Supporting Information

Selective aerobic oxidation of alkyl aromatics on Bi_2MoO_6 nanoplates decorated with Pt nanoparticles under visible light irradiation

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1. Experimental Details

1.1 Materials

Ammonium hydroxide ($NH_3 \cdot H_2O$), glycerol, and ammonium molybdate (($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$)) were supplied from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) was obtained from Tianjin Bodi Chemical Co., Ltd. (Tianjin, China). 4-bromoacetophenone, 1-chloro-4-ethylbenzene, 4-methoxyacetophenone, propiophenone, 4-chloroacetophenone, ethylbenzene, 1-ethyl-4-fluorobenzene, 1-bromo-4-ethylbenzene, 1-indanone, 4-ethylanisole, and 4-fluoroacetophenone were purchased from Alfa Aesar. 1,3-dichlorobenzene was supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Indan, 1,2,3,4-tetrahydronaphthalene, acetophenone, and α-tetralone were supplied from TCI. Diphenylmethane, and benzophenone were obtained from J&K Scientific. Propylbenzene was purchased from Acros Organics. All chemicals were used without further purification. Deionized water used in the synthesis was from local sources.

1.2 Preparation of photocatalysts

Bi_2MoO_6 samples were synthesized by a sample solvothermal method. $Bi(NO_3)_3 \cdot 5H_2O$ (5.0 mmol) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.36 mmol) were dissolved in 60 ml different solvents including water and glycerol (at 50 ^{o}C), respectively and ultrasonicated for 30 min. With continuous stirring, 5% NH_3 (aq.) was added into the mixture by a drop-by-drop process until pH value was 9.0. Then, stirring for 0.5 h, it was added into 100 ml Teflon-lined stainless steel autoclave and maintained at 140 ^{o}C (240 ^{o}C for water) for 24 h. Thereafter, the samples were cooled to room temperature

and recovered by centrifugation at 10000 rpm, washed with deionized water and absolute ethanol, and dried at 80 °C in an oven. Finally, the samples synthesized in glycerol were calcined at 400 °C for 2 h to remove the adsorbed organic compounds.

Metal nanoparticles supported on Bi_2MoO_6 samples were prepared by photodeposition method. Bi_2MoO_6 samples were suspended in methanol aqueous solution (50 vol%) containing chloroplatinic acid under vacuum conditions. The solution was irradiated by a 300 W Xe lamp (PLS-SXE 300, Beijing Perfectlight Co., Ltd.) for 1 h with magnetic stirring, continuously kept at 283 K in a water bath, and then formed Pt-loaded Bi_2MoO_6 samples. Other metals were loaded on Bi_2MoO_6 samples using the same method.

Metal oxide-supported Bi_2MoO_6 samples were prepared by impregnation method. Bi_2MoO_6 samples were suspended in aqueous solution containing corresponding salt. The mixture was evaporated at 353 K with vigorous stirring. The samples were dried at 80 °C for 12 h in an oven. The samples were calcined at 400 °C for 1 h and obtained MO_x-loaded Bi_2MoO_6 samples.

1.3 Characterization

Crystal structures were measured on a powder X-ray diffraction (XRD) instrument Rigaku D/Max-2500/PC using Cu-Kα radiation. Optical properties were performed on an UV-Vis spectrophotometer (JASCO-V550) with $BaSO_4$ as a reference. Morphologies of the samples were recorded with a (Tecnai G^2 Spirit (FEI)) transmission electron microscopy (TEM), a (FEI Quanta 200F) scanning electron

microscopy (SEM), and a (Tecnai G^2 F30 S-Twin) high revolution transmission electron microscopy (HRTEM).

1.4. Evaluation of photocatalytic activity

20 mg catalyst and 0.1 mmol ethylbenzene were mixed in 1.5 mL benzotrifluoride (BTF) solvent. BTF solvent was chosen because it could not be oxidized under such conditions and has high oxygen solubility. The catalyst was dispersed evenly in BTF solution with continuous magnetic stirring for 20 min before light irradiation. Reaction temperature was kept at 17 °C with a water bath. The solution was irradiated by a 300 W Xe lamp with visible light region from 420 to 800 nm. The reaction solution was analyzed with an Aglient Gas Chromatograph (GC7890) equipped with a flame ionization detector and a β-DEX 225 capillary column using 1,3-dichlorobenzene as the internal standard. The chemical structures of products were confirmed by GC-mass spectrometry (MS) (Agilent Technologies, GC6890N-MS5975).

Conversion of ethylbenzene and selectivity of acetophenone were defined as follows:

Conversion (%) = $[(C_0-C_{ethylbenzene})/C_0] \times 100$

Selectivity (%) = $[C_{acetophenone}/(C_0-C_{ethylbenzene})] \times 100$

Where C_0 was the initial concentration of ethylbenzene and $C_{ethylbenzene}$ and $C_{acetophenone}$ were the concentration of the ethylbenzene and the acetophenone, respectively.

The cycling experiments were carried out as following. The oxidation of ethylbenzene was performed as above. After each run of cycling test, the reaction solution was centrifuged, washed with water, ethanol, BTF, dried (80 °C for 12 h), and used for the next run under the same conditions.
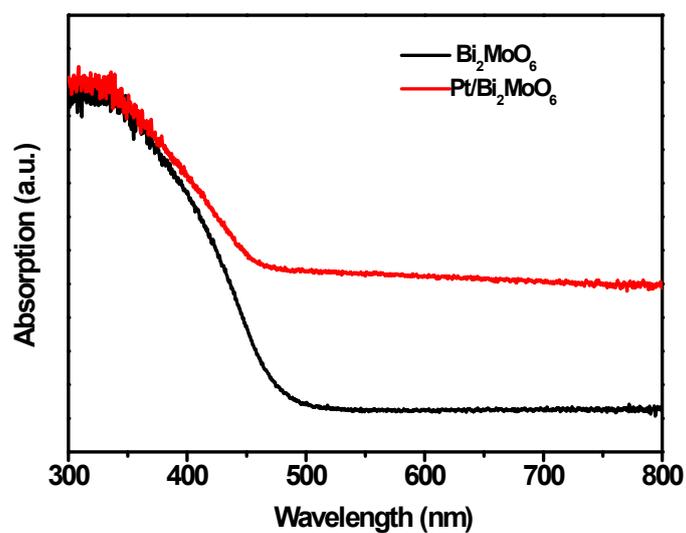
2. **Fig. S1**

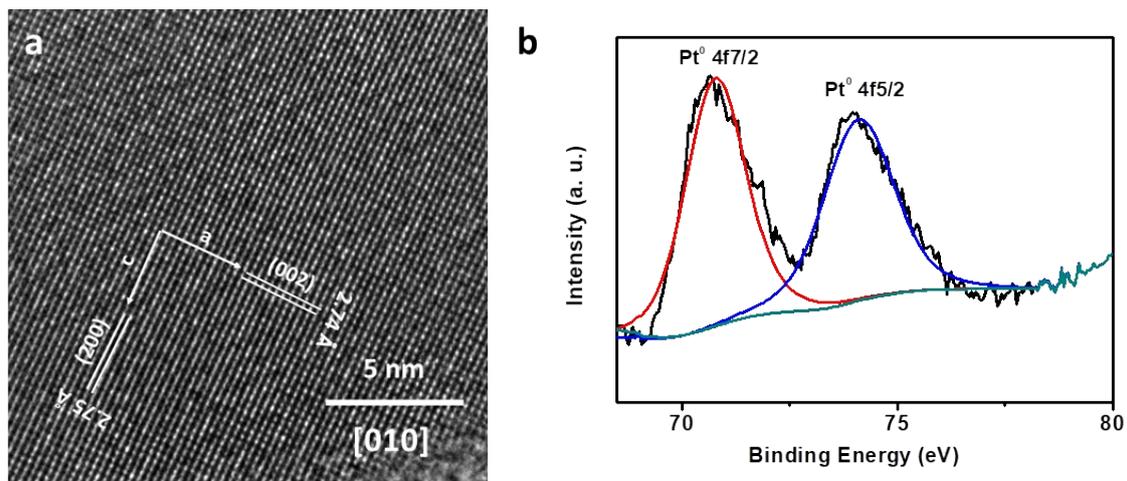**Fig. S1** UV-Vis DRS spectra of Bi_2MoO_6 nanoplates.

3. Fig S2

Fig. S2 (a) HRTEM image and (B) XPS of Pt/Bi$_2$MoO$_6$ nanoplates.

4. Table S1 Controlled experiments

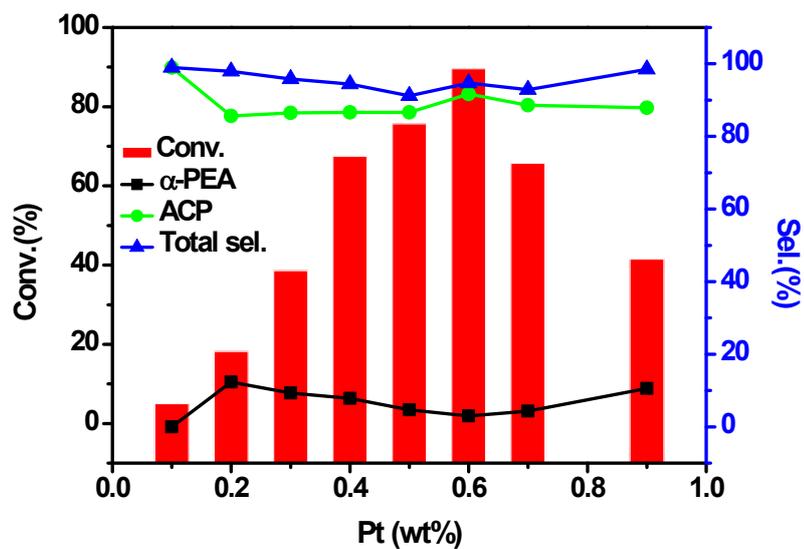| Light	Photocatalyst	O_2	Conv. (%)	Sel. (%)
+	+	+	<1	-
-	+	+	<1	-
+	-	+	<1	-
+	+	-	<1	-

Reaction conditions: catalyst 20 mg, ethylbenzene 0.025 mmol, $C_6H_5CF_3$ 1.5 mL, reaction temperature 17 ^{o}C, reaction time 6 h, O_2 0.1 MPa.

5. Table S2 Photocatalytic aerobic oxidation of ethylbenzene on M/MO_x-Bi_2MoO_6 nanoplates

Photocatalyst	Conv. (%)	α-PEA[a] (%)	ACP[b] (%)	Total Sel.[c] (%)
-	<1	-	-	-
Au	22	12	86	98
Pd	30	15	81	96
Pt	90	3	92	95
Ir	12	16	81	97
Rh	14	7	90	97
Ru	14	22	77	99
CuO_x	5	-	96	96
FeO_x	2	-	99	99
VO_x	3	2	92	94
MnO_x	2	2	98	>99
NiO_x	<1	-	-	-
CoO_x	<1	-	-	-

Reaction conditions: catalyst 20 mg, ethylbenzene 0.025 mmol, $C_6H_5CF_3$ 1.5 mL, reaction temperature 17 ^{o}C, reaction time 6 h, O_2 0.1 MPa, metal loading 0.6 wt%. [a] α-PEA is phenylethyl alcohol. [b] ACP is acetophenone. [c] Total selectivity of products is the selectivity of α-PEA and that of ACP.

6. Fig. S3

Fig. S3 The effect of Pt amount

Reaction conditions: catalyst 20 mg, ethylbenzene 0.025 mmol, $C_6H_5CF_3$ 1.5 mL, reaction temperature 17 °C, reaction time 6 h, O_2 0.1 MPa.

7. Fig. S4
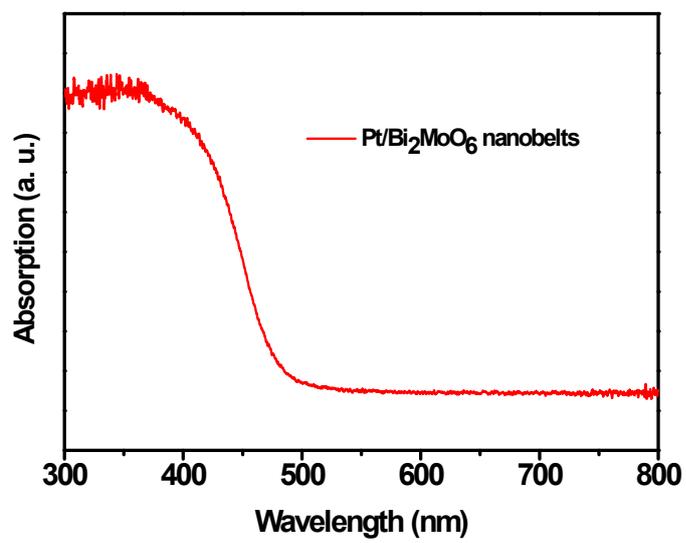
Fig. S4 UV-Vis DRS spectra of Pt/Bi$_2$MoO$_6$ nanobelts.

8. Table S3 BET surface areas of Pt/Bi_2MoO_6 samples

	Pt/Bi_2MoO_6 nanobelts	Pt/Bi_2MoO_6 nanoplates
BET surface areas (m^2/g)	7.3	23.7
The activity of catalyst ($\mu mol \cdot h^{-1} \cdot m^{-2}$)	18.8	41.2

9. Fig. S5
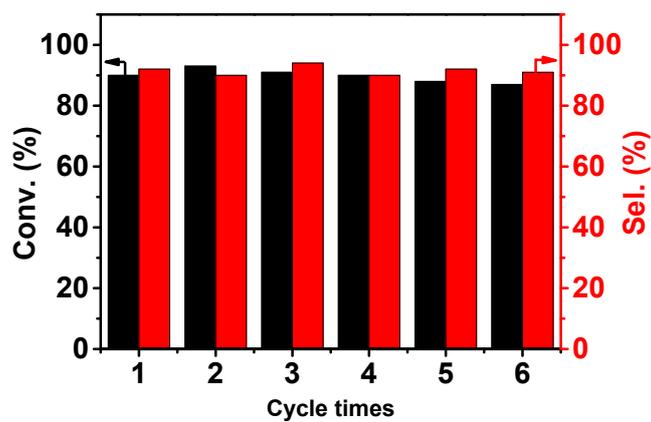
Fig. S5 Cycling experiments of Pt/Bi$_2$MoO$_6$ nanoplates for photocatalytic aerobic oxidation of ethylbenzene.

Reaction conditions: catalyst 20 mg, ethylbenzene 0.025 mmol, C$_6$H$_5$CF$_3$ 1.5 mL, reaction temperature 17 ^{o}C, reaction time 6 h, O$_2$ 0.1 MPa, metal loading 0.6 wt%.

10. Fig. S6
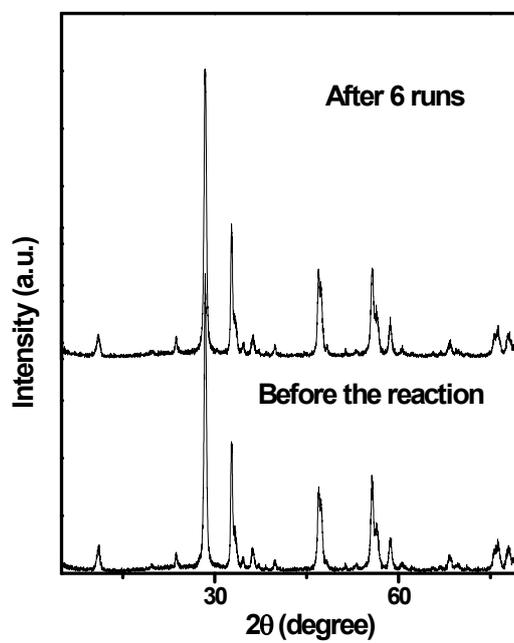
Fig. S6 XRD patterns of Pt/Bi_2MoO_6 nanoplates before the reaction and after 6 runs.

11. Fig. S7
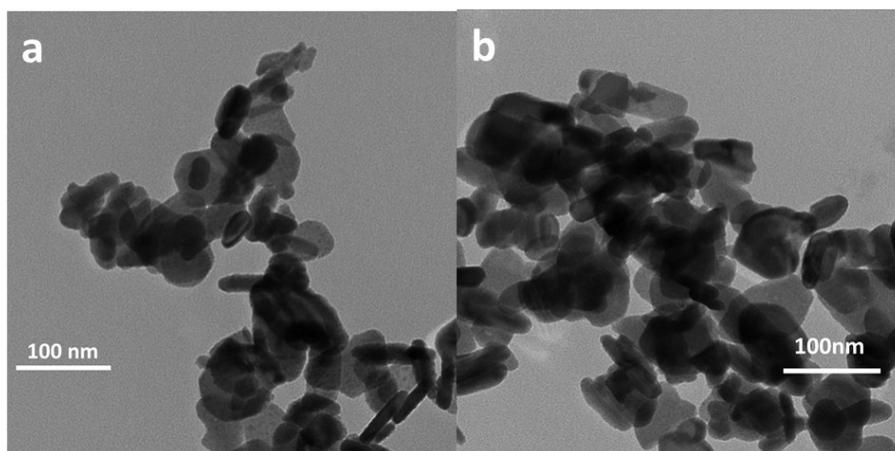
Fig. S7 TEM images of Pt/Bi$_2$MoO$_6$ nanopaltes before the reaction (a) and after 6 runs (b).

12. Fig. S8
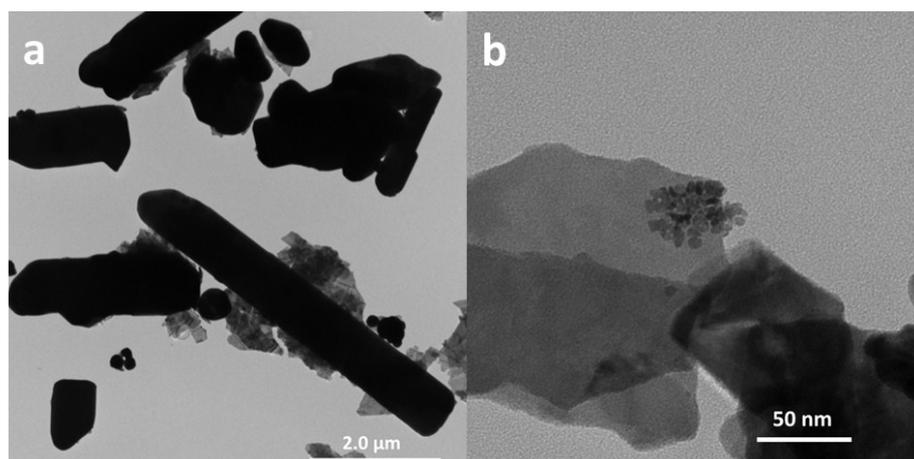
Fig. S8 TEM images of Pt/Bi$_2$MoO$_6$ nanobelts.

13. Note

Table 2 Photocatalytic oxidation of alkyl aromatics on Pt/Bi$_2$MoO$_6$ nanoplates.

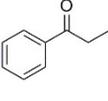| Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
		6	90	92
		10	98	96
		17	92	92
		16	95	95
		2	97	80[a]
		2.5	96	57[b]
		2.5	94	61[c]
		6	92	53[d]
		13	95	88[e]
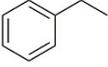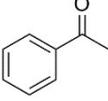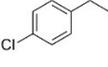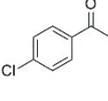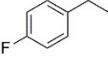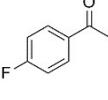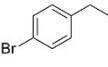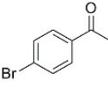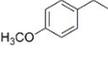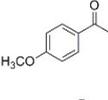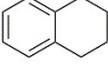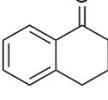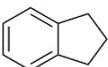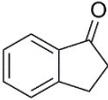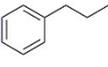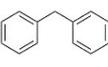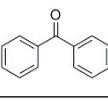
Reaction conditions: catalyst 20 mg, ethylbenzene 0.025 mmol, C$_6$H$_5$CF$_3$ 1.5 mL, reaction temperature 17 °C, λ > 420 nm, O$_2$ 0.1 MPa, metal loading 0.6 wt%. [a] Other products are 4-methoxybenzyl alcohol, anisic aldehyde, p-anisic acid, 4-methoxyphenylethyl alcohol. [b] Other products are 2-propylbenzyl alcohol, 2-propylbenzaldehyde, 2-propylbenzoic acid. [c] Other products are 2-ethylbenzyl acohol, 2-ethylbenzaldehyde, 2-ethylbenzoic acid. [d] Other products are benzyl alcohol or benzaldehyde and benzoic acid. [e] Other product is benzopinacole.

Note 1: Pt/Bi$_2$MoO$_6$ nanoplates could convert most of alkyl aromatics to corresponding ketone and alcohol with high selectivity. For some special substrates, the desirable products are low due to the ketone and alcohol decomposition forming benzyl alcohol, benzaldehyde and benzoic acid.

Note 2: The more reaction mechanism details were provided in below.

With visible light irradiation, the Bi_2MoO_6 nanopaltes are stimulated, and then produce photogenerated holes and electrons. The holes oxidize the ethylbenzene adsorbed on the surface of Bi_2MoO_6 photocatalyst, and forms ethylbenzene cationic radicals. This step is usually regarded as the rate-determining step for the oxidation of alkyl aromatics. Simultaneously, the photogenerated electrons transfer to Pt nanoparticles. Pt nanoparticles as cocatalyst, no only dramatically promote oxygen reduction and suppress the recombination of photogenerated charge, but also activate the C-H bonds of ethylbenzene. The ethylbenzene cationic radicals are recombined by interacting with superoxide radicals. 1-phenylethyl peroxyl radical (PEPR) are generated from the reaction ethylbenzene (EB) cationic radicals and the superoxide radicals. After forming PEPR, there are two pathways for the decomposition of PEPR. The minor reaction pathway is that PEPR abstracts hydrogen from EB, forming 1-phenylethyl hydroperoxide (PEHO), subsequently through β-scission mechanism, and generate benzaldehyde, benzyl alcohol and benzoic acid. The major reaction pathway is that the di-PEPR couple with each other, through Rueesll mechanism, forming acetophenone and phenylethyl alcohol. In these pathways the intermediate (di-PEPR) is more stable in thermodynamically. So, the main products of the ethylbenzene oxidation are acetophenone and phenylethyl alcohol.
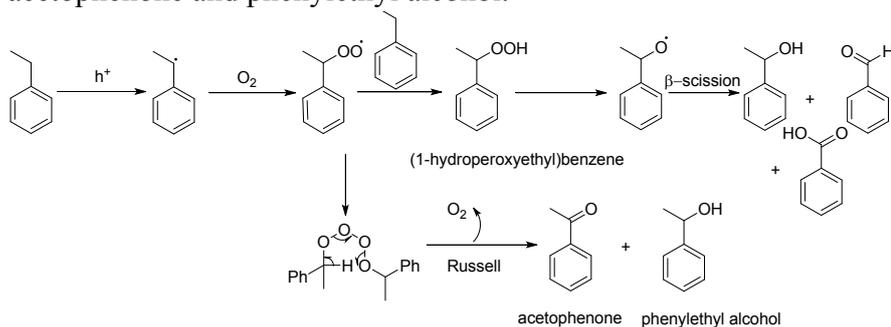
Scheme 1 The reaction pathway of photocatalytic oxidation of ethylbenzene on Pt/Bi_2MoO_6 catalyst