR METHANOL SYNTHESIS GAS

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Gas composed of hydrogen and carbon monoxide with 2:1 volume ratio was supplied by catalytic gasification of wood, when NiO/Al_2O_3 catalyst was employed at 700°C in the presence of water vapor.

The development of techniques for the gasification of coal and heavy oil residue has been desired to exploit new energy resources. Woods are also considered to be one of the energy resources and are expected to supply gases for methanol and Fischer-Tropsch syntheses. The pyrolysis of woods has been extensively studied$^{1)}$ in the presence of steam and oxygen. Woods can be gasified at 300°C and produce gases mainly composed of carbon dioxide, while at temperatures higher than 700°C hydrogen, methane and carbon monoxide are mainly produced besides carbon dioxide. The conversion to gases from woods are, however, as low as around 40% on carbon base. A considerable amount of olefins such as ethylene, propene and so on was formed by pyrolysis of woods, indicating that the gases thus obtained are not suitable for methanol synthesis since these olefinic hydrocarbons are poisons for methanol synthesis catalysts. Hence, catalytic gasification of woods has been of interest$^{2)}$ to improve the conversion of woods to gases and reduce the formation of olefinic compounds.

In the present work the catalytic gasification of woods was studied using various metal oxides catalysts supported over alumina. Several kinds of alumina were employed, their pore size distributions being varied as can be seen in Fig.1. The pore size distributions were measured by a prosimeter

(Sorptomatic 1800 type, Carlo Erba) using nitrogen at its liquid temperature. The relation between mean pore size of alumina support and its catalytic activity was studied using 20 wt% NiO supported on Al_2O_3 catalysts prepared by an usual impregnation method. The catalyst calcined at 500°C in air was mixed with sawdust with a weight ratio of 3:2, then 5 g of this mixture was placed in a reactor made of stainless steel(30 mmϕ). The particle size of alumina support was 1 mmϕ and the mean size of the sawdust particle was also 1 mmϕ. The composition of the sawdust is shown in Table 1. The gasification reaction was carried out at 600°C using a flow reaction system. Ar gas was employed as an inactive gas and it passed through a water reservior heated at 50°C with a flow rate of 200 ml/min, then it was introduced into the reactor. Accordingly, the Ar gas includes about 13.7 vol% of water vapor in it. The gases produced passed through a cold trap to eliminate tarlike fragments and were analysed by gas chromatography using columns packed with molecular sieve 13X and Polapak Q. Tarlike fragments were never trapped in the cold trap during the reaction and the amount of chars left in the reactor was weighed. As is shown in Table 1, the sawdust contains 14 wt% of water vapor and in dry state the sawdust has 48.6 wt% of carbon in it. Therefore, the conversion to gases was calculated by the following equation;

$$\eta=(0.86\mathrm{x}0.486\mathrm{x}W-C)/0.86\mathrm{x}0.486\mathrm{x}W,$$

where η represents the conversion to gases on carbon base, W is the weight of sawdust employed and C means the weight of chars left in the reactor.

Fig. 1. Pore size distribution of alumina

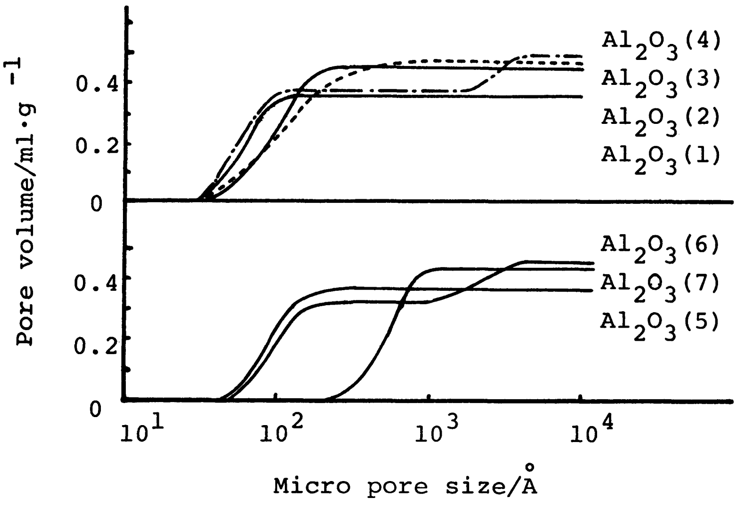

Table 1. Composition of the sawdust in dry state*

Component	wt%
C	48.6
H	7.2
O	43.1
N	<0.3
S	<0.01
Cl	0.19
Ash	0.6

*After removal of water (14.0wt%).

The results obtained are shown in Table 2 together with the result in the absence of a catalyst at 600°C. The mass balance of the atom "A" was estimated by calculating the following equation; n=(number of "A" in gases produced and in chars)/(number of "A" in woods employed). Concerning the carbon atom, the value of n was around 1.0, though the n values for hydrogen and oxygen atoms were higher than 1.0. This is due to the fact that the steam introduced into the reactor was consumed for the wood gasification reaction.

Table 2. Effect of Al_2O_3 support upon wood gasification

Catalyst	Yield(%)	Volume (ml/g-wood)				H_2/CO	CH_4/CO	Residual Carbon(g)
		H_2	CO	CH_4	CO_2			
NiO/Al_2O_3(1)	69	446	194	130	215	2.3	0.67	0.49
NiO/Al_2O_3(2)	77	783	356	43	202	2.2	0.12	0.40
NiO/Al_2O_3(3)	78	874	364	66	179	2.4	0.18	0.38
NiO/Al_2O_3(4)	78	851	213	115	280	4.0	0.54	0.36
NiO/Al_2O_3(5)	80	437	397	67	160	1.1	0.17	0.35
NiO/Al_2O_3(6)	73	565	353	53	163	1.6	0.15	0.46
NiO/Al_2O_3(7)	78	303	379	38	192	0.8	0.10	0.38
Thermal	39	17	150	83	67	0.1	0.56	1.05

In these seven catalysts, NiO/Al_2O_3(1), NiO/Al_2O_3(5), and NiO/Al_2O_3(7) have micropores with diameters around 60, 100, and 300 Å, respectively. So, the following conclusions could be obtained by dicussing on these three results. 1) the conversion to gases becomes maximum when the pore size of the support is ranged from 100 to 300 Å. 2) the amount of methane produced decreased with increase in the pore size. 3) the ratio of H_2/CO produced decreased with increasing the pore size. For the production of gases for methanol synthesis, H_2/CO is desirable to be 2 and methane production must be lowered. Considering these conditions, Al_2O_3(3) support seems to be favorable for the present purpose.

Various kinds of metal oxides were supported over the Al_2O_3(3) by usual impregnation method. The reactions were carried out in the same manner to that mentioned above except that the reaction temperature was set at 700°C. After calcination of the catalysts in air, their activities were measured.

The results are given in Table 3. As it is obvious in Table 3, the catalysts such as MoO_3, V_2O_5, CoO, and Mn_2O_3, which have often employed for oxidation reaction, showed high conversion to gases. This high conversion is, however, attributed to the production of carbon dioxide. Probably, over these typical oxidation catalysts most of carbon monoxide formed was oxidized by oxygen atoms in water vapor or sawdust to form carbon dioxide, resulting in the enhancement of H_2/CO ratio. While over the catalysts such as NiO, Fe_2O_3, and Cr_2O_3, which have been often employed for the reaction involving hydrogen gas, the formation of carbon dioxide was not significant and the ratio of H_2/CO was around 1.7. The formation of methane was also reduced on these catalysts. The ratio of CH_4/CO over NiO/Al_2O_3(3) was as low as 0.09. Now, it was concluded that the most favorable catalyst for wood gasification should be NiO/Al_2O_3(3) when the gases produced are aimed for methanol synthesis.

Table 3. Wood gasification over various metal oxide catalysts

Catalyst	Yield(%)	Volume (ml/g-wood)				H_2/CO	CH_4/CO	Residual Carbon(g)
		H_2	CO	CH_4	CO_2			
V_2O_5/Al_2O_3	81	542	66	21	544	8.2	0.32	0.32
Cr_2O_3/Al_2O_3	77	477	318	127	156	1.5	0.40	0.40
Mn_2O_3/Al_2O_3	77	829	259	150	192	3.2	0.58	0.39
Fe_2O_3/Al_2O_3	79	757	445	98	73	1.7	0.22	0.36
CoO/Al_2O_3	83	515	147	12	488	3.5	0.08	0.26
NiO/Al_2O_3	87	855	475	43	161	1.8	0.09	0.23
CuO/Al_2O_3	89	995	321	125	248	3.1	0.39	0.19
MoO_3/Al_2O_3	81	421	77	9	545	5.5	0.12	0.38

The mechanism of the catalytic gasification of wood is still obscure, but the first stage of the reaction may be thermal cracking of macro carboneous molecules to relatively light compounds. The role of the catalyst is to crack the light carboneous compounds to hydrogen and carbon monoxide with an aide of water vapor.

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