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

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Electronic Supplementary Information (ESI†)

Experimental Details

1. ESR Measurement

Instruments: ESR spectra were recorded at the X-band using a Bruker EMX-10/12 spectrometer with a 100 kHz magnetic field modulation at a microwave power level of 1.0 mW, where the microwave power saturation of the signals does not occur. The magnetic field was calibrated using a 1,1'-diphenyl-2-picrylhydrazyl (DPPH) as standard. Photoirradiation of the sample was carried out using a 500 W Xe lamp (USHIO Inc.).[S1]

Measurements: Each catalyst (50 mg) was placed in a cylindrical quartz ESR tube (capacity, 6 cm^3) and treated with 100 Torr O_2 (1 Torr = 133.3 Pa) at 673 K for 1 h. The tube was evacuated at 473 K for 2 h and cooled to room temperature. The required quantity of O_2 and cyclohexane was then introduced to the tube. The tube was placed on an ESR sample cavity and photoirradiated at 77 K. After photoirradiation for 0.5 h, measurement was then started with photoirradiation.

2. Additional Photocatalytic Reaction

Procedure (i): Reaction was performed with a conventional closed system (capacity, 6 cm^3). Cr-SiO_2(0.1) (50 mg) was spread on the flat bottom (2 cm^2) of the quartz vessel and the vessel was evacuated at room temperature. Cyclohexane (0.5 mmol) was then introduced to the vessel. The sample was photoirradiated (λ > 400 nm) from beneath in a static condition, where the temperature of the bottom of the cell during photoirradiation was 315 K. After the photoirradiation (5 h), the vessel was immediately filled with O_2 (1 atm) and left for 5 min. MeCN (5 ml) was added to the vessel, and the catalyst was rinsed well by ultrasonication for 5 min at room temperature. The resulting MeCN was recovered by centrifugation and then analyzed by GC. The cyclohexanone yield was 0.2 μmol.

Procedure (ii): Cr-SiO_2(0.1) (50 mg) was spread on the above quartz vessel. The vessel was evacuated at room temperature. O_2 (200 Torr) was introduced to the vessel and photoirradiated (λ > 400 nm) for 5 h in a similar manner to that described above. After photoirradiation, cyclohexane (260 Torr; 80 μmol) was immediately introduced to the vessel, and the vessel was left for 5 min. MeCN (5 ml) was added to the vessel, and the catalyst was rinsed well by ultrasonication for 5 min at room temperature. The resulting MeCN was recovered by centrifugation. None of the products was detected by GC analysis.

References

(S1) Y. Shiraishi, N. Saito and T. Hirai, *J. Am. Chem. Soc.*, 2005, **127**, 8304.

Figures

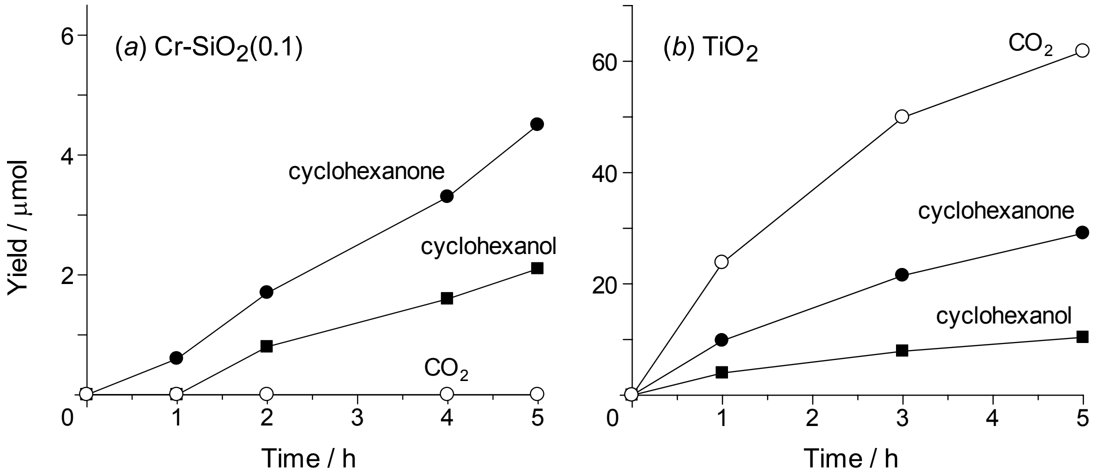

Fig. S1 Change in the product yields during photocatalytic oxidation of cyclohexane on (a) Cr-SiO_2(0.1) and (b) TiO_2 with time. Reaction conditions are: (a) MeCN, 9 ml; cyclohexane 1 ml; catalyst, 50 mg; λ > 400 nm; (b) MeCN, 9 ml; cyclohexane 1 ml; catalyst, 10 mg; λ > 320 nm.

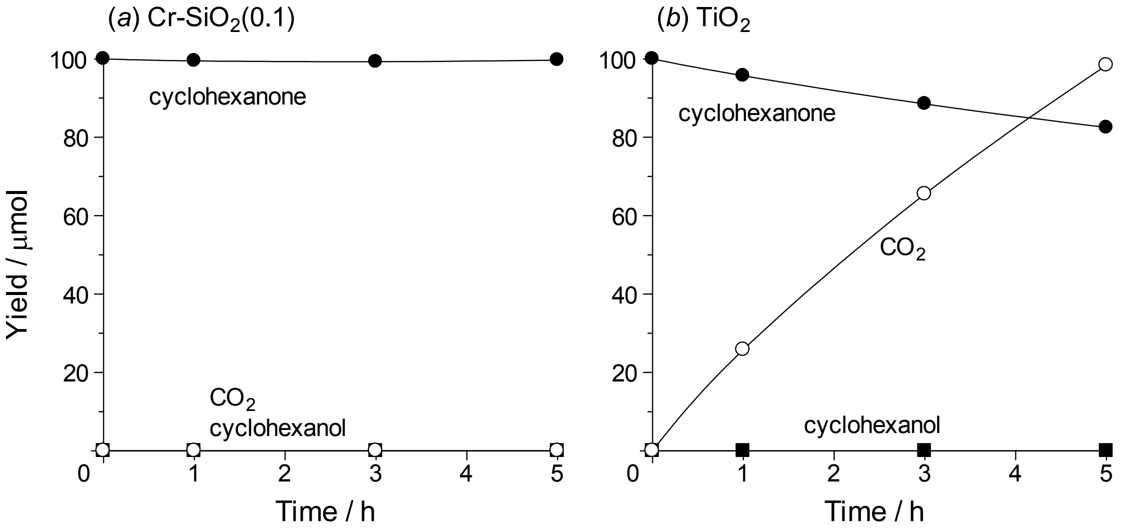

Fig. S2 Change in the product yields during photocatalytic oxidation of cyclohexanone on (a) Cr-SiO_2(0.1) and (b) TiO_2 with time. Reaction conditions are: (a) MeCN, 10 ml; cyclohexanone, 100 µmol; catalyst, 50 mg; λ > 400 nm; (b) MeCN, 10 ml; cyclohexanone, 100 µmol; catalyst, 10 mg; λ > 320 nm.

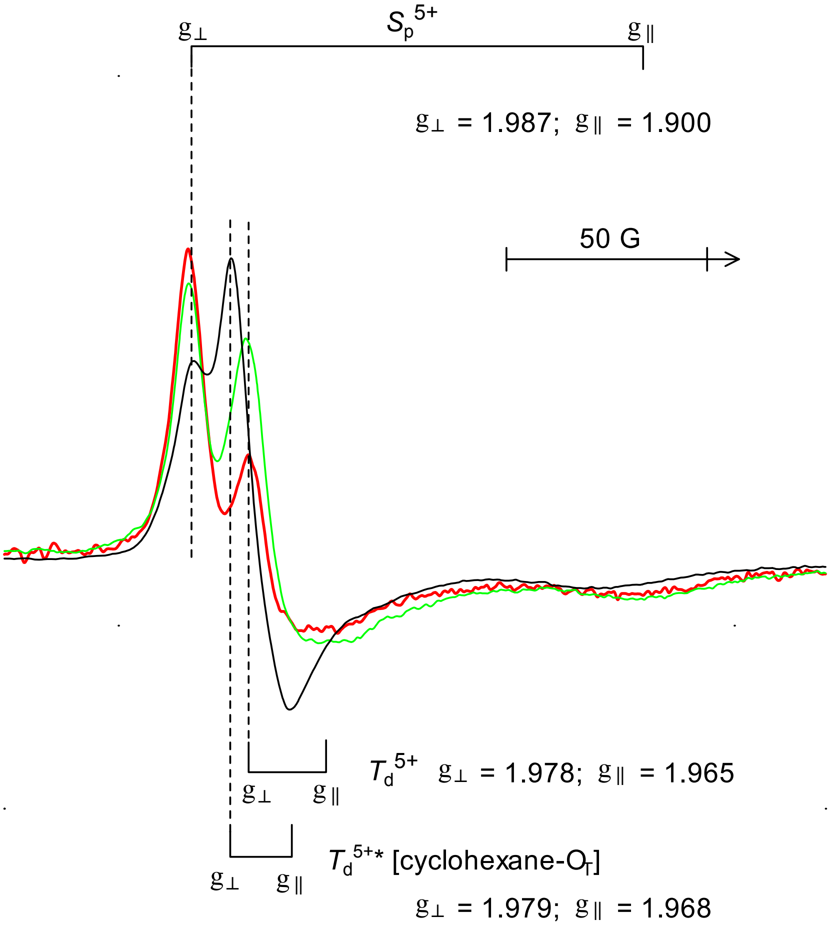

Fig. S3 ESR spectra of Cr-SiO_2(0.1) at 77 K with photoirradiation (red) in vacuo, (green) with 1 Torr O_2, and (black) with 1 Torr cyclohexane.

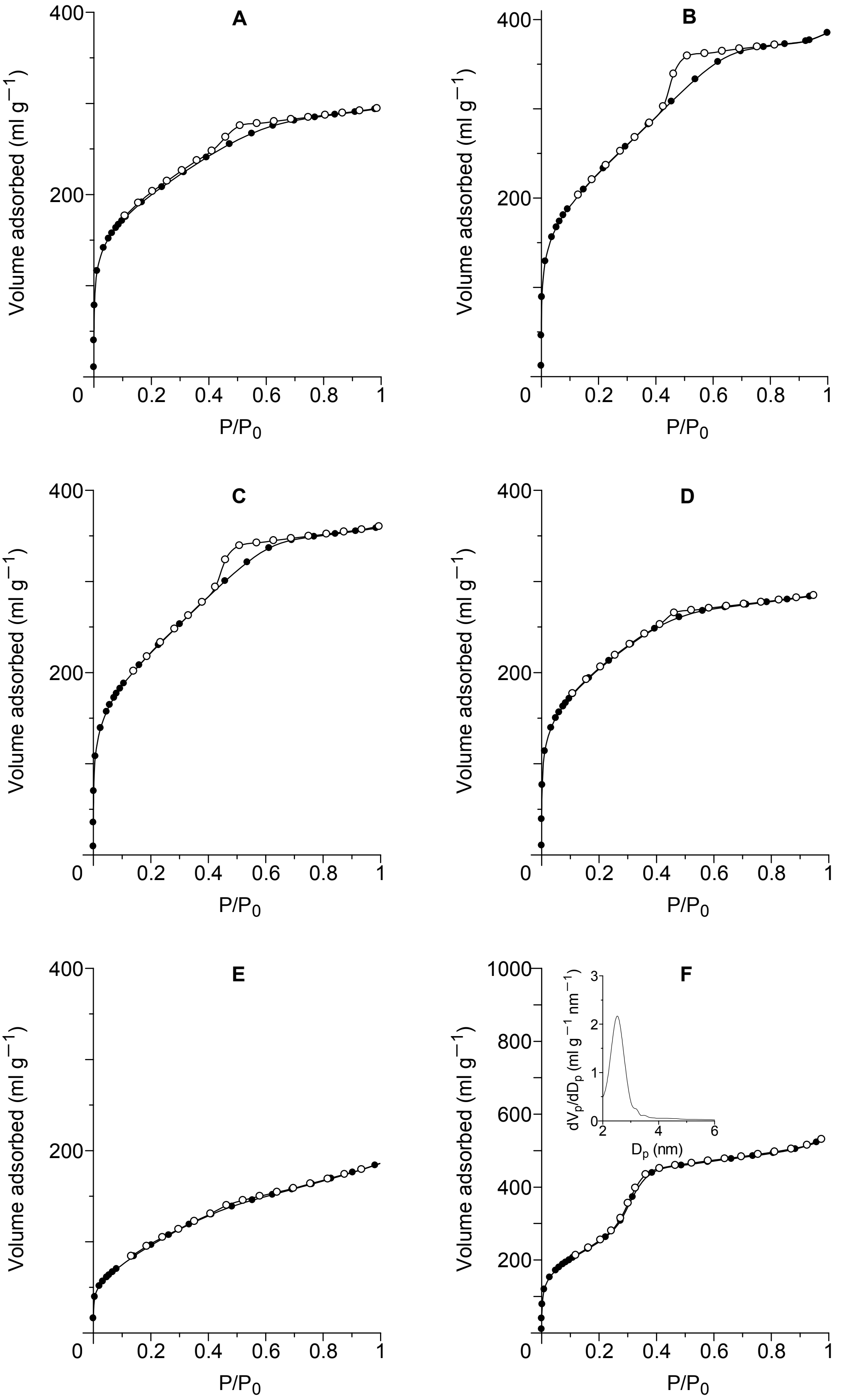

Fig. S4 N_2 adsorption(●)–desorption(○) isotherm and pore size distribution (inset) of the catalysts used. (**A**) Cr-SiO_2(0.1), (**B**) Cr-SiO_2(0.5), (**C**) Cr-SiO_2(1.7), (**D**) Cr-SiO_2(3.1), (**E**) Cr/SiO_2(0.1), and (**F**) Cr$\propto$MCM-41(0.1) (pore volume, 925.3 mm^3/g).