Modification of Highly Dispersed Cerium Oxides on Silica with Highly Dispersed Titanium Oxides as a New Photocatalyst Design for Nonoxidative Direct Methane Coupling

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Modification of ceria-based photocatalyst with titanium oxide resulted in formation of highly dispersed cerium and titanium oxides on silica, where both species exhibited photoactivities for nonoxidative direct methane coupling. A new design of photocatalyst was proposed here.

Nonoxidative direct methane coupling, $2CH_4 \rightarrow C_2H_6 + H_2$, has been reported to occur at room temperature by employing photoenergy and photocatalysts.[1–7] To date, highly dispersed metal oxide species have been suggested as the photoactive sites for the reaction.[1–5] It is expected that the photocatalyst with a large number of photoactive sites would show high photoactivity. Unfortunately, however, when we load a large amount of metal oxide, aggregation of metal oxide tends to occur. Since the highly dispersed species is usually obtained only when the loading amount of metal oxide is low, the number of the photoactive sites is limited to a certain low level. In the present study, silica-supported ceria photocatalyst, which was reported to show high activity for nonoxidative direct methane coupling,[1] was successfully modified with titanium oxides by a double loading method, where both cerium and titanium oxides were highly dispersed on silica and functioned as photoactive sites for the reaction, resulting higher activity than the silica-supported ceria.

As the photocatalyst support, we used amorphous silica that was prepared by sol–gel method[8] followed by calcination in air at 773 K for 5 h. The BET specific surface area was $676\,m^2\cdot g^{-1}$. The silica was impregnated with an aqueous solution of $Ce(NO_3)_3$ or $(NH_4)_2[TiO(C_2O_4)_2]$, followed by drying in an oven overnight and calcining in air at 773 K for 5 h, to obtain $Ce(x)/SiO_2$ or $Ti(y)/SiO_2$, where x or y showed the mol % of Ce or Ti to total amount of metal cations, respectively. In the present study, x and y were around 0.1–0.2 mol % in order to obtain highly dispersed active species.[1–3] The double loading of metal oxides on silica, $Ce(x)/Ti(y)/SiO_2$ sample, was prepared by impregnation of $Ti(y)/SiO_2$ with an aqueous solution of $Ce(NO_3)_3$, followed by drying and calcining. $Ti(y)/Ce(x)/SiO_2$ sample was similary prepared from $Ce(x)/SiO_2$ and $(NH_4)_2[TiO(C_2O_4)_2]$. $Ce(x)Ti(y)/SiO_2$ sample was prepared by impregnation of silica with a mixed solution of $Ce(NO_3)_3$ and $(NH_4)_2[TiO(C_2O_4)_2]$, followed by drying and calcining. The photocatalytic nonoxidative direct methane coupling was carried out in a closed quartz vessel ($30\,cm^3$) in the similar way as in the previous studies.[1–7] Before photoreaction, the sample was treated in O_2 atmosphere (133 Pa) at 1073 K for 1 h, followed by evacuation at 1073 K for 1 h. The sample was irradiated from beneath by a 300-W Xe lamp for 3 h. The light intensity at the reactor was about $10\,mW\cdot cm^{-2}$ when it was measured in the range of 220–300 nm. The products were collected and analyzed by gas chromatography. Ce L_{III}-edge and Ti K-edge XANES spectra were recorded at room temperature at BL 7C station[9] of KEK-PF, Tsukuba, Japan. Diffuse-reflectance (DR) UV–vis spectra were recorded at room temperature on a JASCO V-550 equipped with an integrating sphere covered with $BaSO_4$. Before recording the spectra, the samples were treated as the pretreatment before the photoreaction.

Table 1 shows the photocatalytic activities of the samples for nonoxidative direct methane coupling. No product was detected in the dark or without photocatalysts. The main product was C_2H_6. The addition of small amounts of Ce or Ti on silica promoted the photoactivity of silica support (Table 1, Entries 1, 2, and 4). When the amount of Ce loading increased, photoactivity was slightly decreased (Table 1, Entry 3), suggesting that the sample with higher Ce loading did not exhibit higher photoactivity, probably because of the aggregation of Ce species as reported in the previous study.[1] However, it is noted that the double loading of cerium and titanium oxides on silica, $Ce(0.1)/Ti(0.1)/SiO_2$, showed higher photoactivity than $Ce(0.1)/SiO_2$ or $Ti(0.1)/SiO_2$ (Table 1, Entry 5). The photoactivity of $Ce(0.1)/Ti(0.1)/SiO_2$ sample was close to the sum of photoactivities over $Ce(0.1)/SiO_2$ and $Ti(0.1)/SiO_2$. This suggests that both Ce and Ti species would be highly dispersed without aggregation and behave as the photoactive sites for the reaction. Both hydrocarbons and hydrogen were produced during the photoirradiation, suggesting that the reaction was photocatalytically occurred over the sample. On the other hand, $Ti(0.1)/Ce(0.1)/SiO_2$, prepared in the inversed order, showed lower photoactivity than those of $Ce(0.1)/Ti(0.1)/SiO_2$ and $Ce(0.1)/SiO_2$ (Table 1, Entry 6). In contrast to $Ce(0.1)/Ti(0.1)/SiO_2$, it seemed that at least a part

Table 1. Results of photocatalytic nonoxidative direct methane coupling[a]

Entry	Sample	Total yield[b] $/10^{-1}$ C%	H_2 experimental/ H_2 theoretical[c]
1	SiO_2	0.06	—
2	$Ce(0.1)/SiO_2$	0.75	2.1[d]
3	$Ce(0.2)/SiO_2$	0.70	1.3
4	$Ti(0.1)/SiO_2$	0.53	1.2
5	$Ce(0.1)/Ti(0.1)/SiO_2$	1.17	1.1
6	$Ti(0.1)/Ce(0.1)/SiO_2$	0.64	1.1
7	$Ce(0.1)Ti(0.1)/SiO_2$	1.27	0.8

[a]Reaction temperature was ca. 310 K, sample was 0.2 g, initial methane was 200 μmol. [b]Total of gaseous products and thermally desorbed products obtained after desorption procedure at 573 K for 15 min, based on initial amount of methane. [c]H_2 theoretical was calculated from the amount of produced hydrocarbons. [d]The high ratio might be due to a consecutive reaction to higher hydrocarbons that could not be detected by the employed procedure in the present study.

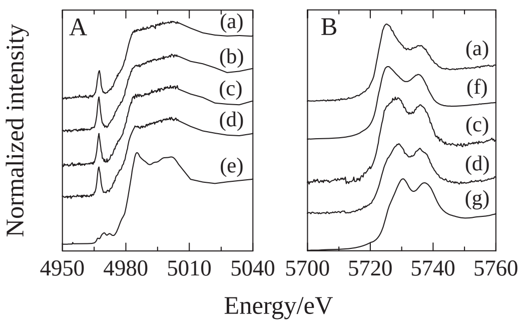

Figure 1. (A) Ti K-edge XANES spectra and (B) Ce L_{III}-edge XANES spectra of (a) $Ce(0.1)/Ti(0.1)/SiO_2$, (b) $Ti/SiO_2(0.1)$, (c) $Ti(0.1)/Ce(0.1)/SiO_2$, (d) $Ce(0.1)Ti(0.1)/SiO_2$, (e) TiO_2, (f) $Ce/SiO_2(0.1)$, and (g) CeO_2 samples.

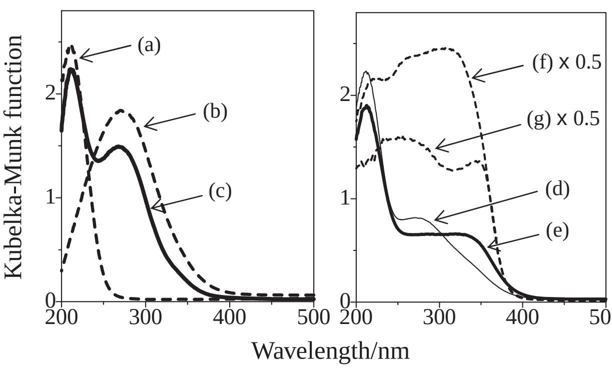

Figure 2. DR UV–vis spectra of (a) $Ti(0.1)/SiO_2$, (b) $Ce(0.1)/SiO_2$, (c) $Ce(0.1)/Ti(0.1)/SiO_2$, (d) $Ti(0.1)/Ce(0.1)/SiO_2$, (e) $Ce(0.1)Ti(0.1)/SiO_2$, (f) TiO_2, and (g) CeO_2 samples. Multiple factor for each spectrum in (f) and (g) is 0.5.

of Ce and Ti species would not be highly dispersed successfully on $Ti(0.1)/Ce(0.1)/SiO_2$. In the case of $Ce(0.1)Ti(0.1)/SiO_2$, high photoactivity was obtained in the same level to $Ce(0.1)/Ti(0.1)/SiO_2$, but hydrogen was not detected stoichiometrically. This suggests that the Ce and Ti species were not fully formed as highly dispersed species on $Ce(0.1)Ti(0.1)/SiO_2$.

In order to confirm the photoactive sites of $Ce(0.1)/Ti(0.1)/SiO_2$, some spectroscopic analyses were carried out. Ti K-edge XANES spectrum of the sample showed that Ti species on the sample was in tetrahedral coordination,[10] as in the case of $Ti(0.1)/SiO_2$ (Figures 1A(a) and 1A(b)). Ce L_{III}-edge XANES spectrum showed that Ce was mainly exist as highly dispersed Ce(III) species,[1,11] similar to the case of $Ce(0.1)/SiO_2$ (Figures 1B(a) and 1B(f)). Figure 2 shows DR UV–vis spectra of the samples. $Ti(0.1)/SiO_2$ showed one sharp absorption band centered around 215 nm (Figure 2a), assignable to highly dispersed titanium oxides species,[10,12] while $Ce(0.1)/SiO_2$ exhibited one absorption band centered at 265 nm (Figure 2b), due to the presence of highly dispersed Ce(III) species on the sample.[1,11,13] $Ce(0.1)/Ti(0.1)/SiO_2$ showed two absorption bands centered at 215 and 265 nm (Figure 2c), suggesting the presence of both highly dispersed titanium oxide species and highly dispersed Ce(III) species, respectively. This result was in agreement with the photocatalytic results, where $Ce(0.1)/Ti(0.1)/SiO_2$ showed photoactivity that was close to the sum of photoactivities over $Ce(0.1)/SiO_2$ and $Ti(0.1)/SiO_2$. Thus, from XANES and DR UV–vis spectra, it was confirmed that the photoactive sites on $Ce(0.1)/Ti(0.1)/SiO_2$ were the highly dispersed Ce(III) species and the highly dispersed tetrahedral Ti oxide species.

On the other hand, in the case of $Ti(0.1)/Ce(0.1)/SiO_2$ and $Ce(0.1)Ti(0.1)/SiO_2$, XANES and DR UV–vis spectra showed that although Ti was obtained as highly dispersed tetrahedral titanium oxide species (Figures 1A(c) and 1A(d), Figures 2d and 2e), Ce was aggregated and mainly existed as Ce(IV) states (Figures 1B(c) and 1B(d), Figures 2d and 2e). It caused the low photoactivity and nonstoichiometric production of H_2 in the photoreaction (Table 1, Entries 6 and 7), because of the photoreduction of Ce(IV) during the reaction, as suggested in the previous study.[1] In the present study, the difference in the aggregation tendency between Ce and Ti was observed, depending on the preparation method, which might be caused by the difference in their chemical affinity to SiO_2.

In conclusion, the highly dispersed cerium oxides on silica can be modified successfully without disturbing the dispersion of cerium species, with addition of titanium oxides by two-step impregnation method, in which the Ti was loaded first, followed by Ce loading. The loading order in the preparation method contributed to the formation of the highly dispersed species. It is expected that the activity of the silica-supported highly dispersed metal oxide photocatalyst with optimum loading amount could be further improved by addition of another metal oxide with moderate loading, according to the present concept.

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References

1 L. Yuliati, T. Hamajima, T. Hattori, H. Yoshida, *Chem. Commun.* **2005**, 4824.
2 H. Yoshida, M. G. Chaskar, Y. Kato, T. Hattori, *J. Photochem. Photobiol. A* **2003**, *160*, 47.
3 L. Yuliati, T. Hattori, H. Yoshida, *Phys. Chem. Chem. Phys.* **2005**, *7*, 195.
4 H. Yoshida, N. Matsushita, Y. Kato, T. Hattori, *Phys. Chem. Chem. Phys.* **2002**, *4*, 2459.
5 H. Yoshida, N. Matsushita, Y. Kato, T. Hattori, *J. Phys. Chem. B* **2003**, *107*, 8355.
6 L. Yuliati, M. Tsubota, A. Satsuma, H. Itoh, H. Yoshida, *J. Catal.* **2006**, *238*, 214.
7 Y. Kato, H. Yoshida, A. Satsuma, T. Hattori, *Microporous Mesoporous Mater.* **2002**, *51*, 223.
8 H. Yoshida, C. Murata, T. Hattori, *J. Catal.* **2000**, *194*, 364.
9 M. Nomura, A. Koyama, M. Sakurai, *KEK Rep.* **1991**, *91-1*, 1.
10 S. Bordiga, S. Collucia, C. Lamberti, L. Marchese, A. Zecchina, F. Boscherini, F. Buffa, F. Genoni, G. Leofanti, G. Petrini, G. Vlaic, *J. Phys. Chem.* **1994**, *98*, 4125.
11 H. Yoshida, L. Yuliati, T. Hamajima, T. Hattori, *Mater. Trans.* **2004**, *45*, 2062.
12 H. Yoshida, C. Murata, T. Hattori, *Chem. Commun.* **1999**, 1551.
13 A. Bensalem, J. C. Muller, F. Bozon-Verduraz, *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 153.

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