Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Preparation and characterization of NiW supported on Al-modified MCM-48 catalyst and its high hydrodenitrogenation activity and stability

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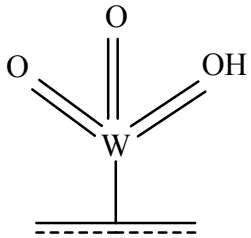

Scheme S1. Surface structure of W atom in oxidic state[1]

Table S1. NH_3-TPD results of MCM-48, Al_Y-MCM-48 (Y=200, 100, 50, 25) samples.

Sample	mmol/g
MCM-48	0.156
Al_{200}-MCM-48	0.142
Al_{100}-MCM-48	0.144
Al_{50}-MCM-48	0.196
Al_{25}-MCM-48	0.235

Table S2. Py-IR results of NiW/MCM-48, NiW/Al_Y-MCM-48 (Y=200, 100, 50, 25) and NiW/γ-Al_2O_3 oxide precursors.

Sample	Brønsted acidity (μmol/g)			Lewis acidity (μmol/g)		
	100℃	200℃	300℃	100℃	200℃	300℃
NiW/MCM-48	33	32	27	412	354	313
NiW/Al_{200}-MCM-48	46	43	41	405	371	311
NiW/Al_{100}-MCM-48	48	45	34	413	359	321
NiW/Al_{50}-MCM-48	55	50	46	403	359	310
NiW/Al_{25}-MCM-48	95	91	85	389	320	313
NiW/γ-Al_2O_3	19	15	13	335	243	204

Table S3.

Py-IR results of NiW/MCM-48, NiW/Al_Y-MCM-48 (Y=200, 100, 50, 25) and NiW/γ-Al_2O_3 sulfide catalysts.

Sample	Brønsted acidity (μmol/g)			Lewis acidity (μmol/g)		
	100℃	200℃	300℃	100℃	200℃	300℃
NiW/MCM-48	26	25	21	336	271	237
NiW/Al_{200}-MCM-48	39	31	29	329	287	242
NiW/Al_{100}-MCM-48	41	37	33	341	287	253
NiW/Al_{50}-MCM-48	49	44	39	336	286	232
NiW/Al_{25}-MCM-48	85	80	72	304	249	233
NiW/γ-Al_2O_3	17	13	10	259	175	123

Table S4.

Metal fractions and Ni/W atomic ratio measured by XPS for nickel and tungsten species present on the surface of sulfided NiW/MCM-48, NiW/Al_Y-MCM-48 (Y=200, 100, 50, 25) and NiW/γ-Al_2O_3 catalysts.

Sample	NiS[a]	NiWS	Ni^{2+}	WS_2	WO_xS_y	W^{6+}	$R_{Ni/W}$[b]	[NiWS](*10^{-4}mol)
NiW/MCM-48	18.8	34.9	46.3	72.5	8.6	18.9	0.39	0.31
NiW/Al_{200}-MCM-48	19.4	36.4	44.2	61.2	10.4	28.4	0.40	0.50
NiW/Al_{100}-MCM-48	21.4	40.4	38.2	58.2	12.2	29.6	0.40	0.61
NiW/Al_{50}-MCM-48	21.1	41.8	37.1	53.0	13.3	33.7	0.41	0.76
NiW/Al_{25}-MCM-48	23.8	42.4	33.8	50.2	9.9	39.8	0.42	0.89
NiW/γ-Al_2O_3	12.1	23.7	64.2	31.2	16.1	52.7	0.41	0.49

a relative amount calculated from XPS results (Eq. (4)).

b Ni/W ratio present on the supports surface calculated from XPS results (Eq. (5)).

Table S5. The HDN_C of quinoline on NiW/MCM-48, NiW/Al_Y-MCM-48 (Y=200, 100, 50, 25) and NiW/γ-Al_2O_3 oxide precursors.

Sample	*HDN_C*(%)		
	300 ℃	330 ℃	360 ℃
NiW/MCM-48	0	0.6	8.9
NiW/Al_{200}-MCM-48	0	0.5	7.6
NiW/Al_{100}-MCM-48	0	0.2	5.6
NiW/Al_{50}-MCM-48	0	0.2	6.1
NiW/Al_{25}-MCM-48	0	0.3	5.8
NiW/γ-Al_2O3	0	0.2	2.3

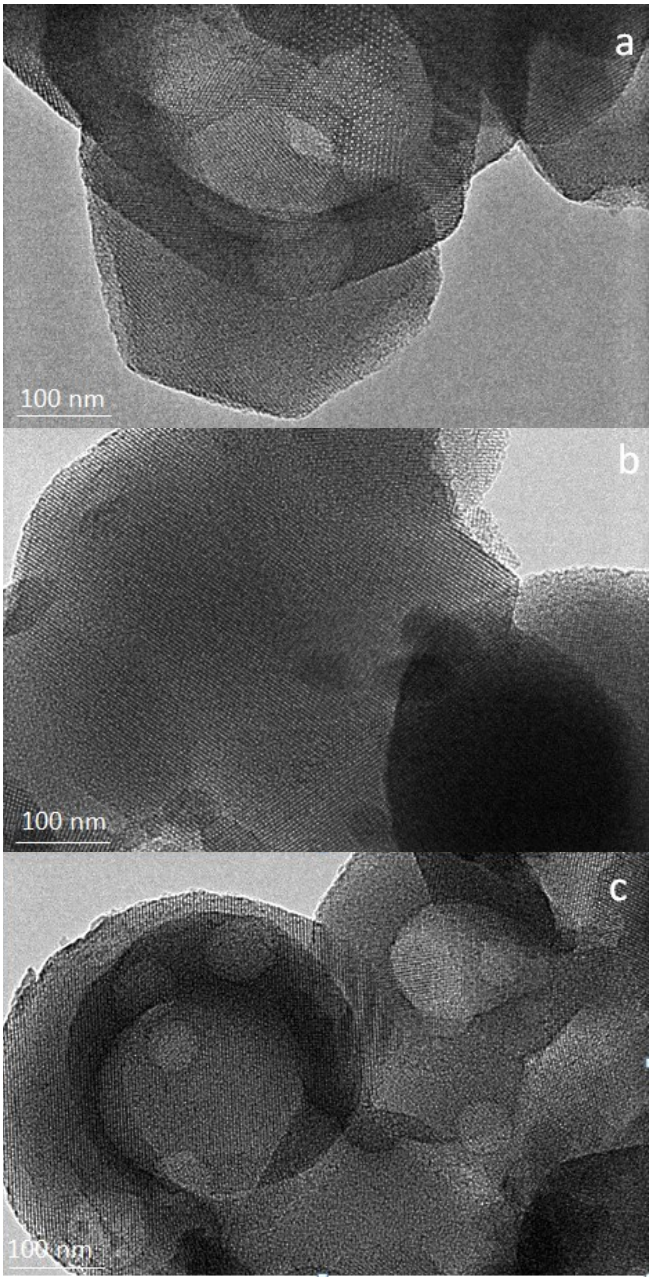

Fig. S1. HRTEM micrographs of (a) aluminum free MCM-48, (b) Al_{100}-MCM-48 and (c) Al_{25}-MCM-48.

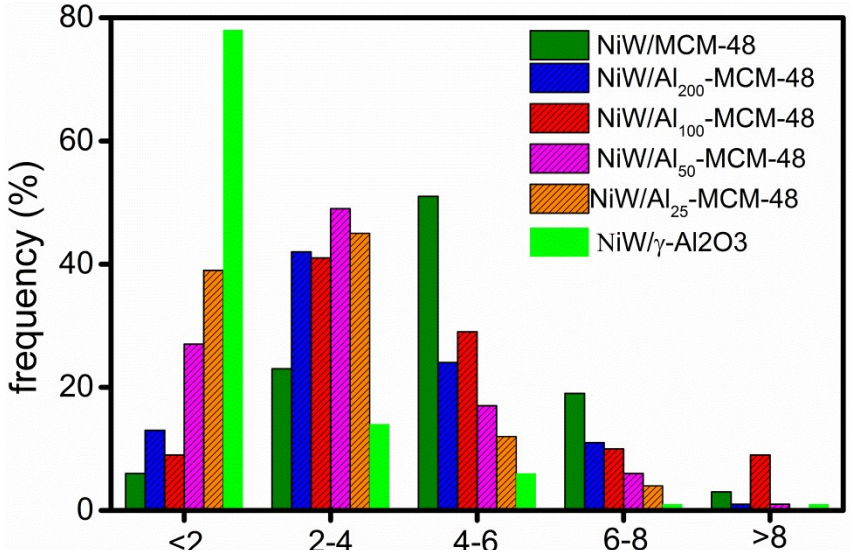

Fig. S2a. Distributions of stacking number of WS_2 slabs of NiW/MCM-48, NiW/Al_Y-MCM-48 (Y=200, 100, 50, 25) and NiW/γ-Al_2O_3 sulfide catalysts in sulfided states.

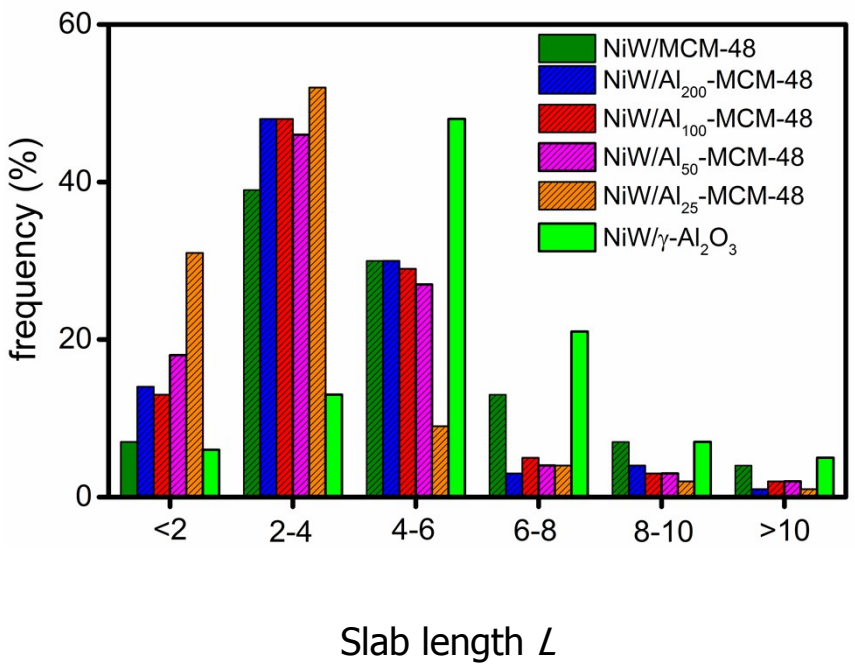

Fig. S2b. Distributions of slab length of WS_2 slabs of NiW/MCM-48, NiW/Al_Y-MCM-48 (Y=200, 100, 50, 25) and NiW/γ-Al_2O_3 sulfide catalysts in sulfided states.

1. J. Bernholc, J. A. Horsley, L. L. Murrell, L. G. Sherman and S. Soled, *J. Phys. Chem. B*, 1987, **91**, 1526-1530.