

Supporting Information

Mo₂C Catalyst Leads to Highly Efficient Hydrogen Transfer of Alcohols and Amines to Synthesize N-alkylamines

Yimei Chen,^a Zhe Wang,^a Zhouyang Long,^{*,b} Yunfei Wang,^a Pingbo Zhang,^a Yan Leng ^{*,a}

^a The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu, China. E-mail: yanleng@jiangnan.edu.cn

^b Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou 221116, China.

Experimental section

Synthesis of TMC-based catalysts

The Mo-containing metal-organic hybrid was prepared by ball milling of tannin (1.0 g) and MoCl₅ (0.3 g) for 30 min. The hybrid was carbonized in nitrogen to yield the black solid sample Mo₂C@C₉₀₀ (from ambient temperature to 400°C at 5°C/min and maintained at 400°C for 1 h, then from 400°C to 900°C at 5°C/min and maintained at 900°C for 2 h). MoO₂@C₆₀₀ and Mo₂C-MoO₂@C₈₀₀ were prepared based on the same method with the maximum calcination temperature of 600°C and 800°C, respectively. WC and NbC were prepared accordingly by using WCl₆ and NbCl₅ as the metal precursors, respectively.

Characterization

X-ray diffraction (XRD) patterns were collected on the Bruker D8 Advance powder diffractometer using Ni-filtered Cu/K α radiation at 40 kV and 20 mA, from 5° to 90° with a scan rate of 5°/min. Transmission electron microscope (TEM) images were obtained with a JEOL JEM-2100 electron microscope operated at 200 kV. Hydrogen temperature-programmed desorption (H₂-TPD) was carried out with a BELCAT- II chemisorption instrument from 50° C to 800° C. X-ray photoelectron spectroscopy (XPS) was conducted with an Axis supra X-ray photoelectron spectrometer equipped with an Al K α radiation source to analyze the chemical environment of each element in the sample. Nitrogen adsorption-desorption analysis was carried out to determine the specific surface area and porous structure of the catalysts using an ASAP2460 fully automated specific surface and porosity analyzer at a temperature of 77 K in liquid nitrogen.

Catalytic tests

Hydrogen transfer coupling of amines and alcohols. A mixture of amine (1 mmol), alcohol (2 mmol), catalyst (20 mg), base (1 mmol), and solvent (1 mL) was added to a pressure tube. Then the tube was purged with nitrogen gas and sealed with a PTFE plug. The reaction was stirred in an oil bath at 150°C for 24 h. On completion, the reaction mixture was cooled to room temperature, the catalyst was filtered off, and the liquid was analyzed by GC-FID (GC 9720). The recovered catalyst was directly used in the next run to test its stability.

Benzyl alcohol dehydrogenation. A mixture of benzyl alcohol (2 mmol), catalyst (20 mg), and xylene (4 mL) was added to a distillation flask. The reaction was then refluxed at 120°C for 6 hours. On completion, the reaction mixture was cooled to room temperature, the catalyst was filtered off, and the liquid was analyzed by GC-FID.

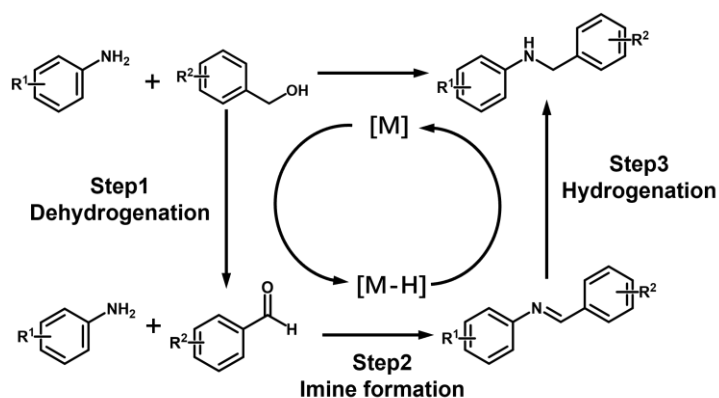
Synthesis of N-benzylideneaniline. A mixture of aniline (1 mmol), benzaldehyde (1 mmol), and toluene (1 mL) was added to a pressure tube. Then the tube was purged with nitrogen and sealed with a PTFE plug. The reaction was stirred in an oil bath at 150 °C for 1 h. On completion, the reaction mixture was cooled to room temperature, and the liquid was analyzed by GC-FID.

Synthesis of N-benzylaniline. A mixture of benzyl alcohol (1 mmol), N-benzylaniline (1 mmol), catalyst (20 mg), and toluene (1 mL) was added to a pressure tube. Then the tube was purged with nitrogen and sealed with a PTFE plug. The reaction was stirred in an oil bath at 150 °C for 8 h. On completion, the reaction mixture was cooled to room temperature, the catalyst was filtered off, and the liquid was analyzed by GC-FID.

Details for DFT calculations

Density functional theory (DFT) calculations in this work were carried out using ORCA (version: 5.0.3), DFT calculations details: Geometry optimization and vibrational frequency calculations were conducted at the B3LYP/def2-SVP (with

DFT-D3 correction) level of theory.¹ The single point calculations for the optimized geometries were performed to obtain accurate energies at the B3LYP/def2-TZVP (with DFT-D3 correction) level of theory level of theory. The RIJCOSX approximation was applied with the def2/J auxiliary basis set.² The solvent effect of toluene was evaluated by the CPCM solvation model. The Gibbs free energies were included in the Gibbs energy correction of unscaled vibrational analysis at the B3LYP/def2-SVP (with DFT-D3 correction) level of theory.



Catalysts for previous:

- (1) Precious metal catalysts: Ru/CeO₂-R, Co₂Rh₂/C, PdCl₂/dppe, etc
- (2) Transition metal catalysts: Ni/θ-Al₂O₃, Fe₂₀-SA@NSC, Cu/CeO₂-P, etc
- (3) Metal organic catalysts: Zn(La)Cl₂, W(phen)(CO)₄, Co(II)-NNN, etc

Catalysts for this work:

Carbonised metal catalyst: Mo₂C

Scheme S1. Hydrogen borrowing (hydrogen transfer) mechanism for N-alkylation of amines with alcohols (M = transition metal) based on catalysts.

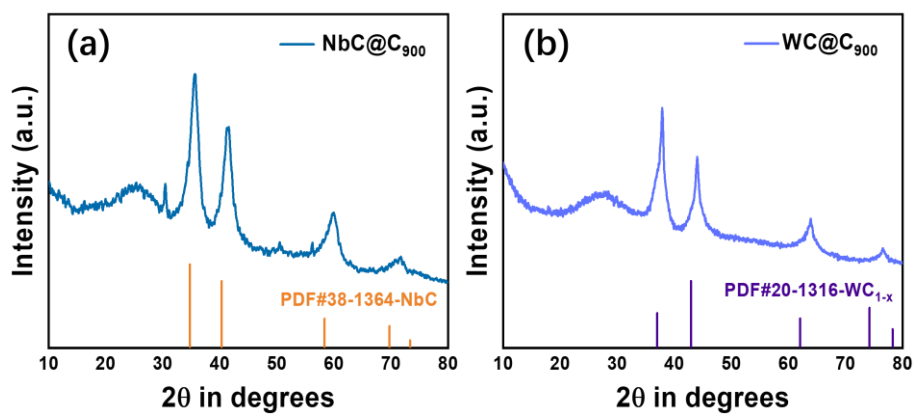


Figure S1. XRD patterns of (a) NbC@C₉₀₀ and (b) WC@C₉₀₀.

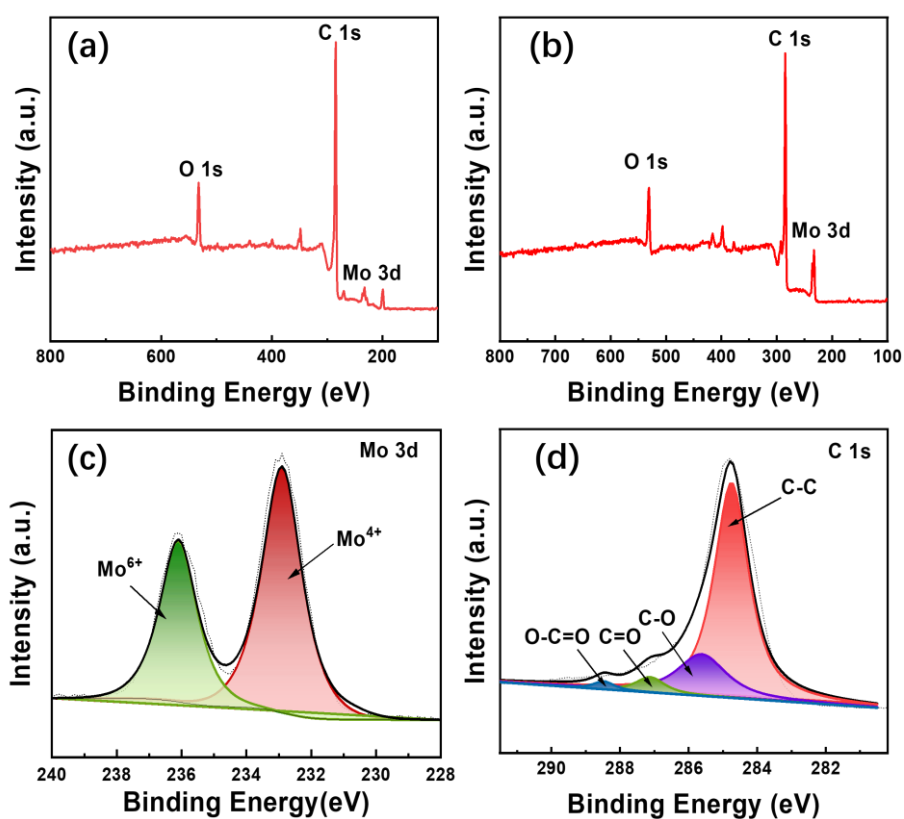


Figure S2. (a) XPS spectrum of Mo₂C@C₉₀₀, (b) XPS spectrum of Mo₂C-MoO₂@C₈₀₀, (c) Mo 3d and (d) C 1s XPS spectra of Mo₂C-MoO₂@C₈₀₀.

Table S1. Results of catalytic performance of hydrogen transfer reactions over various reported catalysts.

Catalyst	Reaction condition	Con (%)	Sel (%)	Yield (%)	Ref.
MnCl ₂	catalyst 10 mol%, PPh ₃ 20 mol%, benzyl alcohol 1.2 equiv, aniline 1 mmol, KOt-Bu 1.2 equiv, PhMe 2 mL, N ₂ , 130°C, 20 h.			82	3
TiOH	catalyst 0.1 g, benzyl alcohol 4.62 mmol, aniline 21.5 mmol, xylene 2 g, N ₂ , 180°C, 15 h.			99.6	4
TiO ₂	catalyst 10mol%, benzyl alcohol 1.3 equiv, aniline 0.35 mmol, KOH 0.27 mmol, toluene 1.0 mL, 140°C, 24 h.			99	5
Zn(La)Cl ₂	catalyst 3.0 mol%, benzyl alcohol 1.2 mmol, aniline 1.0 mmol, KOt-Bu 0.5 equiv, toluene 3 mL, Ar, 120°C, 16 h.			78	6
NiBr ₂	catalyst 0.025 mmol, L1 0.05 mmol, benzyl alcohol 1.0 mmol, aniline 0.25 mmol, KOt-Bu 0.25 mmol, toluene 2.0 mL, N ₂ , 130°C, 48 h.	99		96	7
Ni(COD) ₂	catalyst 3 mol%, benzyl alcohol 1.5 equiv, aniline 0.5 mmol, KOH 0.3 equiv, CPME 2.0 mL, Ar, 140°C, 18 h.	>99	>99		8
Cat-6	catalyst 0.05 mmol, benzyl alcohol 0.6 mmol, aniline 0.5 mmol, KOt-Bu 0.5 mmol, 1,4-dioxane 1.0mL, N ₂ , 130°C, 24 h.	98		95	9
Zn(NO ₃) ₂ ·6H ₂ O	catalyst 15.0 mol%, benzyl alcohol 1.5 mmol, aniline 1.0 mmol, KOt-Bu 1.00 mmol, toluene 1.5 mL, N ₂ , 140°C, 36 h.	100		98	10
Fe ₂₀ -SA@NSC	catalyst 0.02 g, benzyl alcohol 6 mmol, aniline 3 mmol, KOH 0.3 equiv, Ar, 135°C, 24 h.			94	11
Cu/CeO ₂ -P	catalyst 0.05 g, benzyl alcohol 1.2 mmol, aniline 1.0 mmol, toluene 2 mL, Ar, 160°C, 12 h.	>99	88	88	12
Ni/θ-Al ₂ O ₃	catalyst 1 mol%, benzyl alcohol 1.2 mmol, aniline 1.0 mmol, o-xylene 1.5 g, reflux, 144°C, 3 h.	100		99	13
Ni _{9,5} /NC	catalyst 0.1 g, benzyl alcohol 2 mmol, aniline 1 mmol, toluene 10 mL, Ar 1 bar, 160°C, 4 h.	99	92		14
Ni/Ru@SBA	catalyst 3 mol%(Ni), benzyl alcohol 0.5 mmol, aniline 0.5 mmol, neat toluene 2 mL, 120°C, 24 h.	99		99	15
Ru/CeO ₂ -R	catalyst 0.2 g, benzyl alcohol 6 mmol, aniline 2 mmol, p-xylene 2 mL, N ₂ , 160°C, 24 h.	99	88		16
Cu ₂ /NPC-550	catalyst 0.05 g, benzyl alcohol 1 mmol, aniline 0.5 mmol, cyclohexane 3 mL, KOH 0.03g, Ar, 140°C, 12 h.	100	95		17
Mo ₂ C@C ₉₀₀	catalyst 0.025 g, benzyl alcohol 2 mmol, aniline 1 mmol, KOH 1mmol, toluene 1 mL, N₂, 150°C, 24 h.	>99	>99		This work

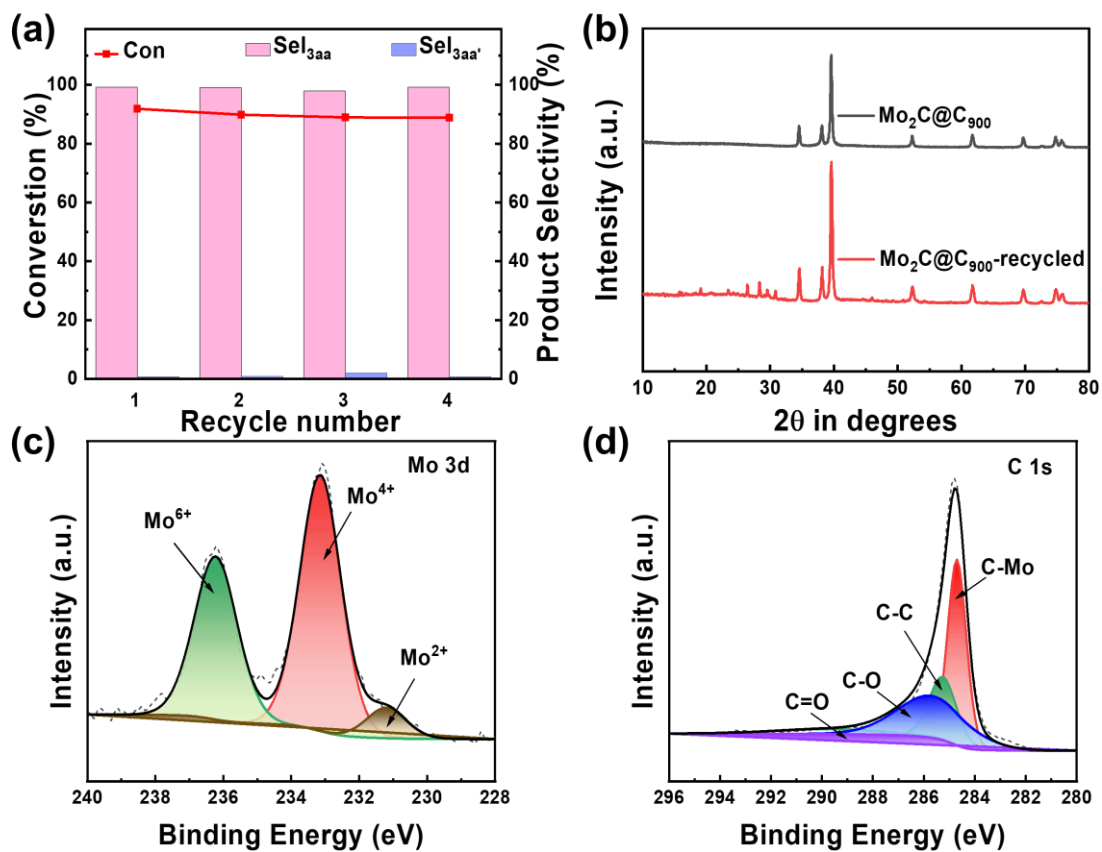
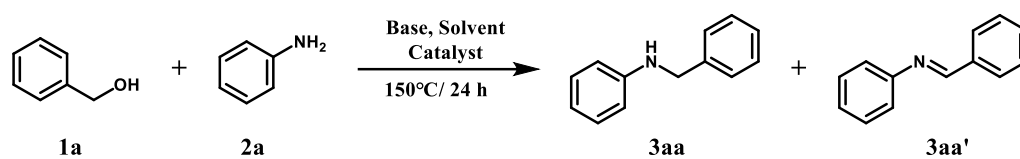


Figure S3. (a) Reusability of $\text{Mo}_2\text{C}@C_{900}$ -catalyzed hydrogen transfer coupling of benzyl alcohol and aniline, (b) XRD patterns of fresh $\text{Mo}_2\text{C}@C_{900}$ and recycled $\text{Mo}_2\text{C}@C_{900}$. (c) Mo 3d and (d) C 1s XPS spectra of recycled $\text{Mo}_2\text{C}@C_{900}$.

Table S2. Optimization of reaction conditions.^a

Entry	Catalyst	Base and amount (mmol)	Solvent	Ratio ^b	Con ^c (%)	Sel ^c (%)		
						3aa	3aa'	Others
1	Mo ₂ C@C ₉₀₀	KOH (0.3)	toluene	2.0:1	34.6	92.1	7.0	0.9
2	Mo ₂ C@C ₉₀₀	KOH (0.5)	toluene	2.0:1	64.3	95.3	4.4	0.3
3	Mo ₂ C@C ₉₀₀	KOH (0.7)	toluene	2.0:1	82.2	98.3	1.4	0.3
4	Mo ₂ C@C ₉₀₀	KOH (1)	toluene	2.0:1	92.7	99.2	0.8	0.0
5	Mo ₂ C@C ₉₀₀	NaOH (1)	toluene	2.0:1	16.6	79.4	18.1	2.5
6	Mo ₂ C@C ₉₀₀	t-KOBu (1)	toluene	2.0:1	50.8	96.8	2.7	0.5
7	Mo ₂ C@C ₉₀₀	K ₂ CO ₃ (1)	toluene	2.0:1	1.7	12.2	65.1	22.7
8	Mo ₂ C@C ₉₀₀	KOH (1)	xylene	2.0:1	40.5	92.9	5.9	1.2
9	Mo ₂ C@C ₉₀₀	KOH (1)	1,4-dioxane	2.0:1	25.3	90.0	9.3	0.6
10	Mo ₂ C@C ₉₀₀	KOH (1)	/	9.2:1	38.6	76.5	7.2	16.3
11	Mo ₂ C@C ₉₀₀	KOH (1)	toluene	1.2:1	46.2	95.9	4.1	0.0
12	Mo ₂ C@C ₉₀₀	KOH (1)	toluene	1.5:1	72.6	99.0	0.9	0.1
13 ^d	Mo ₂ C@C ₉₀₀	KOH (1)	toluene	2.0:1	99.2	99.5	0.5	0.0
14 ^e	Mo ₂ C@C ₉₀₀	KOH (1)	toluene	2.0:1	47.0	95.9	3.5	0.6
15 ^f	Mo ₂ C@C ₉₀₀	KOH (1)	toluene	2.0:1	97.0	99.5	0.5	0.0
16	Mo ₂ C@C ₉₀₀	/	toluene	2.0:1	12.1	50.2	40.0	9.8
17	-	KOH (1)	toluene	2.0:1	21.9	68.8	28.8	2.4

^a Reaction conditions: 1a (2 mmol), 2a (1 mmol), base (1 mmol), Mo₂C@C₉₀₀ (0.02 g), solvent (1 mL), at 150°C for 24 h. ^b Reaction uses different molar ratios of benzyl alcohol and aniline. ^c Conversion and selectivity were determined by GC analysis. ^d Mo₂C@C₉₀₀ (0.025 g). ^e Mo₂C@C₉₀₀ (0.02 g), at 140°C for 24 h. ^f Mo₂C@C₉₀₀ (0.02 g), at 160 °C for 24 h.

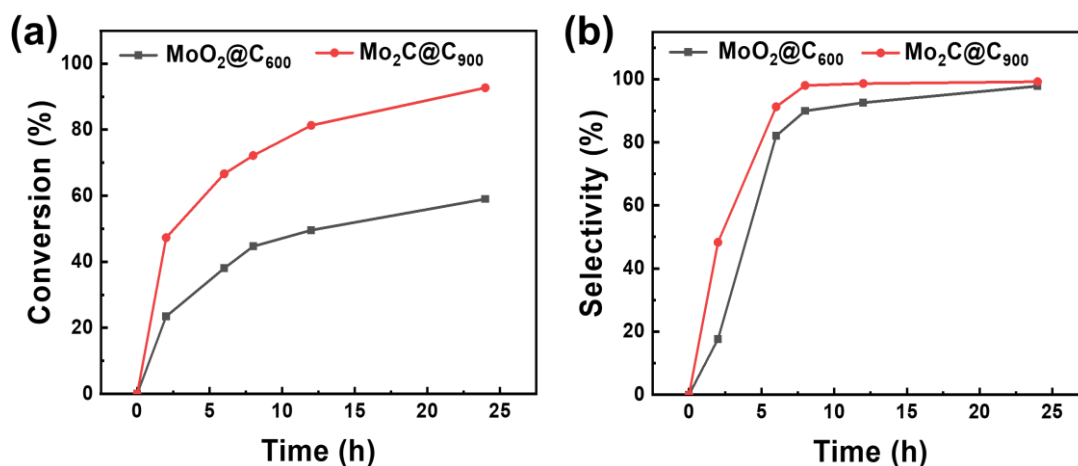
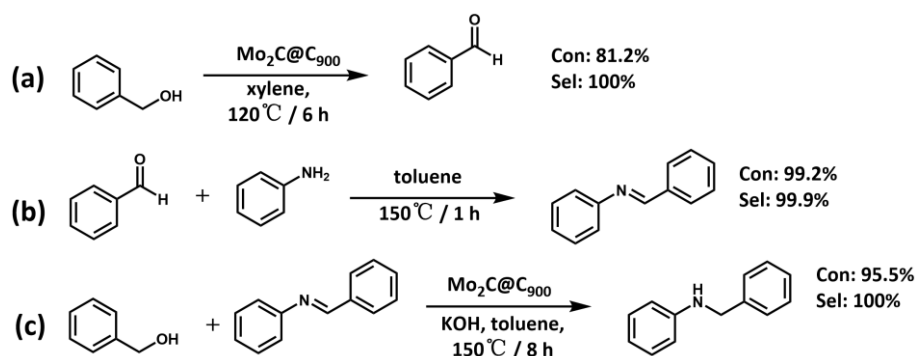


Figure S4. (a) Conversion of aniline on MoO₂@C₆₀₀ and Mo₂C@C₉₀₀ with reaction time, (b) Selectivity of N-benzylaniline on MoO₂@C₆₀₀ and Mo₂C@C₉₀₀ with reaction time.



Scheme S2. (a) The dehydrogenation of benzyl alcohol, (b) The condensation reaction of benzaldehyde and aniline, (c) The hydrogenation of N-benzylideneaniline with benzyl alcohol as hydrogen source.

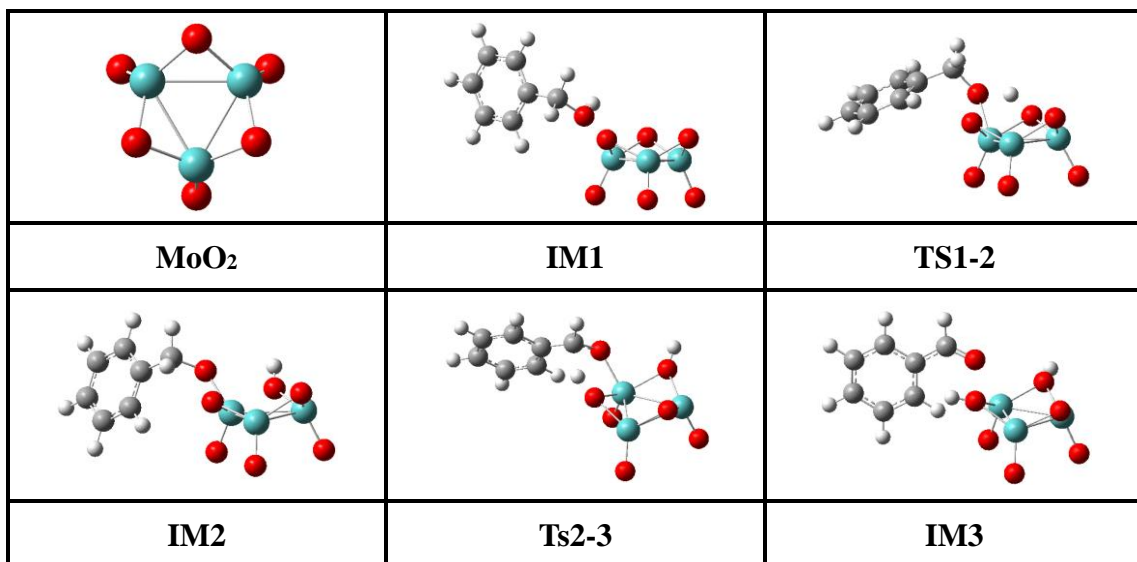


Figure S5. Benzyl alcohol selective oxidation to benzaldehyde on MoO₂ with the initial structure, transition state and the final structure.

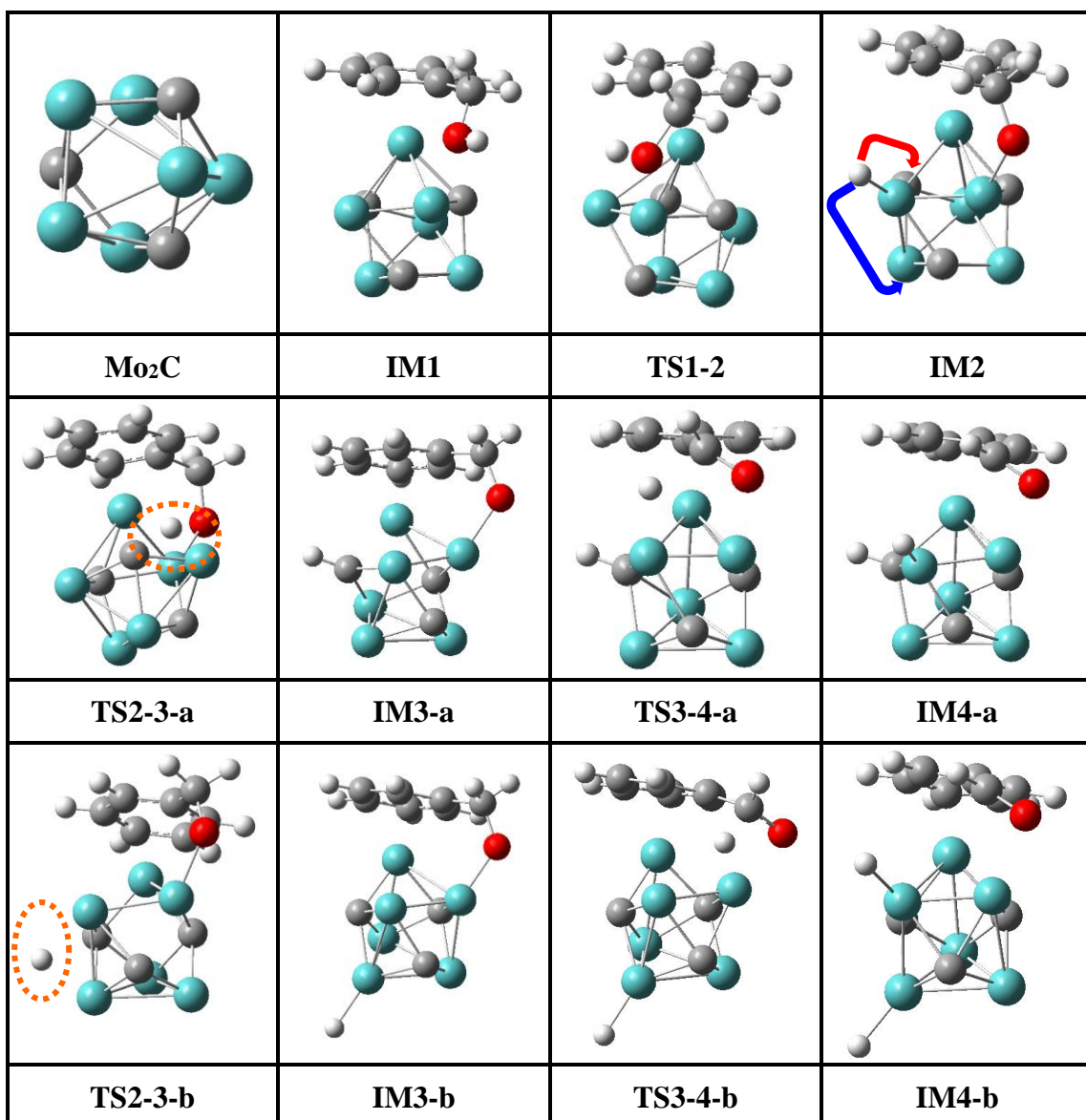


Figure S6. Benzyl alcohol selective oxidation to benzaldehyde on Mo₂C with the initial structure, transition state and the final structure.

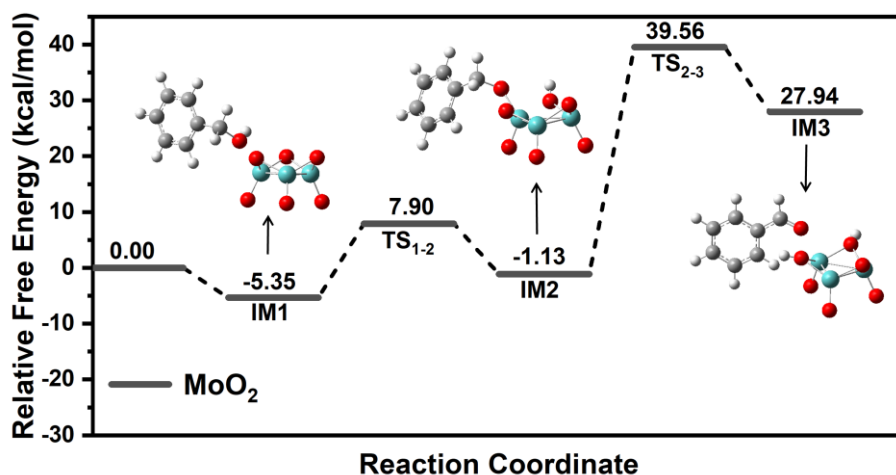


Figure S7. Calculated structures of the intermediates in benzyl alcohol dehydrogenation on MoO₂, and the corresponding energy profile.

Notes and references

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