Supporting Information

Transfer Hydrogenation of Nitroarenes with Hydrazine at Near-Room Temperature Catalysed by a MoO_2 Catalyst

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1. The TEM images and XRD pattern of the MoO_2

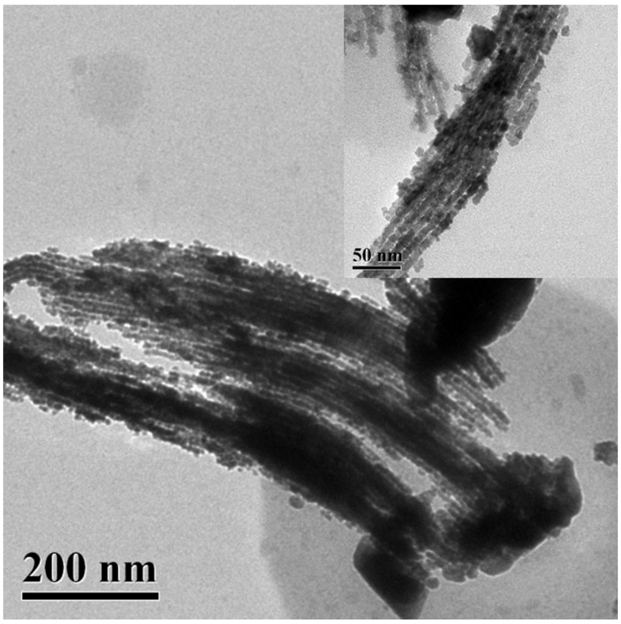


Figure S1. The TEM images of MoO_2.

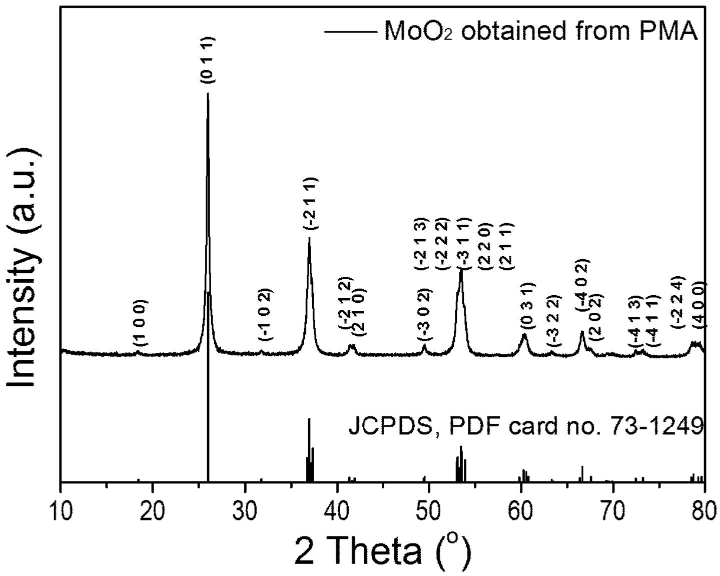


Figure S2. The XRD pattern of MoO_2.

2. Filtration experiment and solvent optimization

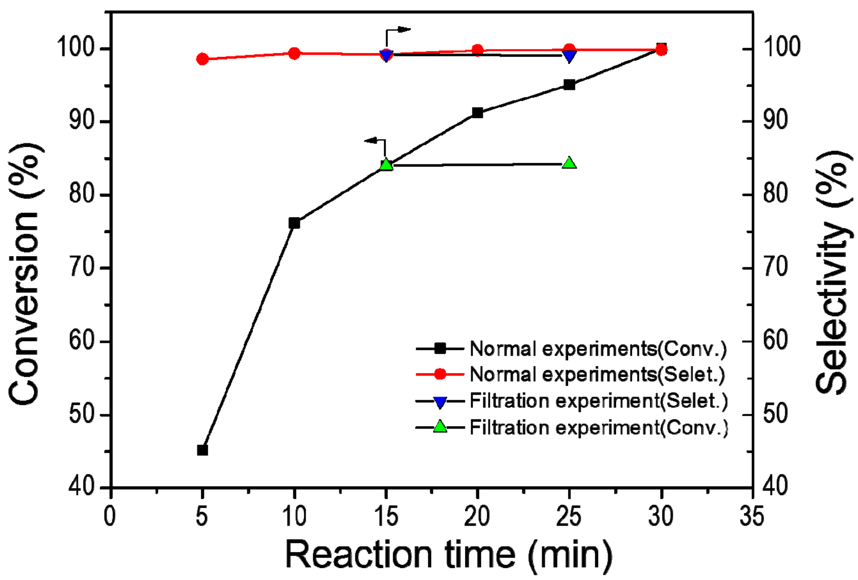


Figure S3. The reduction of nitrobenzene with hydrazine hydrate. Reaction conditions: nitrobenzene 0.5 mmol, hydrazine hydrate 1.5 mmol, ethanol 2.0 mL, MoO_2 20 mg, 50 μL p-xylene, 30 °C.

Table S1: The influence of solvent on the reduction of nitrobenzene by N_2H_4

Entry	Solvent	Conv. (%)	Select. (%)			
			Aniline	Nitroso	Azoxy	Azo
1	Ethanol	>99	>99	0	0	0
2	THF	31.2	64.3	28.9	4.3	2.5
3	DMF	>99	69.4	17.4	8.4	4.8
4	DMSO	88.7	73.6	3.1	16.2	7.1
5	Toluene	23.7	96.6	3.4	0	0
6	H_2O	17.6	>99	0	0	0
7	CH_3CN	51.5	87.9	12.1	0	0
8	Acetone	0	0	0	0	0
9	Ethyl acetate	18.1	77.8	22.2	0	0

Reaction conditions: nitrobenzene 0.5 mmol, solvent 2.0 mL, hydrazine hydrate 1.5 mmol, catalyst (MoO_2) 20 mg, 30 °C, 0.5 h.

3. The reusability and regeneration of the MoO_2

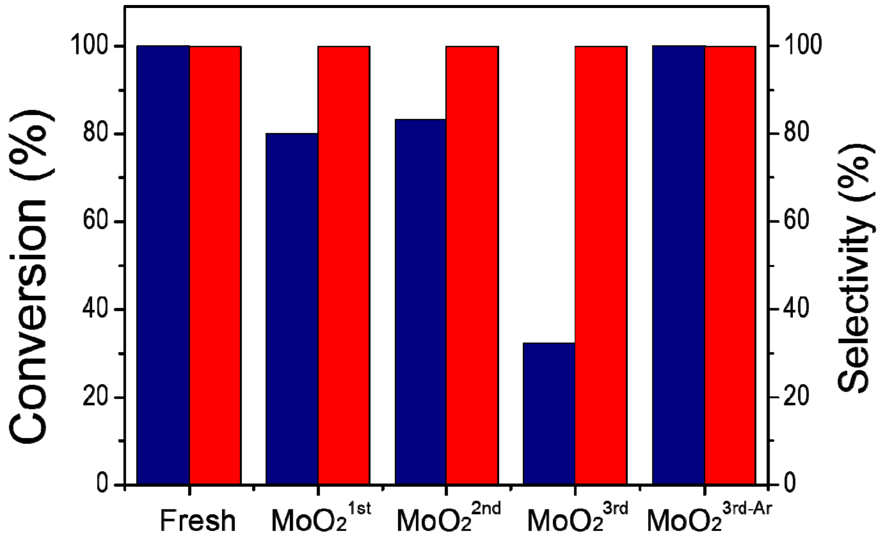


Figure S4. Reusability of the MoO_2 in the nitrobenzene reduction (The left bar stands for the conversion and the right one stands for the aniline selectivity).

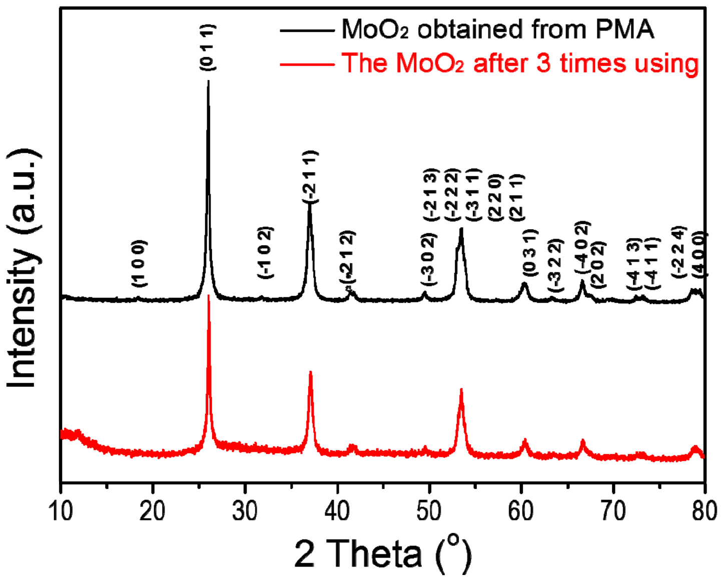


Figure S5. The XRD patterns of the MoO_2 nanoparticles before and after using.

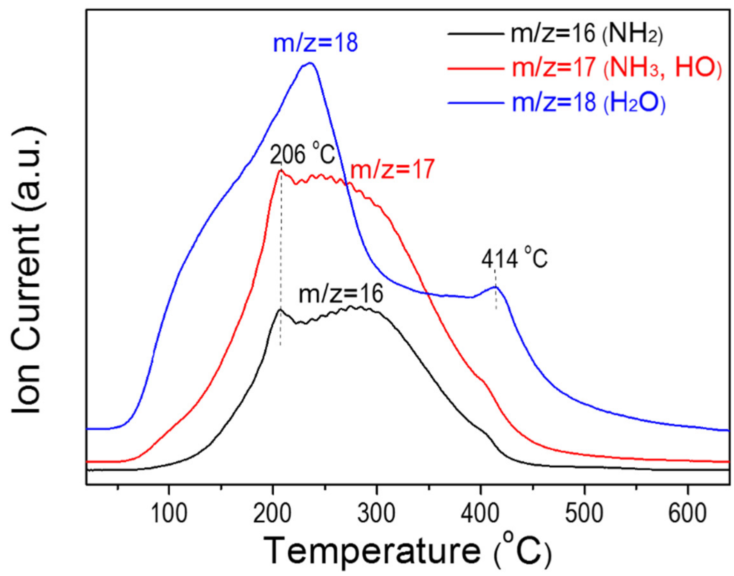


Figure S6. The TPD pattern of MoO_2^{3nd}. Reaction condition: MoO_2^{3nd} 100 mg, Ar (30 mL·min^{-1}), 20~640 °C(10 °C·min^{-1}).

4. The gas composition analysis by mass spectrometer

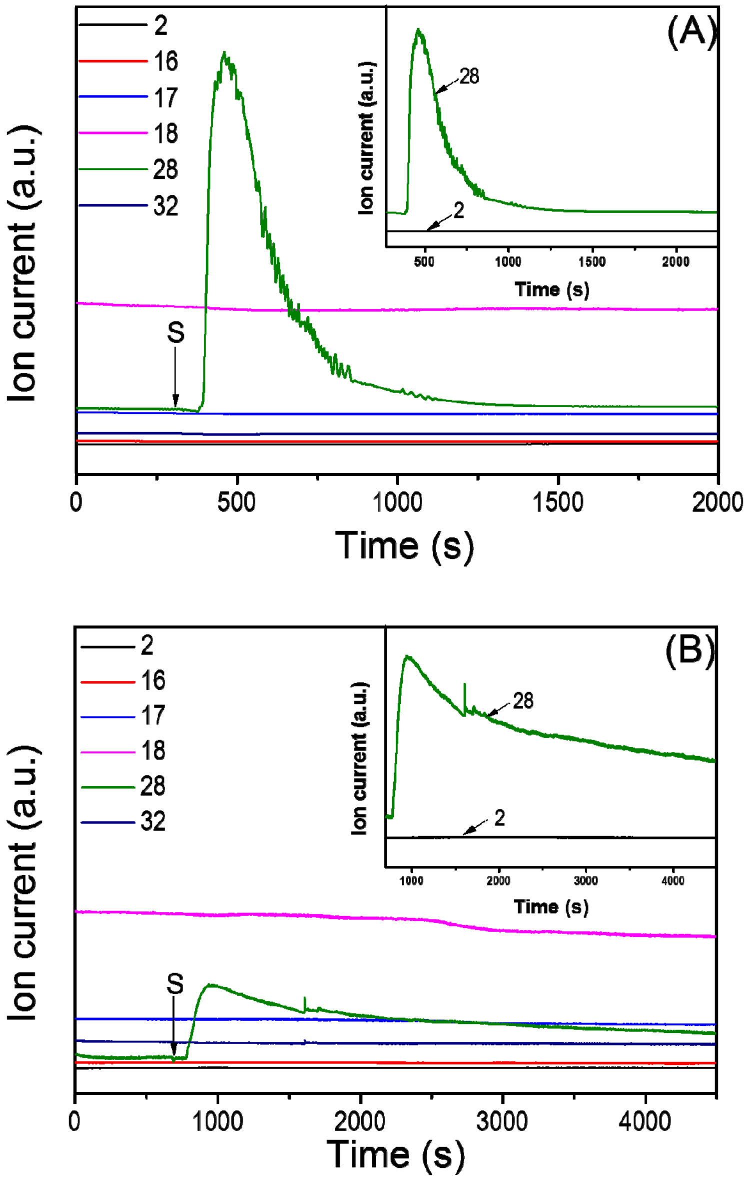


Figure S7. The gas analysis of nitrobenzene reduction with hydrazine (A) and hydrazine decomposition (B) using MoO_2 as catalyst by MS. Reaction condition: MoO_2 50 mg, N_2H_4 1.5 mmol, ethanol 5 mL, 30 °C, Ar as the carrier gas and the "S" stands for the injection of the N_2H_4. A) Nitrobenzene 0.5 mmol; B) no nitrobenzene.

5. The possible routes for the active hydrogen species generation

Table S2. The possible routes for the active hydrogen species generation from the hydrazine decomposition [a]

Route 1A (6 Steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow HN{=}NH + 2H$ $HN{=}NH + 2H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Route 1B (6 Steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow N{=}NH_2 + 2H$ $N{=}NH_2 + 2H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Route 2A (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow NH_2 + N + 2H$ $NH_2 + N + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Route 2B (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow 2NH + 2H$ $2NH + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Cross route 1 (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow NH_2 + N + 2H$ $NH_2 + N + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Cross route 2 (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow 2NH + 2H$ $2NH + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Cross route 3 (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow N{=}NH_2 + 2H$ $N{=}NH_2 + 2H \rightarrow NH_2 + N + 2H$ $NH_2 + N + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Cross route 4 (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow HN{=}NH + 2H$ $HN{=}NH + 2H \rightarrow 2NH + 2H$ $2NH + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Cross route 5 (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow N{=}NH_2 + 2H$ $N{=}NH_2 + 2H \rightarrow N{=}NH + 3H$	**Cross route 6 (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow HN{=}NH + 2H$ $HN{=}NH + 2H \rightarrow N{=}NH + 3H$

$N{=}NH + 3H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	$N{=}NH + 3H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow 2N + 4H$ $2N + 4H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Cross route 5 (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow HN{=}NH + 2H$ $HN{=}NH + 2H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Cross route 6 (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow N_2H_3 + H$ $N_2H_3 + H \rightarrow N{=}NH_2 + 2H$ $N{=}NH_2 + 2H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Cross route 7 (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow NH_2 + N + 2H$ $NH_2 + N + 2H \rightarrow N{=}NH_2 + 2H$ $N{=}NH_2 + 2H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Cross route 8 (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow 2NH + 2H$ $2NH + 2H \rightarrow HN{=}NH + 2H$ $HN{=}NH + 2H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$
Cross route 9 (8 steps) $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow NH_2 + N + 2H$ $NH_2 + N + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$	**Cross route 10 (8 steps)** $N_2H_{4(g)} \rightarrow N_2H_4$ $N_2H_4 \rightarrow 2NH_2$ $2NH_2 \rightarrow NH_2 + NH + H$ $NH_2 + NH + H \rightarrow 2NH + 2H$ $2NH + 2H \rightarrow NH + N + 3H$ $NH + N + 3H \rightarrow N{=}NH + 3H$ $N{=}NH + 3H \rightarrow N{\equiv}N + 4H$ $N{\equiv}N + 4H \rightarrow N{\equiv}N_{(g)} + 4H$

[a] For each intermediate, without special footnote, they are adsorbed specieses on the MoO_2 surface.

6. The MoO_2(011) surface model

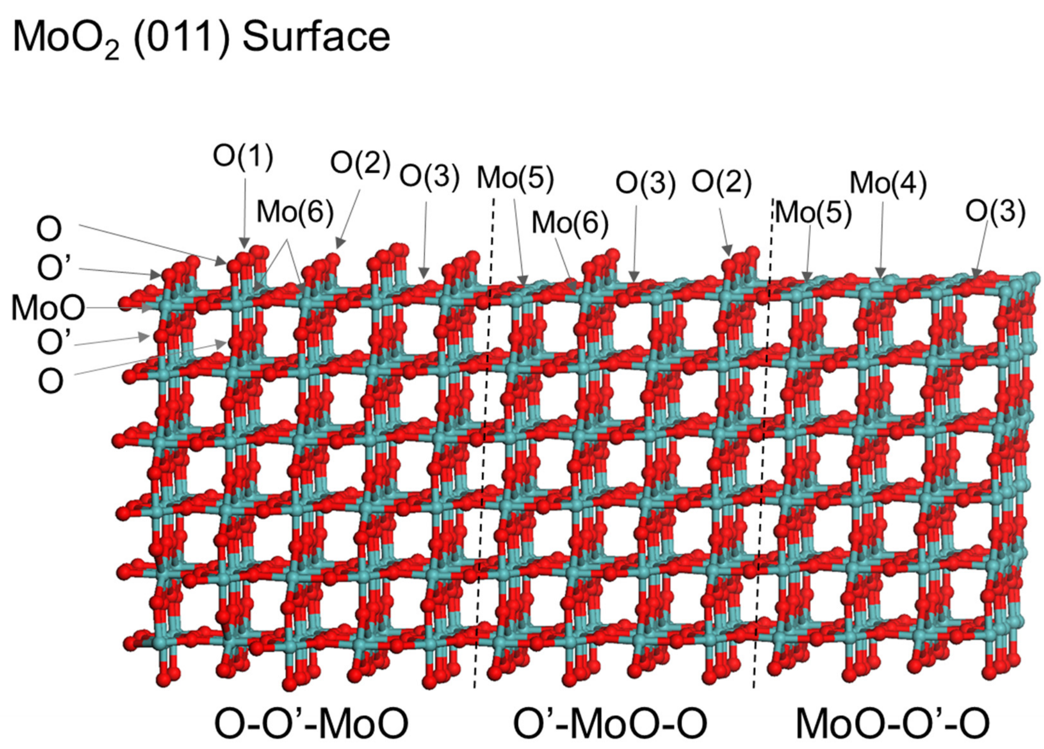
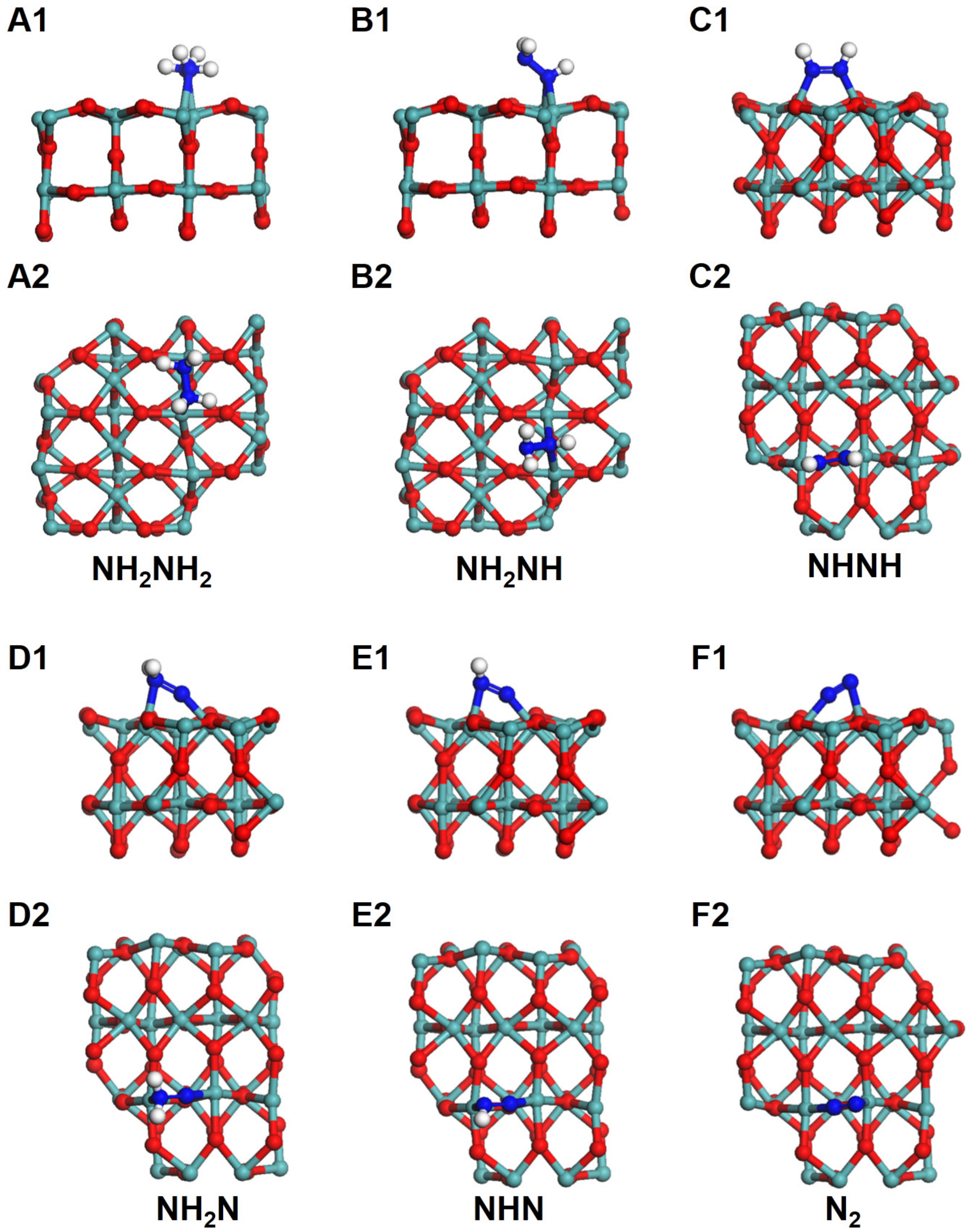


Figure S8. Structure of three ideal terminations of the MoO_2 (011) surface. (a) O-O'-MoO zone; (b) O'-MoO-O zone; (c) MoO-O'-O zone.[1] Different types of surface active centers are indicated: Mo(6), Mo(5) and Mo(5) stand for the six-, five- or four-fold coordinated molybdenum, respectively; O(3), O(2) and O(1)stand for the three, two and one-fold coordinated oxygen atoms, respectively.

7. The adsorption geometries for each species on the MoO_2(011) surface



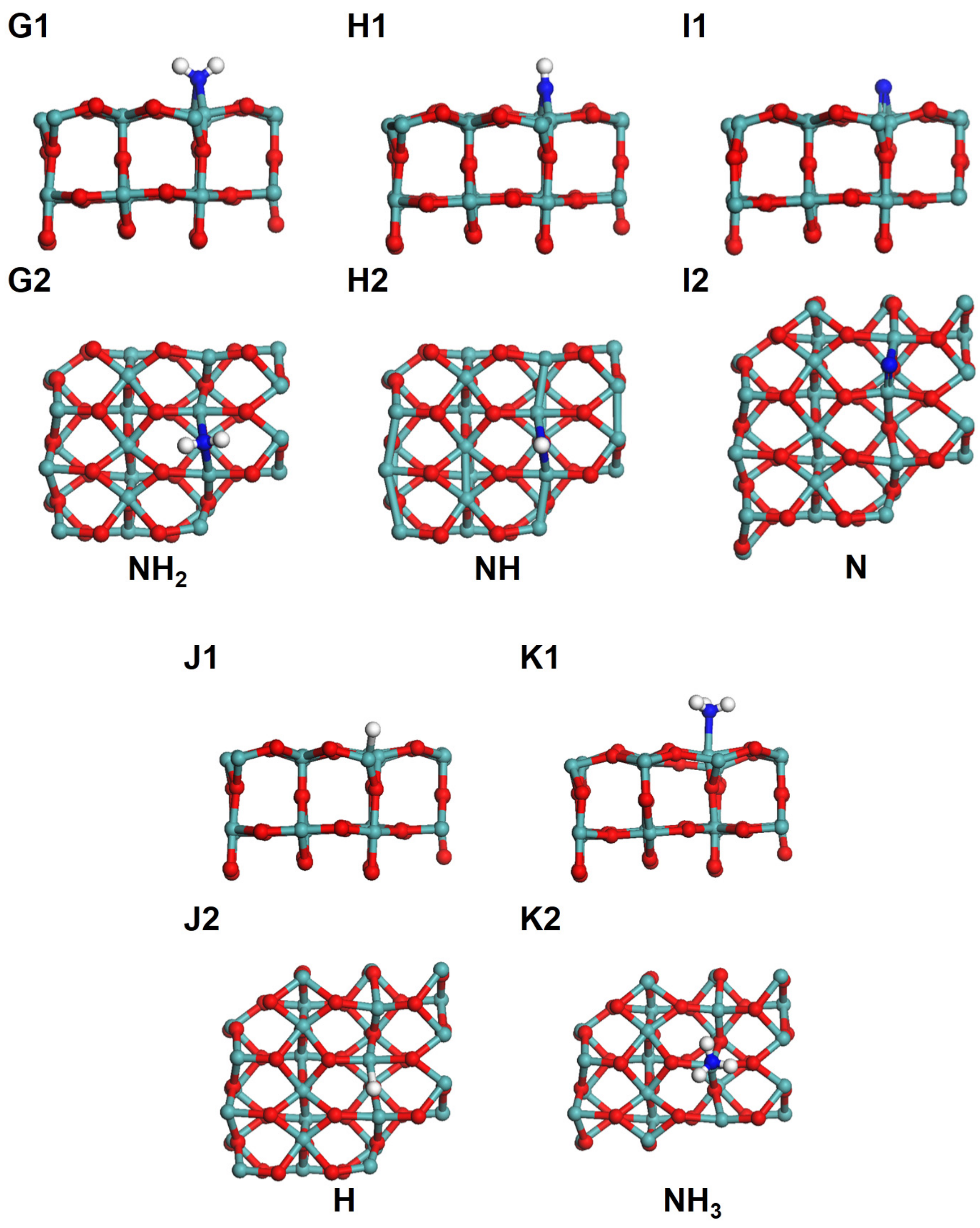


Figure S9. The adsorption geometries for each species on the MoO_2 (011) surface contained in the hydrazine decomposition.

8. References

1 R. Tokarz-Sobieraj; R. Grybos; M. Witko. *Appl. Catal., A*, 2011, **391**, 137-143.