GASIFICATION OF ORGANIC COMPOUNDS BY A RUTHENIUM(IV) OXIDE CATALYST IN SUPERCRITICAL WATER

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Organic compounds including plastics and coals are gasified by the catalysis of RuO_2 in SCW to form CH_4, CO_2 and H_2. The general carbon conversions were nearly quantitative without any solid organic residuals except for coals. Gasification experiment of naphthalene in a RuO_2- supercritical D_2O system indicated that hydrogen atoms of the fuel products originated from water. The catalytic effect of RuO_2 owes to a redox couple of Ru^{IV}/Ru^{II} induced by SCW.

INTRODUCTION

Development of a novel process for converting abundant organic resources, such as biomass, coal and waste plastics, into highly combustive fuels would provide one significant clue to solve a worldwide 'energy problem': the gain of an alternative source of energy to provide against the future inevitable exhaustion of petroleum and natural gas reserves. To exploit such organic resources efficiently, it is essential to convert aromatics and polymers as structral constituents into hydrocarbons suitable for use as fuels. As is well known, however, aromatic compounds are quite stable even under supercritical water (SCW) in the vicinity of critical temperature (critical point: 374?, 22.1 MPa).[1- 5] As for polymers, on the other hand, previous work has clearly demonstrated the difficulty of converting addition polymers into fuels.[6] Here we report a gasification catalysis of ruthenium(IV) oxide (RuO_2) found out in SCW, by which aromatic compounds, as well as other organic compounds including plastics, are converted into CH_4 and CO_2, accompanied by the production of H_2. Stoichiometry on the conversions strongly suggests that hydrogen atoms of CH_4 and H_2 originate from water. In fact, direct evidence supporting this has been obtained by a gasification experiment of naphthalene in supercritical deuterium oxide (D_2O). We afford a simple proposal on the catalytic mechanism of RuO_2 observed in SCW.

MATERIALS AND METHODS

(i) *Gasification experiments of organic compounds*

RuO_2 was purchased from Kanto Chemical Co., and used as received. All experiments were carried out in a 10.8-cm^3 autoclave (reactor) made of C-22 Hastelloy. In each run, an organic sample (100 mg), powdered RuO_2 (20 wt.%) and distilled water (3.0 g) were placed in the reactor, and then sealed. The air inside the reactor was replaced by Ar. The reactor

contents were heated to 450？ with magnetic stirring. The pressure inside the reactor increased autogenously with increase in temperature. The reaction at temperature was conducted for 120 min, during which the pressure autogenously increased with gas produced. After cooling, the reactor was connected to a vacuum glass line equipped with three gas chromatographs (GC) (Shimadzu, GC-8A series). The gaseous products were introduced into the vacuum line and determined free from air by the on-line GCs. Two GCs (Shimadzu, GC-8A series) are equipped with thermal conductivity detectors (TCDs) and the remaining one with a flame ionization detector (FID). Inorganic gases were determined by GC-TCDs (CO_2: silica gel column, He carrier, H_2: molecular sieves 5Å column, Ar carrier) and hydrocarbons (C_1-C_3) were by GC-FID (Porapak Q column, He carrier). Carbon conversions of organic compounds (feed) to gaseous products were calculated according to the following equation; C-conv. (%) = 100× [C] in gaseous products/[C] in feed, where [C] represents the moles of carbon.

(ii) *Gasification experiments of coals*

The gasification experiments were conducted in the basically same manner as described in (i). Each coal sample was weighed out within 20 min after drying at 107？ for 60 min just before its use. Proximate and ultimate analyses of coal samples used are listed in Table 1. Carbon conversions were calculated from moles of carbon based on the data of ultimate analysis in Table 1.

Table 1 : Proximate and ultimate analyses of coal samples

Coal	Proximate analysis (wt.%, dry)				Ultimate analysis (wt.%, daf)				
	Moist.	Ash	V.M.	F.C.	C	H	N	S	O
Morwell	9.3	0.9	47.1	42.7	70.1	4.7	0.6	0.3	24.4
Yallourn	11.1	1.6	45.1	42.2	69.0	4.4	0.6	0.2	25.9

V.M.; volatile matter. F.C.; fixed carbon. daf; dry ash free basis.

(iii) *Supercritical D_2O experiment*

Gasification of naphthalene in D_2O was conducted basically in the same manner as described in (i). A gas chromatography-mass spectrometry (GC-MS) analysis of the gaseous products was performed using a Shimadzu GCMS-QP5000 operated at 70 eV. The GC column used was a J&W scientific DB-5MS capillary column. The MS data were recorded for the GC fraction of methane. The mass of hydrogen was measured after purified by coagulating methane and carbon dioxide with liquid N_2 by a direct inlet method MS, which was performed using a Hitachi M-80B operated at 70 eV.

RESULTS AND DISCUSSION

The experimental results on gasification of aromatic compounds and polymers are shown in Table 1. In each run, a negligibly small CO peak was observed on the GC analysis, although it was not determined quantitatively. Nearly complete gasification of aromatic compounds and polymers was achieved by using RuO_2 in SCW, the amount of which was insufficient for stoichiometric reaction with these organic compounds, to obtain CH_4, CO_2 and

H_2 as major products. The stoichiometric insufficiency of RuO_2 clearly indicates that RuO_2 acts as a gasification catalyst (see $[Org]/[RuO_2]$ and $[O]_{CO_2}/[O]_{Org}$ in Table 2). As is

Table 2 : Experimental results on RuO_2-catalyzed gasification of organic compounds in SCW[a]

Organic compounds (Org)	Atomic ratio		Molar ratio[b]	C-conv. (%)	Product distribution (%)[d]			Molar ratio	
	H/C	O/C	$[Org]/[RuO_2]$		CH_4	CO_2	H_2	$[O]_{CO_2}/[O]_{RuO_2}$	$[H]_{Gas}/[H]_{Org}$[f]
Naphthalene	0.80	0	5.12	96.7	48.8	42.7	8.4	23.1	2.90
Carbazole	0.75	0	3.94	87.9[c]	52.7	40.6	6.7	18.1	2.86
Phenyl ether	0.83	0.08	3.87	99.9	45.8	48.8	5.4	23.9 (22.0)[e]	2.46
Dibenzofuran	0.67	0.08	3.92	101.7	51.0	43.6	5.5	22.0 (20.1)[e]	3.46
Polyethylene	2.00	0	23.5	100.6	66.6	28.0	5.3	14.0	1.47
Polypropylene	2.00	0	15.7	99.9	66.5	26.9	6.5	13.5	1.49
Polystyrene	1.00	0	6.32	100.7	53.7	39.4	6.9	21.5	2.47
Poly(ethylene terephthalate)	0.80	0.40	3.44	97.2	37.3	51.0	11.5	19.3 (12.6)[e]	2.44
Cellulose	1.67	0.83	4.07	97.0	34.2	50.9	14.6	14.0 (4.2)[e]	1.18

[a] Experimental conditions: organic samples, 100 mg; RuO_2, 20 wt.%; water density ($?_w$), 0.28 g cm^{-3}; temperature, 450? ; reaction time, 120 min; final pressure, around 44 MPa. [b] Molar quantities of polymers are apparent values calculated by assuming monomeric units to be molecules. [c] The lower conversion is ascribed to the adsorption of CO_2 by the resulting NH_3; the wt.% conversion based on its feed and recovery was 98.6 wt.%. [d] C_2H_6 and C_3H_8 were detected as minor products, though the proportions ($< 0.2\%$) are not listed here. [e] The values in parentheses were calculated according to ($[O]_{CO_2}$-$[O]_{Org})/[O]_{RuO_2}$. [f] Molar ratios of hydrogen atoms in gaseous products ($[H]_{Gas}$) to those in the organic compounds converted ($[H]_{Org}$). In carbazole, $[H]_{Org}$ was calculated using the wt.% conversion.

demonstrated by the carbon conversions, RuO_2 catalyzes the gasification of organic compounds irrespectively of their structures. The obtained gas had a definite composition (CH_4, CO_2 and H_2) despite the class of organic compounds to be gasified. As seen in Table 2, however, the product distribution changed with hydrogen and oxygen contents. Notably, high hydrogen-to-carbon (H/C) ratios of polyethylene and polypropylene indicated high percentages for CH_4, while high oxygen-to-carbon (O/C) ratios of cellulose and poly(ethylene terephthalate) gave more CO_2 and H_2. In all cases, the molar amounts of hydrogen atoms in the gaseous products increased in comparison with those in the organic compounds gasified (see $[H]_{Gas}/[H]_{Org}$ in Table 2). This suggests that hydrogen atoms of CH_4 and H_2 produced by the present catalytic reactions originate from water molecules.

We attempted to apply the RuO_2- SCW system to Victorian brown coals, Morwell and Yallourn. Carbon conversions and the yields of major products are listed in Table 3. Evidently, the gasification of coals was enhanced by the use of RuO_2 compared with the control experiments under pure SCW without RuO_2 catalysts, although the conversions were

Table 3 : Experimental results on RuO_2-catalyzed gasification of coal in SCW[a]

Coal	Atomic ratio			C-conv.[b] (%)	Yield of Individual gas[c] (NL/100 g of coal (daf))			Molar ratio[d]
	H/C	O/C			CH_4	CO_2	H_2	$[H]_{Gas}/[H]_{Coal}$
Morwell	0.07	0.35	SCW	12.1	2.5	11.0	2.2	1.62
			RuO_2- SCW	32.6	13.8	26.7	9.3	2.35
Yallourn	1.51	2.49	SCW	9.4	1.6	9.5	2.2	1.51
			RuO_2- SCW	42.6	20.2	33.2	9.4	2.49

[a] Experimental conditions: coal samples, 100 mg (dry); RuO_2, 20 wt.%; $?_w = 0.28$ g·cm^{-3}, temperature, 450? ; reaction time, 120 min; final pressure, around 41 MPa. [b] Carbon conversions were calculated from moles of carbon based on the data of ultimate analysis in Table 1. [c] Net yields of product gas were converted to liters in normal state (NL) per 100 g coal (daf). [d] Molar ratios of hydrogen atoms in gaseous products ($[H]_{Gas}$) to those in coals gasified ($[H]_{Coal}$).

not so high at this moment. The large increases in yields of CH_4 and H_2 are worthy of remark, whereas the yields of CO_2 were higher than those of CH_4. The high yields of CO_2 would be attributable to high O/C ratios of coals. In both cases, higher $[H]_{Gas}/[H]_{Coal}$ ratios of about 2.4 to 2.5 were obtained. The results indicate that coals undergo the gasification catalysis of RuO_2 in the same manner as other organic compounds to form CH_4, CO_2 and H_2, the hydrogen atoms of which, as described later, come from water molecules.

In Figure 1(a) is shown a profile of the carbon conversion of naphthalene with increase in temperature and pressure. The carbon conversion increased dramatically at the temperature region of 380 to 420? , reaching the nearly constant value (around 50%) asymptotically. This clearly indicates that the pronounced catalysis of RuO_2 occurs around supercritical temperature, 380 to 420? . The catalytic activity was seemingly saturated above 420? irrespectively of temperature and pressure. At the characteristic temperature region of 380 to 420? , a remarkable change of the product distribution was observed (Figure 1(b)). The production of CH_4 has been facilitated as the catalytic activity of RuO_2 becomes higher. It should be noted that the proportion of H_2 decreased with the increase in that of CH_4. This suggests that H_2 is profoundly related to the production mechanism of CH_4.
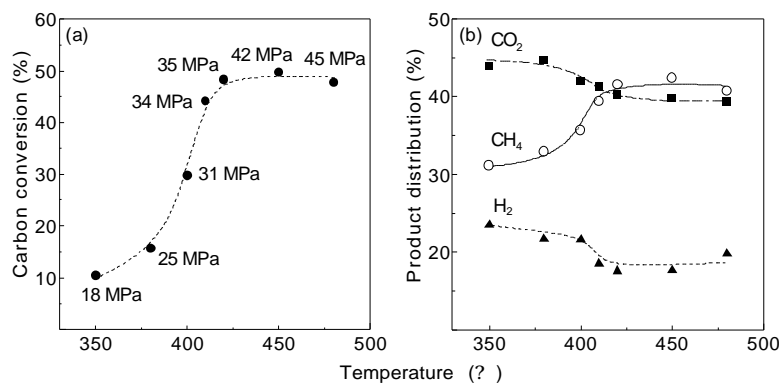

Figure 1 : Profiles of carbon conversion (a) and product distribution (b) on gasification of naphthalene with the elevation of temperature and pressure.

Experimental conditions: naphthalene, 100 mg; RuO_2, 20 wt.%; $?_w = 0.28$ g·cm^{-3}, reaction time, 60 min.

The close correlation between CH_4 and H_2 allowed us to consider that CH_4 would be formed through $\{mCO+nH_2\}$ reactions, *i.e.*, an equimolar reaction (2CO + 2H_2 ? CH_4 + CO_2, ? $H^0 = -247$ kJ mol^{-1}) and a methanation reaction (CO + 3H_2 ? CH_4 + H_2O, ? $H^0 = -206$ kJ mol^{-1}), where a water-gas shift (WGS) reaction (CO + H_2O ? CO_2 + H_2, ? $H^0 = -41$ kJ mol^{-1}) would probably participate. To confirm this we conducted a gasification experiment of naphthalene in the presence of RuO_2 in supercritical D_2O, and the gas obtained was analyzed by gas chromatography-mass spectrometry (GC-MS) and direct inlet method MS. The results of MS analyses indicated that majority of methane and hydrogen produced was not CHD_3 and H_2 (or HD) but an entirely deuterated form CD_4 and D_2, respectively. This strongly support that CD_4 is formed through the $\{mCO+nH_2\}$ reactions between CO and D_2. In consequence, we consider that the gasification of organic compounds by RuO_2 in SCW proceeds primarily through a partial oxidation reaction to produce CO and presumably H_2O, where RuO_2 (*i.e.*, Ru^{IV}) itself would be reduced to a lower oxidation state (*i.e.*, Ru^{II}, see below). Concurrently, H_2 (or D_2) is derived from SCW (or supercritical D_2O). The subsequent $\{mCO+nH_2\}$ reactions are favorable thermodynamically, which strongly shift the product side probably

with competing one another. Although the reverse WGS reaction, which is slightly endothermic, might contribute to the $\{mCO+nH_2\}$ reactions to some extent, there would eventually remain nothing but a small amount of CO.

To identify reduction species of ruthenium formed by the partial oxidation of organic compounds, we measured an absorption spectrum of the solution containing naphthalene and 1,10-phenanthroline in the presence of RuO_2 in SCW. The obtained spectrum showed an absorption band in visible region, the maximum wavelength ($?_{max}$: *ca.* 470 nm) of which was in good agreement with that of the *cis* isomer of bis(1,10-phenanthroline)ruthenium(II) complex.[7] The results support that the gasification reaction is based on the redox reaction between RuO_2 and organic compounds, which proceeds *via* reduction species Ru^{II}.

We propose a catalytic mechanism of RuO_2 in SCW on the basis of the above considerations. The proposed mechanism is illustrated schematically in Figure 2. Organic molecules are partially oxidized by RuO_2 (*i.e.* Ru^{IV}) to form CO and H_2O. Simultaneously, Ru^{IV} is reduced to a lower oxidation sate Ru^{II}. To oxidize an excess number of organic molecules, Ru^{II} must be reoxidized to Ru^{IV}, which is carried out with the reduction of SCW to H_2. The Ru^{IV} regenerated is reduced again to Ru^{II} for further partial oxidation of organic molecules. The CO produced is converted into CH_4 and CO_2 through $\{mCO+nH_2\}$ reactions with H_2 derived from SCW. In this manner, a redox cycle between Ru^{IV} and Ru^{II} is induced by SCW. To the best of our knowledge, presently, it is RuO_2 alone that exhibits the outstanding gasification catalysis in SCW.
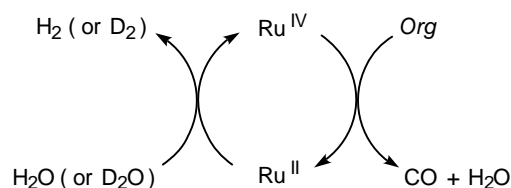

Figure 2 : Schematic representation of the proposed mechanism on gasification catalysis of RuO_2 in SCW.

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