CHEMISTRY LETTERS, pp. 1185-1188, 1981. 1981

PRODUCTION OF HYDROGEN AND HYDROCARBON FROM CELLULOSE AND WATER

Maki KAWAI[*], Tomoji KAWAI[†], and Kenzi TAMARU[††]
The Institute of Physical and Chemical Research, Wako-shi, Saitama 351
[†] Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444
[††] Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

H_2, CH_4 and CO are produced by the thermal reaction (300°C) of cellulose and water vapor using Pt, Pt-TiO_2 and Ru/SiO_2 as catalysts, among which the Ru/SiO_2 catalyst showed the highest activity for direct production of CH_4 and H_2.

The synthesis of hydrocarbons from CO and H_2 or the direct methane formation from carbon and water has been one of the most important problems in catalysis from the view-point of energy conversion. The raw materials of this reaction, coal or oil, are produced by the long-term accumulation of plants or animals. Thus the direct conversion of cellulose, an annually renewable resource, into a gaseous fuel is very attractive. Here we report that hydrocarbons are directly synthesized from cellulose and water by thermal catalytic reactions using supported metal catalysts around 300°C.

Three kinds of catalysts were prepared as follows: 1) Pt; Pt black (Engelhardt), 2) Pt-TiO_2 (Pt 15 wt%); Pt black and TiO_2 (Katayama Kagaku) were mixed and grounded in an agate motar. 3) Ru/SiO_2 (Ru 4.5 wt%); Aqueous solution of $RuCl_3$ was impregnated into SiO_2 (Nihon Aerosil), dried and reduced by 100 Torr of H_2 at 450°C for 1 hr. All the catalysts were used after reducing them by 100 Torr of H_2 at 200°C for 1 hr, followed by an evacuation at the same temperature for 1 hr, after they were mixed with cellulose. The amount of Pt black, Pt-TiO_2 and Ru/SiO_2 used were 0.022, 0.15 and 0.07 g, respectively, in order that the molar ratio of metals to the cellulose was made constant. Cellulose (Toyo filter paper, 45-15 mg) was cut into small peacies (ca. 0.5 mm square) and mixed with each catalyst, so that the powders of catalyst were spread over the cellulose.

Cellulose and catalyst were placed in a closed glass circulation reactor (200 ml) in the presence of water vapor from U trap (liquid H_2O). Gaseous products during the reaction were collected by a trap of -196 and -96°C, and analysed by a mass spectrometer (Hitachi RMS-4).

Table 1

Amount of gaseous products and the conversion of cellulose to gases after 150 min. of reaction at 300°C.

		gaseous products (%)					%
		H_2	CH_4	CO	CO_2	C_2^+	conver-sion
neutral	Cellulose* itself	none	none	55.6	44.4	none	
	Pt-black	23.1	3.0	41.6	32.3	none	1.7
	$Pt\text{-}TiO_2$**	13.0	3.9	41.6	41.6	none	19.2
	after 1200 min	22.0	3.1	46.3	28.6	none	23.0
	Ru/SiO_2	36.2	4.3	19.9	39.5	none	20.5
	after 1200 min	36.5	16.1	3.6	43.8	none	26.5
+KOH***	Pt-black	72.9	5.1	0.07	none	21.9	10.0
	$Pt\text{-}TiO_2$	64.6	3.2	0.45	none	31.7	26.6
	Ru/SiO_2	89.8	2.9	1.3	none	5.4	32.2

* Water produced were trapped during the decomposition.

** The amount of conversion in 150 min changed from 9.0 to 19.2% according to the catalysts used.

*** CO_2 produced in this system was dissolved into KOH.

Table 1 shows the total amount (%) and the component (%) of the gaseous products formed from cellulose in 150 min at 300°C. Cellulose itself decomposed slowly to form CO, CO_2 and H_2O with no H_2 produced in the absence of catalyst. It was, however, demonstrated that H_2, CO, CH_4 and CO_2 were the main products in the presence of water vapor and the catalyst (Pt or Ru). When Ru catalyst was employed, the amount of CH_4 gradually increased with time, whereas in the case of Pt, the ratio of produced CH_4 to CO remained unchanged. It may be interpreted that CO and H_2

produced from cellulose and water reacted to form CH_4 on the Ru surface, since Ru is a well-known catalyst for the CH_4 formation from $CO + H_2$[1]. Accordingly, Ru/SiO_2 exhibited the highest activity for the production of CH_4 and H_2 among these catalyst. The catalyst, $Pt\text{-}TiO_2$ or Ru/SiO_2 was more active than Pt black as is estimated from the amount of cellulose reacted (Table 1). The gaseous products were not observed at all at reaction temperature below 200°C.

The role of H_2O in the reaction is essential for the H_2 production. When H_2O was present, the amount of CO produced decreased whereas H_2 and CO_2 increased. In the case of Ru/SiO_2, the amounts of H_2, CO and CO_2 produced in 300 min without H_2O were 8.2, 20.8 and 10.6 µmol, respectively, whereas they were 90.3, 7.9 and 23.0 µmol with H_2O vapor (Fig 1). It suggests seemingly that water gas shift reaction, $H_2O + CO \rightarrow H_2 + CO_2$, occurs in the presence of H_2O over the Ru or Pt catalyst.

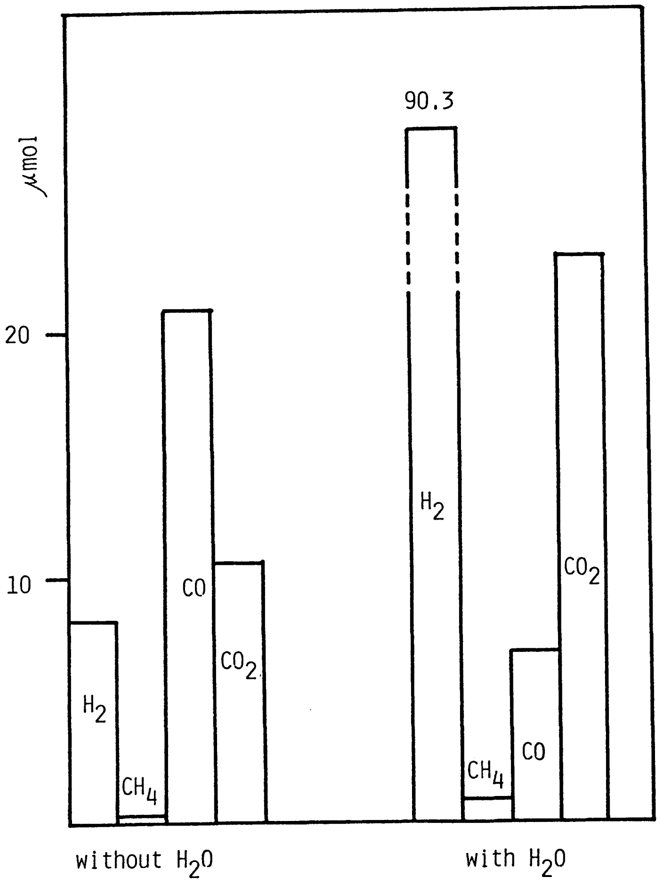

Fig 1. The amount of gases produced by the reaction of cellulose (13.6 mg) without and with H_2O vapor over Ru/SiO_2 (0.015 g) at 300°C for 300 min.

It is of great interest to note that when KOH (1.75×10^{-3} mol) was added to the system, a marked increase in the reactivity and the changes in the reaction products were observed. It was revealed that the amount of CO was less and higher hydrocarbons, ethylene and propylene, were produced with high selectivity (Table 1). The decomposition temperature of cellulose became lower in the presence of KOH or NaOH, in the cellulose sample[2,3], which suggests that the alkali metal ions play an important role in breaking the cellulose skelton, and increase the reactivity of cellulose with water. Since the amount of CO was less when KOH was added to the system, CH_4 formation over Ru catalyst was restrained than that in the case of neutral system.

The reaction mechanism can be considered as follows.

$$(C_6H_{10}O_5)_n \longrightarrow CO,\ CO_2,\ H_2O \qquad (1)$$

$$H_2O + CO \xrightarrow[\text{cat.}]{} H_2 + CO_2 \qquad (2)$$

$$3H_2 + CO \xrightarrow[\text{Ru}]{} CH_4 + H_2O \qquad (3)$$

Cellulose itself decomposes to form CO, CO_2 and H_2O at the first stage (1), followed by the water gas shift reaction over catalysts, which produces H_2 (2). And the produced H_2 and CO reacted to form CH_4 in the case of Ru catalyzed reaction (3).

It is thus demonstrated here that the carbohydrates, which are annually reproducible in a short time cycle, can be easily converted into hydrocarbon and hydrogen by the reaction with water in the presence of Pt or Ru catalysts. H_2, CO and CO_2 were mainly produced over Pt catalyst, while H_2, CH_4 and CO_2 over Ru catalyst. The importance of methane formation may be emphasized in comparison with the photocatalytic reaction by $Pt/TiO_2/RuO_2$ recently reported, in which H_2 and CO_2 are the main products[4].

References

1) M. A. Vannice, J. Catalysis, 37, 449 (1975).
2) T. Tachibana, J. Chem. Soc. Japan, 63, 924 (1942).
3) K. Tamaru, Bull. Chem. Soc. Japan, 24, 164 (1951).
4) T. Kawai and T. Sakata, Nature, 286, 474 (1980).

(Received June 18, 1981)