Electronic Supplementary Information

Preparation of Ru Nanoparticles on TiO_2 by Selective Deposition Method and Their Application to Selective CO Methanation

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Experimental

Catalyst preparation

2wt% Ru/TiO_2 catalysts were prepared by an impregnation method and abbreviated to IMP. The TiO_2 support (JRC-TIO4), comparable to Degussa P25, was provided by the Catalysis Society of Japan. It was impregnated with an aqueous solution of $Ru(NO_3)_3$ solution (50.76 g L^{-1}, Tanaka Co.). All samples were dried at 100 ºC and then calcined at 500 ºC for 3 h in air. These catalysts were abbreviated to IMP. In addition, 2wt% Ru/TiO_2 catalysts were also prepared by a selective deposition method. A volume of 1.97 ml $Ru(NO_3)_3$ solution was diluted to 100 ml with deionized water, adjusted to pH 7 by slowly adding NaOH solution (50%, Aldrich) or NH_3 solution (25%, Wako), and stirred at room temperature for 24 h. Then 4.9 g of TiO_2 (JRC-TIO4) was added under stirring to the solution. The suspension was ultrasonically treated for 30 min and aged at 100 °C for 48 h. The obtained powder was filtered and dried at 100 °C. The Ru/TiO_2 catalysts using NaOH and NH_3 solutions are abbreviated to SD-Na and SD-NH_3, respectively. Furthermore, the powder of SD-Na was washed with copious amounts of water, followed by drying at 100 °C. This powder was named as SD-Na-wash.

Activity test

The catalytic performance for selective CO methanation was evaluated in a 4-mm I.D. fixed-bed quartz tubular reactor at atmospheric pressure. The reaction temperature was measured at the inlet of the catalyst bed by a K-type thermocouple. A quantity of 300 mg of catalyst powder was placed in the reactor, and then reduced at 450ºC for 30 min in 5% H_2/Ar flow prior to each run. The feed gas, which simulates the methane reformate equilibrated at 190 ºC, consists of 0.154% CO, 15.5% CO_2, 62.3% H_2 and

22.0% H_2O (dry base: 0.198% CO, 19.9% CO_2, 79.9% H_2). The gaseous mixture was fed at a space velocity of 11,000 h^{-1}. The gas composition at the reactor outlet was analysed with a micro gas chromatograph (Varian, CP-4900) equipped with MS-5A, COX and PPQ columns and a thermal conductivity detector (TCD). The outlet gas concentrations of CO, CO_2, CH_4, and H_2 were described on the basis of the dry gas composition.

Characterization

The crystalline phase of catalysts was determined by X-ray diffraction (XRD) (Rigaku, RINT 2400 instrument) at voltage of 40 kV and current of 100 mA. Phases were identified from comparison to references from the International Centre for Diffraction Data (ICDD). X-ray photoelectron (XP) spectra were obtained with a JEOL JPS-90SX spectrometer using MgKα radiation. Transmission electron microscopy (TEM, JEOL-2000EX) was used to determine the morphology of the Ru and TiO_2 particles on the catalysts. The chemisorption of CO was measured by a pulse method using a thermal conductivity detector (Quantachrome, CHEMBET-3000). After reduction of the samples with 5% H_2/Ar at 450 ºC for 0.5 h, they were cooled to room temperature in He flow, and then pulses of CO (25 μl_{CO} pulse^{-1}) were passed over the samples until saturation was observed.

Table S1 CO conversion and/or conversion rate over supported Ru catalysts.

Catalyst	Reaction gas		CO conversion			Ref.
	Space velocity	composition	Conv. / %	Conv. Rate / ml min^{-1} g_{cat}^{-1}	Temp / °C	
SD-NH_3	11000 h^{-1}, 0.18 N L min^{-1} g_{cat}^{-1}	$CO/CO_2/H_2/H_2O$ = 0.154/15.5/62.3/22.0	94	0.27	150	This study
2wt%Ru/TiO_2	ca. 10000 h^{-1}	$CO/CO_2/H_2/H_2O$ = 0.2/16.1/65.3/18.4	< 20		150	[1]
2.2wt%Ru/zeolite	5000 h^{-1}	$CO/CO_2/H_2/N_2$ = 0.6/15.5/81.1/2.8		1.8×10^{-6}*	190	[2]
3%Ru/γ-Al_2O_3	0.33 N L min^{-1} g_{cat}^{-1}	$CO/CO_2/H_2/H_2O$ = 0.5/18/45/15	< 10	< 0.17	180	[3]

* Estimated from CH_4 formation rate (62×10^{-6} mol s^{-1} g_{Ru}^{-1}) and selectivity of CO methanation (100%.)

[1] K. Urasaki, K. –I. Endo, T. Takahiro, R. Kikuchi, T. Kojima and S. Satokawa, *Top. Catal.*, 2010, **53**, 707.

[2] S. Eckle, H. –G. Anfang and R. J. Behm, *Appl. Catal. A: Gen.*, 2011, **391**, 325.

[3] C. Galletti, S. Specchia, G. Saracco and V. Specchia, *Chem. Eng. Sci.*, 2010, **65**, 590.

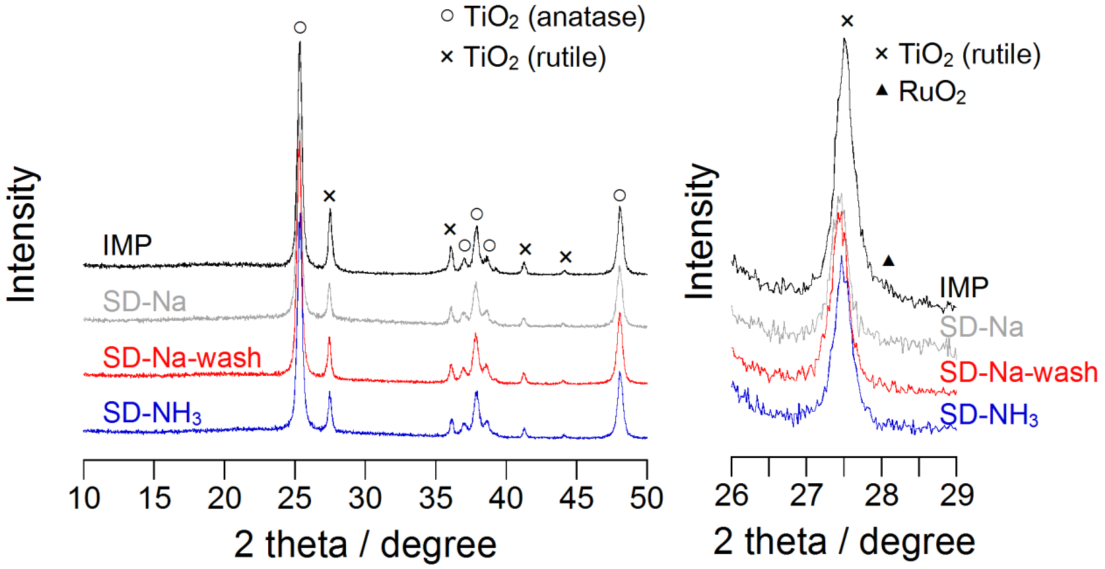

Fig. S1 XRD patterns of IMP, SD-Na, SD-Na-wash, and SD-NH_3. JCPDS-card number: Anatase-type TiO_2 (65-5714) and rutile-type TiO_2 (21-1276).

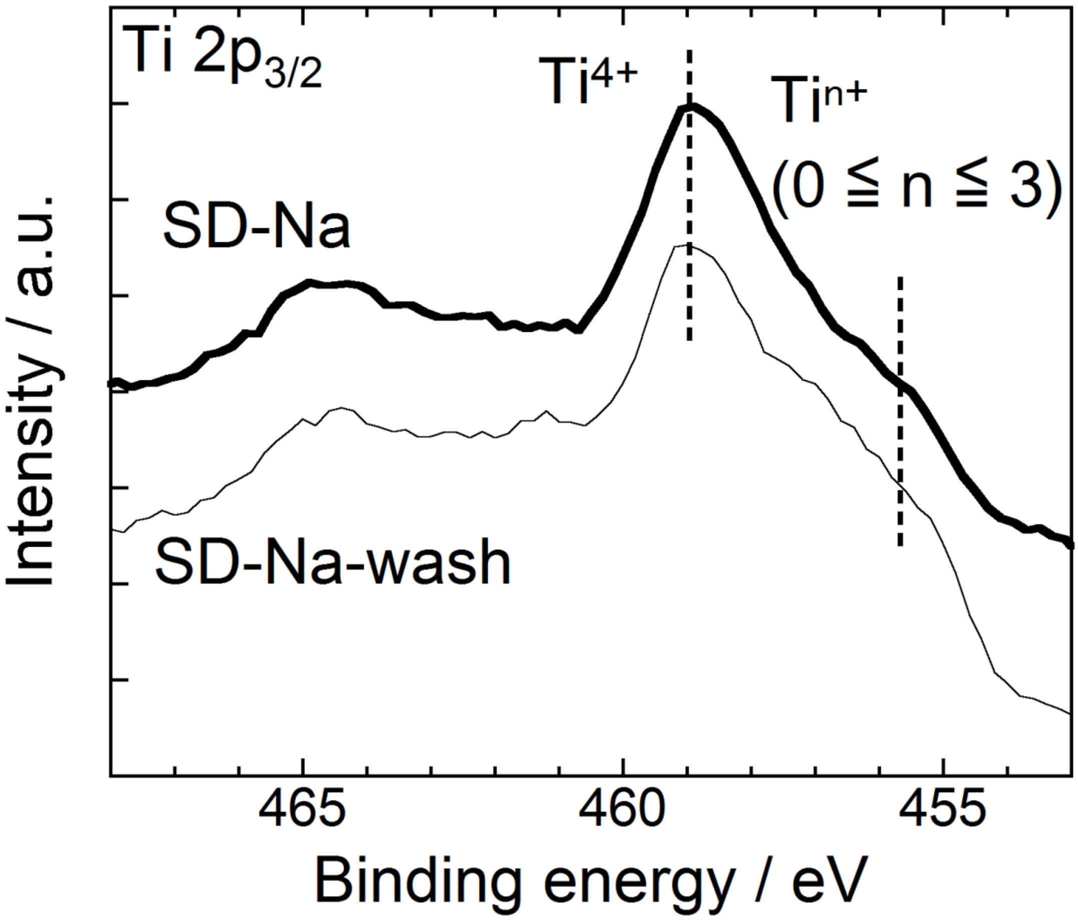

Fig. S2 XP spectra of Ti 2p of SD-NA and SD-Na-wash.[Ref.]

[Ref.] F. Pesty, H. –P. Steinrück and T. E. Madey, *Surf. Sci.*, 1995 , **339**, 83.

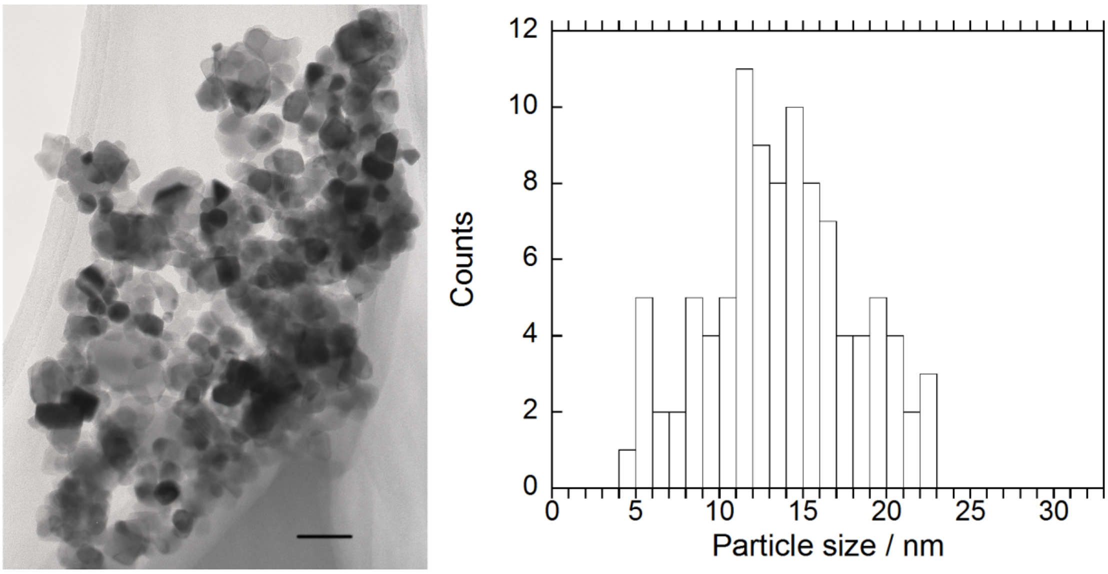

Fig. S3 TEM images of IMP and particle size distribution of Ru on IMP. Bar scale in the TEM image is 50 nm. About 100 Ru particles were counted.

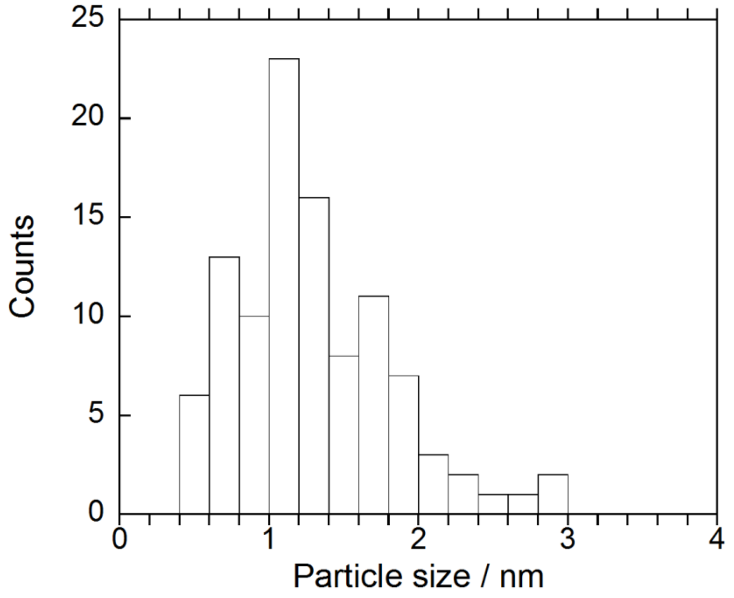

Fig. S4 Particle size distribution of Ru on SD-NH_3 measured by the TEM observation in Fig. 2 (b). About 100 Ru particles were counted.