Supplemental information

Tungsten and molybdenum carbides can shine too

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Supplementary Information 1

A renewed interested in HDO has arisen due the increased use of biomass as a renewable carbon source. In general, biomass-derived feedstocks have a higher oxygen content than fossil fuels and, therefore, need to be deoxygenated. W and Mo carbides have been used in HDO reactions and compared with noble metals. Mostly model compounds such as stearic or oleic acid instead of biomass-derived oils or cresol instead of lignin-derived phenolic compounds were used as substrate.[1, 2] HDS and HDN reactions are usually catalysed by Ni-Mo/Al_2O_3 and take place during the industrial refining process of petroleum feedstocks. Mo and W carbides have been shown to be valuable replacement catalysts for both reaction, HDS and HDN.[3-5] A classical industrial catalyst for isomerisation reactions is platinum. However, also Mo and W have shown to be valuable catalysts for isomerisation reactions. Another benefit of Mo and W, especially for isomerisation, in HDS and HDN reactions is their tolerance towards sulphur (see Table S1). Also for NH_3 synthesis and decomposition, Mo and W have demonstrated to be active and Mo and W carbide are suitable catalysts.

For all reactions, both supported and bulk carbide catalysts studies have been conducted. Mainly carbon and alumina were used as support. Carbonaceous materials have a large surface area and high porosity, durability and stability and therefore are attractive materials to support metal catalysts. Also, aluminium oxide is a widely used material as a support for carbides because of its mechanical and textural properties (e.g., thermal stability, high surface area, surface chemistry).[6] The support ensures stability of the metal particles in the catalytically active phase and enhances the downstream process.

Table S1 Overview of potential reactions using tungsten carbides or molybdenum carbides as replacement for (noble) metal catalyst. Hydrogenation (HYD), hydrodeoxygenation (HDO), hydrodesulphurisation (HDS), hydrodenitrogenation (HDN), isomerisation and NH_3 synthesis/decomposition reactions are shown

Reaction		Catalyst	Replacement	Feedstock
HDO	Bulk	Mo_2C	Pd, Pt, Ru, Rh, Ni, Cu	Acetic acid,[7] acetone,[8] Anisole,[9-12] benzofuran,[4] ethanol,[13] funeral,[9, 14-16] m-cresol,[17] methyl stearate,[18] phenol,[11, 19] propanal,[20] stearic acid,[18]
	Bulk	W_2C	Pd, Pt, Ru, Rh, Ni, Cu	acetaldehyde,[21] acetic acid,[21] benzofuran[22] ethylene glycol[21]
	Supported	Mo_2C/C	Pt, Pd, Ru, Rh (supported)	Decanal,[23] guaiacol,[24] lignin,[25] methoxyphenol[26] oleic acid,[1, 27, 28] stearic acid,[18, 23, 29] vegetable oil,[18, 27, 30, 31]
	Supported	Mo_2C/Al_2O_3	CoMo and NiMo supported on Al_2O_3	Acrylic acid,[32] benzofuran,[33]
	Supported	Wo_2C/C		Guaiacol,[24] oleic acid and palmitic acid[28]
HDS	Bulk	Mo_2C	Pt/Al_2O_3, MoS_2/Al_2O_3	Dibenzothiophene[4, 34]
	Bulk	W_2C	Ni	Thiophene[5]

	Sup	Mo_2C/AC	$Ni-Mo/Al_2O_3$	Dibenzothiophene,[3] thiophene[35]
		Mo_2C/Al_2O_3	Ni	Dibenzothiophene,[4, 33, 34, 36] hexane,[37] thiophene[38-40]
HDN	Bulk	Mo_2C	sulfide $Ni-Mo/Al_2O_3$	Amines[41] carbazole,[42-44] indole,[45, 46] pyridine,[47] quiniline[48, 49]
		W_2C		Carbazole[43]
	Sup	Mo_2C/Al_2O_3	$Ni-Mo/Al_2O_3$	Coal-derived feeds,[50, 51] pyridine,[52] quinoline[33, 52]
		Mo_2C/AC		Indole [3, 53]
Isomerisation	Bulk	Mo_2C	Pt	butane[54, 55] and heptane,[56-58]
		W_2C		Butane,[54] dimethylpentane,[59] heptane,[57, 58] neopentane,[59, 60] nethylcyclohexane[59]
	S	Mo_2C/CNF		Vegetable oils[23]
		W_2C/Al_2O_3	Pt/SiO_2	Heptane[61]
HYD	Bulk	Mo_2C	Pt, Pd/Al_2O_3	Benzene,[62] butane,[54] CO,[63-65] CO_2,[66-68] ethane,[69] ethanol,[13] ethylene,[70] furfural,[71] levulinic acid,[72] long-chain alkadienes,[73] nitroarenes[74], toluene,[75, 76],
		W_2C	Pt	Butane,[54] CO[5, 65]
	Supported	Mo_2C/CNT	Ru	Levulinic acid[77]
		Mo_2C/Al_2O_3		Benzene,[78] CO_2,[79] CO,[63, 80] ethylene glycol[81]
		W_2C/C		Ethylene glycol[81], pentene[5]
		W_2C/Al_2O_3		Ethylene glycol[81]
NH_3 synthesis		α & β Mo_2C	Iron, Mo nitride	(N_2+3H_2)[82]
NH_3 decomposition		W_2C	Ru, Fe NH_3	Ammonia[83-85]
		Mo_2C	Mo_2N	Ammonia[86, 87]

Supplementary Information 2

Table S2 lists the N and S content of coals from the following mines: the Zhundong (ZD) coal from the Xinjiang province, Yimin (YM) lignite from Inner Mongolia, Zhaotong (ZT) lignite produced in the Yunnan province and Shenmu from the Shanxi province, lignites from Mequinenza (Spain) and Labin (Croatia), highly volatile bituminous coals from Czeczot and Siersza and medium volatile bituminous coal from Zofio´wka (Poland).

Table S2 N and S content of coals from different origins

Name and origin	N (wt%)	S (wt%)	Ref.
ZD_ Zhundong (Xinjiang province, China)	0.57	0.38	[88]
YM_Yimin (Mongolia)	0.81	0.13	[88]
ZT_haotong (Yunnan province, China)	1.82	0.57	[88]
Shenmu (Shanxi province, China)	1.11	0.34	[89]
Mequinenza (Spain)	0.80	10.30	[90]
Labin (Croatia)	1.20	10.00	[90]
Czeczot (Poland)	1.00	1.40	[90]
Siersza (Poland)	1.10	1.10	[90]
Zofio´wka (Poland)	1.50	0.60	[90]

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