Highly dispersed Ce(III) species on silica and alumina as new photocatalysts for non-oxidative direct methane coupling

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Highly dispersed cerium oxide species on silica and alumina, which mainly exist as Ce(III) species, promote non-oxidative direct methane coupling photocatalytically around room temperature, while Ce(IV) species as CeO_2 particles do not behave as a catalyst for this reaction.

Direct conversion of methane to hydrogen and higher hydrocarbons under non-oxidative conditions is thermodynamically difficult and prohibited at room temperature, *e.g.*, $2CH_4 \rightarrow C_2H_6 + H_2$ $\Delta G = 68.6$ kJ mol^{-1}. However, it has been reported that some silica-based photocatalysts such as silica-alumina,[1–3] silica-supported zirconia[4,5] and silica supported-magnesia[6] showed activities for this reaction around room temperature when the catalysts were activated through evacuation at high temperature, such as 1073 K, before photoreaction.

On the other hand, rare earth oxides have been widely investigated for several applications such as lasers, optical amplifiers, light emitting diodes, *etc.*[7,8] Rare earth ions generally can be photoexcited by absorbing light *via* f–d or f–f transitions, implying their possibilities as photocatalysts. However, only a few studies on the photocatalysis of rare earth ions have been reported, *e.g.* photoactivities of Eu ions for conversion of α-methylstyrene[9] and isolated Pr(III) on metal oxide supports and zeolites for photodecomposition of N_2O.[10,11] These facts suggest that rare earth ions have potential abilities to induce various kinds of reactions photocatalytically.

Cerium is the most abundant rare earth oxide and one of the most interesting elements. The roles of cerium in catalysis have been recognized in three-way catalysis (TWC), fluid catalytic cracking (FCC), wet catalytic oxidation of organic pollutants[12–14] and so on due to their unique properties such as redox and oxygen release–storage abilities. In addition, since cerium oxide can be photoexcited by absorbing photoenergy higher than the band gap (2.95 eV), cerium oxide has been examined as a semiconductor photocatalyst for some reactions such as water splitting[15,16] and toluene photooxidation.[17,18] Cerium has also been employed as a dopant for the modification of TiO_2 photocatalytic activity.[18–21] However, photocatalytic activity of the cerium ion itself has not been revealed yet. In the present study, we first report the photocatalytic activity of cerium ions as a novel type of photocatalyst for non-oxidative direct methane coupling, which was much higher than those of other silica-based photocatalysts previously reported.[1–6]

As the photocatalyst support we used silica and alumina. Silica was prepared from $Si(OEt)_4$ by the sol–gel method followed by calcination in dry air at 773 K for 5 h[22] (BET specific surface area 660 m^2 g^{-1}). Alumina was a reference catalyst, JRC-ALO-8, donated from the Catalysis Society of Japan, with specific surface area of 163 m^2 g^{-1}. Each support was impregnated with an aqueous solution of $Ce(NO_3)_3$ (Kishida), dried at 383 K in an oven over night and calcined at 773 K in a flow of dry air for 5 h. The cerium oxide samples supported by silica or alumina are referred to as $Ce/SiO_2(x)$ or $Ce/Al_2O_3(x)$, where x is the mol% of Ce to total cation of Ce and Si or total cation of Ce and Al. Unsupported CeO_2 (Kishida) was employed, with specific surface area of 3 m^2 g^{-1}.

The reaction tests were carried out in a similar way to previous studies in a closed quartz reaction vessel (30 cm^3).[1–6] The standard procedure was as follows. The catalyst sample (0.2 g) was spread over the flat bottom of reactor (14 cm^2) and treated in a 100 Torr (1 Torr = 133 Pa) oxygen atmosphere at 773 K for 1 h, followed by evacuation at 773 K for 1 h to clean up the catalyst surface. Methane (200 μmol) was introduced at room temperature. The catalyst sample was irradiated from beneath by a 300 W Xe lamp (used at 17.5 A, 15 V) for 3 h. Light intensity measured in the range of 220–300 nm was about 10 mW cm^{-2} at the reactor. The products in the gaseous phase were separately collected and analyzed by gas chromatography. The adsorbed products at room temperature were thermally desorbed by heating at 573 K for 15 min, collected and analyzed by gas chromatography.

The Ce L_{III}-edge XANES measurements were performed at room temperature in transmission mode (Ce > 1 mol%) and fluorescence mode (Ce < 1 mol%) at the BL-9A station of KEK-PF, Tsukuba, Japan, with a Si(111) double-crystal monochromator in a similar way to the previous study.[23] Some samples were measured at the BL-7C station. Before recording the spectra, the same pre-treatment was carried out as before the photoreaction test. Then, the sample was sealed with a polyethylene film in a dry atmosphere. Diffuse reflectance UV-visible spectra were recorded at room temperature on a JASCO V-570 equipped with an integrating sphere covered with $BaSO_4$. Before recording the spectra, the sample in a specially designed *in-situ* cell was treated just as for the pre-treatment mentioned above. Thus, the sample was transferred to the optical part without exposure to the atmosphere. X-Ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer RINT 1200 using Ni-filtered Cu-Kα radiation (40 kV, 20 mA).

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Table 1 Results of the non-oxidative direct methane coupling upon photoirradiation[a]

Entry	Sample[b]	Gaseous product/10^{-2} μmol			Thermally desorbed products [b]/10^{-2} μmol	Total yield [c]/10^{-2} μmol	H_2/10^{-2} μmol	H_2 experimental/H_2 calculated from hydrocarbon products
		C_2H_4	C_2H_6	C_3H_8				
1	SiO_2	0.03	0.10	n.d.	n.d.	0.13	n.d.	0
2	Ce/SiO_2*(0.01)*	n.d.	3.10	0.06	tr.	3.15	5.50	1.7
3	Ce/SiO_2*(0.1)*	0.06	7.43	0.21	0.33	8.03	16.4	3.3
4	Ce/SiO_2*(2)*	n.d.	12.0	0.13	0.69	12.8	n.d.	0
5	Al_2O_3	n.d.	6.81	0.14	2.98	9.93	12.9	1.0
6	Ce/Al_2O_3*(0.01)*	n.d.	7.43	0.22	2.56	10.2	15.4	1.1
7	Ce/Al_2O_3*(0.1)*	n.d.	11.0	0.26	3.43	14.7	8.39	0.5
8	Ce/Al_2O_3*(5)*	n.d.	14.9	0.05	5.58	20.6	n.d.	0
9	CeO_2	n.d.	0.24	n.d.	0.17	0.41	n.d.	0
10[d]	Ce/SiO_2*(0.01)*	n.d.	23.0	1.24	0.92	25.2	85.1	3.1
11[e]	Ce/SiO_2*(0.1)*	0.09	7.81	0.29	0.42	8.61	18.5	1.9
12[f]	Ce/SiO_2*(0.1)*	n.d.	7.70	0.26	tr.	7.96	27.0	2.0

[a] Reaction temperature was *ca.* 310 K, sample was 0.2 g, initial methane was 200 μmol, irradiation time was 3 h. [b] The italic numbers in parentheses show the content of Ce (mol%) on the supports. [c] These products such as C_2H_4, C_3H_6, *etc* were desorbed by heating at 573 K for 15 min after the photoreaction and collected in a liquid nitrogen trap. [d] The sum of the yield of the gaseous phase and the thermal desorption products. [e] Irradiation time was 36 h. [f] Evacuation pre-treatment was performed at room temperature. [g] Oxidation and evacuation pre-treatment was performed at 1073 K. tr. = trace, n.d. = not detectable.

The photoactivities of the samples are shown in Table 1. It was confirmed that no product was detected in the dark. Upon photoirradiation, all the samples exhibited formation of C_2H_6 as the main gaseous product, without any CO_x formation. In some cases, C_2H_4 and C_3H_8 were also detected as minor products. Amorphous silica showed a trace amount of product (entry 1). Alumina gave a higher yield of hydrocarbons and hydrogen than silica did (entry 5). The addition of Ce to both the silica and alumina supports increased the activity (entry 2–4, 6–8), suggesting that Ce played an important role in the photoreactions. However, CeO_2 itself without supporting material showed only a small amount of products without hydrogen (entry 9).

On both silica and alumina supports, the sample with low loadings of Ce produced both hydrocarbons and hydrogen, indicating the possibility that the reactions, methane coupling and consecutive ones, proceeded catalytically. The amount of hydrogen obtained over Ce/SiO_2 samples was higher than that expected from detected hydrocarbons. This suggests that the photoreactions over these samples may also consecutively give higher hydrocarbons that were not detectable with the thermal desorption procedure employed here. Meanwhile, it was confirmed that the TON (turnover number) of the photoreaction over Ce/SiO_2*(0.01)* was 2.5 after 36 h (entry 10), where the TON was defined as the amount of produced H_2 per amount of Ce ion. A TON more than unity indicates that the reaction proceeded photocatalytically over the sample. On the other hand, even though more hydrocarbon products were obtained over samples with high loadings of Ce, the formation of hydrogen was not observed (entry 4, 8), suggesting that the whole photoreaction mechanism over the samples with low loadings of Ce and high loadings of Ce would be different from each other.

Fig. 1 shows the XANES spectra of the samples and references. $Ce(NO_3)_3$ was used as a reference for Ce(III) and CeO_2 was used for Ce(IV).[23] Samples with low loadings of Ce (0.01 mol%) on both silica and alumina showed a dominant peak assignable to Ce(III) at 5726.1 eV (Fig. 1a, d), while high loading samples (2 and 5 mol%) showed peaks similar to those for CeO_2 (Fig. 1c, f). This suggests that Ce species in low loading samples would be highly dispersed on the supports mainly as Ce(III) cations, while those in high loading samples would mainly exist as Ce(IV) cations in CeO_2 small particles.

Fig. 2 shows diffuse reflectance UV-visible spectra of the samples and bulk CeO_2. As the bare silica and alumina did not

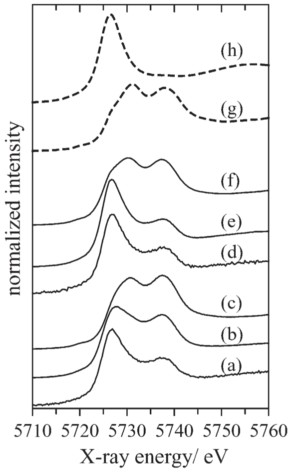

Fig. 1 Ce L_{III}-edge XANES spectra of (a) Ce/SiO_2*(0.01)*, (b) Ce/SiO_2*(0.1)*, (c) Ce/SiO_2*(2)*, (d) Ce/Al_2O_3*(0.01)*, (e) Ce/Al_2O_3*(0.1)*, (f) Ce/Al_2O_3*(5)*, (g) CeO_2 and (h) $Ce(NO_3)_3$.

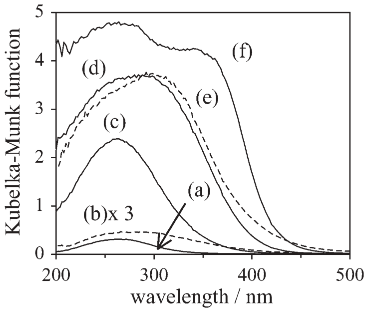

Fig. 2 Diffuse reflectance UV-visible absorption spectra of (a) Ce/SiO_2*(0.01)*, (b) Ce/Al_2O_3*(0.05)*, (c) Ce/SiO_2*(0.1)*, (d) Ce/SiO_2*(2)* (e) Ce/Al_2O_3*(5)*, and (f) CeO_2. The intensity of spectrum (b) was multiplied by three.

exhibit strong absorption bands, the bands in these spectra should be due to cerium species. The bulk CeO_2, which is a wide-bandgap semiconductor, showed a large absorption band less than 420 nm (Fig. 2f), which corresponds to the charge transfer from O (valence band) to Ce (conduction band). High loading samples (2 and 5 mol%) exhibited a large band (Fig. 2d, e), where the absorption edge shifted to shorter wavelength than that of bulk CeO_2 probably due to the quantum size effect.[24,25] This suggests that the Ce species in the high loading samples would be nano-sized CeO_2 particles. Samples with low loadings of Ce exhibited an absorption band at 265 nm (Fig. 2a–c), that was assignable to Ce(III) species.[23] This absorption band corresponds to the charge transfer from oxygen to Ce(III) (LMCT, ligand-to-metal charge transfer),[26] or the 4f–5d transition of the Ce(III) ion.[27,28] The formation of Ce^{3+} species at low Ce loadings is in agreement with other literature.[26,29]

XANES and UV-visible spectra suggested that the samples with low content (0.01–0.1 mol%) would predominantly have highly dispersed cerium oxide species on the supports, not CeO_2 particles. Samples with high content (2 and 5 mol%) would have mainly CeO_2 nano-sized particles that were also confirmed by XRD patterns. Since hydrogen was not detected in the photoreactions over high loading samples, it is suggested that the Ce(IV) species consumed hydrogen that should be produced in the photoreaction. The highly dispersed cerium oxide species on both the supports, which mainly exist as Ce(III) species, would be the photocatalytic active sites for non-oxidative direct methane coupling.

This novel kind of photocatalyst showed much higher photoactivity (about five times) than silica-based photocatalysts reported before, such as silica-alumina, silica-supported zirconia, and silica-supported magnesia.[1–6] In the case of these silica-based photocatalysts, evacuation pretreatment at high temperature such as 1073 K is required to produce the active species, *i.e.* active Si–O–M linkages (M = metal), through dehydroxylation on the surface.[30,31] In the case of highly dispersed cerium oxide on silica samples, mainly Ce(III), it was found that the photoactivities did not much depend on the pre-treatment temperature of the samples (Table 1, entries 3, 11 and 12). Even the sample evacuated at room temperature showed similar photoactivity to those treated at higher temperature, suggesting that this photocatalyst is a different type from the previously reported silica-based photocatalysts.[1–6] This suggests that the photoactive sites of the silica-supported ceria will not be described as the active Si–O–M linkages. Furthermore, since highly dispersed cerium oxide not only on silica but also on alumina showed photoactivities for non-oxidative direct methane coupling, it is strongly suggested that the photoactivity of these ceria-based photocatalysts come from the Ce(III) species itself that is highly dispersed on any suitable support, though it can not be clearly revealed here whether the photoexcitation would occur with the LMCT or the 4f–5d transition in Ce(III).

In another experiment, it was also confirmed that Ce mainly existed as the Ce(III) species on TiO_2 supports with low loadings. However, hydrogen was not detected on it, which would be due to the consumption of hydrogen for the reduction of TiO_2 upon photoirradiation. This shows another important point that the support materials should have durability under photoreductive conditions.

In conclusion, highly dispersed cerium oxide species on silica and alumina, which mainly exist as Ce(III) cations, were found to promote non-oxidative direct methane coupling photocatalytically. On the other hand Ce(IV) species would inhibit the formation of H_2 and would not catalyse this photoreaction. It would be expected that the highly dispersed cerium oxide species on any suitable support would be active for this reaction if stable under a reductive atmosphere.

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