

Gasification reaction of organic compounds catalyzed by RuO₂ in supercritical water

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Nearly complete gasification of organic compounds has been achieved by stoichiometrically insufficient amounts of RuO₂ in supercritical water (SCW) to provide CH₄, CO₂ and H₂, all the hydrogen atoms of which originate from water, and the catalytic effect of RuO₂ results from a redox couple of Ru^{IV}/Ru^{II} induced by SCW.

Abundant organic resources such as biomass, coal and waste plastics can be regarded not only as a chemical feedstock but also as a potential source of energy. To exploit such organic resources efficiently, it is essential to convert aromatics and polymers as structural constituents into hydrocarbons with higher hydrogen contents suitable for use as fuels.

Previous works on the reactivity of supercritical water (SCW, critical point of water: 374 °C, 22.1 MPa) have shown the high stability of aromatic compounds and the difficulty in converting addition polymers into fuels.^{1–3} Supercritical water oxidation (SCWO), including catalytic SCWO with metal oxide catalysts, is a prominent approach for the decomposition of such stable organic compounds.⁴ However, SCWO provides not fuel products but CO₂ as a major product. Here we present a catalytic gasification reaction of organic compounds by ruthenium(IV) oxide (RuO₂) in SCW, where aromatic compounds, as well as other organic compounds including plastics, are converted into CH₄ and CO₂, accompanied by the production of H₂. Stoichiometry on the conversions strongly suggests that the hydrogen source of the fuel products is water. In fact, direct evidence supporting this has been obtained by a gasification experiment of naphthalene in a RuO₂-supercritical deuterium oxide (D₂O) system. We afford a simple mechanism for the catalytic effect of RuO₂ in SCW.

Experiments[†] were conducted under Ar atmosphere in an autoclave at 450 °C and around 44 MPa for 120 min. The gas produced was quantitatively analyzed by on-line gas chroma-

tography (GC). In each run, a negligibly small CO peak was observed in the GC analysis, though it was not determined quantitatively. Nearly complete gasification of aromatics and polymers was achieved by RuO₂, the amount of which is insufficient for stoichiometric reactions, to obtain CH₄, CO₂ and H₂ as major products (Table 1). The quantitative insufficiency of RuO₂ indicates that the gasification reaction catalytically proceeds by the action of RuO₂ (see [Org]/[RuO₂] and [O]_{CO₂}/[O]_{RuO₂} in Table 1). The results were largely different from those of SCWO by excess amounts of O₂: the SCWO of such stable organic compounds did not proceed at 450 °C, producing more or less carbonaceous deposits except for CO₂ as a major gaseous product. In the present RuO₂-SCW system, there remained almost no solid organic residuals, and an unchanged composition of gas (CH₄, CO₂ and H₂) was obtained despite the class of organic compounds to be gasified. As seen in Table 1, however, the product distribution changed with the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios of organic compounds. Notably, high H/C ratios of polyethylene and polypropylene resulted in high percentages of CH₄, while high O/C ratios of cellulose and poly(ethylene terephthalate) gave more CO₂ and H₂. 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 1). This suggests that hydrogen atoms of the fuel products originate from water molecules.}

In Fig. 1(a) is shown a profile of the carbon conversion of naphthalene with increasing temperature and pressure. The gasification catalysis of RuO₂ became marked around the supercritical temperature, 380 to 420 °C. The catalytic activity was seemingly saturated above 420 °C. This means that the catalytic rate becomes maximal at this temperature. At the characteristic temperature region of 380 to 420 °C, a remarkable change of the product distribution was observed (Fig. 1(b)). The

Table 1 Summary of the experimental results on gasification reactions of organic compounds by RuO₂ in SCW^a

Organic compounds (Org)	Atomic ratio		Molar ratio ^b		Product distribution (%) ^c			Molar ratio	
	H/C	O/C	[Org]/[RuO ₂]	C-conv. (%) ^c	CH ₄	CO ₂	H ₂	[O] _{CO₂}/[O]_{RuO₂}}	[H] _{Gas} /[H] _{Org} ^g
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 ^d	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) ^f	2.46
Dibenzofuran	0.67	0.08	3.92	101.7	51.0	43.6	5.5	22.0 (20.1) ^f	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) ^f	2.44
Cellulose	1.67	0.83	4.07	97.0	34.2	50.9	14.6	14.0 (4.2) ^f	1.18

^a Experimental conditions: organic samples, 100 mg; RuO₂, 20 wt.%; water density (ρ_w), 0.28 g cm⁻³; temperature, 450 °C; 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 C-conv. (carbon conversion) (%) = 100 × [C] in gaseous products/[C] in organic compounds loaded. ^d The lower conversion is ascribed to the adsorption of CO₂ by the resulting NH₃; the wt.% conversion based on its feed and recovery was 98.6 wt.%. ^e C₂H₆ and C₃H₈ were detected as minor products, though the proportions (<0.2%) are not listed here. ^f The values in parentheses were calculated according to ([O]_{CO₂} - [O]_{Org})/[O]_{RuO₂}. ^g 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.

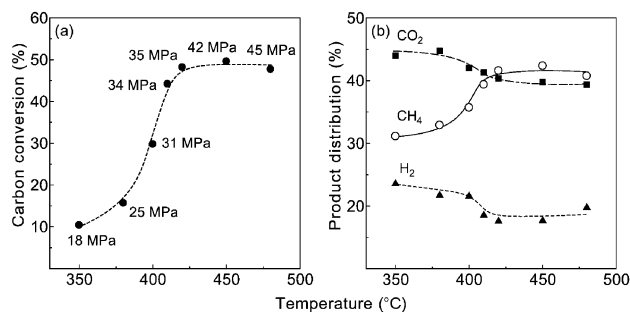


Fig. 1 Profiles of carbon conversion (a) and product distribution (b) on gasification of naphthalene with the elevation of temperature and pressure. Experimental conditions: naphthalene, 100 mg; RuO₂, 20 wt.%; $\rho_w = 0.28$ g cm⁻³; reaction time, 60 min.

production of CH₄ has been facilitated as the catalytic activity of RuO₂ becomes higher. It should be noted that the proportion of H₂ decreased with the increase in proportion of CH₄. This suggests that H₂ is profoundly related to the production mechanism of CH₄.

The close correlation between CH₄ and H₂ allowed us to consider that CH₄ would be formed through $\{m\text{CO} + n\text{H}_2\}$ reactions, *i.e.*, an equimolar reaction ($2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{CO}_2$, $\Delta H^0 = -247$ kJ mol⁻¹) and a methanation reaction ($\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$, $\Delta H^0 = -206$ kJ mol⁻¹), where a water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, $\Delta H^0 = -41$ kJ mol⁻¹) would probably participate. To confirm this we conducted a gasification experiment of naphthalene in the presence of RuO₂ in supercritical D₂O, and the gaseous products were analyzed by gas chromatography-mass spectrometry (GC-MS) and direct inlet method MS.[‡] The results of the MS analyses indicated that the majority of the methane and hydrogen produced were not CHD₃ and H₂ (or HD) but the entirely deuterated forms CD₄ and D₂, respectively. This strongly supports that CD₄ is formed through the $\{m\text{CO} + n\text{H}_2\}$ reactions between CO and D₂. It is therefore concluded that the gasification reaction proceeds primarily through a partial oxidation of organic compounds by RuO₂ to produce CO and probably H₂O, where RuO₂ (*i.e.*, Ru^{IV}) itself would be reduced to a lower oxidation state (*i.e.*, Ru^{II}, see below), while concurrently H₂ (or D₂) is derived from SCW (or supercritical D₂O). The subsequent $\{m\text{CO} + n\text{H}_2\}$ reactions are quite favorable thermodynamically, which strongly shift towards the product side while competing with one another.⁵ The reverse WGS reaction, which is slightly endothermic, might contribute to the $\{m\text{CO} + n\text{H}_2\}$ reactions to some extent, though there would eventually remain nothing but a small amount of CO.

Next we measured an absorption spectrum of the solution containing naphthalene and 1,10-phenanthroline in the presence of RuO₂ under supercritical conditions. Phenanthroline is a well-known bidentate ligand, which generally forms stable chelate complexes with the 2+ ions of transition metals including Ru^{II}.⁶ The obtained spectrum showed a broad absorption band in visible region, the maximum wavelength (λ_{max}) of which was *ca.* 470 nm (Fig. 2). The λ_{max} is in good

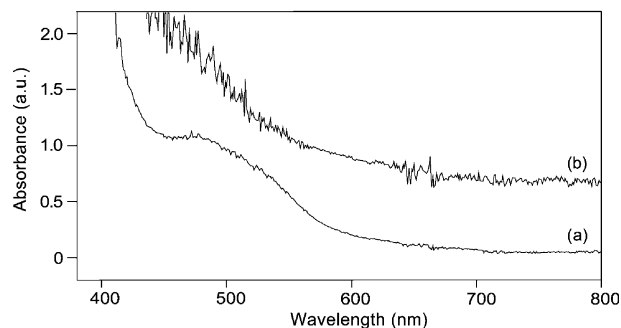


Fig. 2 Absorption spectra of 1,10-phenanthroline-ruthenium(II) complex (a) and free ligand (b) observed in SCW at 450 °C.

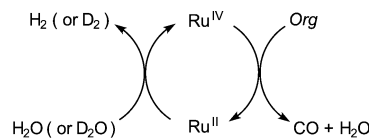


Fig. 3 SCW-induced redox cycle between Ru^{IV} and Ru^{II} catalyzing the gasification of organic compounds.

agreement with that of the *cis* isomer of the bis(1,10-phenanthroline)ruthenium(II) complex.⁷ The result suggests that Ru^{II} exists as an intermediate in the catalytic mechanism of RuO₂, and also supports that the catalytic mechanism is based on the redox reactions caused by RuO₂.

A proposed mechanism on the gasification catalysis of RuO₂ in SCW is illustrated schematically in Fig. 3. Organic molecules are partially oxidized by RuO₂ to form CO and H₂O, where Ru^{IV} is reduced to a lower oxidation state of 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 H₂. The Ru^{IV} regenerated is reduced again to Ru^{II} for further partial oxidation of organic molecules. The CO produced is converted into CH₄ and CO₂ through $\{m\text{CO} + n\text{H}_2\}$ reactions with H₂ derived from SCW. A redox cycle between Ru^{IV} and Ru^{II} is induced by SCW, whereby the gasification reaction of organic compounds proceeds catalytically. To the best of our knowledge, presently, it is RuO₂ alone that exhibits outstanding gasification catalysis in SCW.

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Notes and references

† RuO₂ was purchased from Kanto Chemical Co., and used as received. All experiments were carried out in a 10.8 cm³ autoclave (reactor) made of C-22 Hastelloy. In each run, an organic sample (100 mg), powdered RuO₂ (20 wt.%) and distilled water (3.0 g) were placed in the reactor, which was then sealed. The air inside the reactor was replaced by Ar. The reactor contents were heated to 450 °C with magnetic stirring. The pressure inside the reactor increased autogenously with increasing 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. Inorganic gases were determined by GC-TCDs (CO₂: silica gel column, He carrier, H₂: molecular sieves 5 Å column, Ar carrier) and hydrocarbons (C₁–C₃) by GC-FID (Porapak Q column, He carrier).

‡ Gasification of naphthalene in D₂O was conducted basically in the same manner as described above. The GC-MS analysis 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 GC-MS data obtained for the GC fraction of methane; *m/z* (%): 20 (100.0) [M⁺], 18 (76.3), 19 (8.4), 16 (8.2), 14 (3.6), 17 (3.6), 21 (1.1), 12 (1.0). The direct inlet method MS was performed using a Hitachi M-80B operated at 70 eV. The mass of hydrogen was measured after purified by coagulating methane and carbon dioxide with liquid N₂. The MS spectrum showed only one peak at *m/z* = 2.

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