COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Fine structural photoluminescence spectra of silica-supported zirconium oxide and its photoactivity in direct methane conversion

Hisao Yoshida,*[a] Manohar G. Chaskar,[ab] Yuko Kato[a] and Tadashi Hattori[a]

[a] *Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan. E-mail: yoshidah@apchem.nagoya-u.ac.jp; Fax: +81-52-789-3193*

[b] *Department of Chemistry, Annasaheb Mager College, Pune District Education Association, Pune 4110028, India*

Received (in Cambridge, UK) 11th June 2002, Accepted 31st July 2002
First published as an Advance Article on the web 12th August 2002

Highly dispersed zirconium oxide species on silica exhibit fine structure in phosphorescence emission spectra showing the vibration energy of the photoactive Zr–O–Si linkage to be 955 cm^{-1}, and the species promotes the photoinduced non-oxidative methane coupling at room temperature.

Photoluminescence is a sensitive and selective spectroscopy to detect and investigate photoactive species. So far it has been applied to study many local species on solid materials such as coordinatively unsaturated surface sites of bulk oxides, dispersed metal oxide species on support oxides, and so on.[1] Although usually broad bands are observed in the spectra, many matters on the surface of heterogeneous catalysts have been clarified by photoluminescence over the years.[1,2]

In some special cases, fine structure can be observed on photoluminescence spectra, which is typically due to the vibration mode of the photoexcited metal–oxygen bond in the luminescence species. The fine structure helps us to understand the structure of the photoactive sites. Unfortunately, however, reports of clear fine structural photoluminescence spectra have been limited to only a few systems. Since the fine structural spectra of highly dispersed vanadium oxide species on silica[3] was first reported in 1975, only those of the dispersed oxide species of the light transition metals (Ti,[4,5] V,[6] and Cr[7]) and non-transition metals (Mg,[8,9] Al[10,11]) on/in silica matrix and that of ZnO powder[12] have been published. In these cases, the vibration energy of the luminescence sites on/in silica matrix was estimated from the fine structure: *e.g.*, 1040 cm^{-1} for the V=O bond,[1] 965 cm^{-1} for Ti–O–Si linkage,[4] and 985 cm^{-1} for Al–O–Si linkage.[10]

In the present study, the fine structural photoluminescence spectrum of a silica-supported Zr system was observed for the first time. Zirconium–silicon oxide systems are known as catalysts for acid/base reaction,[13] oxidation,[14] and photoisomerization.[15] Here, in addition, the photoexcited Zr–O–Si sites were found to promote photo-induced direct conversion of methane to ethane and higher hydrocarbons; this reaction was quite recently discovered on silica–alumina systems[16,17] upon photoirradiation.

Amorphous silica (679 m^2 g^{-1}) was prepared from $Si(OEt)_4$ (Kishida) by sol–gel method, followed by calcination in a flow of air at 773 K for 5 h.[18] Amorphous silica (3 g) was impregnated in an aqueous solution (50 ml) of zirconyl nitrate (Nacalai), dried at 383 K overnight (12 h) and calcined at 773 K in a flow of dry air for 5 h to obtain silica-supported zirconium oxide samples referred to as $ZrO_2/SiO_2(x)$, where x is mol% of Zr.† Commercially obtained ZrO_2 powder sample was employed (7.0 m^2 g^{-1}, Kishida).

Before recording the spectra, the samples were treated with 60 Torr oxygen (1 Torr = 133 Nm^{-2}) for 1 h at 1073 K, followed by evacuation for 1 h at 1073 K. The photoluminescence (phosphorescence) spectra were recorded with Hitachi F-4500 fluorescence spectrophotometer at 77 K, where the fluorescence emission was cut off electrically.

The reaction tests were carried out in a closed quartz reaction vessel (82 cm^3) with flat bottom (19.6 cm^2) in a similar way to the previous studies.[16,17] The sample (0.5 g) was treated with 60 Torr oxygen for 1 h at 1073 K, followed by evacuation for 1 h at 1073 K. Photoirradiation of the sample was carried out for 3 h in the presence of methane (200 μmol). Reaction temperature was *ca.* 310 K. Products in the gaseous phase and thermally desorbed products were separately collected and analysed by gas chromatography. The yield (C%) is based on the initial amount of methane.

Fig. 1A shows the phosphorescence emission spectra of the samples evacuated at 1073 K. The wavelength of the excitation light was 300 nm. The silica sample (Fig. 1Aa) exhibited a broad band centred around 450 nm which would originate from surface silanols.[8,10] For the $ZrO_2/SiO_2(0.01)$ (Fig. 1Ab), the band maximum was shifted to around 520 nm, and some unclear shoulders similar to the fine structure were observed. The band intensity is larger than that of SiO_2, but still low and noisy. It is noted that the $ZrO_2/SiO_2(0.1)$ (Fig. 1Ac) exhibited a clear fine structural spectra centred at 522 nm; the maxima observed were at 434, 454, 476, 498, 522, 549 and 581 nm. Emission intensity was highest in the present study (see the multiplication factor shown). For the $ZrO_2/SiO_2(0.5)$ samples, the fine structure became unclear and the intensity decreased (Fig. 1Ad). The $ZrO_2/SiO_2(1.0)$ sample exhibited a complex band centred around 470–480 nm without fine structure (Fig. 1Ae) which is similar to a reported spectrum of zirconium–silicon binary oxide catalyst.[15]

In Fig. 1B is shown the excitation spectra of these samples. The monitoring emission light was 520 nm which corresponded to the centre of the fine structural emission band. The samples

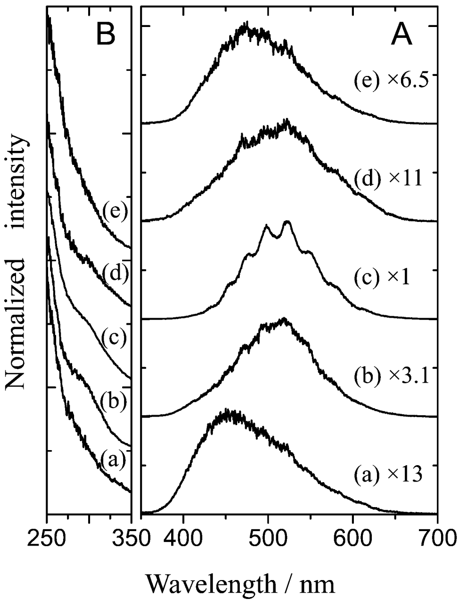

Fig. 1 Phosphorescence emission [A] and excitation spectra [B] of the samples: SiO_2 (a), $Zr/SiO_2(0.01)$ (b), $Zr/SiO_2(0.1)$ (c), $Zr/SiO_2(0.5)$ (d) and $Zr/SiO_2(1.0)$ (e). The excitation wavelength for A was 300 nm. The monitoring emission wavelength for B was 520 nm. The multiplication factor for each spectrum is shown.

DOI: 10.1039/b205575a

of ZrO_2/SiO_2(0.01), ZrO_2/SiO_2(0.1), and ZrO_2/SiO_2(0.5) showed a shoulder band at 300 nm (Fig. 1B b–d). Other samples, silica (Fig. 1Ba) and ZrO_2/SiO_2(1.0) (Fig. 1Be), did not exhibit such a band. These results suggest that the band in the excitation spectrum corresponds to the fine structural emission band centred around 520 nm. These mean that the photoactive sites on ZrO_2/SiO_2 samples containing moderate amounts of zirconium oxide are excited by the light of around 300 nm and emit the intense phosphorescence centred around 520 nm.

In the case of TS-1 (Ti-silicalite),[4] only the samples of the low Ti content (typically 0.5 mol% of Ti) show the fine structural photoluminescence spectra. Also in the case of silica–alumina,[16] only isolated tetrahedral Al species in silica matrix (less than 20 mol% of Al) show clearly the fine structure on the photoluminescence spectra. In the present study, the fine structural phosphorescence spectra were observed on the samples of low zirconium content such as 0.01 and 0.1 mol% (Fig. 1Ab and 1Ac). Thus, it is suggested that the luminescence species are the highly dispersed zirconium oxide species. An increase of Zr loading of more than 0.1 mol% reduced the emission intensity and diminished the fine structure, probably due to the formation of zirconium oxide aggregates at the expense of highly dispersed zirconium oxide species.

The vibration energies of the excited sites were calculated from the difference between each maximum of the fine structure in the emission spectra (Fig. 1Ac) to be 1044, 1006, 919, 930, 927, 991 and 852 cm^{-1}, respectively. Since the error of each maximum value was estimated *ca.* ±50 cm^{-1}, the average value‡ of 955 cm^{-1} was employed as the vibration energy of the luminescence moiety on the ZrO_2/SiO_2(0.1). This value is close to that for Ti–O–Si in TS-1 (965 cm^{-1})[4] and Al–O–Si in silica–alumina (985 cm^{-1})[10] in photoluminescence spectroscopy, but different from that for V=O (1040 cm^{-1}) in VO_4 on the surface of silica. For ZrO_2–SiO_2 glasses treated at 973 K,[19] broad Raman bands observed at 954 cm^{-1} and an infrared band at 975 cm^{-1} are assigned to Zr–O–Si linkage. Silica-supported zirconia[20] shows an infrared band at 945 cm^{-1}, and zirconium silicates[21] shows an infrared band at 960 cm^{-1}; both are attributed to the symmetric stretching vibration of the Zr–O–Si linkage. These values are in good agreement with the present value obtained from photoluminescence spectroscopy, suggesting that the photoluminescence site is Zr–O–Si linkage. Photoexcitation on the Ti–O–Si in TS-1 is explained as charge transfer from ligand oxygen to titanium (LMCT, ligand-to-metal charge transfer). On the analogy of Ti system to Zr system, it is suggested the photoexcitation occurred by charge transfer from oxygen to zirconium on the Zr–O–Si linkage of the highly dispersed zirconium oxide species in ZrO_2/SiO_2.

We examined the activity of the representative samples of ZrO_2/SiO_2 in the photoinduced non-oxidative methane coupling. On the silica sample, only a small amount of C_2H_6 (0.021 C%) was obtained. The ZrO_2/SiO_2(0.1) sample, which exhibited the fine structural photoluminescence spectrum, showed 5 times higher activity than silica; the C_2H_6 and C_3H_8 products were obtained in the gas phase (0.109 C% and 0.003 C%, respectively), while a trace amount C_2H_4 was observed as adsorbed product. On the other hand, the ZrO_2/SiO_2(1.0) sample containing 10 times the amount of Zr, which exhibited a broad band without fine structure in photoluminescence spectrum, showed only half the activity (0.052 C%) of the ZrO_2/SiO_2(0.1) sample. On the zirconium oxide without silica-support, no products were obtained. On this non-supported sample, the number of surface zirconium sites was estimated to be equivalent or superior to the supported samples, meaning that the bulk zirconium oxide obviously has less specific activity for this reaction than the dispersed zirconium species on silica. Thus, it was found that the silica-supported zirconium oxide of low zirconium content typically around 0.1 mol%, which exhibited the fine structural photoluminescence spectra, exhibited high photoactivity in the photo-induced non-oxidative methane coupling. Since the photo-induced reaction would be promoted by the surface photoexcited sites, it is very likely that the highly dispersed zirconium oxide species exhibiting the fine structure in photoluminescence spectra are the highly active sites for this photo-induced reaction.

In conclusion, highly dispersed zirconium oxide species having Zr–O–Si linkage on silica exhibit fine structure in photoluminescence spectra, and the vibration energy of the Zr–O–Si linkage was confirmed as 955 cm^{-1}. In addition, the highly dispersed zirconium species were found to promote photo-induced non-oxidative methane coupling.

This work was partly supported by a Grant-in-Aid for Exploratory Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. H.Y. acknowledges the Nitto Foundation and Japan Chemical Innovation Institute (JCII) for the financial supports.

Notes and references

† $x = N_{Zr}/(N_{Zr}+N_{Si}) \times 100$ (mol%), N_M is the number of M atoms in the sample.

‡ The average is calculated as the mean of the middle five values, ignoring the first and the last values. When all seven values are used for the calculation, the average is 953 cm^{-1}.

1 M. Anpo and M. Che, *Adv. Catal.*, 2000, **44**, 119–257 and references therein.

2 L. Marchese, T. Maschmeyer, E. Gianotti, S. Coluccia and J. Thomas, *J. Phys. Chem. B*, 1997, **101**, 8836–8838; B. Wichterlová, J. Dědeček, Z. Sobalik, A. Vondrová and K. Klier, *J. Catal.*, 1997, **169**, 194–202; P. Nachtigall, M. Davidová and D. Nachtigallová, *J. Phys. Chem. B*, 2001, **105**, 3510–3517; H. Garcá, J. M. López Nieto, E. Palomares and B. Solsona, *Catal. Lett.*, 2000, **69**, 217–221.

3 A. M. Gritscov, V. A. Shvets and V. B. Kazansky, *Chem. Phys. Lett.*, 1975, **35**, 511–512.

4 A. S. Soult, D. D. Pooré, E. I. Mayo and A. E. Stiegman, *J. Phys. Chem. B*, 2001, **105**, 2687–2693.

5 M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis and E. Giamello, *J. Phys. Chem.*, 1985, **89**, 5017–5021.

6 M. Anpo, I. Tanahashi and Y. Kubokawa, *J. Phys. Chem.*, 1980, **84**, 3440–3443; M. Iwamoto, H. Furukawa, K. Matsukami, T. Takenaka and S. Kagawa, *J. Am. Chem. Soc.*, 1983, **105**, 3719–3720.

7 M. F. Hazenkamp and G. Blasse, *J. Phys. Chem.*, 1992, **96**, 3442–3446.

8 H. Yoshida, T. Tanaka, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2107–2111.

9 T. Tanaka, H. Yoshida, K. Nakatsuka, T. Funabiki and S. Yoshida, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2297–2298.

10 Y. Kato, H. Yoshida and T. Hattori, *Phys. Chem. Chem. Phys.*, 2000, **2**, 4231–4236.

11 H. Yoshida, T. Tanaka, A. Satsuma, T. Hattori, T. Funabiki and S. Yoshida, *Chem. Commun.*, 1996, 1153–1154.

12 M. Anpo and Y. Kubokawa, *J. Phys. Chem.*, 1984, **88**, 5556–5560.

13 K. Tanabe, M. Nisono, Y. Ono and H. Hattori, *Stud. Surf. Sci. Catal.*, 1989, **51**, 1; H. J. M. Bosman, E. C. Kruissink, J. van der Spoel and F. van den Brink, *J. Catal.*, 1994, **148**, 660–672; M. Niwa, N. Katada and Y. Murakami, *J. Catal.*, 1992, **134**, 340–348.

14 X. Gao, J. L. G. Fierro and I. E. Wachs, *Langmuir*, 1999, **15**, 3169–3178; V. Ramaswamy, B. Tripathi, D. Srinivas, A. V. Ramaswamy, R. Cattaneo and R. Prins, *J. Catal.*, 2001, **200**, 250–258; C. Palazzi, L. Oliva, M. Signoretto and G. Strukul, *J. Catal.*, 2000, **194**, 286–293.

15 S. C. Moon, M. Fujino, H. Yamashita and M. Anpo, *J. Phys. Chem. B*, 1997, **101**, 369–373.

16 H. Yoshida, N. Matsushita, Y. Kato and T. Hattori, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2459–2465.

17 Y. Kato, H. Yoshida and T. Hattori, *Chem. Commun.*, 1998, 2389–2390; H. Yoshida, Y. Kato and T. Hattori, *Stud. Surf. Sci. Catal.*, 2000, **130**, 659–664; Y. Kato, H. Yoshida and T. Hattori, *Micropor. Mesopor. Mater.*, 2002, **51**, 223–231.

18 H. Yoshida, C. Murata and T. Hattori, *J. Catal.*, 2000, **194**, 364–372.

19 S. W. Lee and R. A. Condrate Sr, *J. Mater. Sci.*, 1988, **23**, 2951–2959.

20 Z. Dang, B. G. Anderson, Y. Amenomiya and B. A. Morrow, *J Phys. Chem.*, 1995, **99**, 14437–14443.

21 B. Rakshe, V. Ramashe, V. Ramaswamy and A. V. Ramaswamy, *J. Catal.*, 1996, **163**, 501–505.