

SUPPLEMENTARY INFORMATION

Direct cyanomethylation of aliphatic and aromatic hydrocarbons with acetonitrile over metal loaded titanium oxide photocatalysts

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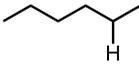
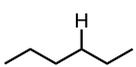
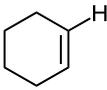
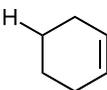
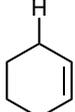
Table S1 The C–H bond dissociation energies in various organic compounds.

Table S2 The cyanomethylation of n-hexane with acetonitrile over the M/TiO₂ photocatalyst.

Fig. S1 The mass fragments of a standard material and the main product from cyanomethylation of cyclohexene.

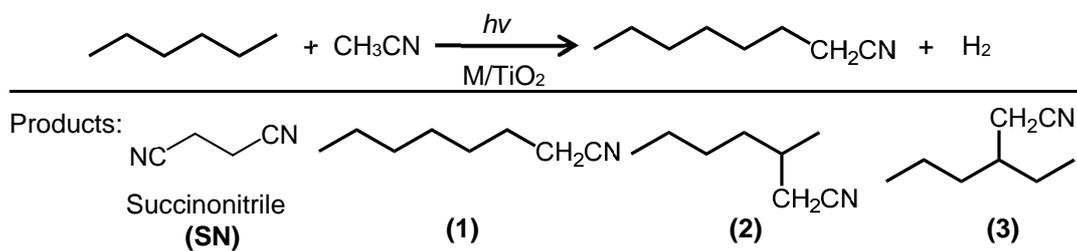
Table S3 Adsorbed amount of CO on the samples, metal dispersions, and metal particle sizes.

Table S1 The C–H bond dissociation energies in various organic compounds. ^a

Compounds	C–H bonds	Bond dissociation energy /kJ mol ⁻¹
acetonitrile	H–CH ₂ CN	406
cyclohexane	H–C ₆ H ₁₁	416
n-hexane		414
		410
cyclohexene ^b		415
		457
		415
		350
benzene	H–C ₆ H ₅	440

^a These values except cyclohexene were cited from ref. S1. ^b The values of cyclohexene were cited from ref. S2.

Table S2 Results of the photocatalytic reaction tests for the cyanomethylation of n-hexane with acetonitrile over a M/TiO₂ photocatalyst. ^a



Entry	Catalyst	Products / μ mol				C ₁₂ H ₂₆	H ₂
		SN	1	2	3		
1	Pt/TiO ₂	6.2	0.29	0.81	1.0	n.d. ^b	70
2	Pd/TiO ₂	2.9	0.12	0.49	0.54	n.d.	35

^a Reaction conditions: M/TiO₂ catalyst 0.2 g, n-hexane 0.76 mmol (0.1 mL), water 5.6 mmol (0.1 mL), acetonitrile 74.7 mmol (3.9 mL). Reaction time was 1 h. Reaction temperature was ca. 310 K. The wavelength of irradiation was 365 \pm 20 nm and the intensity was 27mW cm⁻² measured at 360 \pm 15 nm. ^b not detected.

The cyanomethylation of n-hexane with acetonitrile was also examined with the Pd/TiO₂ and Pt/TiO₂ samples (Table S2). The cyanomethylated products were obtained in the presence of these photocatalysts, and the Pt/TiO₂ sample gave the products in higher yield than the Pd/TiO₂ sample. Among cyanomethylated products, the compound **2** and **3** were obtained more than the compound **1**. The cyanomethylation at the primary carbon less proceeded because the primary carbon radical species would be rather unstable compared to the secondary and tertiary carbon radical species. However, the product selectivity was not so clear because of the small difference in the C–H bond dissociation energy as shown in Table S1.

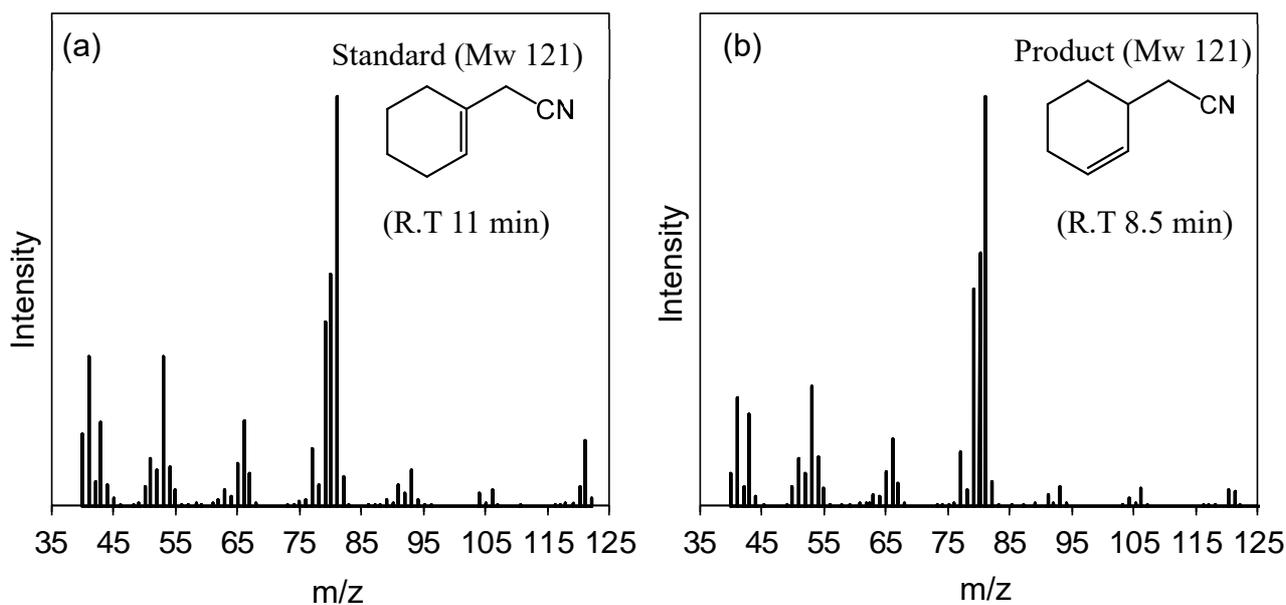


Fig. S1 GC-Mass fragments of (a) the standard compound and (b) the product obtained from the direct cyanomethylation of cyclohexene with acetonitrile over the Pt/TiO₂ sample.

Table S3 Adsorbed amount of CO on the samples, metal dispersions, and metal particle sizes.^a

Entry	Catalysts	Adsorbed amount / $\mu\text{mol g}^{-1}$	Metal dispersion (%)	Particle size /nm
1	Pt(0.1)/TiO ₂	2.8	54	2.1
2	Pd(0.1)/TiO ₂	4.8	50	2.2
3	Pd(0.1)/Al ₂ O ₃	2.7	28	3.9
4	Pd(1.0)/Al ₂ O ₃	45.9	49	2.3
5	Pd(2.0)/Al ₂ O ₃ ^b	45.6	24	4.6

^a The catalyst samples used was 50 mg. As a pretreatment, metal loaded TiO₂ samples were reduced at 473 K, while metal loaded Al₂O₃ samples were reduced at 673 K. Metal dispersion and particle size were calculated from the adsorption amount of CO.

^b After the reduction, the sample was kept in argon atmosphere at 673 K for 40 min, and then cooled down to room temperature in argon atmosphere.

Reference

- [S1] Y-R. Luo, *Handbook of bond dissociation energies in organic compounds*, CRS press, 2007.
 [S2] Z. Tian, A. Fattahi, L. Lis, and S.R. Kass, *J. Am. Chem. Soc.*, 2006, **128**, 17087.