



Selective synthesis of carbon monoxide via formates in reverse water–gas shift reaction over alumina-supported gold catalyst

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ABSTRACT

Thermal decomposition of formic acid on SiO₂, CeO₂ and γ -Al₂O₃ was studied as an elementary step of reverse water–gas shift reaction (RWGS) over supported Au catalysts. γ -Al₂O₃ showed the highest CO selectivity among the tested oxides in the decomposition of formic acid. Infrared spectroscopy showed the formation of four formate species on γ -Al₂O₃: three η^1 -type and one μ^2 -type species, and these formates decomposed to CO at 473 K or higher. Au-loaded γ -Al₂O₃ samples were prepared by a deposition-precipitation method and used as catalysts for RWGS. The supported Au catalyst gave CO with high selectivity over 99% from CO₂ and H₂, which is attributed to the formation of formates on Au and subsequent decomposition to CO on γ -Al₂O₃.

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1. Introduction

Carbon dioxide (CO₂) has been recognized as an abundant and inexpensive carbon resource for chemical industry [1–4]. Reverse water–gas shift reaction (RWGS, Eq. (1)) is one of the most important reactions in C1 chemistry, because the resulting carbon monoxide (CO) [5–9] can be utilized as feedstock for the production of valuable compounds such as methanol, dimethyl ether and hydrocarbons [5,8]. Cu/ZnO/Al₂O₃ is known as an active catalyst for RWGS and methanol synthesis from syngas (CO/H₂), and methanol can be directly obtained from CO₂ and H₂ [5,10–12]. Methanol synthesis from CO₂ and H₂ has been currently tested in a pilot plant with a copper-based catalyst [13]. In contrast to the direct synthesis of methanol, the production of syngas from CO₂ is one of the key technologies for sustainable chemical production, because syngas can be converted to a variety of useful compounds in the Fischer–Tropsch synthesis [5,8,14,15].



Gold (Au) nanoparticles supported on various oxides have been investigated by Haruta et al. for the hydrogenation of CO₂ [16]. CO is a main product in this system, because the Au

catalysts cannot catalyze CO hydrogenation to CH₄ or CH₃OH. Moreover, CO₂ conversion and product selectivity greatly depend on the acid–base property of the oxide supports. Au catalysts on acidic supports produce CO and a small amount of CH₄. On the other hand, Au catalysts on basic supports give low CO₂ conversion due to a strong interaction of CO₂ with basic sites.

It is known that formate species are formed as a key intermediate in the CO₂ hydrogenation over Au catalysts [5,17–20]. Since Au nanoparticles do not decompose the formate species [20,21], the decomposition of formate species is strongly influenced by the property of supports. In this paper, we studied the decomposition of formate species on oxide supports such as SiO₂, γ -Al₂O₃ (hereafter Al₂O₃) and CeO₂ as an elementary step in RWGS over Au catalysts. Amphoteric Al₂O₃ converted formate species into CO with higher selectivity than SiO₂ and CeO₂. Thermal decomposition of formates on Al₂O₃ was evaluated by diffusible reflectance infrared Fourier transform spectroscopy (DRIFT). Then, Au-loaded Al₂O₃ samples were prepared and their catalytic activity was tested in RWGS.

2. Experimental

2.1. Reagents

Al₂O₃ was purchased from Tokyo Chemical Industry Company (Japan). Formic acid, HAuCl₄•3H₂O and diethyl ether with highest

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Table 1. Adsorption and thermal decomposition of formic acid on Al₂O₃, CeO₂ and SiO₂.

Oxide	Amount of adsorbed formic acid (mmol/g) ^a	Surface area (m ² /g)	Density of adsorbed formic acid (nm ⁻²)	CO/CO ₂ ratio ^b
Al ₂ O ₃	1.3	160	4.9	50
CeO ₂	1.0	130	4.6	3
SiO ₂	0.8	290	1.7	1

^a Determined by TOC analysis.^b CO and CO₂ were analyzed by GC-TCD.

grade were obtained from Wako Pure Chemical Industries (Japan) and used without any purification treatment.

2.2. Thermal decomposition of formate species on metal oxides

Formic acid was immobilized on metal oxides (CeO₂, SiO₂, and Al₂O₃) by simple adsorption treatment. Each metal oxide (1.0 g) was added to a mixture of formic acid (1 mL) and diethyl ether (25 mL), and the solution was stirred at room temperature for 6 h under air. After filtration, the resulting materials were washed repeatedly with diethyl ether, and then dried under vacuum for 12 h. The amount of formic acid on each metal oxide was estimated by a total organic carbon analyzer (TOC, Shimadzu SSM-5000A). The samples were heated in an IR cell from 298 to 773 K with a heating rate of 2 K/min under a mixed gas flow of Ar (2 mL/min) and He (18 mL/min). The outlet gas was analyzed by gas chromatography (Shimadzu GC 8A, thermal conductivity detector, active carbon column (2 m), temperature 383 K) to monitor the evolved CO and CO₂. FT-IR spectra were obtained at a resolution of 1 cm⁻¹ using a spectrometer (Spectrum 100, PerkinElmer) equipped with a mercury cadmium telluride (MCT) detector. A total of 16 scans were averaged for each spectrum. Deconvolution of peaks was performed by assuming Gaussian profiles of the peaks.

2.3. Catalyst preparation and catalytic reaction

An Au-loaded Al₂O₃ sample was prepared by a deposition-precipitation (DP) method [22]. Al₂O₃ was immersed in an aqueous solution of HAuCl₄ (pH 8), which was aged for 1 h. The resulting solid was filtered, washed with H₂O, dried at 383 K and reduced in H₂ at 573 K for 3 h to afford Al₂O₃-supported Au catalyst (denoted Au-DP). For comparison, an Al₂O₃-supported Au catalyst (Au 5 wt%) was prepared by a conventional impregnation method using HAuCl₄·3H₂O (99.9%, Wako). After immobilization of Au species on Al₂O₃ by vacuum evaporation and drying at 298 K, the sample was reduced in H₂ at 573 K for 3 h to obtain Al₂O₃-supported Au catalyst (denoted Au-Imp). Structural characterization of the catalysts was performed by X-ray fluorescence spectroscopy (XRF, EDX-720, Shimadzu), nitrogen adsorption (Belsorp-mini II, Microtrac-BEL), X-ray diffraction (XRD, Rigaku, Ultima IV, Cu Kα) and transmission electron microscopy (TEM, JEM-2100F, JEOL, 200 kV).

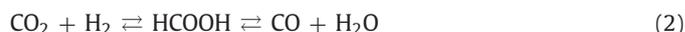
Hydrogenation of CO₂ was conducted in a fixed-bed flow reactor (inner diameter 9.5 mm) made of SUS316 (Fig. S1). Mass flows of CO₂ (99.95%), H₂ (99.999%), He (99.999%) and Ar (99.999 %, internal standard) were regulated by mass flow controllers (HORIBA STEC). The catalyst (0.3 g) was diluted with glass beads (diameter 0.2 mm, 1 g) and charged in the reactor. After reduction of the catalyst in H₂ flow (20 mL/min) at 673 K for 1 h and subsequent treatment in He flow (20 mL/min) at 673 K for 15 min, a gas mixture (CO₂ 15%, H₂ 75%, Ar 10%, flow rate 20 mL/min, space velocity (SV) 4000 mL/g/h, 0.1 MPa) was fed into the reactor. Products in the liquid phase collected by a water-trap were analyzed by high-performance liquid chromatography (HPLC, Shimadzu LC10ATVP, UV detector) with a Shodex Sugar SH-1011 column (ø8 × 300 mm; eluent: water 0.5 mL/min; 323 K). The outlet gas was analyzed by gas chromatography (Shimadzu GC 8A, the

thermal conductivity detector, active carbon column (2 m), temperature 383 K).

3. Results and discussion

3.1. Thermal decomposition of formic acid on metal oxides

Thermal decomposition of formic acid produces CO₂ + H₂ or CO + H₂O (Eq. 2). In the reaction from the left to the right (RWGS), formic acid (HCOOH) is assumed to be an intermediate and selective decomposition of HCOOH to CO is important. Hence, the effect of supports on the decomposition of HCOOH was studied.



Here we used three metal oxides for the decomposition of HCOOH into CO to find the most appropriate support of Au for RWGS. Table 1 compares the amount of adsorbed HCOOH and CO/CO₂ ratio in the decomposition of HCOOH. Similar amounts of HCOOH adsorbed on metal oxides estimated by TOC. However, the densities of immobilized HCOOH for Al₂O₃ and CeO₂ are larger than that for SiO₂. This difference is attributed to weakly basic property of Al₂O₃ and CeO₂ to stabilize HCOOH by the formation of formate. Decomposition of adsorbed species was examined by heating these oxides from room temperature to 773 K under inert gas atmosphere. SiO₂ decomposed HCOOH into CO and CO₂ equally (CO/CO₂ = 1). CeO₂ and Al₂O₃ produced CO more favorably than CO₂, and Al₂O₃ gave the highest CO/CO₂ ratio among the three oxides. Fig. 1 shows dependence of CO and CO₂ formation on reaction temperature over Al₂O₃. CO evolution starts at 473 K and rapidly increases up to 543 K. On the basis of CO evolution, decomposition is completed below 673 K. From these results, decomposition of HCOOH on Al₂O₃ was monitored by IR at 483–683 K.

Fig. 2 shows a DRIFT spectrum of HCOOH-adsorbed Al₂O₃ at 483 K under inert gas atmosphere. Broad bands at 3000–2800 cm⁻¹, 1800–1400 cm⁻¹ and 1400–1200 cm⁻¹ are assignable to C–H stretching, C–O stretching and C–H bending modes of adsorbed formic acid, respectively. Tamaru et al. reported that a formate species with the η¹-type structure is an intermediate in the

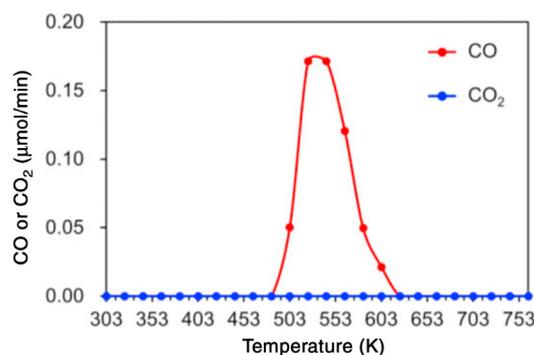


Fig. 1. Dependence of CO (red) and CO₂ (blue) formation on reaction temperature over Al₂O₃. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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