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COMMUNICATION

Highly efficient and selective sunlight-induced photocatalytic oxidation of cyclohexane on an eco-catalyst under a CO_2 atmosphere

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Highly efficient and selective sunlight-induced photocatalytic oxidation of cyclohexane to cyclohexanone and cyclohexanol was achieved on TiO_2 (P25) modified with iron oxide under a CO_2 atmosphere.

Production of chemicals and fuels through heterogeneous photocatalysis driven by sunlight is one of the most compelling objectives in modern chemistry. Titanium dioxide is a promising material for the purpose due to availability, low toxicity, and chemical stability; however, it responds only to UV light, occupying 3–4% of sunlight, and tends to be nonselective for synthetic reactions.[1] Accordingly, after the discovery of the photocatalytic nature of TiO_2,[2,3] great endeavors are continuously being done to modify TiO_2 by doping with metal[4] and nonmetal elements[5] or hybridization with organic dyes[6] and nanoparticles,[7] as well as to design novel catalysts such as molecular-sieve-like TiO_2 [8–11] and non-TiO_2 materials,[12–16] to achieve efficient and selective photocatalysis under sunlight. Besides catalyst design, there have been several studies on the influence of reaction environments on heterogeneous photocatalysis.[10,17–23] Very recently, we have found that sunlight-induced photocatalytic oxidation of aqueous benzene to phenol over TiO_2-supported gold nanoparticles was substantially improved to give a higher yield and selectivity when the reaction was conducted under a CO_2 atmosphere.[23] This result motivated us to investigate various sunlight-driven photocatalytic selective oxidations on more economically favorable catalysts under CO_2.

Selective oxidation of cyclohexane to cyclohexanone and cyclohexanol is one of the most important synthetic reactions, since the partially oxidized products are an important intermediate in ε-caprolactam synthesis, which is used in the manufacture of nylon polymers. However, there have been few efficient photocatalytic processes under sunlight or visible light irradiation.[24–27] In this communication, we report a high level of efficient and selective sunlight-induced cyclohexane oxidation on TiO_2 (P25) modified with iron oxide[28,29] by conducting the reaction under CO_2. This photocatalyst is economically favorable, as well as environmentally benign, since iron is harmless and abundant in nature.

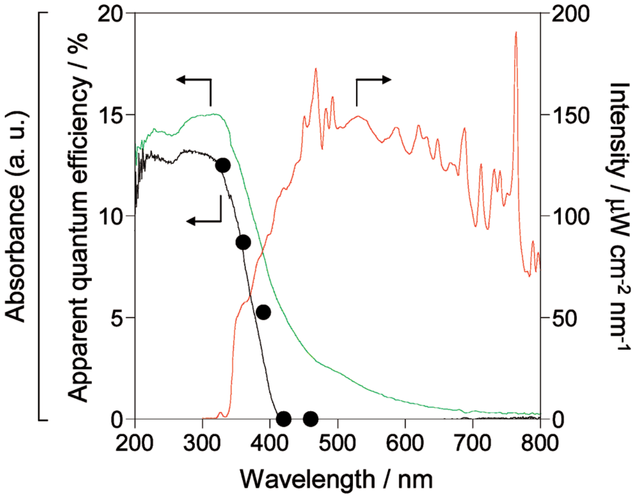

Fig. 1 Diffused reflectance spectra of (—) P25 and (—) FeO@P25, (●) action spectrum in cyclohexanone formation on FeO@P25, and (—) radiation spectrum of solar simulator used in this study.

An iron oxide-modified P25 (named as FeO@P25) was synthesized using iron(III) acetylacetonate complex according to the literature.[28] In the XRD pattern and TEM image of FeO@P25, diffraction peaks only due to TiO_2 were detected and particles other than P25 were not observed, respectively. The adsorption spectrum of FeO@P25 showed a shoulder centered at 500 nm (Fig. 1). These results imply the presence of molecular-level iron oxide adjacent to the P25 surface.[28,29] An iron(III) acetylacetonate complex has been reported to irreversibly react with surface titanol groups to form Ti–O–Fe covalent bond *via* ligand exchange reaction.[28] The amount of the immobilized iron oxide in FeO@P25 was estimated to be 0.81 Fe^{3+} ions nm^{-2}. Taking the amount (more than 4 groups nm^{-2}) of titanol on P25 into account,[30,31] iron oxide on P25 is thought to exist as patchy molecular-level particles, rather than a contentious ultrathin layer.

Photocatalytic conversions were carried out by photoirradiation with solar simulator (San-Ei Electric Co., Ltd) to a mixture of catalyst (30 mg) and O_2-saturated acetonitrile (18 mL) solution of cyclohexane (2 mL) in a stainless-made closed container equipped with Pyrex glass (75 mL) under controlled atmosphere at 42 °C, with shaking. The CO_2 pressure was tuned by changing the amount of the added dry ice in the mixture and the irradiation was started after the sublimation of

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Table 1 Results of cyclohexane oxidation on P25, FeO@P25 and $FeO@SiO_2$ under simulated sunlight[a]

Entry	Catalyst	Added CO_2/μmol (kPa)	Yield/μmol CHone[b]	CHnol[c]	CO_2	[CHone + CHnol] TON[d]	[CHone + CHnol] Selectivity/%[e]
1	P25	0[f]	39.7	13.6	126.0	—	71.7
2		909 (51)	24.6	8.0	183.0	—	51.7
3		1818 (102)	47.1	15.1	252.4	—	59.6
4		2273 (127)	30.5	3.3	821.2	—	19.8
5		2727 (153)	29.6	13.7	373.3	—	41.0
6		3409 (191)	30.3	10.0	503.5	—	32.4
7	FeO@P25	0[f]	3.6	Trace	Trace	5.3	>99.9
8		455 (26)	2.5	Trace	n.d.	3.7	>99.9
9		909 (51)	6.3	Trace	n.d.	9.3	>99.9
10		1818 (102)	5.4	Trace	75.1	7.9	30.0
11		2727 (153)	4.8	Trace	50.6	7.1	36.2
12		909 (51)[g]	18.8	7.0	n.d.	38	>99.9
13		909 (51)[h]	78.8	60.7	n.d.	206	>99.9
14		909 (51)[i]	4.3	Trace	n.d.	6.3	>99.9
15		909 (51)[j]	6.2	Trace	n.d.	9.2	>99.9
16		0[k]	9.2	Trace	154.7	14	26.2
17	$FeO@SiO_2$	0[f]	n.d.	n.d.	n.d.	—	—

[a] Solar simulator irradiation time, 6 h; catalyst, 30 mg; O_2-saturated solution of cyclohexane (2 mL) in acetonitrile (18 mL). [b] Cyclohexanone. [d] Cyclohexanol. [d] Estimated on the basis of Fe amount. [e] [formed CHone] + [formed CHnol]/[formed CHone] + [formed CHnol] + 1/6[formed CO_2] × 100. [f] In air. [g] Irradiation time, 12 h. [h] Irradiation time, 24 h. [i] Sunlight with a wavelength shorter than 420 nm was cut-off. [j] After the reaction (entry 9), the catalyst was recovered, washed with acetonitrile, and then used for reaction. [k] Argon was purged.

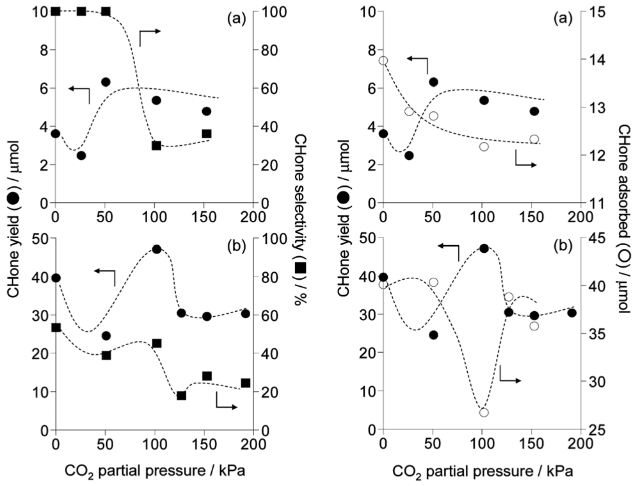

Fig. 2 (left) CO_2 pressure-dependence of photocatalytic oxidation activity of cyclohexane to cyclohexanone on (a) FeO@P25 and (b) P25 under sunlight irradiation for 6 h. (right) Comparison between (●) CO_2 pressure-dependence of cyclohexanone formation on (a) FeO@P25 and (b) P25 (plots same to those in Fig. 1) and (○) that of cyclohexanone adsorption from acetonitrile on (a) FeO@P25 and (b) P25.

the added dry ice. The container was placed by *ca.* 30 cm away from the light source to irradiate 1 solar (1000 W m^{-2})-power light to the mixture. CO_2 and organic compounds were quantitatively analyzed by GC-TCD (the measurement accuracy was within 1.0%) and GC-FID, respectively. Toluene was used as internal standard for GC-FID. Pristine P25 and iron oxide-modified SiO_2 (named as $FeO@SiO_2$)† were also used for comparison. For all photocatalytic reactions, only three products, cyclohexanone, cyclohexanol, and carbon dioxide, were detected by gas chromatographic analyses.

Table 1 summarizes all the results and Fig. 2 (left) shows the CO_2 pressure dependence of the yield and the selectivity for cyclohexanone formation on FeO@P25 and P25 under typical conditions. When the reaction was done on FeO@P25 under 51 kPa of a CO_2 atmosphere for 24 h, the best result, with a TON value of more than 200 and a selectivity of *ca.* 100%, was attained (Table 1, entry 13). A notable finding is that even the reaction on FeO@P25 in air gives a selectivity of *ca.* 100%, and by conducting the reaction under 51 kPa of CO_2, even when the irradiation time was prolonged, the yield is substantially improved with a selectivity maintained at *ca.* 100% (Table 1, entries 7, 9, 12 and 13, and Fig. 2, left (a)). To the best of our knowledge, 100% selectivity is the highest among those that had been reported for photocatalytic cyclohexanone production under visible light.[24–27] Also, the yield (more than 200 TON) was considerably higher than those obtained in other selective photocatalytic cyclohexane oxidations under visible light.[24–27] For example, 68% selectivity and 2.5 TON for cyclohexanone production were obtained on Cr–Si binary oxide[25] and 99% selectivity and 22 TON for cyclohexanone and cyclohexanol production were attained on hydrophobically modified Cr–Si binary oxide.[27] In the present study, it is also worth mentioning that the photocatalytic performance of pristine P25 is improved to give a higher yield with a selectivity maintained to some extent by conducting the reaction under CO_2 (Table 1, entries 1 and 3, and Fig. 2, left (b)). All of the results described above suggest that effective and selective sunlight-induced organic synthesis is possible even on cheap and abundant photocatalysts just by conducting the reaction under CO_2 atmosphere.

Interestingly, a high level of effective and selective cyclohexane oxidation was attained only when FeO@P25 was irradiated by sunlight including UV light (320 nm < λ) (Table 1). P25 produced much larger amount of CO_2 when irradiated by sunlight (excitation with UV light (λ < 420 nm), Fig. 1), resulting in much lower selectivity (Table 1, entries 1–6). It is well-known that valence band holes possess strong oxidation power; therefore, highly selective cyclohexane oxidation is difficult on

P25, even under CO_2. On the other hand, when FeO@P25 was irradiated by sunlight, only with a wavelength longer than 420 nm (only molecular iron oxide was excited, Table 1, entry 14), smaller amount of cyclohexanone formed on FeO@P25 if compared to that obtained by sunlight irradiation (320 nm < λ, Table 1, entry 9), although similar selectivity (*ca.* 100%) were attained. Also, no products were detected on FeO@SiO_2 under identical conditions (Table 1, entry 17), showing that the iron oxide functioned as the photocatalysis of cyclohexane oxidation only when it was adjacent to TiO_2. Moreover, no products were detected on FeO@P25 without any irradiation, which revealed that iron oxide did not work as a thermocatalyst. From these observations, we considered a possible role of iron oxide in the selective cyclohexane oxidation over FeO@P25 as follows: electrons, which transfer from both the TiO_2 valence band by UV excitation, and iron oxide by visible light excitation (possibly due to the d–d transition of molecular iron oxide)[28,29] to the TiO_2 conduction band, effectively reduce adsorbed O_2 to generate O_2^-. The obtained superoxide anion plays an important role in the selective cyclohexane oxidation over FeO@P25. Lower amount of cyclohexanone formed on FeO@P25 when only the iron oxide was excited (Table 1, entries 9 and 14), which was explained by that smaller amount of electrons, which were necessary to generate O_2^-, were transferred to the conduction band of TiO_2. The action spectrum (from 330 to 460 nm) in cyclohexanone formation on FeO@P25 was in good agreement with the UV-vis spectrum of P25 rather than that of FeO@P25 (Fig. 1), supporting the above hypothesis. The mineralization of cyclohexane and the successive oxidation of cyclohexanone and cyclohexanol hardly occurred to give only trace amounts of CO_2 on FeO@P25 (especially under lower loading levels of CO_2), since iron oxide efficiently prevented the interactions between bulky molecules, cyclohexane and the partially oxidized products, with the valence band holes on the P25 surface. The coating of TiO_2 particles with silica and alumina layers is useful to suppress the photocatalytic decomposition activity of organic compounds.[32–34]

When the atmosphere was changed from CO_2 (or air) to Ar (purged), larger amounts of cyclohexanone and CO_2 formed on FeO@P25 (Table 1, entry 16). Moreover, the yield and the selectivity for cyclohexanone and cyclohexanol formation on FeO@P25 and P25 varied with CO_2 pressure (Table 1 and Fig. 2, left). These results imply that CO_2 dissolves in the liquid phase and/or adsorbs on the catalyst surface depending on CO_2 pressure, affecting the present photocatalysis. CO_2 is known to adsorb on metal oxides,[35] so that the surface modification of P25 with CO_2 possibly promotes the desorption of the formed cyclohexanone and cyclohexanol to suppress the successive oxidation. It is also thought that dissolved CO_2 changes the polarity of the liquid phase to influence the adsorption or the desorption of the partially oxidized products, since it has been reported that the adsorption behavior of cyclohexanone on TiO_2 dramatically varies with solvents.[36,37] To confirm the hypothesis, the adsorption of cyclohexanone from acetonitrile on FeO@P25 and P25 was investigated under controlled CO_2 pressure.‡ As shown in the right of Fig. 2, the amount of the adsorbed cyclohexanone on FeO@P25 and P25 varied with CO_2 pressure, and the curves almost mirrored the curves for CO_2 pressure dependence of the photocatalytic performance. Accordingly, it is plausible that under an appropriate CO_2 loading (*ca.* 50 and 100 kPa for FeO@P25 and P25, respectively) a balanced combination between the CO_2-modified surface properties of the catalysts and the polarity of the liquid phase makes the formed cyclohexanone and cyclohexanol promptly desorb from the catalysts surface, which prevents the successive oxidation of the partially oxidized products.

As shown in Table 1 (entry 15), FeO@P25 was able to be reused without significant loss of the activity. Moreover, it was possible to synthesize the catalyst at larger scale by increasing the amount of the added P25, iron source and solvent. These facts show merits of the present system for practical applications.

In summary, we have reported a highly effective and selective sunlight-induced photocatalytic oxidation of cyclohexane, in acetonitrile, to cyclohexanone and cyclohexanol on TiO_2 (P25) modified with iron oxide under a CO_2 atmosphere. The present success opens up new opportunities to synthesize a wide variety of fine chemicals in an economically and environmentally favorable fashion.

Notes and references

† FeO@P25 was synthesized according to the literature:[28] P25 (1.0 g, Nippon Aerosil) was added to 6.5 × 10^{-4} mol L^{-1} of a iron(III) acetylacetonate in a mixed solvent (100 mL, ethanol/hexane = 3 : 17 v/v) and the mixture was stirred at room temperature for 24 h. The product was separated by centrifugation (3000 rpm, 20 min), washed repeatedly with the same solvent, and calcined at 500 °C for 1 h. The reaction was repeated three times. FeO@SiO_2 was synthesized in a similar way, where SiO_2 (Wako gel Q-63) was used instead of P25.

‡ Adsorption tests were done in a similar way that conducted in photocatalytic conversions except that 10 mg of the catalyst and a solution of cyclohexanone (2 mL) in acetonitrile (18 mL), which was not bubbled with O_2, were mixed.

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