Supporting Information (SI)

Development and study of a bifunctional photocatalyst based on SAPO-34 molecular sieve

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Complementary methods.

Preparation of catalysts

Preparation of Bi_2WO_6

Put 5mmol $Bi(NO_3)_3 \cdot 5H_2O$ crystals with 2.00g citric acid in 30.00 mL deionised water, stir for a certain time, add 2.5 mmol $Na_2WO_4 \cdot 2H_2O$ crystals, stir for a certain time, put in a hydrothermal synthesis kettle and react at 180 °C for 20 h, wash the resulting solid with deionised water and anhydrous ethanol respectively for 3 times, and at 80°C Dried at 80 °C for 12 h to obtain Bi_2WO_6 crystals.

Preparation of BiOI

Mix ethylene glycol monomethyl ether with water according to 1:1 (volume ratio); Liquid A: add 2.5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ crystals to 25.00 ml of the mixture and stir; Liquid B: dissolve 2.5 mmol KI in 25.00 ml of the mixture and stir; add Liquid B to Liquid A drop by drop and stir for a certain time, then place it in a hydrothermal synthesis kettle. The synthesis was carried out at 160 °C for 6 h. The synthesized solid was washed with deionized water by centrifugation for 3 times, placed in an oven and dried at 80 °C for 12 h to obtain BiOI crystals.

Preparation of Bi_2WO_6 @ SAPO-34

After placing 5mmol $Bi(NO_3)_3 \cdot 5H_2O$ crystals with 2.00 g citric acid in 30mL deionised water and stirring for a certain time, 2.5mmol $Na_2WO_4 \cdot 2H_2O$ crystals were added, and after stirring to form a crystalline solution, a certain amount of SAPO-34 molecular sieve sample was added and stirring was continued for 6 h. The synthetically modified SAPO-34 molecular sieves, respectively, were prepared by hydrothermal synthesis, noted as Bi_2WO_6 @ SAPO-34.

Preparation of BiOI @ SAPO-34

Ethylene glycol monomethyl ether and water were mixed according to 1:1 (v/v); Liquid A: 2.5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ crystals were added to 25.00 ml of the mixture and stirred; Liquid B: 2.5 mmol KI was dissolved in 25.00 ml of the mixture and stirred; Liquid B was added to Liquid A drop by drop, and after stirring to form the crystallized liquid, a certain amount of SAPO -34 molecular sieve sample, continue to stir for 6 h, and then prepare synthetically modified SAPO-34 molecular sieve by hydrothermal synthesis, respectively, noted as BiOI @ SAPO-34.

Theoretical calculations

Optimisation of the structure of the SAPO-34 molecular sieve

All quantum chemistry calculations were performed in Gaussian 09. The structure of the molecular sieve was initially optimised in ChemDraw using MM2/Minimize Energy, followed by geometry optimisation and frequency calculations using b3lyp/6-311+G(d,p), taking into account the effect of hydrogen bonding on the dispersion correction of the basis set. The HOMO and LUMO energy levels of the molecular sieve were analysed to indirectly infer the redox ability and determine whether the reaction occurred according to frontier molecular orbital theory. The transition state of the formaldehyde reaction mechanism was searched for the reaction products and reactants according to the TS method, which was further calculated using the M062X/6-311+G(d,p) method to obtain a high level energy map.

Density Flood Theory calculations for Bi-based catalysts

Calculations based on density flooding theory (DFT) were carried out using MedeA software. A pseudopotential of conservative parametric number is chosen for structural optimisation and electronic calculations, taking into account spin polarisation effects. Taking BiVO4 as an example, during the energy band calculation, the optimisation K-point is set to 3 x 3 x 3, the cut-off energy

is 571.40 eV, the electron energy is 1.0 x 10-6 eV, the maximum displacement is 0.001 A, the interatomic interaction force accuracy is 0.03 eV/nm and the intracrystal stress accuracy is 0.05 GPa.

Determination of formaldehyde content

Configuration of acetylacetone solution

Weigh 12.50g of ammonium acetate crystals, add the appropriate amount of water to dissolve, add 1.5ml of glacial acetic acid, add to a 50ml volumetric flask, shake well and add 0.125ml of acetylacetone, adjust the pH of the solution = 6, add deionised water to fix the volume. Store in a refrigerator at 2-5°C.

Configuration of formaldehyde standard solution

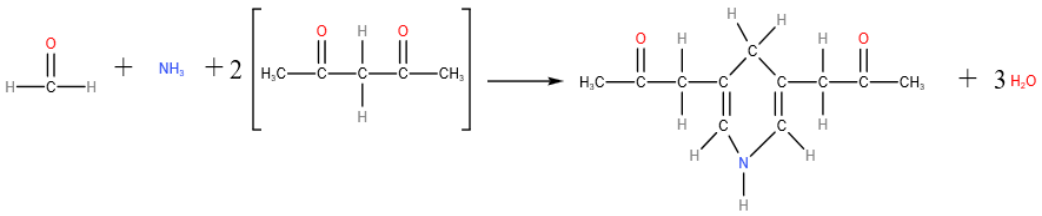
Measure 2.6ml of 38% formaldehyde solution accurately, add a small amount of water and shake well, then use a glass rod to drain into a 100ml volumetric flask and add deionised water to fix the volume. A standard solution of 1g/ml of formaldehyde can be obtained.

Accurately measure 1ml of the configured formaldehyde standard solution, add to a 100ml volumetric flask and fix the volume to obtain 1μg/ml of formaldehyde solution.

Determination of formaldehyde content by UV spectrophotometer

Accurately measure 2.00ml of formaldehyde solution (0.1mg/ml), add into a 200ml volumetric flask and fix the volume. A formaldehyde solution can be obtained.

Measure 50ml of the formaldehyde solution, add it to a 100ml conical flask, add 2.5ml of the previously prepared acetylacetone solution, react in a water bath at 60°C for 30min, a yellow complex appears in the reaction solution, remove 3-4ml of the reaction solution, measure the UV absorption wavelength and a UV absorption peak appears at 413nm.



Formaldehyde content standard curve plotting

Dilute the configured formaldehyde standard solution according to different ratios of gradient, add 2.5ml of previously equipped acetylacetone solution, react in a water bath at 60℃ for 30min, yellow complexes appear in the reaction solution, take out 3-4ml of the reaction solution, measure the UV absorption wavelength, and the standard curve of formaldehyde content can be obtained, see Figure S1.

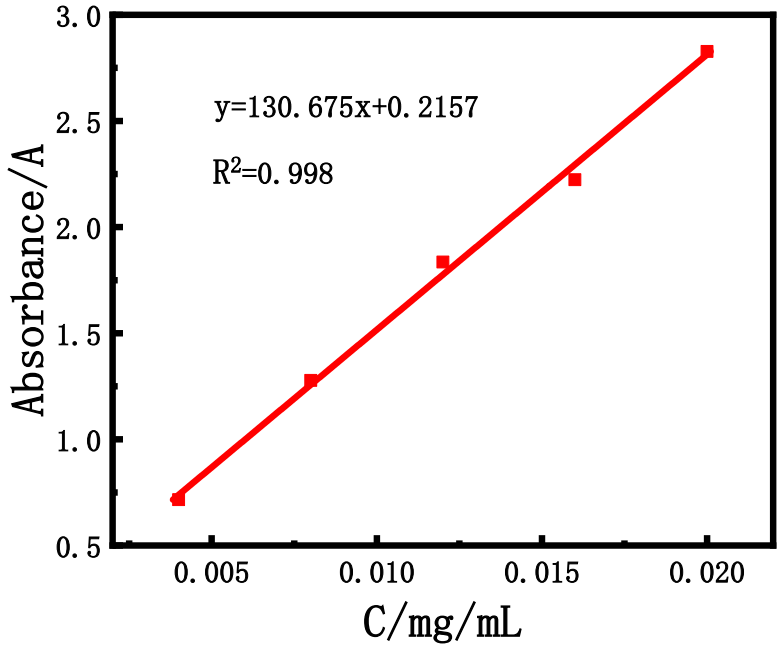


Figure S1. Standard curve of formaldehyde content

Determination of formaldehyde content in the reaction solution

Photocatalytic degradation experiments were carried out by preparing 0.5mg/mL of aqueous formaldehyde solution as the reaction solution and 2.5g/L of catalyst, which was irradiated in a mercury lamp. During the degradation, a 0.50mL sample of the reaction solution was removed

according to a predetermined time gradient. It was transferred over to a liquid sampling bottle and the formaldehyde in the reaction solution was quantified using the acetylacetone UV spectrophotometer method. The procedure was as follows: 0.24ml of the filtered reaction solution was accurately pipetted, 1.00ml of acetylacetone buffer (0.25%, wt) was added to it, the volume was fixed to 10.00ml with deionised water, heated at 91°C in a water bath for 6min and then removed, and the UV absorbance of the reaction solution was measured after it had cooled to room temperature.

Table S1. Standard card information for Bi-based catalysts and SAPO-34 molecular sieves

	JCPDS	**2-Theta（°）**
$BiVO_4$	83-1700	18.98、18.67、28.81、28.95、30.53、35.21、46.72、53.28、59.67
Bi_2WO_6	73-112	28.31、32.80、32.93、46.98、47.16、55.68、56.00
BiOI	73-2062	9.68、29.74、31.74、45.49、51.49、55.3
SAPO-34	47-0429	9.5、13.0、16.2、20.7、26.0、31.0

Table S2. Pore size and specific surface area of composite molecular sieve catalysts

	Surface Area (m²/g)	**Pore Volum (cm³/g)**	**Pore Size (nm)**
$BiVO_4$	5.4018	0.01576	24.4777
Bi_2WO_6	4.0925	0.01493	25.5395
BiOI	25.9333	0.12746	20.7095
SAPO-34	946.4700	0.47058	1.98878
$BiVO_4$ @ SAPO-34	287.6750	0.15569	2.16485
$BiVO_4$ - SAPO-34	462.1212	0.23708	2.05209
$BiVO_4$ / SAPO-34	387.2077	0.19556	2.02023
Bi_2WO_6 @ SAPO-34	326.8095	0.29904	3.6601
BiOI @ SAPO-34	353.6933	0.16684	1.8869

Table S3. Band gap of composite molecular sieve catalysts

	Eg（eV）
$BiVO_4$	2.06
Bi_2WO_6	2.56
BiOI	1.68
SAPO-34	-----
$BiVO_4$ @ SAPO-34	2.21
$BiVO_4$ - SAPO-34	2.08
$BiVO_4$ / SAPO-34	2.02
Bi_2WO_6 @ SAPO-34	2.92
BiOI @ SAPO-34	1.68

Table S4. ICP-AES of composite molecular sieve catalyst $BiVO_4$@SAPO-34

Sample quality m_0（g)	**Constant volume V_0（mL)**	**Test element**	**Test solution element concentration Co（mg/L)**	**Dilution ratio f**	**Sample element content Cx（mg/kg)**	**Sample element content W（%)**
0.0540	25	Si	2.665	10	12336.9	1.23%
0.0540	25	Al	1.202	100	55651.0	5.57%
0.0540	25	Bi	3.845	100	177997.0	17.80%
0.0540	25	P	3.105	100	143753.3	14.38%
0.0540	25	V	2.153	100	99693.6	9.97%

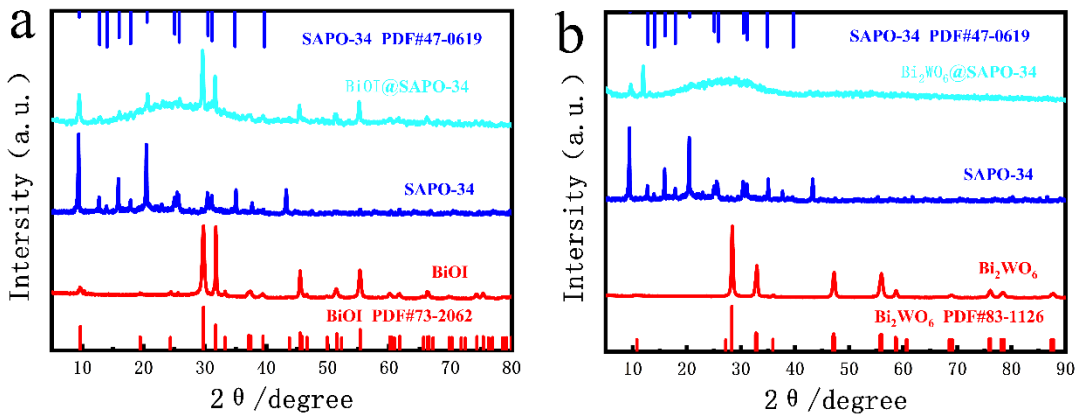


Figure S2. XRD patterns of BiOI, BiOI@SAPO-34 catalysts (a); Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts

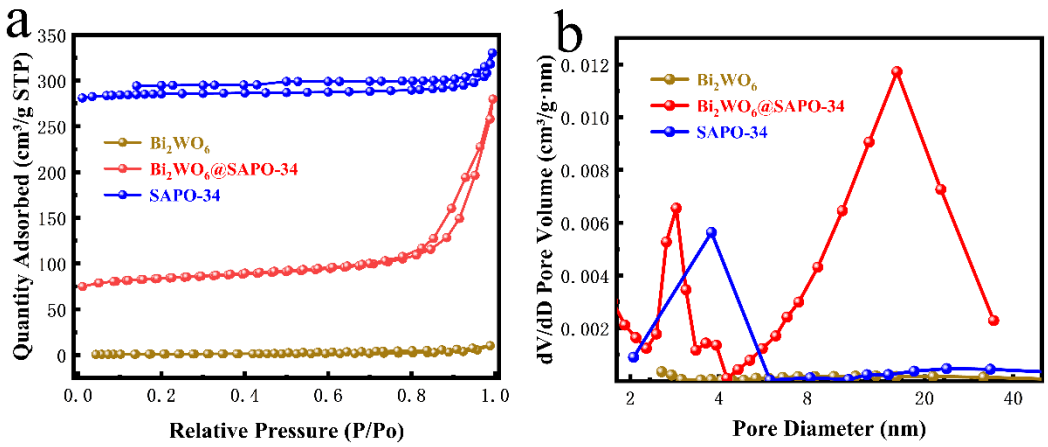


Figure S3. Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts and N_2 adsorption and desorption profiles (a) pore size distribution (b)

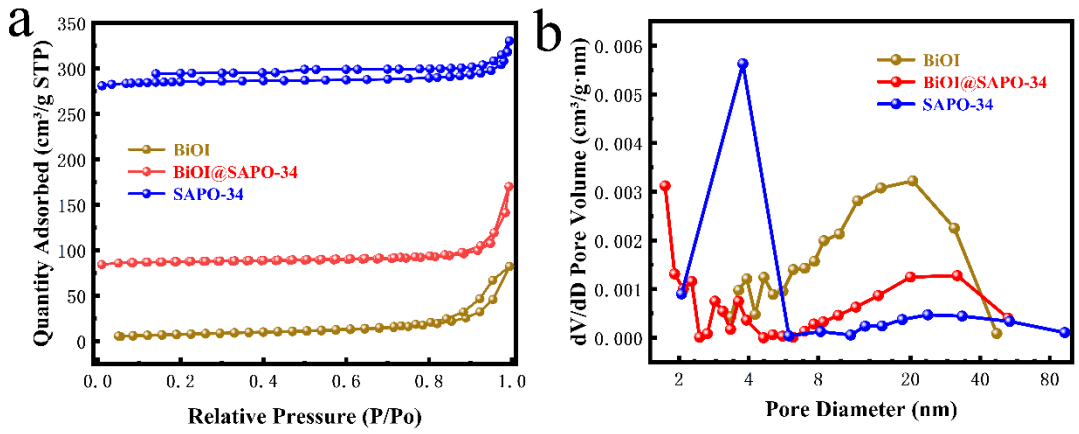


Figure S4. Plots of BiOI, BiOI@SAPO-34 catalysts and N_2 uptake and desorption curves (a) pore size distribution (b)

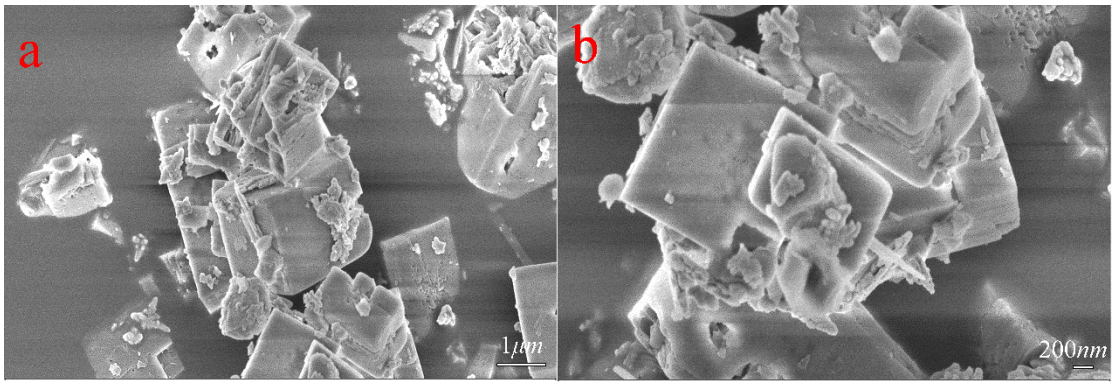


Figure S5. Scanning electron micrograph of $BiVO_4$ / SAPO-34 composite molecular sieve catalyst

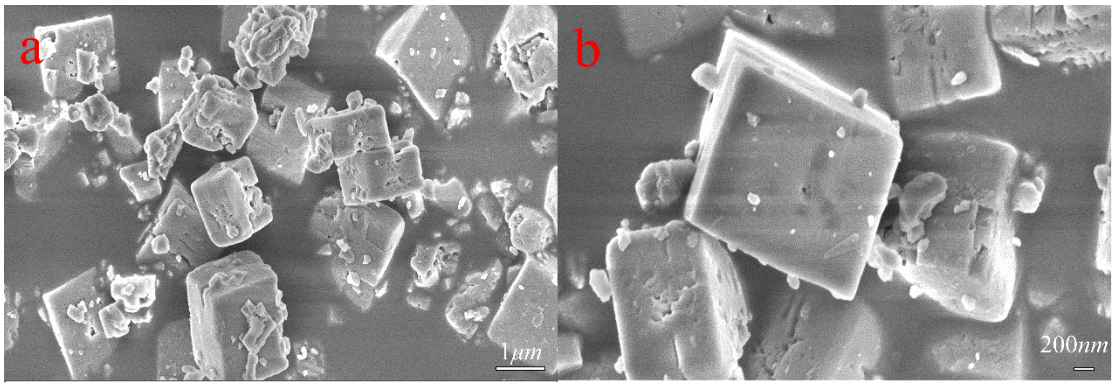


Figure S6. Scanning electron micrograph of $BiVO_4$ - SAPO-34 composite molecular sieve catalyst

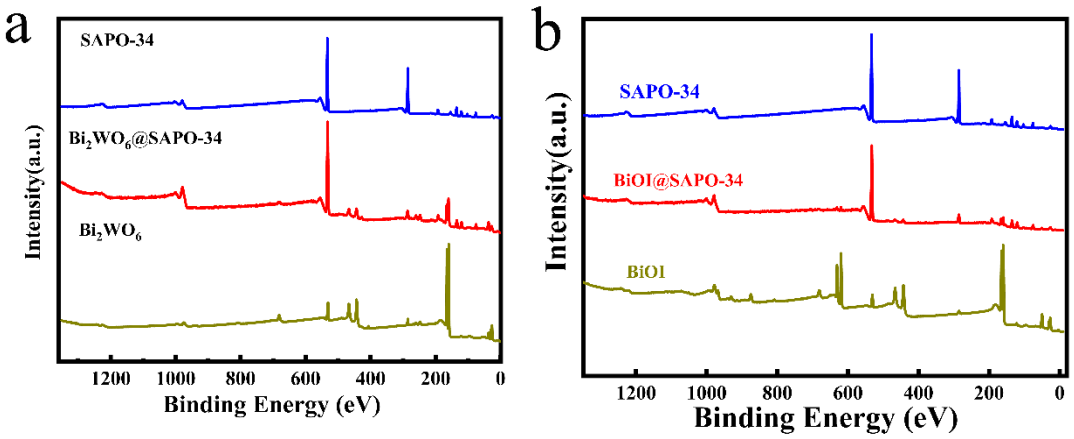


Figure S7. XPS patterns of Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts (a); XPS patterns of BiOI, BiOI@SAPO-34 catalysts (b)

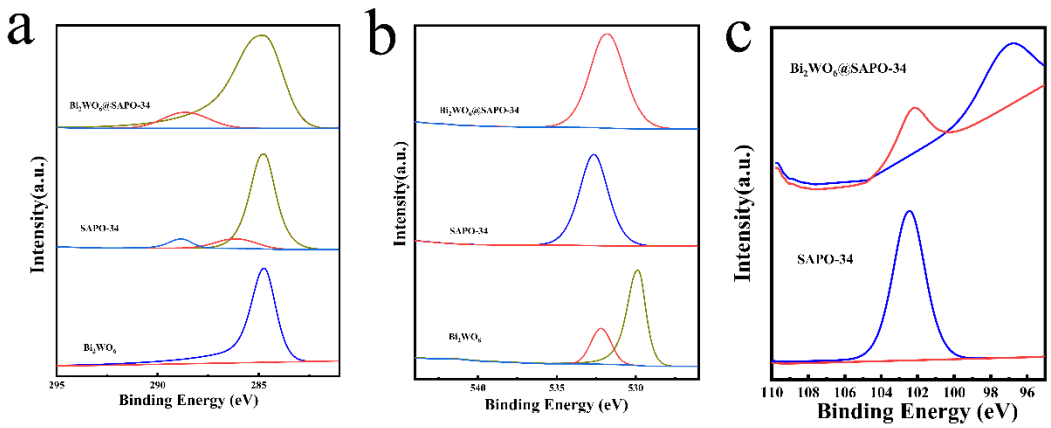


Figure S8. XPS fine spectra of Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts C1s (a); O1s (b); Si3n (c)

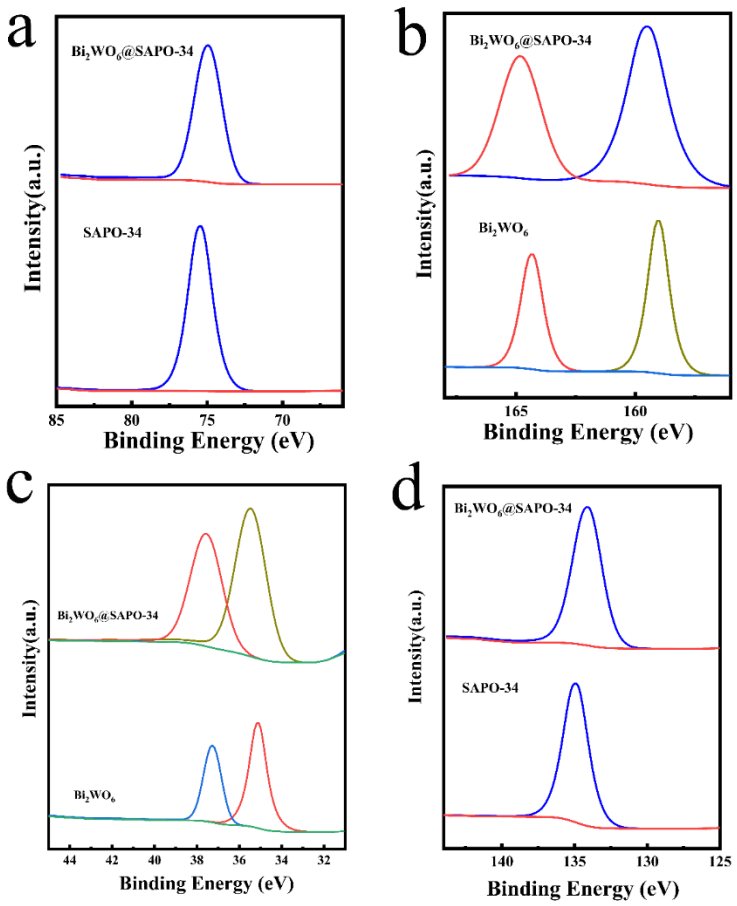


Figure S9. XPS fine spectra of Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts Al2p (a); Bi4f (b); I3d (c); P2p (d)

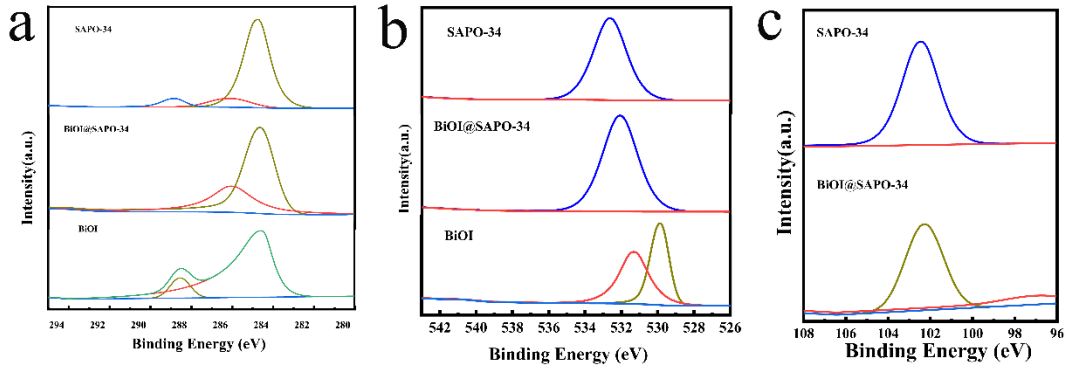


Figure S10. XPS fine spectra of BiOI, BiOI@SAPO-34 catalysts C1s (a); O1s (b); Si3n (c)

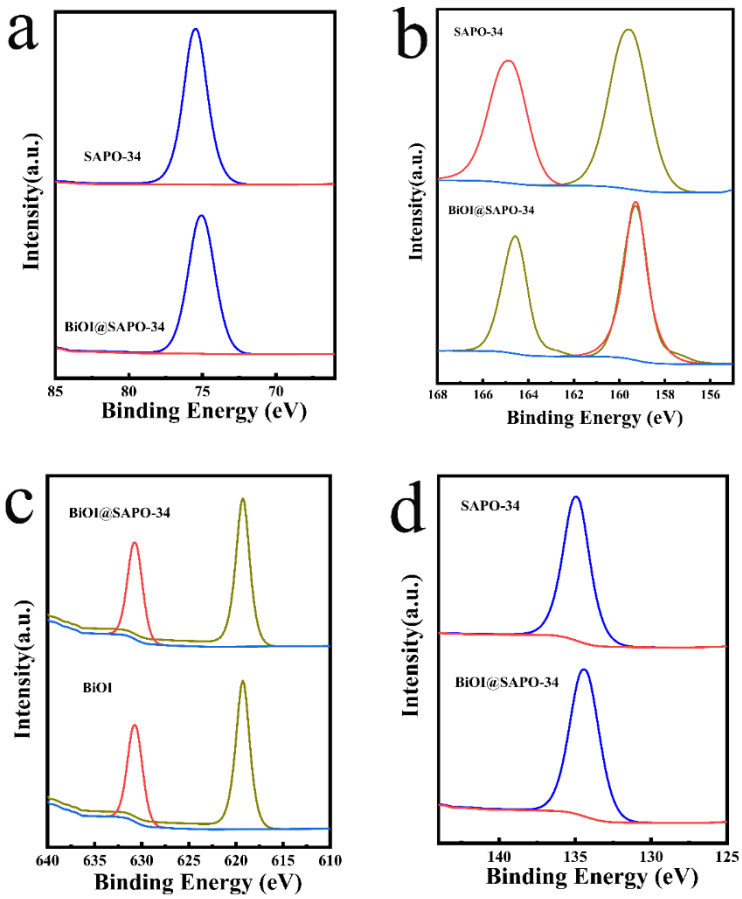


Figure S11. XPS fine spectra of BiOI, BiOI@SAPO-34 catalysts Al2p (a); Bi4f (b); I3d (c); P2p (d)

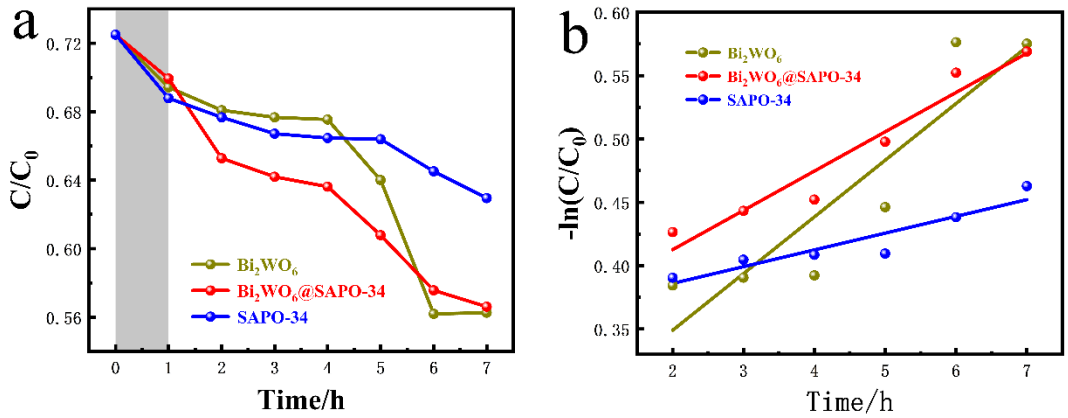


Figure S12. Degradation of aqueous formaldehyde solutions by Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts under mercury lamp conditions

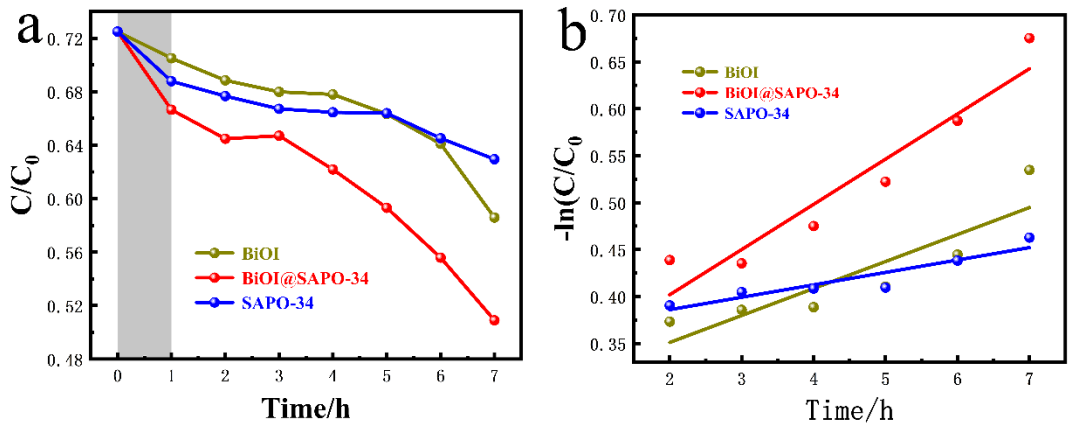


Figure S13. Degradation of aqueous formaldehyde solutions by BiOI, BiOI@SAPO-34 catalysts under mercury lamp conditions

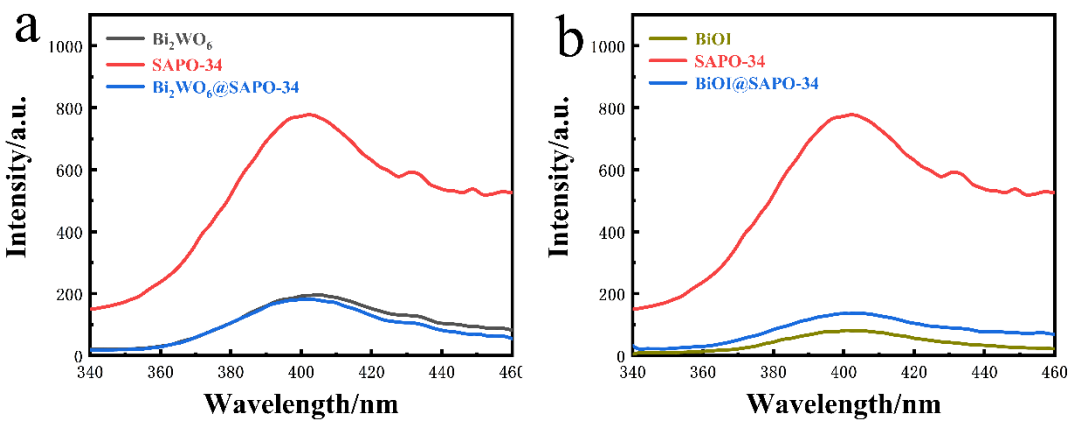


Figure S14. PL profiles of Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts (a); PL profiles of BiOI, BiOI@SAPO-34 catalysts (b)

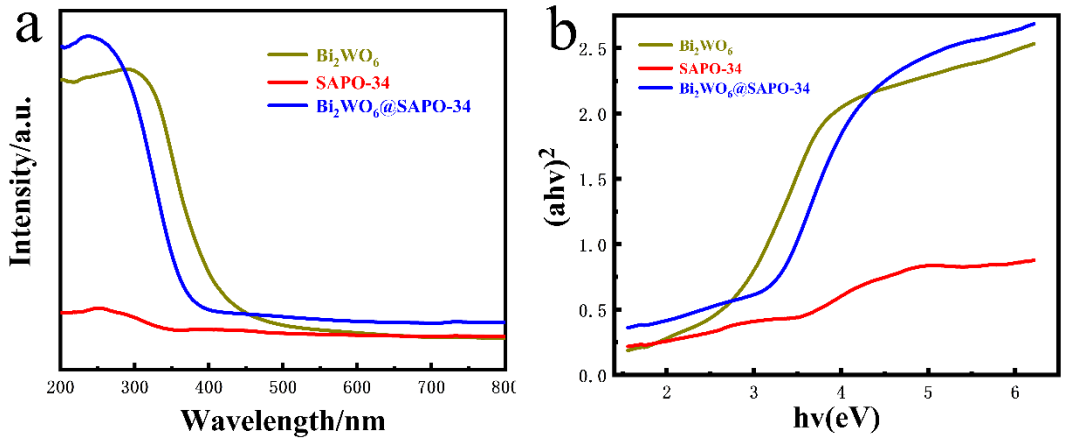


Figure S15. UV-Vis spectra of Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts

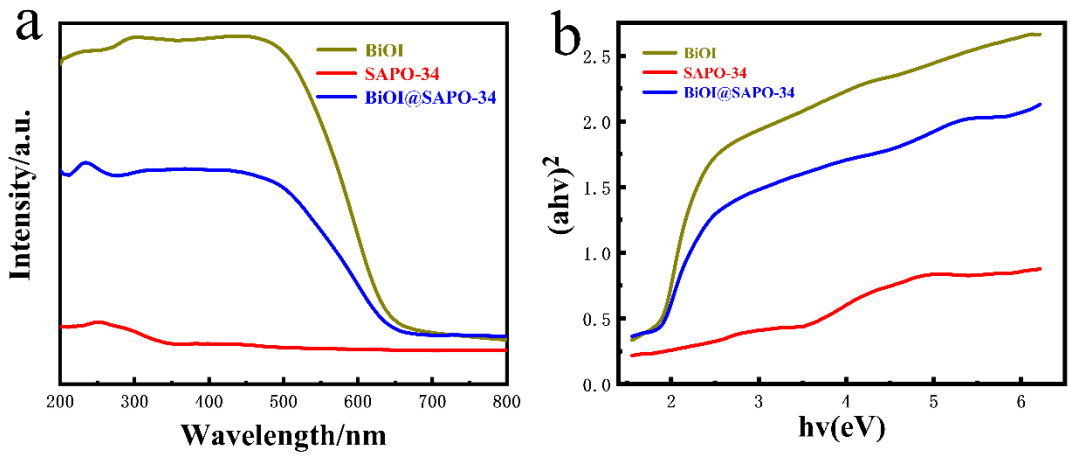


Figure S16. UV-Vis spectra of BiOI, BiOI@SAPO-34 catalysts

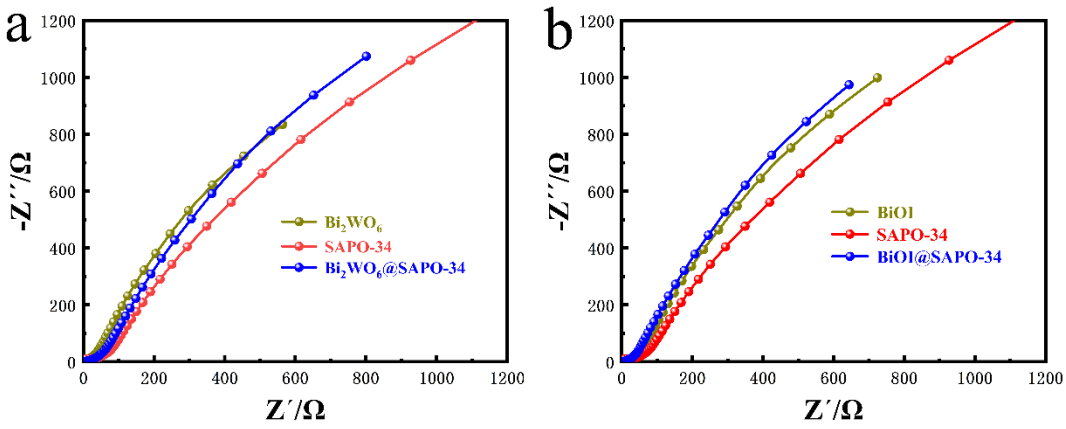


Figure S17. EIS profiles of Bi_2WO_6, Bi_2WO_6@SAPO-34 catalysts (a); EIS profiles of BiOI, BiOI@SAPO-34 catalysts (b)

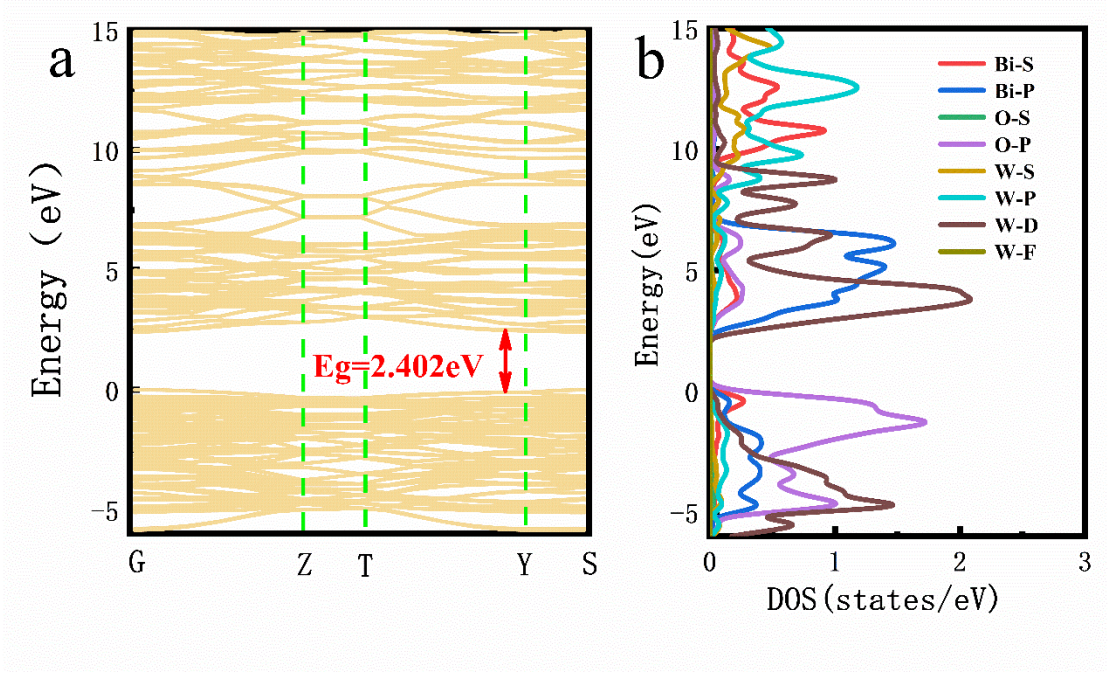


Figure S18. Energy band structure diagram of the Bi_2WO_6 catalyst (a); PDOS (b)

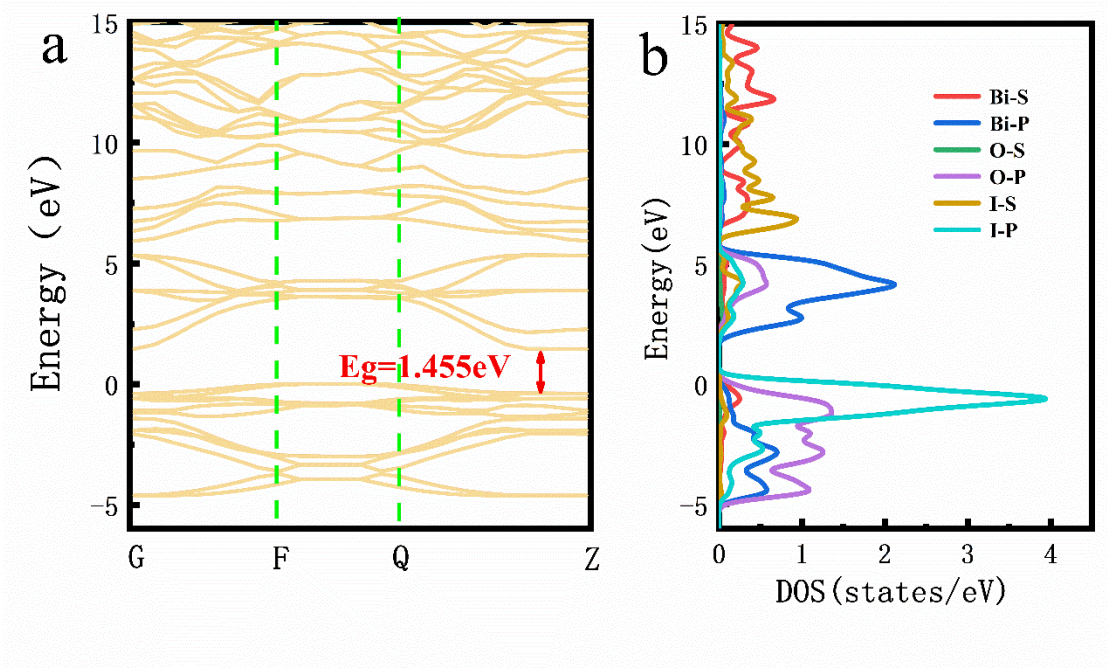


Figure S19. Energy band structure diagram of the BiOI catalyst (a); PDOS (b)

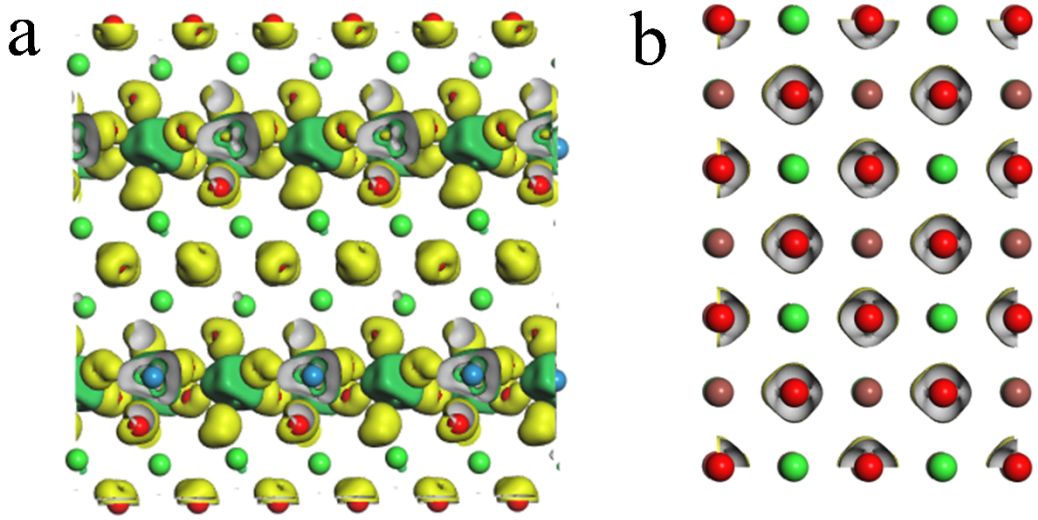


Figure S20. Differential charge diagram for Bi_2WO_6 catalyst (a); differential charge diagram for BiOI catalyst (b)

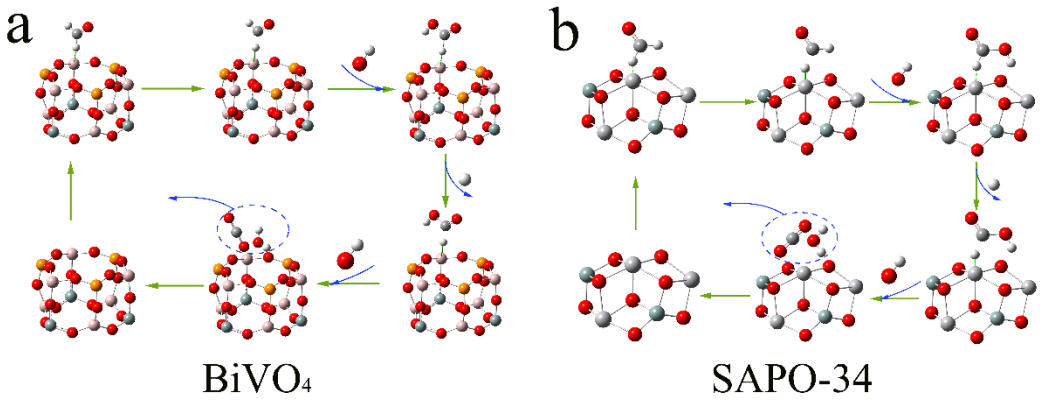


Figure S21. Reaction history of formaldehyde molecules on the surface of $BiVO_4$ catalyst (a); reaction history of formaldehyde molecules on the surface of SAPO-34 molecular sieve (b)

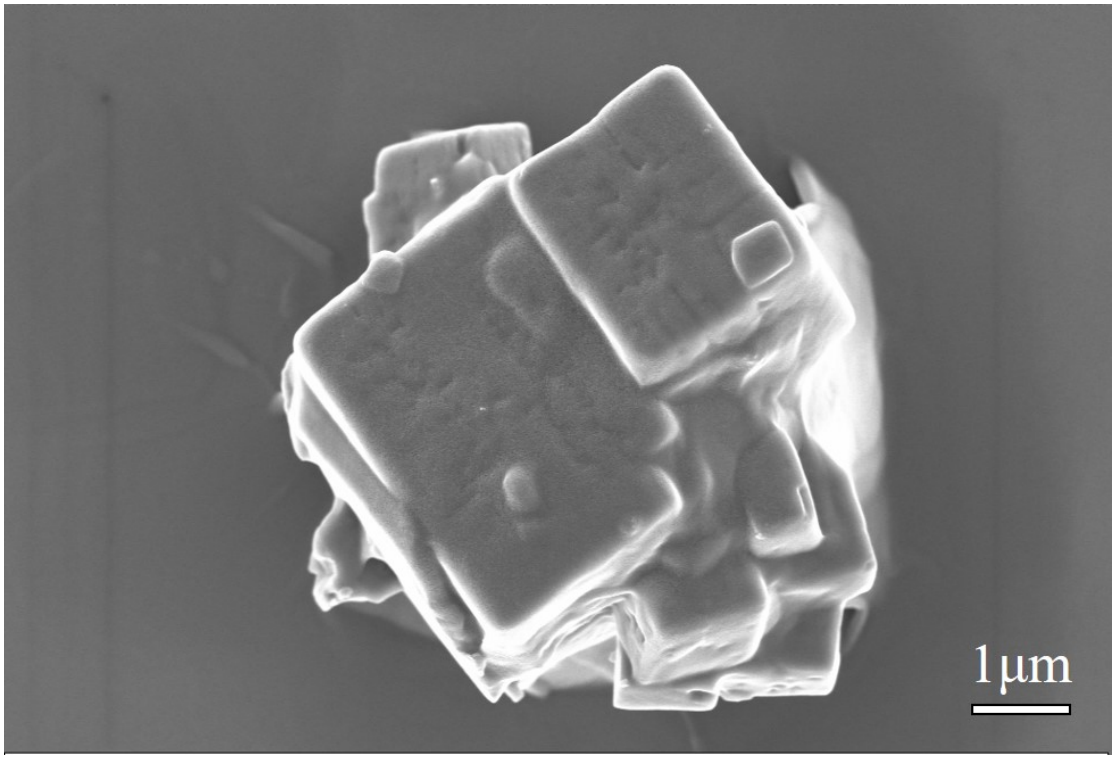


Figure S22. SEM after the reaction of composite molecular sieve catalyst $BiVO_4$@SAPO-34

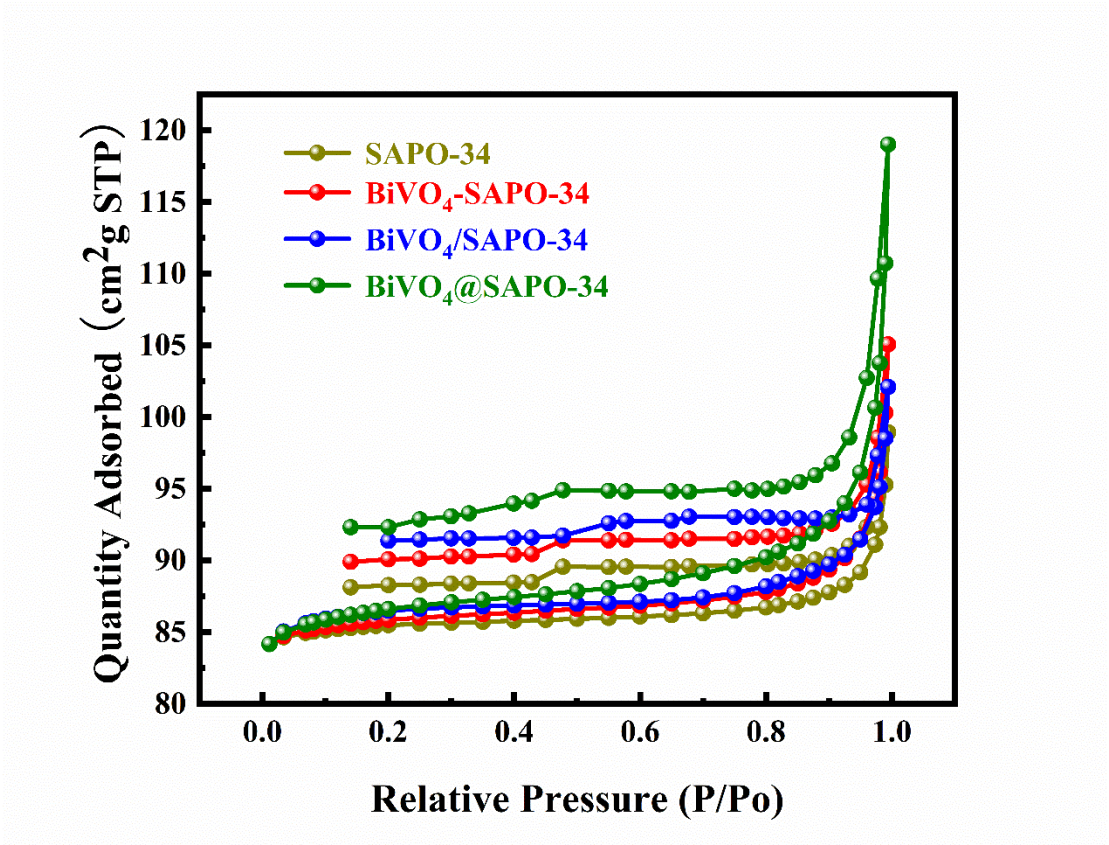


Figure S22. N_2 adsorption and desorption curves of the composite molecular sieve catalysts

Energies and Cartesian Coordinates (Å) for the Optimized Structures

SAPO34

B3lyp/6-31g SCF energy: -19259.464892 Hartree

Si	-4.116833	-3.333605	-4.840575
Al	-3.731218	0.798182	5.159898
O	-2.461527	-2.924525	-5.045385
O	-5.029140	-2.784845	3.935800
O	-4.057263	-0.831396	5.544152
O	-2.159888	3.951335	-3.933962
P	-0.507794	4.487039	-3.834304
Al	-1.013997	5.239967	-0.733639
O	-0.679136	5.477544	-2.418633
O	0.196027	-4.203438	-1.205140
Si	-4.114320	5.863724	-0.464125
Al	-3.733864	-4.866583	-1.890415
O	-2.458989	5.828753	-0.005421
O	-5.034558	-2.013257	-4.379593
O	-4.063798	-4.384880	-3.493438
O	0.192986	3.147682	-3.053666
O	-2.151404	1.427562	5.385572
P	-0.498371	1.076969	5.795173
Al	-1.007786	-1.978045	4.907348
O	-0.667028	-0.643438	5.961946
Si	-4.108633	-2.524547	5.308013
Al	-3.737014	4.074942	-3.268617
O	-2.453243	-2.902128	5.051073
O	-5.036727	4.804957	0.445398
O	-4.061766	5.221814	-2.048685
P	-0.501101	-5.556183	-1.968422
Al	-1.014164	-3.258597	-4.174439
O	-0.673289	-4.835808	-3.538706
O	0.198142	1.055082	4.241725
O	-2.154619	-5.380486	-1.459037
O	0.071066	4.232452	0.149566
Al	1.446777	-3.246958	-0.458708
O	0.851755	-2.178123	0.850999
Si	1.204797	-1.978394	2.438069
O	2.121569	-0.496227	2.819951
Al	3.710589	-2.126674	-2.826140
O	2.723294	2.440317	3.347053
O	2.695903	-1.028604	-3.885082
O	4.886803	0.372544	-4.616221
P	3.299459	3.981289	3.023185
Al	1.438524	2.021219	-2.594047
O	0.841472	0.354339	-2.320572
Si	1.196701	-1.120939	-2.936167
O	2.109190	-2.193241	-1.840319
O	0.072848	-2.241239	3.590828
Al	3.717028	3.518369	-0.432699
O	2.722906	-4.116378	0.437862
O	2.703695	3.879426	1.051087
O	4.894068	3.807925	2.637678
P	3.291268	-4.610651	1.936329
Si	1.206057	3.104068	0.494783
O	2.116440	2.699672	-0.984893
O	0.066738	-1.986629	-3.744174
Al	1.448439	1.228031	3.041178
O	0.855557	1.829062	1.461160
P	3.293370	0.622623	-4.960570
Al	3.717999	-1.388579	3.256144
O	2.720140	1.674982	-3.787380
O	2.699959	-2.851863	2.832565
O	4.886339	-4.194763	1.983502
Al	-9.194107	1.781639	-2.328363
O	-9.845526	2.729100	-1.052215
O	-9.819222	0.291428	-2.903326
Si	-9.425306	3.457842	0.447056
O	-7.748701	3.542846	0.438102
Al	6.044513	0.245987	-3.234281
O	5.830855	1.643622	-2.233812
O	4.714835	-3.617848	-2.731673
O	5.317242	-1.267131	-2.503499
Si	6.033022	3.088862	-1.486336
O	7.628443	3.523577	-1.427244
O	-7.548443	-3.572002	-0.484188
P	-5.945040	-3.213026	-0.412582
Al	-6.013245	-2.060507	2.685229
O	-5.572350	-2.708519	1.066873
O	-5.580445	-0.286003	2.596808
O	-5.035078	1.634998	4.315045
O	7.743526	-3.029927	1.804635
P	9.424068	-3.221156	1.563993
Al	9.119789	-0.297758	2.862961
O	9.909478	-1.705797	2.253105

O 9.531002 1.316185 2.481140
Al -9.191021 1.117812 2.717243
O -9.847056 -0.457859 2.908880
O -9.812992 2.358228 1.708795
Si -9.420390 -2.119963 2.785034
O -7.741868 -2.140394 2.848566
O -7.552391 2.205945 -2.850975
P -5.948513 1.966695 -2.574441
Al -6.018217 -1.292535 -3.125995
O -5.576457 0.432825 -2.875531
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O -5.037921 -4.553054 -0.743727
Al 6.047559 2.676907 1.827672
O 5.826787 1.105575 2.522253
O 4.724125 4.181404 -1.770037
O 5.321582 2.810482 0.153733
Si 6.032275 -0.259826 3.406709
O 7.628306 -0.519913 3.756181
O 7.740501 -0.051494 -3.504234
P 9.420534 0.254479 -3.568284
Al 9.110038 -2.330502 -1.698786
O 9.914146 -1.105875 -2.612727
O 9.509798 -2.799519 -0.105827
Si -9.425542 -1.351648 -3.222000
O -7.746945 -1.392908 -3.275330
Al -9.191344 -2.908725 -0.379271
O -9.846279 -2.283672 -1.838797
O -9.811583 -2.658135 1.199930
Si 6.026758 -2.829915 -1.929316
O 7.620951 -2.996679 -2.339798
P -5.944436 1.248957 2.991115
Al -6.019602 3.359523 0.445473
O -5.578870 2.278681 1.813240
O -5.591514 2.393919 -1.046735
O -5.041891 2.924830 -3.567971
Al 6.049097 -2.936932 1.406776
O 5.831907 -2.762649 -0.302833
O 4.723816 -0.555325 4.496164
O 5.324534 -1.547293 2.352472
O -7.547660 1.361072 3.341369
P 9.424843 2.970623 2.007310
Al 9.115619 2.633263 -1.164637
O 9.920141 2.817332 0.352465
O 9.517676 1.484821 -2.363977
O 7.744740 3.053120 1.704297