

Hydrodesulfurization of sulfur-containing aromatic compounds via WGSR over dispersed Ni–Mo sulfide catalysts

Baygildin I.G.¹, Vutolkina A.V.¹, Maksimov A. L.^{1,2}, Karakhanov E.A.¹

¹Lomonosov Moscow State University, Chemistry Department, Moscow, 119991, Russia

²Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991, Russia

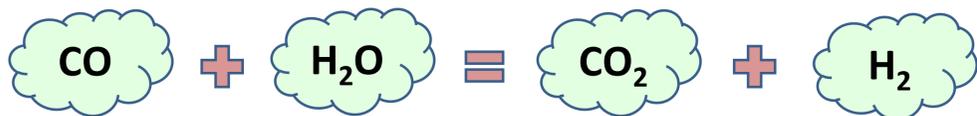
E-mail: i.baygildin@bk.ru

Catalytic hydrodesulfurization (HDS) is a vital step in the processing of petroleum into useful hydrocarbon products. Petroleum carries many sulfur-containing compounds, which are limited by ecological restrictions. So, development of active catalysts for HDS is necessary. Unsupported dispersed catalysts have essential benefits for effective oil upgrading.

Advantages of unsupported catalysts:

- Formation in situ by decomposition of oil/water soluble precursors under hydrogenation conditions
- High specific surface area (up to 300 m²/g)
- Absence of mass transfer limitations for large molecules
- High content of active sites (80-100%)
- Resistance to catalyst poisons

Ni(Co)-Mo sulfides active in water gas shift reaction:



The present work is devoted to testing of dispersed unsupported Ni-Mo sulfide catalysts formed *in situ* by decomposition of water soluble metal precursors in HDS of benzothiophene (BT) and dibenzothiophene (DBT) in aqueous medium under CO pressure.

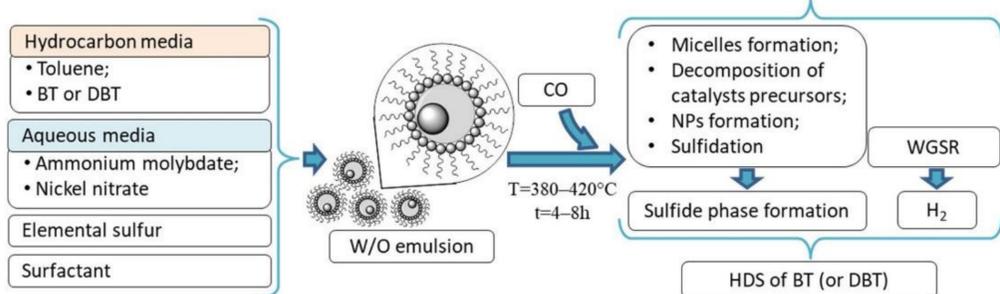


Fig. 1. The proposed reaction scheme for the HDS of BT and DBT via H₂, generated through the WGSR, over Ni-Mo-S catalysts formed in situ from water-soluble metal precursors.

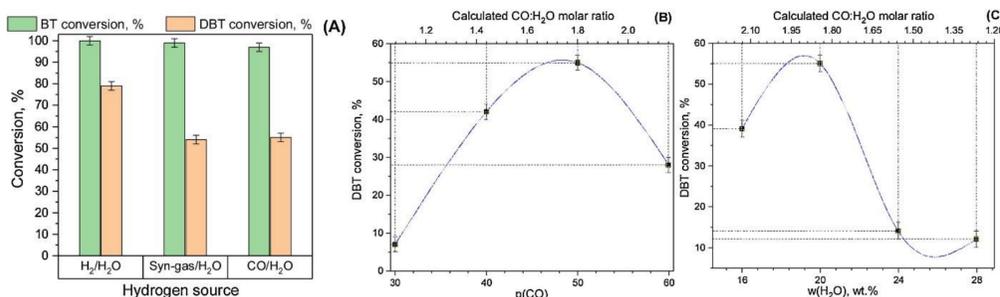


Fig. 2. The influence of hydrogen source on BT and DBT conversion (A); DBT conversion versus carbon monoxide pressure (B) and water content (C). Reaction conditions: T = 400 °C, t = 6 h, ω(Mo) = 0.08 wt.%, ω(S) = 2.5 wt.%, ω(SPAN-80) = 4.0 wt.%; for (A): p(CO) = 5 MPa, CO:H₂O = 1.8 (mol/mol), ω(H₂O) = 20 wt.%, p(H₂) = 5 MPa, p(syn-gas) = 5 MPa; for (B): ω(H₂O) = 20 wt.%; for (C): p(CO) = 5 MPa.

The optimal reaction conditions: CO/H₂O = 1,8, p(CO) = 5 MPa.

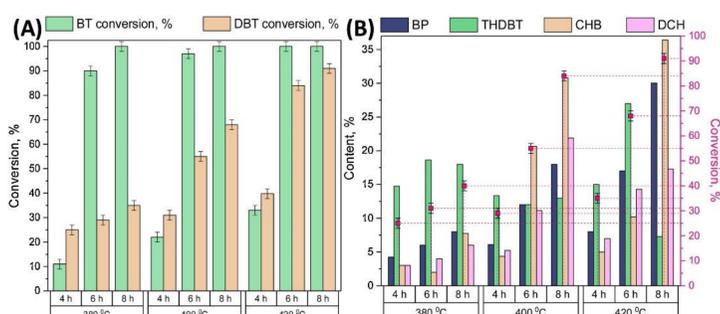


Fig. 3. Temperature and time-dependent conversion of BT and DBT (A) and product distribution for HDS of DBT (B) over dispersed Ni-Mo sulfide catalysts obtained in situ from water-soluble precursors under WGSR conditions. Reaction conditions: ω(Mo) = 0.08 wt.%, ω(S) = 2.5 wt.%, ω(SPAN-80) = 4.0 wt.%, ω(H₂O) = 20 wt.%.

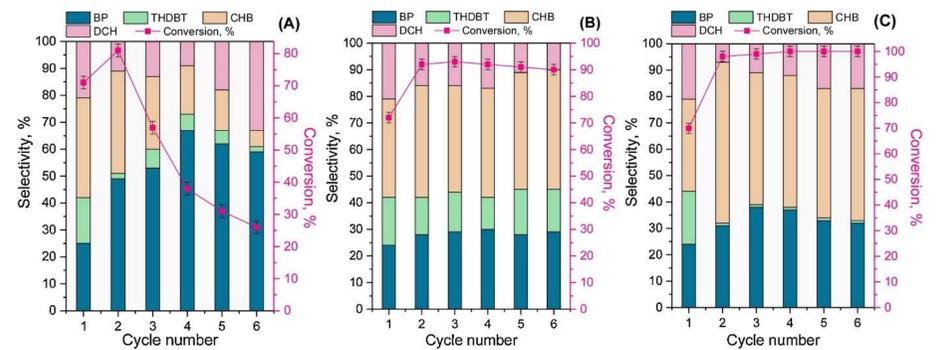


Fig. 4. Recycle tests of Ni-Mo sulfide catalysts in HDS of DBT; for (A): the sulfur was added only for the first cycle; for (B): sulfur-assisted recycle tests; for (C): sulfur-assisted recycle tests under hydrogen pressure without water. Reaction conditions: t = 6 h, ω(Mo) = 0.16 wt.%, ω(S) = 2.5 wt.%, ω(SPAN-80) = 4.0 wt.%, ω(H₂O) = 20 wt.%, for (C): p(H₂) = 5 MPa.

The catalysts were subjected to extensive studies by FT-IR, XRD, TEM, EDX mapping, and XPS techniques for the active phase investigation. Also, the study of thermal decomposition of catalyst precursors by TGA-DSC was of great importance to evaluate the efficiency of such a way preparation of Ni-Mo sulfide catalysts

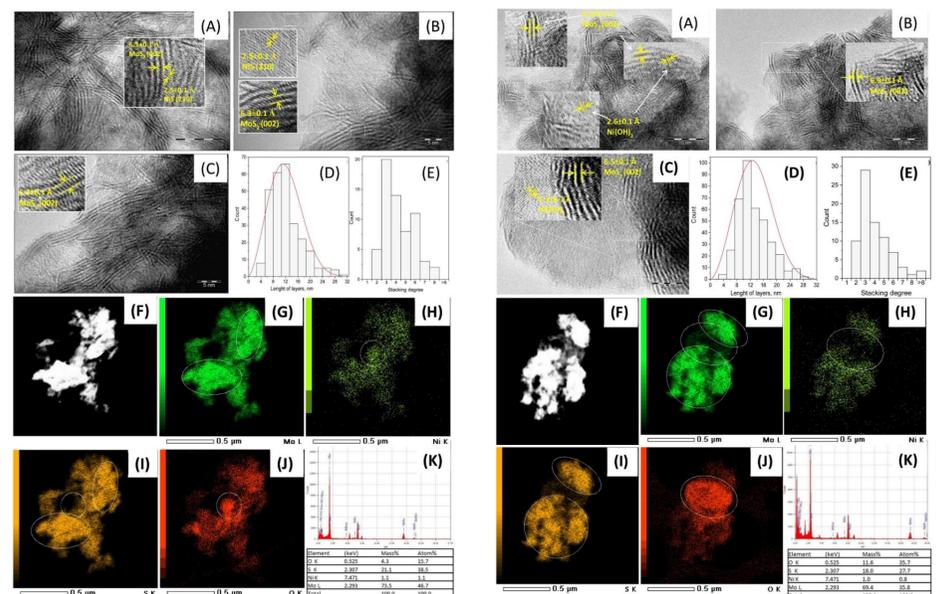


Fig. 5. TEM images (A-C), slab length distribution (D), and slab stacking degree (E) obtained from TEM and STEM (F) and EDX mapping (G-K) for Ni-Mo catalyst formed in situ from water-soluble precursors under WGSR conditions

Fig. 6. TEM images (A-C), slab length distribution (D), and slab stacking degree (E) calculated from TEM and STEM (F) and EDX mapping (G-K) images for Ni-Mo catalyst after recycling.

Surface concentration (at.%) and components ratio

Mo 3d	Ni 2p	S 2p	O 1s	C 1s	Ni/Mo	S/ (Ni + Mo)
11,60	3,20	27,60	28,60	25,30	0,30	1,90

Mo 3d5/2, eV (content, %)			Ni 2p3/2, eV (content, %)			S 2p3/2, eV (content, %)			
MoS ₂	MoS _x O _y	Mo ⁶⁺	NiS _x	NiMoS	NiMoO ₄	Ni ²⁺	S ²⁻	S ²⁻ or SeI	SO ₄ ²⁻
228.8 (79.1)	229.9 (12.6)	232.6 (8.3)	852.9 (13.2)	854.1 (38.2)	856.0 (30.2)	856.8 (18.4)	161.7 (80.2)	163.3 (7.9)	168.8 (11.9)

Table 1. The composition of sulfide catalysts (from XPS data), the quantitative XPS analysis of the Mo 3d5/2, Ni 2p3/2, and S 2p3/2 core levels

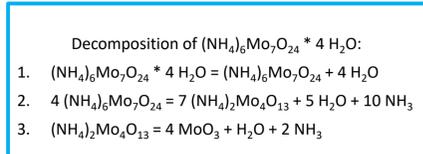
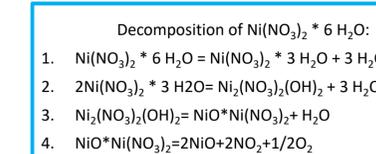
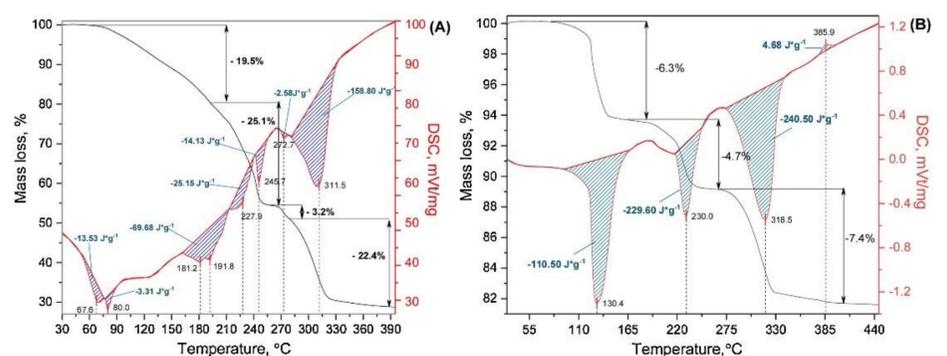


Fig. 7. The TGA-DSC curves and decomposition pathways for Ni(NO₃)₂·6H₂O (A) and (NH₄)₆Mo₇O₂₄·4H₂O (B) obtained under flowing nitrogen at a heating rate of 10 °C/min.

Acknowledgements

The research is supported by grant of the Russian Science Foundation (project № 19-79-00259). Find more: A.V. Vutolkina, I.G. Baygildin et al. In Applied Catalysis B: Environmental. – 2021. – Vol. 282.