Supplementary Materials

Deposition of Co onto supported MoS_2 by water-assisted spreading: Increased activity promotion in hydrodesulphurization reaction of 1-benzothiophene

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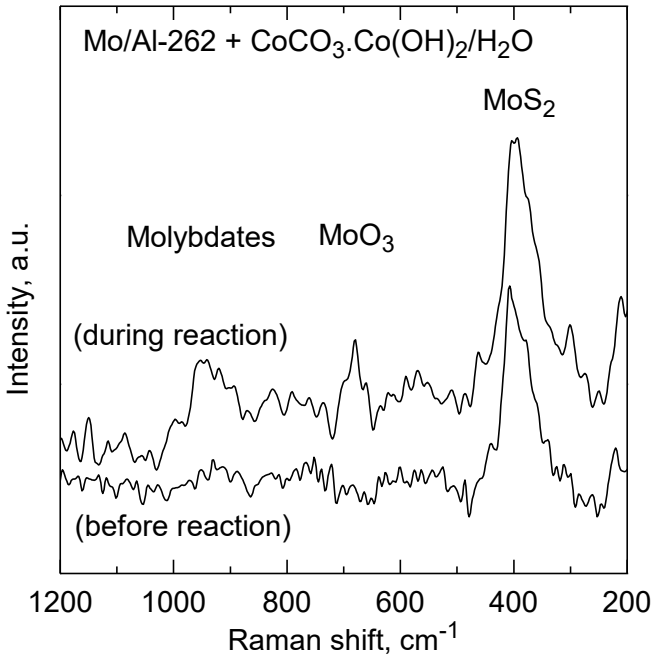
Content:

1. Additional information on re-oxidation of supported Mo sulphides

Raman spectroscopy hardly recognized partial re-oxidation of sulphided Mo/Al-262 surface during WAS_{sulph} in Figure S1. The samples clearly exhibited main bands of MoS_2 layers [20, 21] near 400 cm^{-1}, which remained the same during the continuation of WAS_{sulph} experiment. However, hardly recognized bands of oxidic Mo species at about 995-820 or 670 cm^{-1} [22-25] were formed after 1 h reaction of Mo/Al-262 with $CoCO_3.Co(OH)_2$ / H_2O slurry both at 25 °C or at 95 °C. No other changes were observed during additional 14 day reaction at 25 °C or 24 h heating at 95 °C. It was concluded that partial re-oxidation of Mo sulphide layers proceeded below the proof limit of our Raman spectroscopy method.

O_2 up-takes determined over sulphided Mo/Al-262 at -72, 25, and 90 °C were 18, 32 and 56 μmol g^{-1}. The first value is considered as a number of free sulphur vacancies of Mo/Al-262, while the other two values should be considered as a measure of partial re-oxidation of supported MoS_2. Nevertheless, this 56 μmol g^{-1} represents of about one order of magnitude lower value of sorption sites than it should be expected for sorption of Co. The saturated amount of Co achieved by WAS_{sulph} is listed in the article in Table 2.

Figure S1: Raman spectroscopy of reaction of Mo/Al-262 with $CoCO_3.Co(OH)_2/H_2O$ slurry: bottom line – 0 min (dried sulphided Mo/Al-262), upper line – example of patterns achieved between 1h – 14 days of the WAS_{sulph} reaction at 25 °C or between 1 h – 24 h of the WAS_{sulph} reaction at 95 °C.



1.1. Methods of O_2 chemisorption and Raman spectroscopy

Sulphided Mo/Al-262 catalyst was analysed by O_2 chemisorption. The catalysts were re-sulphided in situ, flushed by helium at 400 °C for 1 h and cooled down. The amount of chemisorbed O_2 was determined at -72 °C (cooling in a mixture of dry ice and ethanol), at 25 °C (cooled at laboratory temperature), or at 90 °C (heating in a hot water). Pulses of O_2 (Linde Gas a.s., Czech Republic) added to the flow of He were monitored with a thermal conductivity detector VICI (Valco Instrument Inc., USA) and an HP3394A integrator (Hewlett Packard, USA).

Raman spectra were collected over the reaction slurry of sulphided Mo/Al-262 catalyst and $CoCO_3.Co(OH)_2$ after selected time intervals. The WAS_{sulph} method is described in the article. A reaction slurry was placed on tungsten plate and measured using a dispersive Nicolet Almega XR spectrometer equipped with the Olympus BX51 microscope, excitation laser source (473 nm), and with a maximum incident power of 50 mW with 128 expositions with 0.5 s exposition time. For all experiments, the laser beam was focused by 50 x objective on spot with area around 1 μm^2 resulting in maximum irradiance5 MW/cm^2.

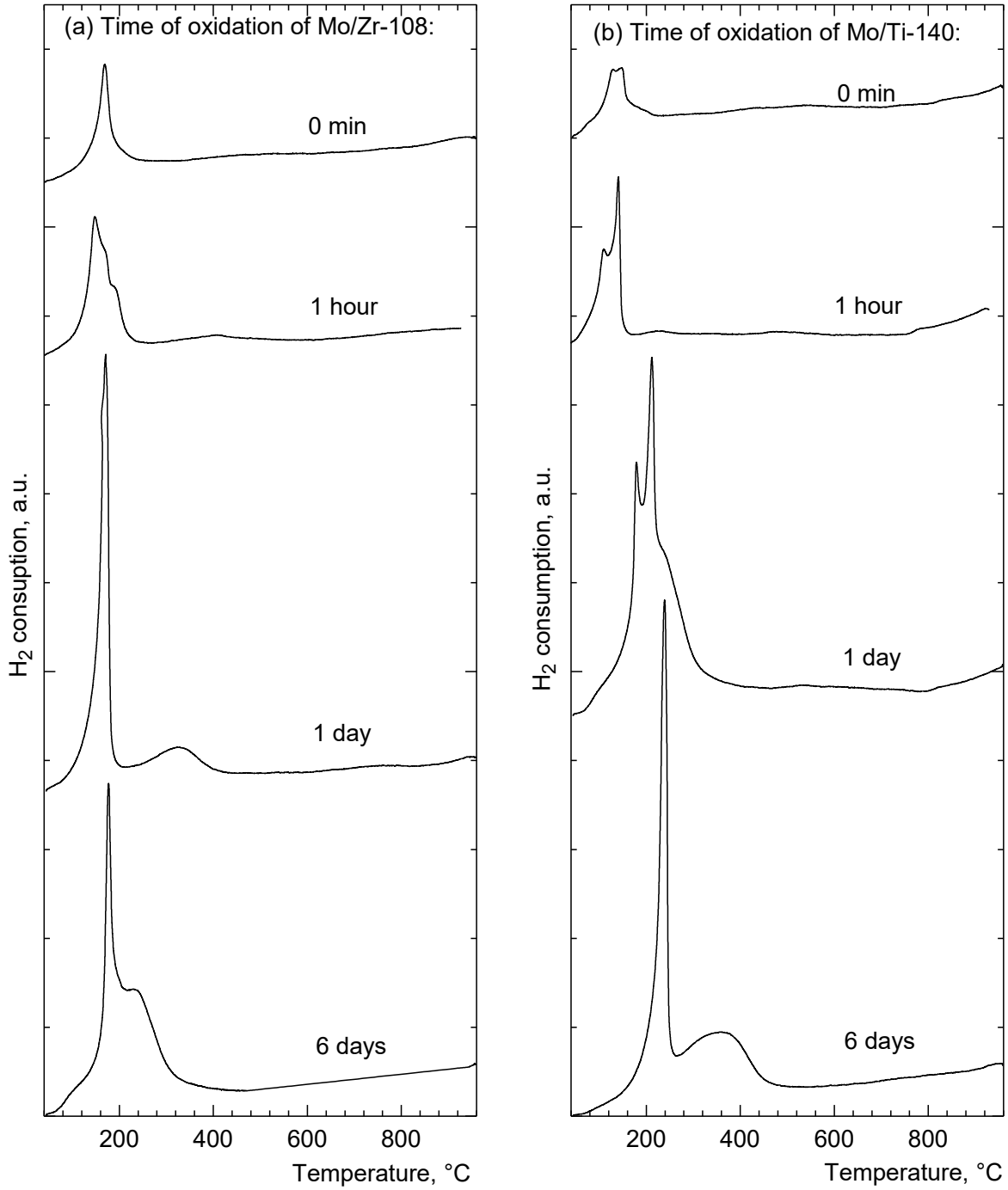


Figure S2: Re-oxidation of sulphided Mo/Zr-108 (**a**) and Mo/Ti-140 (**b**) followed by H_2-TPR.

2. Sorption of Co on sulphided Mo supported on Zr-108-e and Ti-140-e by SEM-EDX

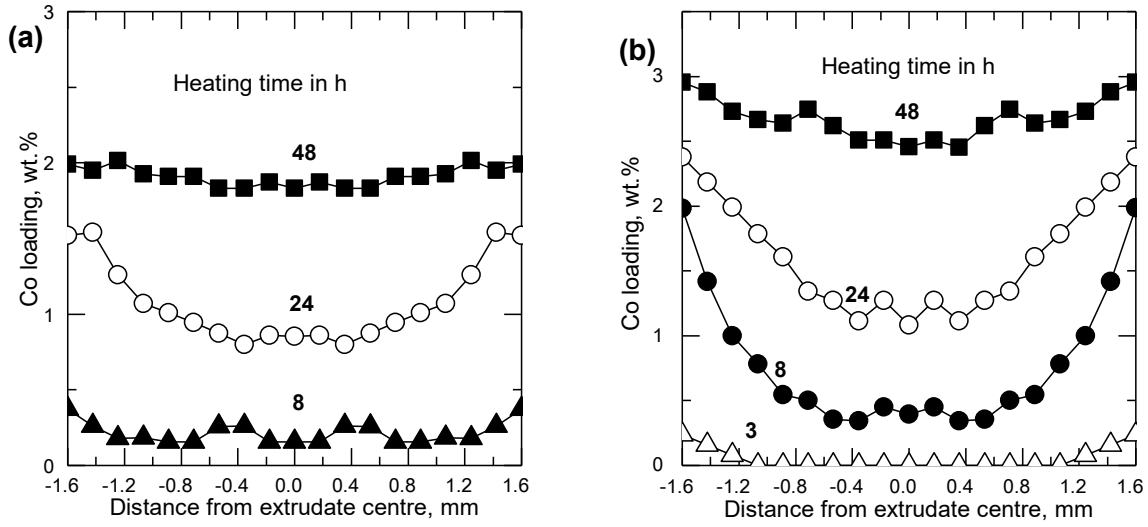


Figure S3: Saturation of Mo/Zr-108-e (**a**) and Mo/Ti-140-e (**b**) by $CoCO_3.Co(OH)_2/H_2O$ slurry.

3. H_2-TPR of sulphided MoO_3, $CoCO_3.Co(OH)_2$ and the reference CoMo catalyst

For the matter of comparison, the results of H_2-TPR of sulphided individual starting compounds MoO_3 and $CoCO_3.Co(OH)_2$ and the reference catalyst are shown in Figure S4. It was found that reduction of sulphided MoO_3 starts at temperatures above 400 °C with maximum of hydrogen consumption at about 800 °C while sulphided $CoCO_3.Co(OH)_2$ exhibited two maxima at about 230 and 830 °C. The reference sulphided catalyst exhibits typical features of supported CoMo catalysts, which are discussed in the article.

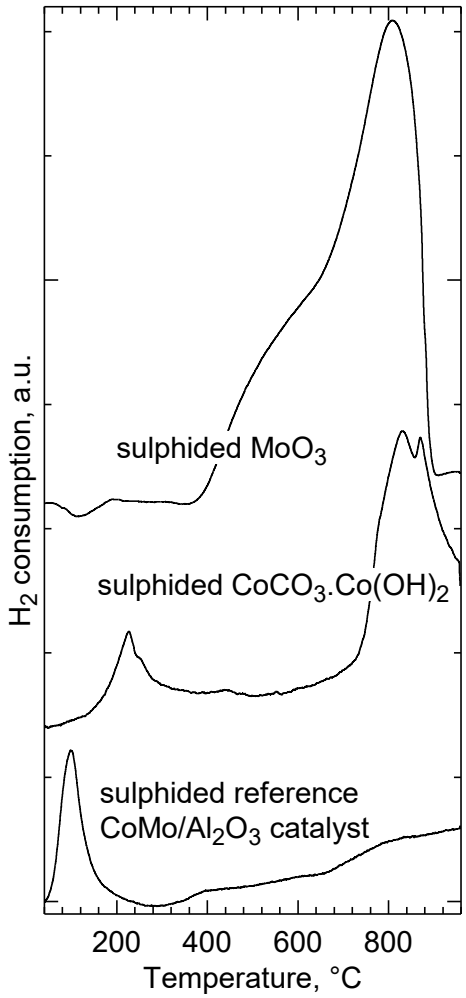


Figure S4: H_2-TPR patterns of sulphided individual starting compounds and the reference commercial CoMo catalyst.

4. XPS surface analysis of selected sulphided catalysts

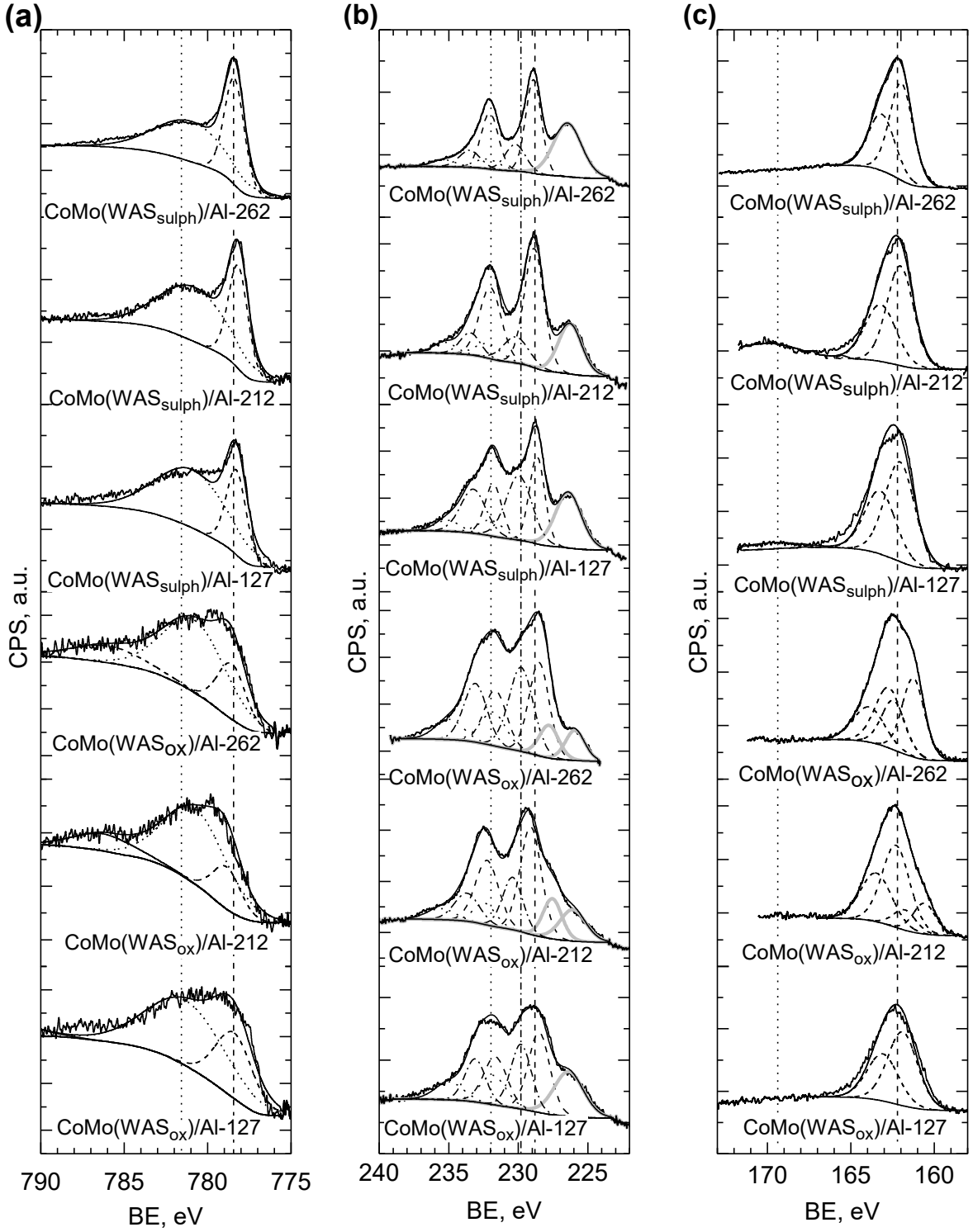


Figure S5. XPS Co $2p_{3/2}$ (a), Mo $3d_{5/2}$ (b), and S $2p_{3/2}$ (c) spectra. Binding energies (BE): **(a)** dot line – oxidic Co^{2+} (781.6 ± 0.5 eV), dash line – sulphidic Co^{2+} (778.3 ± 0.5 eV); **(b)** dot line – oxidic Mo^{6+} (232.0 ± 0.5 eV), dash dot line – MoS_xO_y (229.8 ± 0.5 eV), dash line –

sulphidic Mo^{4+} (228.7 ± 0.5 eV), grey solid line – sulphur S 2s; **(c)** dot line – sulphates SO_4^{2-} (169.5 ± 0.5 eV), dash line – sulphides S^{2-} (162.4 ± 0.5 eV).

5. Selectivity to dihydrobenzothiophene (DH) during 1-benzothiophene (BT) HDS

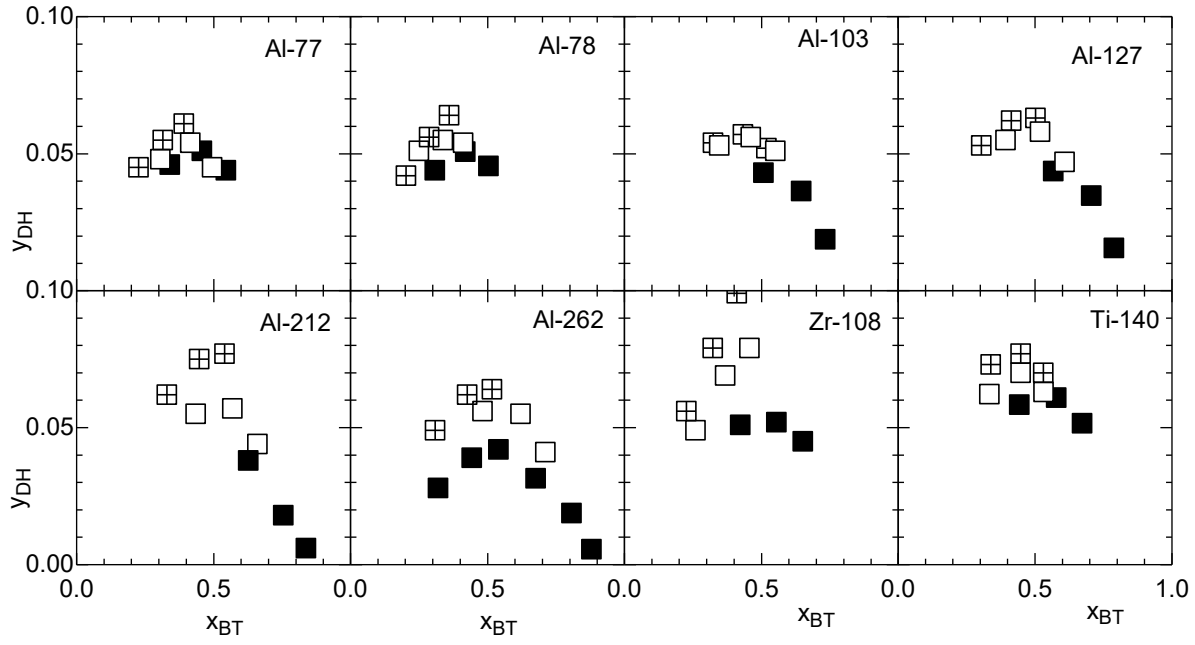


Figure S6. Selectivity to dihydrobenzothiophene (y_{DH}) during 1-benzothiophene (x_{BT}) HDS: crossed squares – CoMo(CIM_{ox}), open squares – CoMo(WAS_{ox}), and solid squares – CoMo(WAS_{sulph}).