Supporting Information

Molybdenum-Incorporated Mesoporous Silica: Surface Engineering toward Enhanced Metal-Support Interactions and Efficient Hydrogenation

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Figure S1. Mo K-edge XANES of *x*Mo-KIT-6 ($x = 0.5 \sim 8.0$) and the MoO₃ reference.

Samples	Surface area $(m^2/g)^a$	Pore volume (cm ³ /g) ^b	Pore diameter (nm) ^b	$a_0 (nm)^c$	$\delta \left(nm ight)^d$
KIT-6	745	0.97	7.5	23.1	4.1
0.1Mo-KIT-6	761	1.19	7.7	24.0	4.3
0.5Mo-KIT-6	636	1.20	8.4	25.0	4.1
3.0Mo-KIT-6	629	1.23	8.3	24.9	4.2
6.0Mo-KIT-6	539	0.91	8.7	25.5	4.1
8.0Mo-KIT-6	397	0.51	7.8	27.4	5.4
3.0Mo/KIT-6	457	0.74	6.5	23.1	5.1

Table S1. Textural properties of *x*Mo-KIT-6.

^a Analyzed by N₂ isothermal sorption; ^b Calculated by BJH method; ^c XRD unit-cell parameter estimated from the position of the (211) diffraction line ($a_0=6^{1/2}d_{211}$); ^d The pore wall thickness $\delta = a_0/2$ -D_p.

Samples	Surface area $(m^2/g)^a$	$d(nm)^{b}$	D _{Ir} (%) ^c
4.9%Ir/KIT-6	541	2.0	55
5.0%Ir/0.1Mo-KIT-6	560	2.0	55
4.9%Ir/0.5Mo-KIT-6	439	2.0	55
4.9%Ir/3.0Mo-KIT-6	433	2.1	52
4.8%Ir/6.0Mo-KIT-6	375	2.1	52
4.9%Ir/8.0Mo-KIT-6	261	2.2	50
4.9%Ir/3.0Mo/KIT-6	256	3.9	28
4.8%Ir/SiO ₂	341	2.5	44
4.9%Ir/MoO ₃	40	2.5	44

 Table S2. Textural properties of Ir-based catalysts.

^a Analyzed by N₂ isothermal sorption; ^b Particle size determined by TEM; ^c Ir dispersion ($D_{Ir} = 1.1/d_{Ir}$).



Figure S2. HAADF-TEM images of (a) Ir/KIT-6, (b) Ir/0.1Mo-KIT-6, (c) Ir/0.5Mo-KIT-6, (d) Ir/3.0Mo-KIT-6, (e) Ir/6.0Mo-KIT-6, (f) Ir/8.0Mo-KIT-6 and (g) Ir/3.0Mo/KIT-6 with a consistent Ir loading $(4.9 \pm 0.1 \text{ wt}\%)$.



Figure S3. (a) XRD pattern and (b) HR-TEM image of the Ir/3.0Mo-KIT-6. Due to the ultrafine size (~ 2.2 nm), the XRD pattern doesn't present visible diffraction peaks for Ir. However, the HR-TEM clearly identifies the (111) facet of *fcc* Ir.



Figure S4. EDS profile of Ir/3.0Mo-KIT-6.



Figure S5. XPS profiles of Mo 3d in a series of Ir/xMo-KIT-6 catalysts obtained after reduction by H₂/Ar at 300 °C.

Entry	Catalysts ^b	Conv. (%)
1	4.9%Ir/3.0Mo-KIT-6	85
2	3.0Mo-KIT-6	< 5
3	4.9%Ir/3.0Mo/KIT-6	8
4	4.9%Ir/MoO ₃	19
5	4.8%Ir/SiO ₂	< 5

Table S3. N-acetylmorpholine hydrogenation over supported Ir catalysts.^a

^a Reaction conditions: N-acetylmorpholine (0.5 mmol), DME (10 mL), catalyst (0.1 g), temperature (130 °C), H₂ (3 MPa), 4 Å M.S. (0.4 g), stirring rate (600 rpm), time (4 h). ^b All the samples were reduced by 5 vol% H₂/Ar at 300 °C.



Figure S6. N-acetylmorpholine hydrogenation over supported Ir, Pt and Pd catalysts (metal loading :4.9 \pm 0.1 wt%).

Table S4. Cinnamaldehyde hydrogenation over supported Ir catalysts.^a

Entry	Catalysts ^b	Cinnamaldehyde Conv. (%)	Cinnamyl alcohol Sel. (%)
1	4.9%Ir/3.0Mo-KIT-6	75	96
2	4.9%Ir/3.0Mo/KIT-6	28	96
3	4.9%Ir/MoO ₃	33	95

^a Reaction conditions: cinnamaldehyde (0.8 mmol), $H_2O(9 \text{ ml})$, EtOH (21 ml), catalyst (30 mg), temperature (30 °C), H_2 (2 MPa), stirring rate (600 rpm), time (3 h). ^b All the samples were reduced by 5 vol% H_2/Ar at 300 °C.



Figure S7. (a) TEM image of Ir/3.0Mo-KIT-6 after five successive runs, and (b) corresponding size distribution of the Ir NPs.