

# Effect of Adding Chelating Ligands on the Catalytic Performance of Rh-Promoted MoS<sub>2</sub> in the Hydrodesulfurization of Dibenzothiophene

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**Abstract:** Hydrodesulfurization (HDS) is a widely used process currently employed in petroleum refineries to eliminate organosulfur compounds in fuels. The current hydrotreating process struggles to remove organosulfur compounds with a steric hindrance due to the electronic nature of the current catalysts employed. In this work, the effects of adding chelating ligands such as ethylenediaminetetraacetic acid (EDTA), citric acid (CA) and acetic acid (AA) to rhodium (Rh) and active molybdenum (Mo) species for dibenzothiophene (DBT) HDS catalytic activity was evaluated. HDS activities followed the order of RhMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (88%) > RhMo-AA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (73%) > RhMo-CA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (72%) > RhMo-EDTA/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (68%). The observed trend was attributed to the different chelating ligands with varying electronic properties, thus influencing the metal–support interaction and the favorable reduction of the Mo species. RhMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> offered the highest HDS activity due to its (i) lower metal–support interaction energy, as observed from the RhMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> band gap of 3.779 eV and the slight shift toward the lower BE of Mo 3d, (ii) increased Mo–O–Mo species ( $N_{\text{Mo–O–Mo}} \sim 1.975$ ) and (iii) better sulfidation of Rh and MoO in RhMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> compared to the chelated catalysts. The obtained data provides that HDS catalytic activity was mainly driven by the structural nature of the RhMo-based catalyst, which influences the formation of more active sites that can enhance the HDS activity.

**Keywords:** hydrodesulfurization (HDS); chelating ligands; molybdenum disulfide (MoS<sub>2</sub>); dibenzothiophene; RhMo-(L)- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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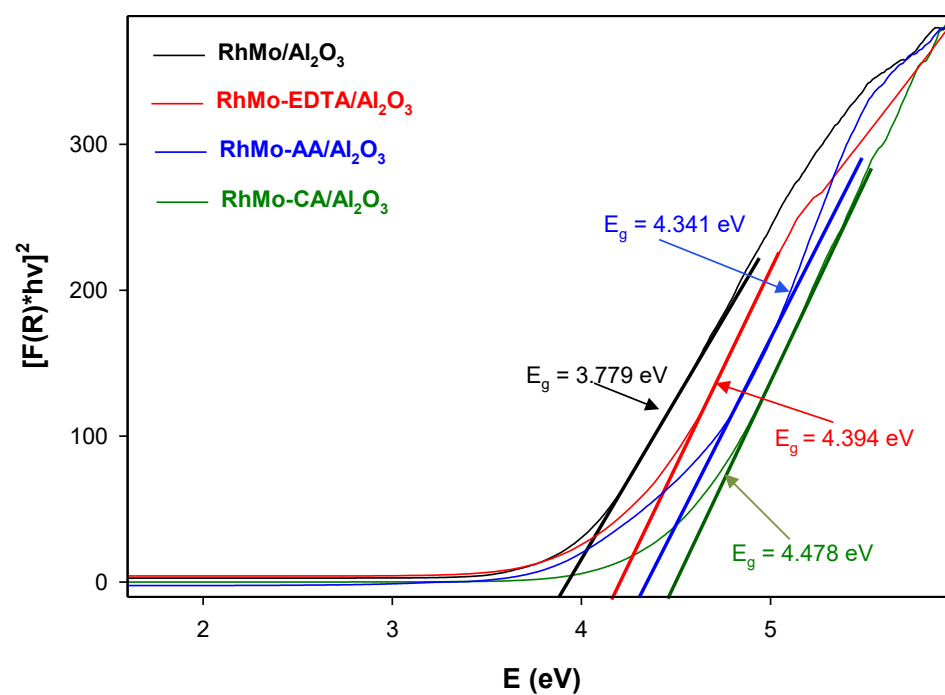
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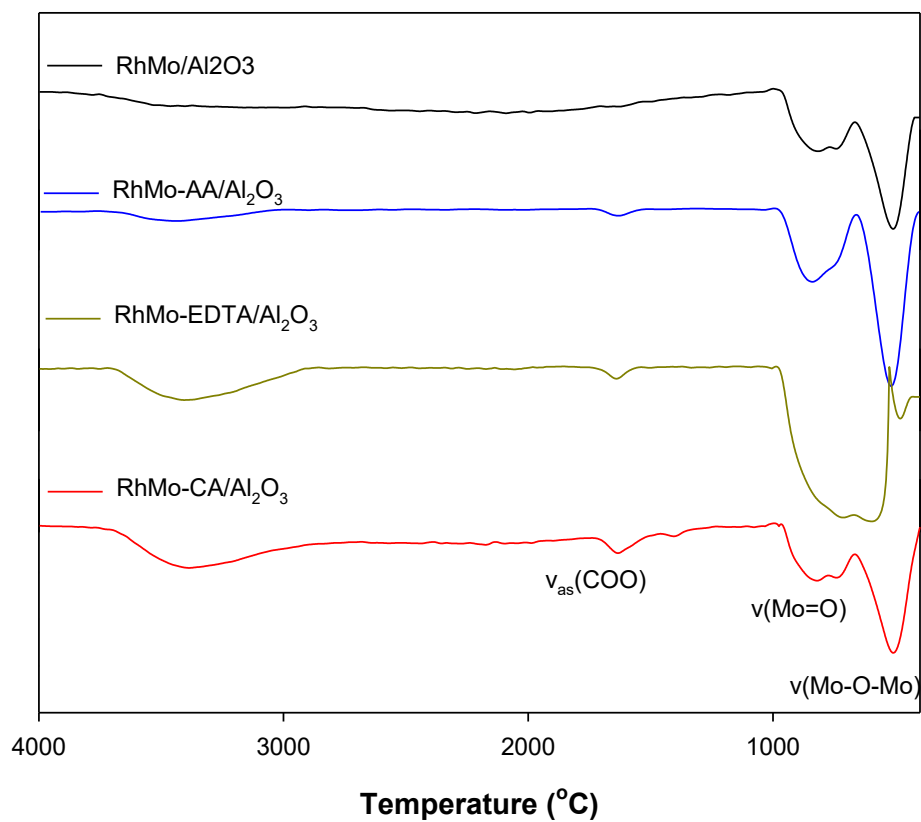
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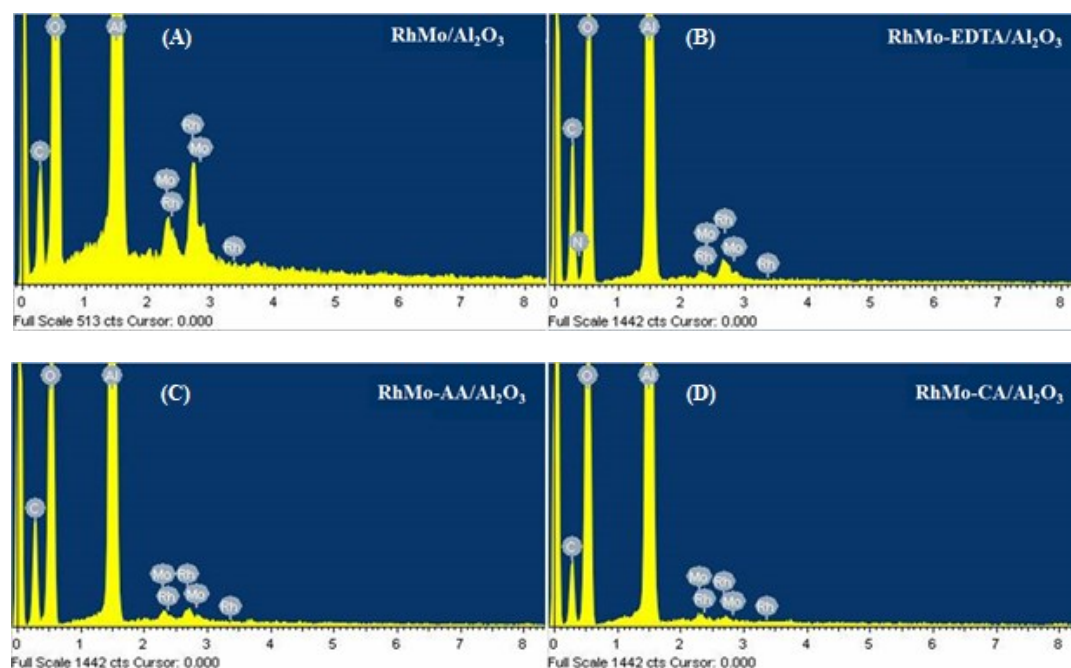
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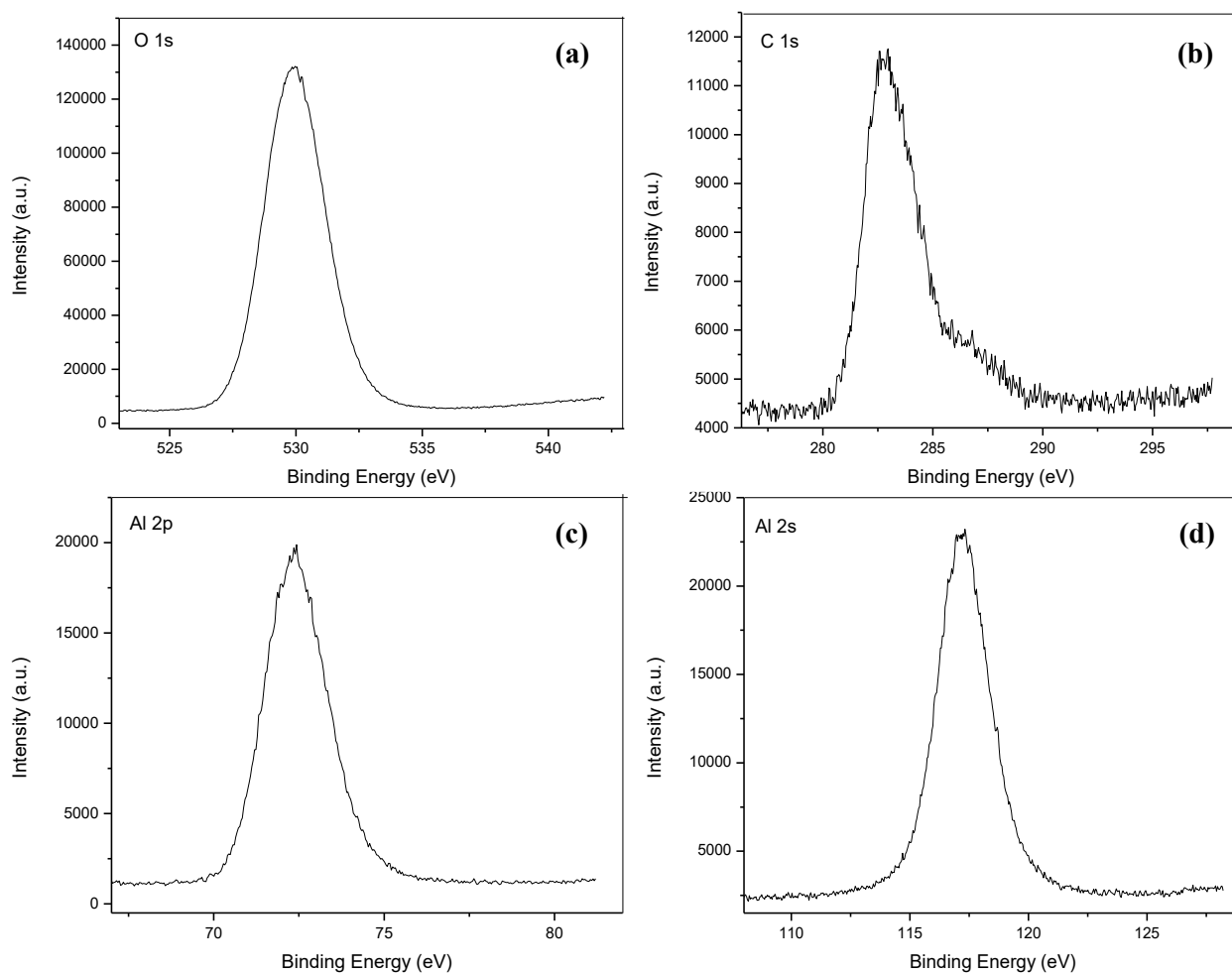
**Figure S1.** The  $E_g$  values for  $\text{RhMo}/\text{Al}_2\text{O}_3$ ,  $\text{RhMo-}x/\text{Al}_2\text{O}_3$  ( $x = \text{EDTA}$ ,  $\text{AA}$ ,  $\text{CA}$ ) obtained from a UV-Vis spectra.



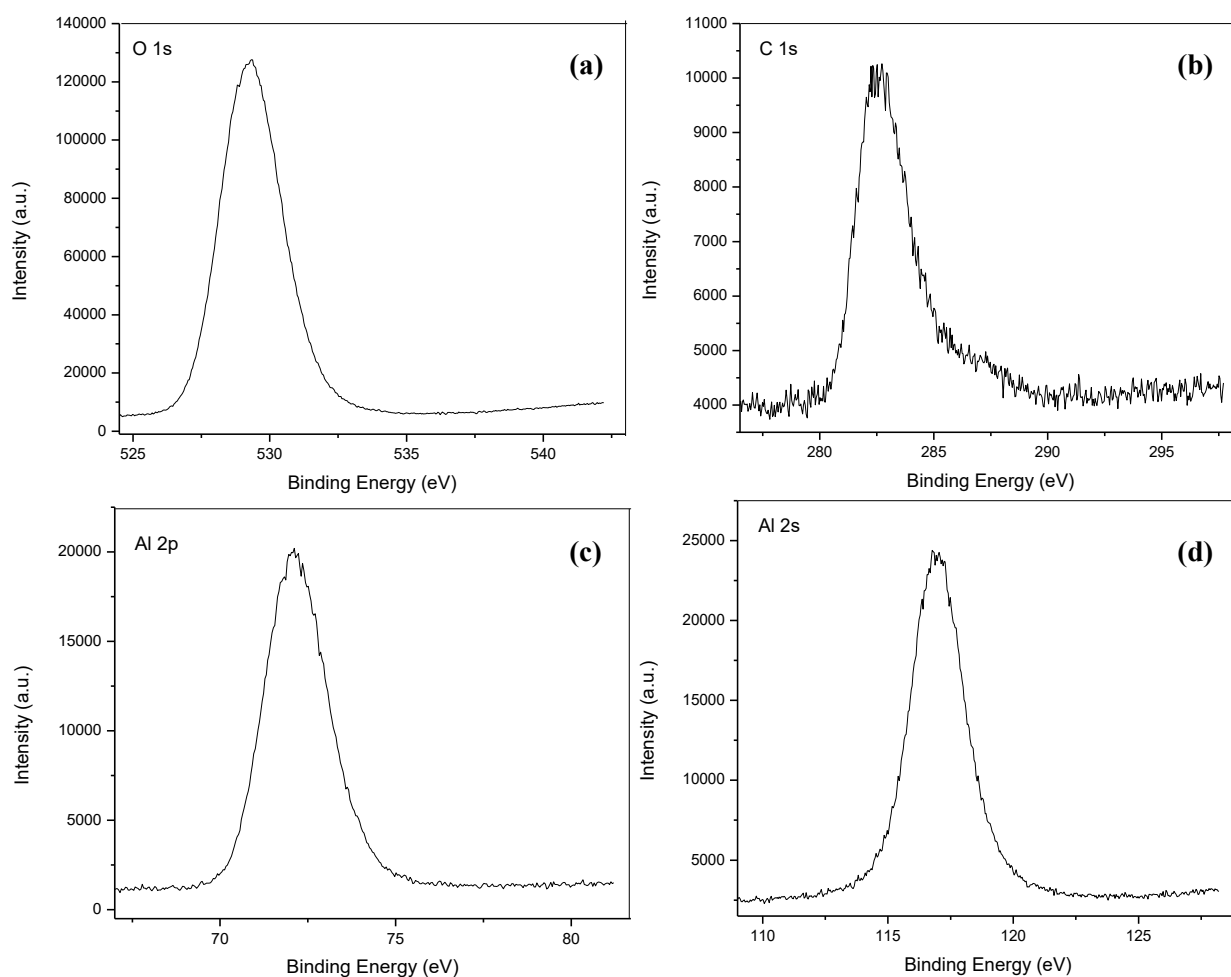
**Figure S2.** FT-IR spectra of  $\text{RhMo}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{RhMo-EDTA}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{RhMo-AA}/\gamma\text{-Al}_2\text{O}_3$ , and  $\text{RhMo-CA}/\gamma\text{-Al}_2\text{O}_3$  catalysts.



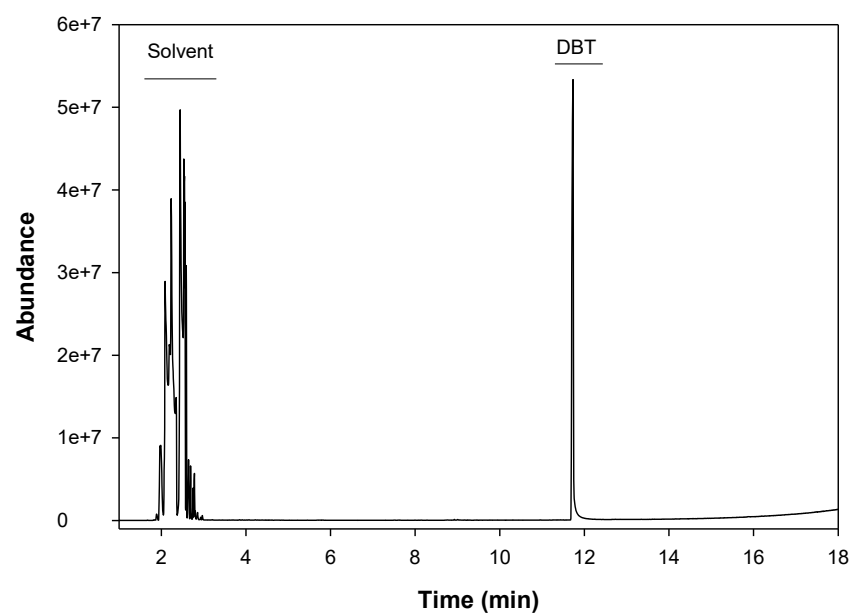
**Figure S3.** EDX analysis for (a) RhMo/Al<sub>2</sub>O<sub>3</sub>, (b) RhMo-EDTA/Al<sub>2</sub>O<sub>3</sub>, (c) RhMo-AA/Al<sub>2</sub>O<sub>3</sub>, (d) RhMo-CA/Al<sub>2</sub>O<sub>3</sub> catalysts.



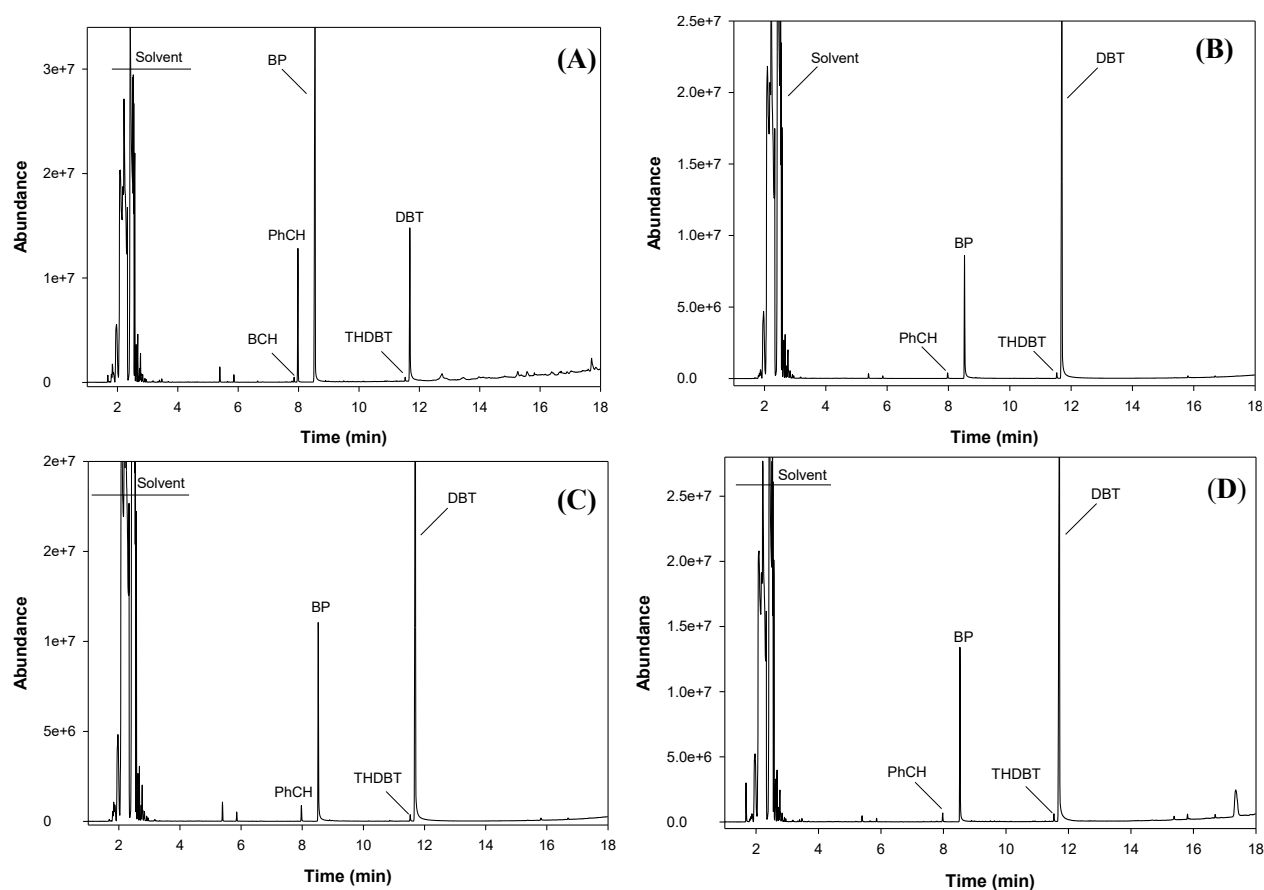
**Figure S4.** XPS spectra for RhMo/Al<sub>2</sub>O<sub>3</sub> different elemental contributions of (a) O 1s, (b) C 1s, (c) Al 2p, (d) Al 2s.



**Figure S5.** XPS spectra for CoMo-EDTA/γ-Al<sub>2</sub>O<sub>3</sub> different elemental contributions of (a) O 1s, (b) C 1s, (c) Al 2p, (d) Al 2s.



**Figure S6.** GC chromatogram of DBT before HDS.



**Figure S7.** GC chromatogram of DBT after HDS using (A) RhMo/Al<sub>2</sub>O<sub>3</sub>, (B) RhMo-EDTA/Al<sub>2</sub>O<sub>3</sub>, (C) RhMo-AA/Al<sub>2</sub>O<sub>3</sub>, (D) RhMo-CA/Al<sub>2</sub>O<sub>3</sub>, DBT = dibenzothiophene, BP = biphenyl, PhCH = biphenyl cyclohexane, BCH = bicyclohexyl, THDBT = tetrahydrodibenzothiophene.

**Table S1.** XPS parameters of the different distributions (BE) of Mo 3d obtained for chelated and unchelated RhMo/Al<sub>2</sub>O<sub>3</sub> catalysts.

Catalysts	BE (eV) Mo 3d <sub>5/2</sub>			BE (eV) S 2p		Mo distribution (%)		
	Mo <sup>4+</sup>	Mo <sup>5+</sup>	Mo <sup>6+</sup>	S 2p <sub>3/2</sub>	S 2p <sub>1/2</sub>	Mo <sup>4+</sup>	Mo <sup>5+</sup>	Mo <sup>6+</sup>
RhMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	229.2	230.1	233.4	162.3	163.5	63	17	21
RhMo-EDTA/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	229.9	230.0	233.0	160.1	163.5	60	27	13

**Table S2.** XPS parameters of the contributions of Rh 3d obtained for unchelated and chelated RhMo/Al<sub>2</sub>O<sub>3</sub> catalysts.

Catalysts	BE (eV) Rh 3d <sub>5/2</sub>			BE (eV) Rh 3d <sub>3/2</sub>		
	Rh <sub>2</sub> O <sub>3</sub>	Rh <sub>2</sub> S <sub>3</sub>	RhSO <sub>x</sub>	Rh <sub>2</sub> O <sub>3</sub>	Rh <sub>2</sub> S <sub>3</sub>	RhSO <sub>x</sub>
RhMo/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	306.1	307.7	309.3	313.2	311.2	310.2
RhMo-EDTA/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	308.3	310.5			311.4	