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Visible light-induced selective oxidation of cyclohexane to cyclohexanone on Cr–Si binary oxide with molecular oxygen†

Yasuhiro Shiraishi,* Yugo Teshima and Takayuki Hirai

Received (in Cambridge, UK) 9th June 2005, Accepted 15th July 2005
First published as an Advance Article on the web 17th August 2005
DOI: 10.1039/b508172f

Cr–Si binary oxide prepared by a sol–gel method, when activated by visible light, catalyses highly selective oxidation of cyclohexane to cyclohexanone with molecular oxygen.

Selective oxidation of cyclohexane to cyclohexanone is one of the most important synthetic reactions, because cyclohexanone is an important intermediate in ε-caprolactam synthesis, which is used in the manufacture of nylon polymers.[1] Catalytic cyclohexanone synthesis, driven by a heterogeneous catalyst with molecular oxygen (O_2), has attracted much attention.[2] Photocatalytic versions have been investigated extensively using various catalysts, such as TiO_2,[3] Fe porphyrin-modified TiO_2,[3b,4] polyoxotungstate-modified SiO_2,[5] and V_2O_5-impregnated Al_2O_3,[6] in a liquid/solid system. These systems, however, require UV light for catalyst activation. A photocatalytic system, driven by visible light (>400 nm), was first proposed by Frei *et al.*, employing zeolite Y as a catalyst and enabling quantitative formation of cyclohexanone.[7] This innovative system was, however, conducted in a gas/solid system. Development of a "handy" liquid/solid system driven by visible light, capable of promoting selective cyclohexanone synthesis, is now the focus of attention.

As well known, Cr oxide species, which are highly dispersed on an inorganic support, have LMCT (ligand-to-metal charge transfer) absorption at >400 nm.[8] Earlier reports reveal that hydrothermally-synthesized Cr-containing mesoporous silica (Cr$\propto$HMS) and Cr-impregnated HMS (Cr/HMS) and ZSM-5 (Cr/ZSM-5) promote NO decomposition and propane oxidation by visible light irradiation with O_2.[9] A recent report shows that Cr–Si binary oxide (Cr–SiO_2), prepared by a sol–gel method, catalyzes epoxidation of propene by visible light with O_2.[10] Here, we describe that this Cr–SiO_2 catalyst promotes a selective oxidation of cyclohexane to cyclohexanone by visible light with O_2. This is a liquid/solid photocatalytic system showing the highest cyclohexanone selectivity among those that had been reported.

We used four kinds of Cr–SiO_2(x) [x(mol %) = Cr/(Cr + Si) ratio; x = 0.1, 0.5, 1.7, 3.1] prepared by a sol–gel method with TEOS and $Cr(NO_3)_3 \cdot 9H_2O$ as Si and Cr sources (Table 1).[11]‡ Catalytic conversions were carried out by photoirradiation with a Xe lamp (λ > 320 and > 400 nm) to a suspension of catalyst (50 mg) in O_2-saturated MeCN (9 ml) with cyclohexane (1 ml).§

Table 1 summarizes the results of cyclohexane oxidation on Cr–SiO_2. All of these catalysts promote oxidation both by UV and visible light, indicating that these are active for visible light-induced cyclohexane oxidation. Cr–SiO_2(0.5) gives higher product yields than Cr–SiO_2(0.1) of lower Cr content, but Cr–SiO_2(1.7) and (3.1) of higher Cr content give lower product yields than Cr–SiO_2(0.5). Highest turnover number (TON) for cyclohexanone production is obtained for Cr–SiO_2(0.1), where TON value decreases with an increase in Cr content of the catalyst.

Fig. 1 shows diffuse-reflectance spectra of the catalysts. Cr–SiO_2(0.1) and (0.5) show distinctive three absorption bands

Table 1 Results of cyclohexane photooxidation (5 h) over various catalysts[a]

Catalyst	S_{BET}[b]/m^2g^{-1}	Light irradiated, λ/nm	Yield/µmol			Cyclohexanone select. (%)[c]	TON[d]
			Cyclohexanone	Cyclohexanol	CO_2		
Cr–SiO_2(0.1)	702.9	>400	4.5	2.1	Trace	68	2.5
		>320	7.0	4.0	Trace	64	3.9
Cr–SiO_2(0.5)	802.0	>400	9.7	5.6	1.8	62	1.0
		>320	16.2	7.1	2.2	68	1.7
Cr–SiO_2(1.7)	779.8	>400	5.8	3.9	Trace	60	0.2
		>320	9.4	6.2	0.2	60	0.3
Cr–SiO_2(3.1)	709.2	>400	4.7	2.7	Trace	64	0.1
		>320	5.7	3.6	Trace	61	0.1
Cr/SiO_2(0.1)	359.6	>400	1.8	0.8	Trace	68	0.9
		>320	1.5	0.8	0.4	63	0.8
Cr$\propto$MCM-41(0.1)	925.8	>400	0.3	0.1	Trace	69	0.2
Cr_2O_3[e]		>320	ND	ND	ND		
TiO_2(P-25)[e]		>320	29.1	10.4	61.8	58	

[a] Catalyst, 50 mg; MeCN, 9 ml; cyclohexane, 1 ml. [b] See N_2 adsorption–desorption data (Fig. S4). [c] Cyclohexanone select. = [cyclohexanone/(cyclohexanone + cyclohexanol + (1/6)CO_2)] (Refs. 3e and 6b). [d] TON = [(cyclohexanone formed)/(Cr amount on catalyst)]. [e] Catalyst, 10 mg.

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka, 560-8531, Japan. E-mail: shiraish@cheng.es.osaka-u.ac.jp; Fax: +81-6-6850-6273; Tel: +81-6-6850-6271

† Electronic supplementary information (ESI) available: Experimental details; change in product yield with time when cyclohexane (Fig. S1) or cyclohexanone (Fig. S2) is used as a starting material; ESR spectra (Fig. S3); N_2 adsorption–desorption isotherm of catalyst (Fig. S4). See http://dx.doi.org/10.1039/b508172f

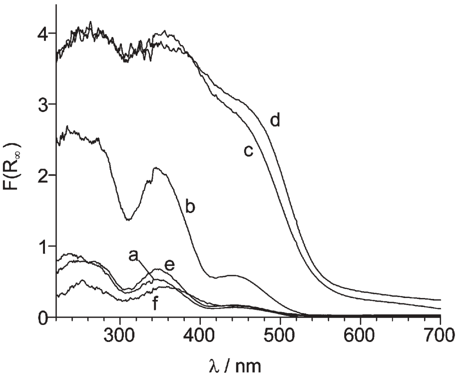


Fig. 1 Diffuse-reflectance spectra of the catalyst used. (a) Cr–SiO_2(0.1), (b) Cr–SiO_2(0.5), (c) Cr–SiO_2(1.7), (d) Cr–SiO_2(3.1), (e) Cr/SiO_2(0.1), (f) Cr$\propto$MCM-41(0.1).

at 245, 330, and 460 nm, assigned to LMCT (from O^{2-} to Cr^{6+}) transitions of chromate species, which are highly dispersed on silica matrixes and isolated from each other.[12] In contrast, Cr–SiO_2(1.7) and (3.1) show red-shifted absorption at 500–800 nm, which is assigned to the d–d transition of octahedral Cr^{3+} in the Cr_2O_3 cluster,[12] indicating that these catalysts contain polymerized Cr^{3+} species. Use of Cr_2O_3 as catalyst does not promote reaction even by UV light (Table 1), suggesting that the polymerized Cr^{3+} species are inactive for oxidation. The low activity of Cr–SiO_2(1.7) and (3.1) (Table 1) is therefore due to the formation of polymerized Cr^{3+}, indicating that the isolated chromate species act as the active site for cyclohexane oxidation.

A notable feature of Cr–SiO_2 is the high cyclohexanone selectivity (Table 1): Cr–SiO_2(0.1) with visible light achieves 68% selectivity, whereas TiO_2 with UV shows a lower value (58%). 68% selectivity is the highest among those that had been reported for the liquid/solid photocatalytic system.[3–6] In addition, the amount of CO_2 formed on Cr–SiO_2 is significantly lower than that on TiO_2 (Table 1; Fig. S1†), indicating that Cr–SiO_2 promotes partial oxidation of cyclohexane. Some TiO_2 systems show higher cyclohexanone selectivity than Cr–SiO_2.[3b–e] However, when TiO_2 was used for reaction of cyclohexanone, CO_2 formation was observed (Fig. S2†), indicating that, on TiO_2, the cyclohexanone formed is sequentially decomposed. In contrast, Cr–SiO_2 does not promote decomposition of cyclohexanone (Fig. S2†), suggesting that Cr–SiO_2 is more selective for cyclohexanone production. TON for cyclohexanone production on Cr–SiO_2(0.1) exceeds 1 (Table 1), indicating that the reaction proceeds catalytically.

The most notable fact is that such high photocatalytic activity of chromate species appears exceptionally on the catalyst prepared by a sol–gel method (Cr–SiO_2): chromate species created by other methods show much lower activity. We used two additional catalysts prepared by an impregnation method using amorphous silica as support[13] [Cr/SiO_2(0.1)‡] and by a templating method[14] [Cr$\propto$MCM-41(0.1)‡], which have the same Cr content as Cr–SiO_2(0.1). Both catalysts show absorption spectra assigned to chromate species (Fig. 1) as also for Cr–SiO_2(0.1), and promote cyclohexane oxidation by both UV and visible light (Table 1). However, cyclohexanone yield and TON obtained on both catalysts are much lower than those obtained on Cr–SiO_2(0.1).

Chromate species form tetrahedral (T_d^{6+}) and square-pyramidal (S_p^{6+}) structures on silica matrixes.[12] Fig. 2 shows ESR spectra of the catalysts (50 mg) measured *in vacuo* at 77 K (see Experimental details†).[15] Cr–SiO_2 and Cr/SiO_2 show signals assigned to the reduced T_d and S_p species (T_d^{5+} and S_p^{5+}), while Cr$\propto$MCM-41 shows only the T_d^{5+} signal. Upon photoirradiation to the Cr$\propto$MCM-41 sample, the T_d^{5+} signal disappears and a new signal appears, which is assigned to the excited state T_d^{5+} species (T_d^{5+}*), formed by photoinduced charge transfer (PCT) between Cr and terminal oxygen (O_T).[9c] Photoirradiation to Cr/SiO_2 also leads to T_d^{5+}* signal formation, while change in the S_p^{5+} signal is not observed. Cr–SiO_2 also does not show the change in the S_p^{5+} signal. This indicates that S_p species scarcely form excited states and that T_d species act as the active site for cyclohexane oxidation.

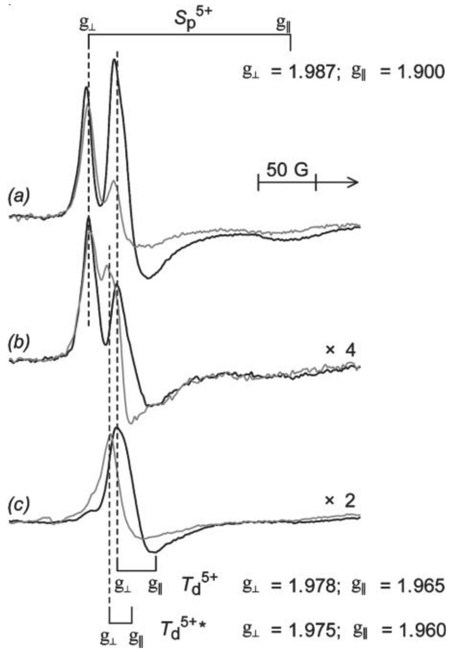
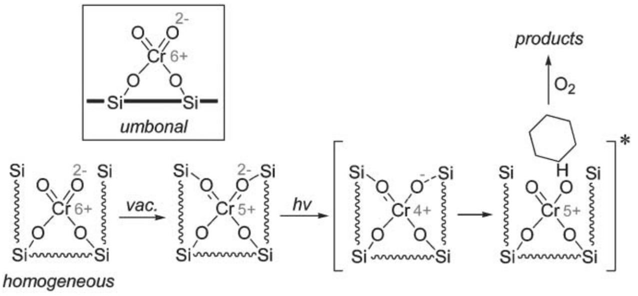


Fig. 2 ESR spectra of (a) Cr–SiO_2(0.1), (b) Cr/SiO_2(0.1), and (c) Cr$\propto$MCM-41(0.1), obtained at 77 K *in vacuo* (black) in the dark and (grey) with photoirradiation.

Interestingly, on Cr–SiO_2, the T_d^{5+}* signal does not appear (Fig. 2), despite the disappearance of the T_d^{5+} signal. This indicates that T_d^{5+} on Cr–SiO_2 is photoreduced to the species of lower oxidation number (Cr^{4+}, Cr^{3+}, Cr^{2+}). In the spectrum, the distinctive Cr^{3+} signal does not appear.[12] Cr^{2+} species are easily oxidized by O_2 to Cr^{3+}.[16] However, photoirradiation to Cr–SiO_2 with O_2 (1 Torr = 133.3 Pa) still does not lead to Cr^{3+} signal formation. These imply that Cr^{4+} is involved in the excited T_d species on Cr–SiO_2 and the T_d^{4+}* species acts as the site for effective oxidation, although direct observation of the species had not been done. A question arises as to why the T_d species on Cr–SiO_2 is photoreduced to Cr^{4+}. For Cr/SiO_2, T_d species are anchored on the SiO_2 surface, forming "umbonal" structure (Scheme 1).[9c] Cr$\propto$MCM-41 is synthesized by a simultaneous hydrolysis of $CrCl_2$ and TEOS. The rate of $CrCl_2$ hydrolysis is, however, higher than that of TEOS, such that Cr species rapidly surround the template micelle.[17] As a result, Cr species still form the umbonal structure on the surface of the MCM-41 pore. In contrast, on Cr–SiO_2, Cr and Si species are arranged randomly, thus forming an "homogeneous" structure (Scheme 1). As shown in Fig. 2, T_d^{5+} signal intensity on Cr–SiO_2, obtained *in vacuo*, is



Scheme 1

much higher than that on the other catalysts. The reduction of Cr^{6+} to Cr^{5+} occurs due to a O_T–Si bond formation, associated with H_2O removal from adjacent Si species.[12] On Cr–SiO_2 with homogeneous T_d^{6+}, the O_T–Si bond forms more easily than on the other catalysts with umbonal T_d^{6+}, resulting in high T_d^{5+} signal intensity. On stabilized T_d^{5+}, PCT between O_T and Cr occurs easily, thus probably promoting the formation of T_d^{4+*} (Scheme 1). This may result in high Cr–SiO_2 activity.

The mechanism of cyclohexane oxidation on T_d^{4+*} must be clarified. Upon photoirradiation to Cr–SiO_2 with O_2 (1 Torr) at 77 K (see Fig. S3†), none of the signals assigned to oxygen radicals (O_2^-, O_3^-) appear.[15] Photoirradiation to Cr–SiO_2 with cyclohexane (1 Torr) without O_2 at 77 K (see Fig. S2†) leads to an appearance of a new signal ($g_\perp = 1.979$, $g_\parallel = 1.968$), which is not attributable to a cyclohexanyl radical[18] but agrees with the T_d^{5+*} signal observed on Cr/SiO_2 and Cr$\propto$MCM-41 (Fig. 2). The O_T^- formed by PCT has electrophilic character.[15] The T_d^{5+*} signal may be attributable to formation of a [cyclohexane–O_T] complex *via* proton attraction by electrophilic O_T^- (Scheme 1), which may lead to oxidation of T_d^{4+*} to T_d^{5+*}. Cyclohexanone may form *via* reaction of this complex with O_2 (Scheme 1). To confirm this, the following experiments were carried out (see Experimental details†): (i) photoirradiation to Cr–SiO_2(0.1) with cyclohexane, followed by addition of O_2 while stopping photoirradiation; and (ii) photoirradiation to Cr–SiO_2(0.1) with O_2, followed by addition of cyclohexane. Only the former procedure promoted cyclohexane oxidation. The results strongly support the above mechanisms.

In conclusion, we have found that Cr–SiO_2, prepared by a sol–gel method, acts as an efficient and selective photocatalyst for oxidation of cyclohexane to cyclohexanone, driven by visible light. The catalytic activity of the chromate species depends strongly on the environment of the species. The present catalytic system has the potential to become a very powerful tool for development of economically- and environmentally-friendly catalytic oxidation processes. The results presented here will be useful for development of more efficient photocatalytic systems driven by visible light.

This research was supported by the Grant-in-Aid for Scientific Research (No. 15360430) and on Priority Areas “Fundamental Science and Technology of Photofunctional Interfaces (417)” (No. 15033244) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

Notes and references

‡ Catalyst preparation. **Cr–SiO_2(*x*)**: TEOS (20.8 g) and $Cr(NO_3)_3 \cdot 9H_2O$ [0.04 g ($x = 0.1$); 0.2 ($x = 0.5$); 0.6 ($x = 1.7$); 1.2 ($x = 3.1$)] dissolved in ethylene glycol (16 g) were stirred at 363 K for 3 h. H_2O (80 g) was added to the mixure and stirred at 363 K for 5 h. The obtained gel was calcined at 773 K for 5 h under air. **Cr/SiO_2(0.1)**: amorphous silica (2 g) and $Cr(NO_3)_3 \cdot 9H_2O$ (0.008 g) dissolved in water (50 g) was stirred at 353 K for 12 h. The obtained gel was calcined at 773 K for 5 h. **Cr$\propto$MCM-41(0.1)**: tetraethylammonium hydroxide (35% aqueous solution, 10 g) and cetyltrimethylammonium bromide (6.2 g) dissolved in water (49 g) was stirred at 323 K for 0.5 h. Fumed silica (6 g) and $CrCl_3 \cdot 6H_2O$ (0.014 g) dissolved in water (5 g) was added to this solution whose pH was adjusted to 11.5 with H_2SO_4. The obtained gel was left for 2 days at 423 K within an autoclave and then calcined at 823 K for 15 h under air.

§ Reaction was conducted within a Pyrex glass tube (20 ml) using a 2 kW Xe lamp, filtered through aqueous $NaNO_2$ (3 wt %) or $CuSO_4$ (10 wt %) solution, to give >400 nm (light intensity at 400–530 nm: 16.0 mW m^{-2}) or >320 nm (320–530 nm: 25.1 mW m^{-2}), with magnetic stirring.

1 (*a*) U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. de Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinace and E. L. Pires, *Appl. Catal. A*, 2001, **211**, 1; (*b*) G. Bellussi and C. Perego, *Cattech*, 2000, **4**, 4; (*c*) A. Castellan, J. C. J. Bart and S. Cavallaro, *Catal. Today*, 1991, **9**, 237.
2 For example: (*a*) R. Zhao, D. Ji, G. Lv, G. Qian, L. Yan, X. Wang and J. Suo, *Chem. Commun.*, 2004, 904; (*b*) T. Hayashi, A. Kishida and N. Mizuno, *Chem. Commun.*, 2000, 381; (*c*) R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 11926.
3 (*a*) C. Giannotti, S. Le Greneur and O. Watts, *Tetrahedron Lett.*, 1983, **24**, 5071; (*b*) R. Amadelli, M. Bregola, E. Polo, V. Crassiti and A. Maldotti, *J. Chem. Soc., Chem. Commun.*, 1992, 1355; (*c*) G. Lu, H. Gao, J. Suo and S. Li, *J. Chem. Soc., Chem. Commun.*, 1994, 2423; (*d*) P. Boarini, V. Carassiti, A. Maldotti and R. Amadelli, *Langmuir*, 1998, **14**, 2080; (*e*) A. Sclafani and J. M. Herrmann, *J. Phys. Chem.*, 1996, **100**, 13655; (*f*) S.-I. Shimizu, T. Kaneko, T. Fujishima, T. Kodama, H. Yoshida and Y. Kitayama, *Appl. Catal. A.*, 2002, **225**, 185; (*g*) C. B. Almquist and P. Biswas, *Appl. Catal. A.*, 2001, **214**, 259; (*h*) M. A. Brusa and M. A. Grela, *J. Phys. Chem. B.*, 2005, **109**, 1914; (*i*) M. A. Gonzalez, S. G. Howell and S. K. Sikdar, *J. Catal.*, 1999, **183**, 159.
4 A. Molinari, R. Amadelli, L. Antolini, A. Maldotti, P. Battioni and D. Mansuy, *J. Mol. Catal. A*, 2000, **158**, 521.
5 A. Maldotti, A. Molinari, G. Varani, M. Lenarda, L. Storaro, F. Bigi, R. Maggi, A. Mazzacani and G. Sartori, *J. Catal.*, 2002, **209**, 210.
6 (*a*) K. Teramura, T. Tanaka, T. Yamamoto and T. Funabiki, *J. Mol. Catal. A*, 2001, **165**, 299; (*b*) K. Teramura, T. Tanaka, M. Kani, T. Hosokawa and T. Funabiki, *J. Mol. Catal. A*, 2004, **208**, 299.
7 (*a*) H. Sun, F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1996, **118**, 6873; (*b*) F. Blatter, H. Sun, S. Vasenlov and H. Frei, *Catal. Today*, 1998, **41**, 297; (*c*) G. Li, M. Xu, S. C. Larsen and V. H. Grassian, *J. Mol. Catal. A*, 2003, **194**, 169; (*d*) R. G. Larsen, A. C. Saladino, T. A. Hunt, J. E. Mann, M. Xu, V. H. Grassian and S. C. Larsen, *J. Catal.*, 2001, **204**, 440.
8 (*a*) M. Anpo, *Photofunctional Zeolites*, Nova Science Publishers Inc., New York, 2000; (*b*) M. Matsuoka and M. Anpo, *J. Photochem. Photobiol. C*, 2003, **3**, 225.
9 (*a*) H. Yamashita, K. Yoshizawa, M. Ariyuki, S. Higashimoto, M. Che and M. Anpo, *Chem. Commun.*, 2001, 435; (*b*) H. Yamashita, S. Ohoshiro, K. Kida, K. Yoshizawa and M. Anpo, *Res. Chem. Intermed.*, 2003, **29**, 881; (*c*) H. Yamashita, M. Ariyuki, K. Yoshizawa, K. Kida, S. Ohoshiro and M. Anpo, *Res. Chem. Intermed.*, 2004, **30**, 235.
10 C. Murata, H. Yoshida and T. Hattori, *Chem. Commun.*, 2001, 2412.
11 A. Ueno, H. Suzuki and Y. Kotera, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 127.
12 (*a*) B. M. Weckhuysen, A. A. Verberckmoes, A. L. Buttiens and R. A. Schoonheydt, *J. Phys. Chem.*, 1994, **98**, 579; (*b*) B. M. Weckhuysen, I. E. Wachs and R. A. Schoonheydt, *Chem. Rev.*, 1996, **96**, 3327.
13 H. Yoshida, C. Murata and T. Hattori, *J. Catal.*, 2000, **194**, 364.
14 Z. Zhu, Z. Chang and L. Kevan, *J. Phys. Chem. B*, 1999, **103**, 2680.
15 Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.*, 2005, **127**, 8304.
16 B. M. Weckhuysen, R. A. Schoonheydt, J.-M. Jehng, I. E. Wachs, S. J. Cho, R. Ryoo, S. Kijlstra and E. Poels, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3245.
17 (*a*) N. Hüsing, B. Launay, D. Doshi and G. Kickelbick, *Chem. Mater.*, 2002, **14**, 2429; (*b*) C. J. Brinker and G. W. Scherer, *Sol–Gel Science*, Academic Press, New York, 1990.
18 H. Koizumi, T. Takada, T. Ichikawa and A. Lund, *Chem. Phys. Lett.*, 2001, **340**, 256.