Supplementary Information

Effect of Fe, Co and Ni promoters on MoS_2 based catalysts for chemoselective hydrogenation of nitroarenes

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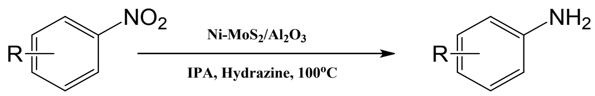
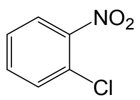
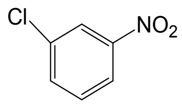
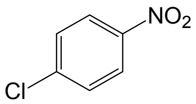
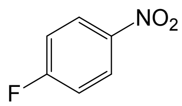
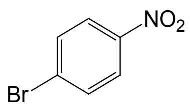
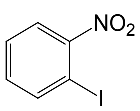
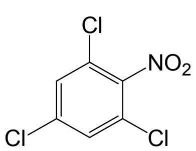
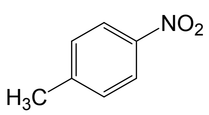
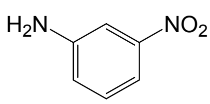
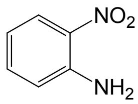
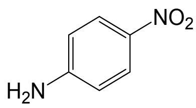
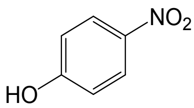
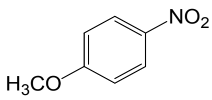
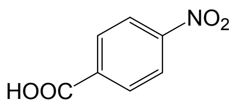
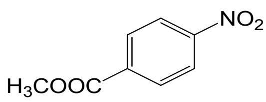
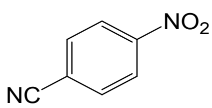
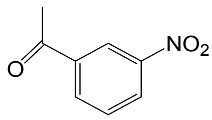
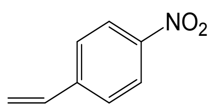
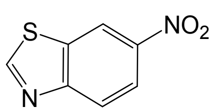
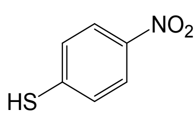
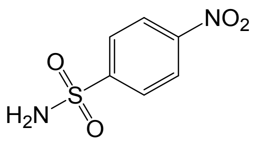
1. The evaluation on compatibility and stability over Ni-MoS$_2$/γ-Al$_2$O$_3$ catalyst

Table S1. Summary on the hydrogenation of various nitroarenes over Ni-MoS$_2$/γ-Al$_2$O$_3$ catalyst.



Entry	Substrate	$N_2H_4 \cdot H_2O$ (equiv.)	Time/ h	Sel./ yield[a] (%)
1		3	2	99/99
2		3	6	99/99
3		3	4	99/99
4		3	4	98/97
5		3	4	99/99
6		5	8	98/97
7		5	8	99/99
8		5	12	100/99

9		8	4	100/99
10		8	10	99/98
11		8	6	100/99
12		6	16	99/99
13		5	8	99/98
14		5	8	99/99
15		5	8	99/99
16		3	4	99/99
17		5	8	99/98
18		3	2	98/98
19		5	4	99/99
20		5	8	99/99

21		5	8	99/98

Reaction conditions: 0.1 g catalyst, 1 mmol substrate, 100 ^oC, 15 mL isopropyl alcohol, 1 MPa N_2, n equiv. $N_2H_4 \cdot H_2O$, calibration concentration of $N_2H_4 \cdot H_2O$ is 79.2%.

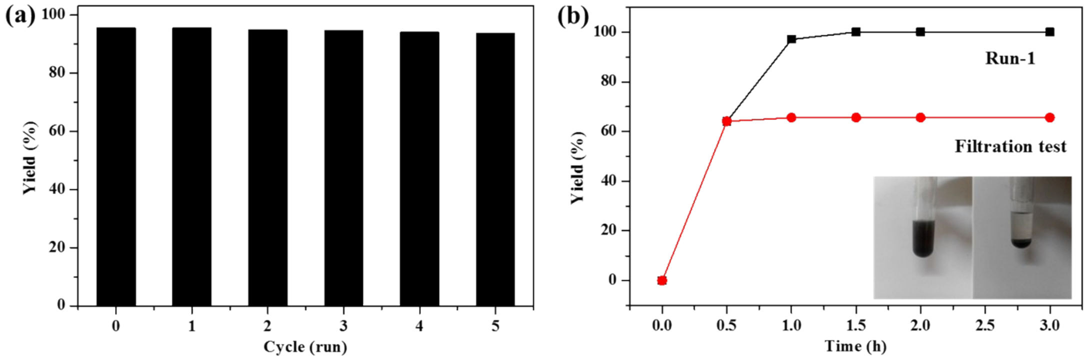


Fig. S1. (a) Recyclability test; (b) Hot filtration test. After reaction for 0.5 h, the catalyst was separated under the reaction conditions. Inset of (b): The photographs showing before and after the facile separation via the centrifugation. Reaction conditions: 0.1 g catalyst, 1 mmol nitrobenzene, 100 ^oC, 15 mL isopropyl alcohol, 1 MPa N_2, 2 equiv. $N_2H_4 \cdot H_2O$, 1 h.

2. Catalysts characterization

ICP-AES

Table S2. The ICP-AES analysis of the metal loading.

Catalysts	Content of metals
$NiO_x/\gamma\text{-}Al_2O_3$	Ni 2.32wt%
$MoO_3/\gamma\text{-}Al_2O_3$	Mo 9.67wt%
$Fe\text{-}MoO_3/\gamma\text{-}Al_2O_3$	Fe 2.30wt%; Mo 9.71wt%
$Co\text{-}MoO_3/\gamma\text{-}Al_2O_3$	Co 2.26wt%; Mo 9.75wt%
$Ni\text{-}MoO_3/\gamma\text{-}Al_2O_3$	Ni 2.34wt%; Mo 9.77wt%

XRD

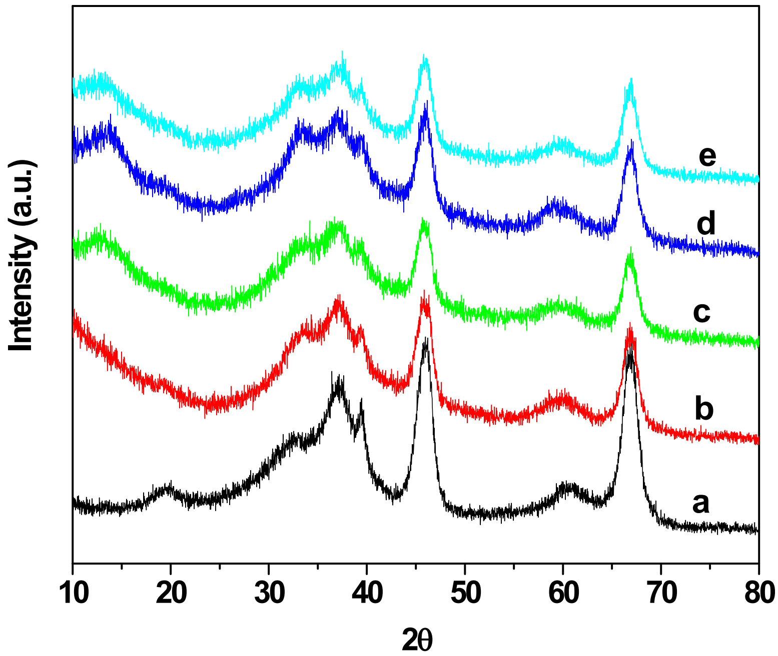


Fig. S2. XRD patterns of γ-Al_2O_3 (a), MoS_2/γ-Al_2O_3 (b), Co-MoS_2/γ-Al_2O_3 (c), Ni-MoS_2/γ-Al_2O_3 (d) and Fe-MoS_2/γ-Al_2O_3 (e) catalysts.

XPS

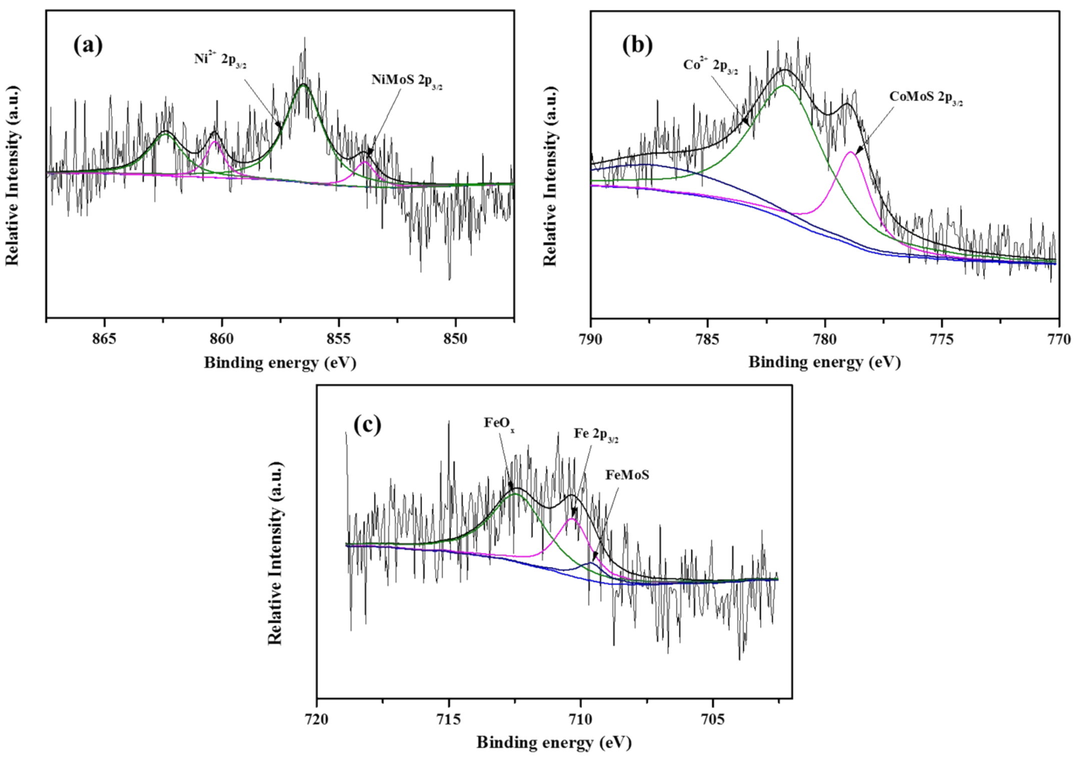
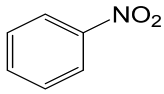
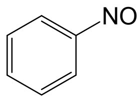
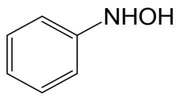
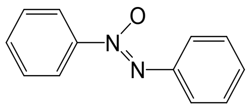
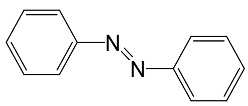


Fig. S3 XPS spectra showing the binding energies of Ni $2p_{3/2}$ (a), Co $2p_{3/2}$ (b) and Fe $2p_{3/2}$ (c) in various catalysts.

Table S3. Synthesis of aniline using different intermediates as substrates over the Ni-MoS_2/γ-Al_2O_3 catalyst [a]

Entry	Reactant	Conv. (%)	Select. (%)
1		67	99
2		95	98
3		99	99
4		7	92
5		10	98

[a] Reaction conditions: 0.1 g catalyst, 1 mmol substrate, 100 °C, 0.5 h, 15 mL isopropyl alcohol, 1 MPa N_2, 2 equiv. $N_2H_4 \cdot H_2O$.

Table S4. The NO adsorption on Mo edge by DFT calculation

	Adsorption (eV)	kJ/mol
Mo	-0.356	-34.346
Fe	-0.365	-35.260
Co	-0.446	-43.062
Ni	-0.348	-33.560