Electronic Supplementary Information

Physical mixing of TiO_2 with sponge nickel creates the new active sites for selective CO methanation

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Experimental

A commercial sponge Ni (99.9%) catalyst was obtained from STREAM chemicals, and TiO_2 (P-25 and P-90) was obtained from Evonik Degussa. The following metal oxides were provided by the Catalysis Society of Japan: SiO_2 (JRC-SIO-6), γ-Al_2O_3 (JRC-ALO-6), ZrO_2 (JRC-ZRO-3) and TiO_2 (JRC-TIO-7 and JRC-TIO-11). As a comparison of the metal oxides, α-Al_2O_3 was prepared by calcination of γ-Al_2O_3 at 1300°C for 2 h. Catalysts were obtained by physical mixing of the above-mentioned metal oxides, sponge Ni, and a small amount of ethanol using a mortar and pestle. In addition, the physical mixture of NiO particles and TiO_2 (named as Ni_{np}-TiO_2) was prepared as described above for sponge Ni system. The NiO was obtained by calcination of nickel (II) nitrate hexahydrate (Kanto Kagaku) at 500 °C. The Ni amount for the catalysts was 10wt%. Finally, 10wt%Ni/TiO_2 (named as Ni/TiO_2) was prepared by a conventional impregnation method. TiO_2 was impregnated with an aqueous solution of nickel (II) nitrate hexahydrate at 80°C. The crude material was dried at 110°C overnight, and then calcined at 500°C for 2 h.

The catalytic performance for selective CO methanation was evaluated in a 6-mm I. D. fixed-bed quartz tubular reactor under atmospheric pressure. The reaction temperature was measured at the catalyst bed by a K-type thermocouple. After loading 300 mg of a catalyst powder in the reactor, the catalyst was treated under a flow of 10%H_2/He at 450°C for 30 min. After cooling to 150°C in a He flow, a flow of $CO/CO_2/H_2/H_2O$ (0.20/16.4/64.8/18.6, $W/F_{CO} = 0.75\ kg_{cat}\ h\ mol_{CO}^{-1}$) was passed through the catalyst bed. The feed gas simulates the methane reformate equilibrated at 180°C. The products were analyzed by an online gas chromatograph (Shimadzu, GC-8A) equipped with a SHINCARBON ST 50-80 column (Shinwa Chem. Ind.) and a thermal conductive detector. Values of the outlet gas concentrations were described as a basis of the dry gas composition. The lower detection limit of CO concentration was 10 ppm.

The crystalline phase of catalysts was determined by powder X-ray diffraction (Rigaku, Ultima IV), equipped with CuKα radiation source, at a voltage of 40 kV and a current of 40 mA.

Scanning transmission electron microscopy (Hitachi HD-2000 STEM) was used to observe the morphology of the sponge Ni-TiO_2 mixture. At the same time, X-ray energy dispersive spectroscopy (EDS) mapping was conducted.

X-ray photoelectron spectroscopy (XPS) data of Ni 2p level were obtained with a JEOL JPS-9010MC spectrometer using MgKα radiation operated at 20 W and 10 kV. The binding energy was calibrated with respect to C 1s peak of the contaminated carbon (284.6 eV).

N_2O titration was carried out according to the methods.[1] The number of accessible Ni surface atoms was estimated according to **eq. (S1)**. About 50 mg of catalysts were placed in the quartz tube, connected to a flow system (BEL Japan, BELCAT-B) and treated at 450 ºC for 0.5 h in a H_2 flow. He gas was used as a carrier gas, and the successive doses of 10%N_2O/He gas were subsequently introduced into the He stream by means of a calibrated injection valve (70 μL_{N2O} (stp) $pulse^{-1}$) at 50ºC. The amount of outlet gas was analyzed by a thermal conductive detector.

$$Ni + N_2O \rightarrow NiO + N_2 \qquad \text{(S1)}$$

Table S1 Property of TiO_2.

Sample	Phase	Preparation method	SSA / $m^2\ g^{-1}$	contaminants
P-25[a]	Anatase	Chlorine method	50±15	HCl < 0.3
P-90[a]	Anatase	Chlorine method	90±20	HCl < 0.3
JRC-TIO-7 [b]	Anatase	Sulfuric acid method	270	$SO_3 \approx 0.57$
JRC-TIO-11 [b]	Anatase	Chlorine method	97	Cl < 0.6

a Reported by Evonik Degussa. b Reported by the Catalysis Society of Japan.

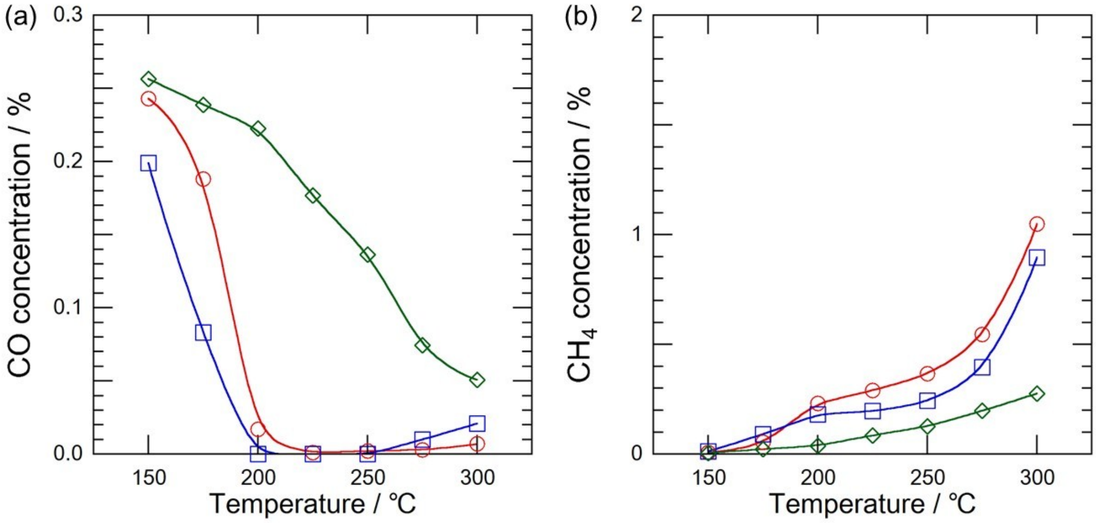

Fig. S1 (a) CO and (b) CH_4 concentration over Ni-TiO_2 (○), Ni/TiO_2 (□), and Ni_{np}-TiO_2 (◊). Reaction condition: $CO/CO_2/H_2/H_2O$ = 0.20/16.4/64.8/18.6 (the concentration of CO in a dry gas was 0.25%), W/F_{CO} = 0.75 kg_{cat} h mol_{CO}^{-1}. Ni amount: 10wt%.

Fig. S1 (a) shows the CO concentration dependency against reaction temperatures over Ni-TiO_2, Ni/TiO_2 (prepared by an impregnation method), and Ni_{np}-TiO_2 (physical mixture of NiO particles and TiO_2). For both Ni-TiO_2 and Ni/TiO_2, the CO concentration rapidly decreased with temperature: the concentration fell to less than 200 ppm at more than 200°C. Less CO production for these catalysts was detected than that for the physical mixture of sponge Ni and metal oxides, indicating that RWGS reaction hardly occurred on the catalyst surface of Ni-TiO_2 and Ni/TiO_2. For Ni_{np}-TiO_2, CO concentration gradually dropped with reaction temperature, but only to 500 ppm at 300°C.

Fig. S1 (b) shows the CH_4 concentration curves over Ni-TiO_2, Ni/TiO_2, and Ni_{np}-TiO_2. For Ni-TiO_2 and Ni/TiO_2, the initial increase in the CH_4 concentration to *ca.* 0.25% ended at 200°C and a plateau in the concentration appeared to 250°C. Above 250°C, the concentration started to increase sharply. For Ni_{np}-TiO_2, on the other hand, the CH_4 concentration gradually and monotonically increased with increasing reaction temperatures.

Accordingly, reaction behaviour of Ni-TiO_2 seems to be similar to that of Ni/TiO_2, and Ni_{np}-TiO_2 was much less active in CO/CO_2 methanation than Ni-TiO_2 and Ni/TiO_2.

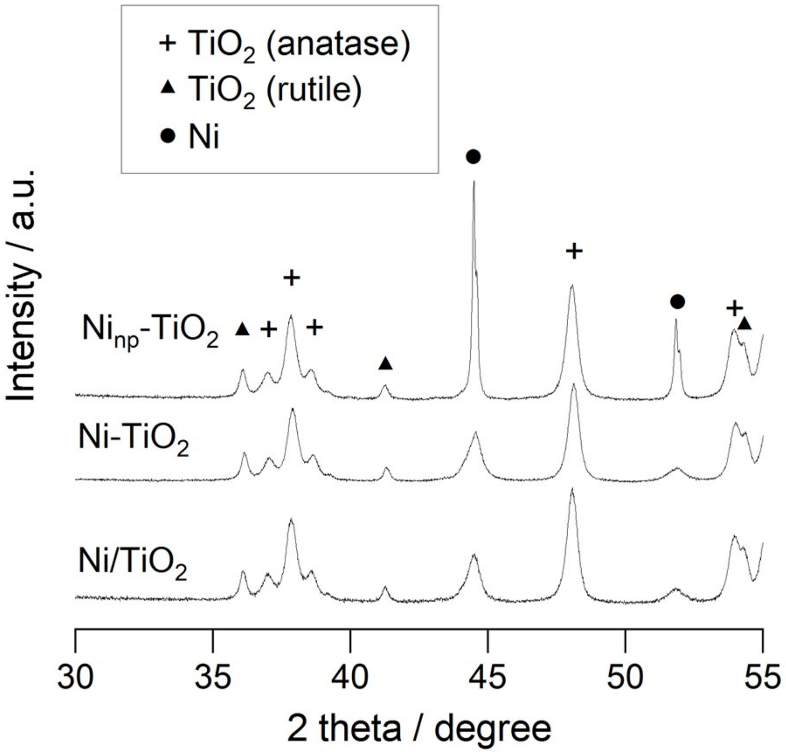

Fig. S2 XRD patterns of spent Ni_{np}-TiO_2, Ni-TiO_2, and Ni/TiO_2.

Fig. S2 shows the powder XRD patterns for the three types of TiO_2 supported Ni catalysts.

All catalysts had multiple peaks assignable to anatase- and rutile-type TiO_2. Thus, there is no apparent difference in the crystalline characteristics of TiO_2 support. In addition, peaks assignable to metallic Ni were observed at 44.5 and 51.9°. The crystallite size of metallic Ni was estimated from the Ni (111) plane (at 44.5°) by Scherrer's equation (eq. 2 in the main text). The size for Ni_{np}-TiO_2, Ni-TiO_2, and Ni/TiO_2 was 41, 13, and 15 nm, respectively.

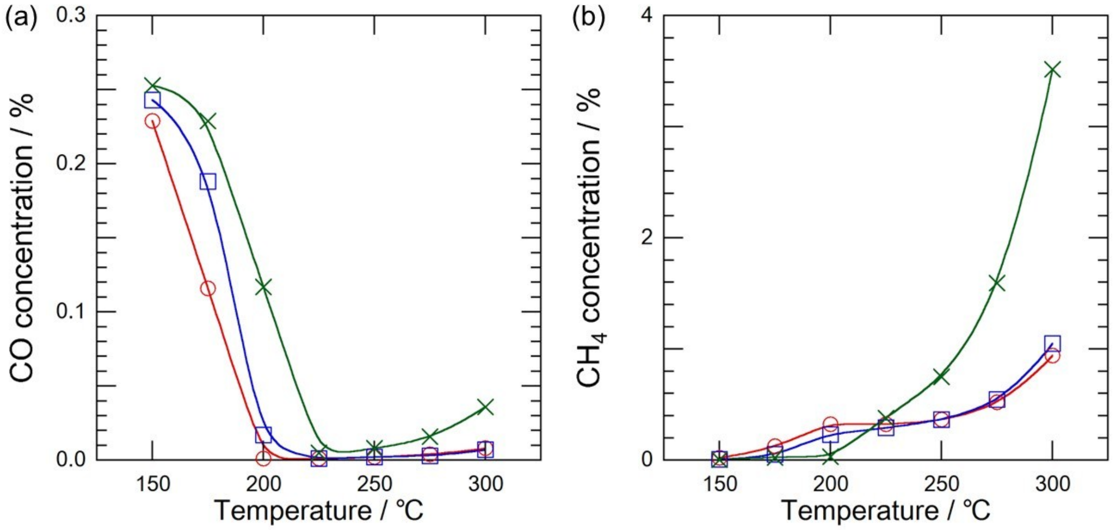

Fig. S3 (a) CO and (b) CH_4 concentration over Ni-TiO_2 reduced at 350°C (○), 450°C (□), and 650°C (×). Reaction condition: $CO/CO_2/H_2/H_2O$ = 0.20/16.4/64.8/18.6 (the concentration of CO in a dry gas was 0.25%), $W/F_{CO} = 0.75\ kg_{cat}\ h\ mol_{CO}^{-1}$. Ni amount: 10wt%.

Fig. S3 (a) shows the CO concentration dependency against reaction temperatures over Ni-TiO_2 reduced at 350, 450, and 650°C. CO concentration curve was shifted to higher temperature with increasing reduction temperature, indicating that Ni-TiO_2 reduced at higher temperature is less active in CO methanation. **Fig. S3 (b)** shows the CH_4 concentration dependency against reaction temperatures over Ni-TiO_2 reduced at 350, 450, and 650°C. CH_4 concentration curve of Ni-TiO_2 reduced at 350°C was similar to that for Ni-TiO_2 reduced at 450°C. For the both catalysts, in other words, the initial increase in the CH_4 concentration to *ca.* 0.25% ended at 200°C and a plateau in the concentration appeared to 250°C. Above 250°C, the concentration started to increase sharply. For Ni-TiO_2 reduced at 650°C, CH_4 concentration increased sharply with increasing reaction temperature from 200°C. In consequence, the Ni-TiO_2 reduced at 650°C exhibited the highest CO_2 methanation activity in the three Ni-TiO_2, and the Ni-TiO_2 reduced at less than 450°C should be suitable for selective CO methanation.

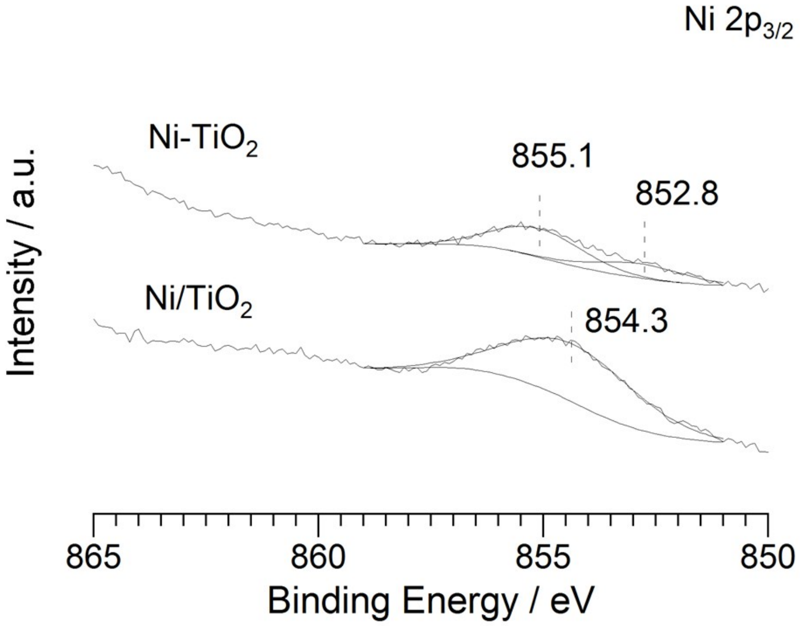

Fig. S4 XPS spectra of Ni $2p_{3/2}$ of Ni-TiO_2 and Ni/TiO_2. The peak at *ca.* 855 eV is attributed to NiO,[2] Ni_2O_3,[3] or $Ni(OH)_2$,[4,5] while the peak at ca. 853 eV is attributed to metallic Ni.[6]

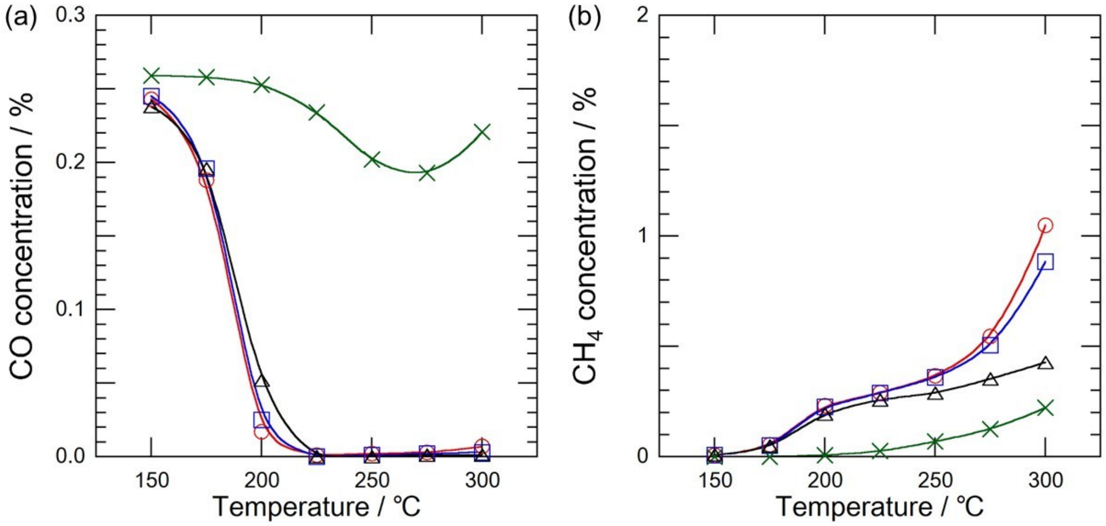

Fig. S5 (a) CO and (b) CH_4 concentration over the physical mixtures of sponge Ni and TiO_2. P-25 (○), P-90 (□), JRC-TIO-7 (×), and JRC-TIO-11 (△). Reaction condition: $CO/CO_2/H_2/H_2O$ = 0.20/16.4/64.8/18.6 (the concentration of CO in a dry gas was 0.25%), W/F_{CO} = 0.75 kg_{cat} h mol_{CO}^{-1}. Ni amount: 10wt%. The properties of the TiO_2 is summarized in **Table S1**.

When TiO_2 prepared by a chlorine method (P-25, P-90, and JRC-TIO-11) was used, CO and CH_4 concentration trends for the physical mixture of sponge Ni and the TiO_2 was almost the same. On the other hand, when TiO_2 prepared by a sulfuric acid method (JRC-TIO-7) was used, CO and CH_4 concentration over the physical mixture of sponge Ni and the TiO_2 was changed gradually and minutely, leading to almost no activity of CO/CO_2 methanation.

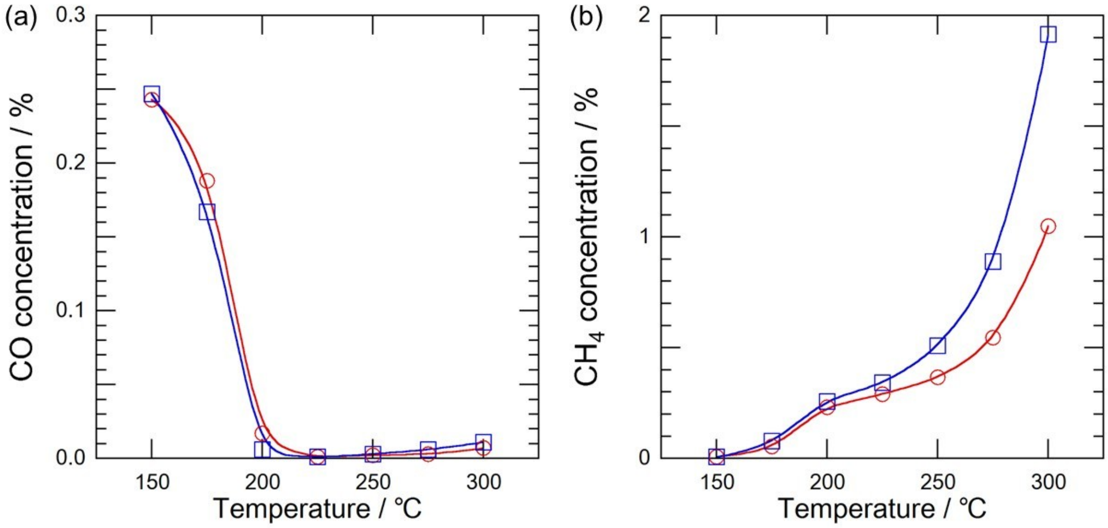

Fig. S6 (a) CO and (b) CH_4 concentration over the physical mixtures of sponge Ni and TiO_2. P-25 (○) and P-25 calcined at 500°C (□). Reaction condition: $CO/CO_2/H_2/H_2O$ = 0.20/16.4/64.8/18.6 (the concentration of CO in a dry gas was 0.25%), $W/F_{CO} = 0.75\ kg_{cat}\ h\ mol_{CO}^{-1}$. Ni amount: 10wt%.

Pre-calcination of TiO_2 changed only the trend of CH_4 concentration: CH_4 concentration increased more rapidly over the physical mixture of sponge Ni and P-25 calcined at 500°C than that over the physical mixture of sponge Ni and P-25. Thus, the catalyst with P-25 calcined at 500°C exhibited higher activity of CO_2 methanation than the catalyst with P-25.

References

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[5] A.N. Mansour, *Surf. Sci. Spectra*, 1994, **3**, 239-246.

[6] S. Tada, R. Kikuchi, K. Wada, K. Osada, K. Akiyama, S. Satokawa and Y. Kawashima, *J. Power. Sources*, 2014, **264**, 59-66.