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# Formation of Ru active species by ion-exchange method for aqueous phase reforming of acetic acid

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## ABSTRACT

NaY-zeolite was employed as a support of ruthenium catalysts for aqueous phase reforming of acetic acid. Catalytic activities of the supported ruthenium species on NaY-zeolite depended on oxidation state controlled by preparation conditions. Catalyst NaY(exc), whose 5 wt% ruthenium precursors were supported through cation-exchanging process, produced H<sub>2</sub> continuously for 10 h when the catalysts were used without reducing by H<sub>2</sub> prior to usage. Decreasing the loading amounts of ruthenium on NaY(exc) led to improve the selectivity toward complete reforming of acetic acid giving H<sub>2</sub> and CO<sub>2</sub> because of the strong interaction between positively charged ruthenium particle and the support. However, contents of sodium cations controlled by the pH of precursor solutions did not affect the catalytic performances.

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## Introduction

It has been generally accepted that hydrogen fuel cells are environmentally clean and highly efficient devices for electrical power generation [1–3]. They cannot have, however, a high impact on solving environmental problems without overcoming the shortage of hydrogen production from high-temperature steam reforming of non-renewable hydrocarbon feedstock [4–6]. The full environmental benefit of generating power from hydrogen fuel cells is achieved when hydrogen is produced from renewable sources such as solar power and biomass which are promising major challenges as the global energy generation moves toward a “hydrogen society”.

Fifteen years ago, it was reported for the first time that the liquid phase reactions of methanol, ethylene glycol, glycerol and other oxygenates with water were catalyzed by supported Pt and Ni metals, which can be a model catalytic reaction for biomass conversion [7,8]. The mechanism of H<sub>2</sub> production from ethylene glycol was recognized to involve the cleavages of C–C and C–H bonds to form adsorbed CO followed by water-gas shift to H<sub>2</sub> and CO<sub>2</sub> formation [9,10]. Consequently, a good catalyst for aqueous phase reforming (APR) process must be active in the cleavage of C–C bonds and water-gas shift reaction, but it must inhibit the cleavage of C–O bond and methanation reactions. It has been generally accepted that alcohols such as methanol, ethylene glycol and glycerol, where the C–H bond of each carbon atom is activated by adjacent OH groups, might be converted selectively to H<sub>2</sub> and CO<sub>2</sub> [7,11–13].

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For ethanol, however, it is rather difficult to obtain H<sub>2</sub> and CO<sub>2</sub> selectively as complete reforming products because of the non-activated methyl group, which is easily transformed to CH<sub>4</sub> [14–16]. Accordingly we will obtain a 1:1 ratio of CH<sub>4</sub> and CO<sub>2</sub> together with acetic acid, and formed CO or CO<sub>2</sub> is transformed into CH<sub>4</sub> through a methanation reaction which results in an excess CH<sub>4</sub> compared to CO<sub>2</sub> [17]. However, a possibility of reforming acetic acid in steam reforming (SR) as well as APR reactions exists at lower temperatures.

Recently we have studied APR reactions of ethanol (EtOH) and acetic acid (AcOH) as model compounds of biomass for hydrogen production over various supported precious metal catalysts [17]. In the case of EtOH-APR over TiO<sub>2</sub> supported 5 wt % metal catalysts, the activity as well as the selectivity differ depending on the kind of metals with the following activity order: Ru > Rh > Pt > Ir. Over Pt/TiO<sub>2</sub> and Ir/TiO<sub>2</sub>, a large amount of AcOH was formed by the hydration of acetaldehyde (AcH) with smaller amounts of CO<sub>2</sub> and CH<sub>4</sub> (1:1 ratio), indicating the absence of complete reforming process with water. On the other hand, over Rh/TiO<sub>2</sub> and Ru/TiO<sub>2</sub> catalysts, major products were CH<sub>4</sub> and CO<sub>2</sub> with a small amount of liquid phase products and excess CH<sub>4</sub> was formed afterward indicating the operation of an unfavorable methanation reaction.

We have also studied the metal particle size effects upon the APR reactions of ethanol and acetic acid over Ru/TiO<sub>2</sub> catalysts to clarify the controlling factors for the selectivity of this reaction [18]. Decomposition processes from AcH and AcOH occurred over larger Ru metals, forming 1:1 ratio CH<sub>4</sub> and CO (or CO<sub>2</sub>). On the other hand, positively charged (Ru<sup>δ+</sup>) Ru species would be the active sites for the hydration of AcH where CO<sub>2</sub> methanation was inhibited completely. From AcH and AcOH, a certain extent of complete reforming process to form H<sub>2</sub> and CO<sub>2</sub> was observed especially over smaller Ru metal catalysts. At this stage, however, detailed active site structure and the mechanism of the complete reforming process were not clarified yet.

In the present study, we have designed Ru/NaY-zeolite catalysts for APR reaction of AcOH. NaY zeolite has unique three-dimensional ordered porous structure as well as cation-exchangeable ability. Such characteristics would be efficient for controlling the structural and electronic properties of supported ruthenium species. As we have expected, Ru/NaY-zeolite catalysts exhibit high selectivity for complete reforming. In this work, we have tried to characterize the efficient active site formed on NaY zeolite.

## Experimental

### Preparation of catalysts and reaction procedures

Supported ruthenium catalysts were prepared by simple impregnation of a precursor compound or cation-exchanging method. A cationic ruthenium(III) complex, [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>, was employed as a precursor of all the supported ruthenium catalysts.

### Impregnation method

The supports (NaY zeolite, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>) were dispersed in pure water and stirred for 30 min. To this slurry,

an aqueous solution of [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> (5 wt% of the support) was added and the resulting mixture was stirred for 30 min at room temperature. After additional stirring for 1 h at 333 K, volatiles were evaporated. The obtained solids were dried overnight at 373 K and grinded. Prior to employ as catalyst, the solids were reduced at 623 K under H<sub>2</sub> stream.

### Cation-exchanging method

NaY zeolite (2.95 g) was dispersed to de-ionized water (400 mL) and stirred for 30 min at room temperature. To this slurry, aqueous HCl (1 mol L<sup>-1</sup>) was added to adjust the pH to a desired value (4.5–7.0). In another vessel, [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> (an appropriate amount of ruthenium regarding to the support; 0.5 wt%–5 wt%) was dissolved in water (50 mL). This solution was stirred for 30 min at ambient temperature and then dilute aqueous HCl (0.1 mol L<sup>-1</sup>) was added to adjust the pH as 4.5. The resulting ruthenium precursor solution was added to the support-dispersed solution. After stirring the mixture at room temperature for 24 h, solid materials were collected by centrifugation. The resulting catalysts were washed with water (300 mL × 3) and dried by vacuum at room temperature overnight. The loading amounts of ruthenium and sodium were quantified by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS), respectively. The resulting catalysts, x wt % Ru/NaY(exc) (pH y) [where x = 5, 2, 1, or 0.5 on y = 4.5 (changing the loading amounts of ruthenium), and, y = 4.5, 5.0, 5.5, 6.0, 6.5, or 7.0 when x = 5 (changing the pH of the catalyst-preparing solution)] were applied to the reaction with or without pre-reduction treatment under H<sub>2</sub> streaming at 623 K.

Catalyst SA(exc), namely SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> based ruthenium catalysts, was also prepared by cation-exchanging method via similar manner. The support SA, whose cation was exchanged from H<sup>+</sup> to NH<sub>4</sub><sup>+</sup>, was dispersed in pure water. To this support-dispersed slurry, the precursor solution was added immediately and stirred for 24 h at room temperature. Then the solids were collected by filtration and washed with 1 L of de-ionized water. Contents of ruthenium in the washed water were quantified by ICP-MS to estimate the exchanged ratio of cations. The resulting catalysts were evacuated at room temperature overnight. The resulting 3.4 wt% Ru/SA(exc) was applied to the reaction with or without pre-reduction treatment.

### Aqueous phase reforming of acetic acid with water

The catalyst (0.5 g) was put into a stainless steel autoclave (400 mL). After purging by pure N<sub>2</sub>, 80 mL of degassed aqueous solution of acetic acid (1 vol%: AcOH = 28.0 mmol g<sub>cat</sub><sup>-1</sup>) was introduced into the reactor under nitrogen atmosphere. The reforming reaction was conducted in a batch mode, which was connected to an online TCD gas chromatograph to analyze the gas phase products during the reaction (molecular sieve 13X column and Porapak Q column). After quick heating (about 60 min), the reaction was started at 473 K under 2.5–3.0 MPa pressure. During the reaction, the liquid phase content of the autoclave was stirred vigorously by a magnetic stirrer. A small part of the liquid phase products was sampled using an online sampling tube (1 mL) and analyzed using an FID gas chromatograph (CP PoraBond Q column).

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