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Electronic Supplementary Information

# Highly selective demethylation of anisole to phenol over $H_4Nb_2O_7$ modified $MoS_2$ catalyst

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## SECTION S1 SUPPLYMENTARY FIGURES

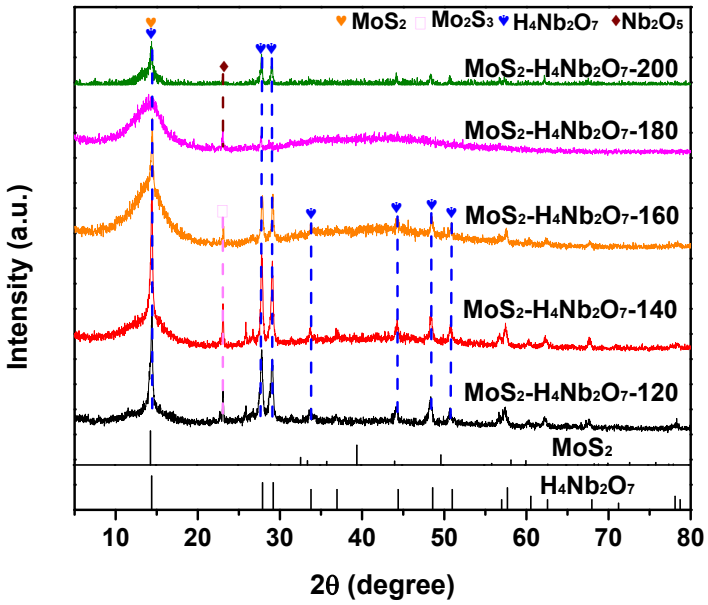


**Figure S1.** XRD spectra of the samples prepared under different temperatures.

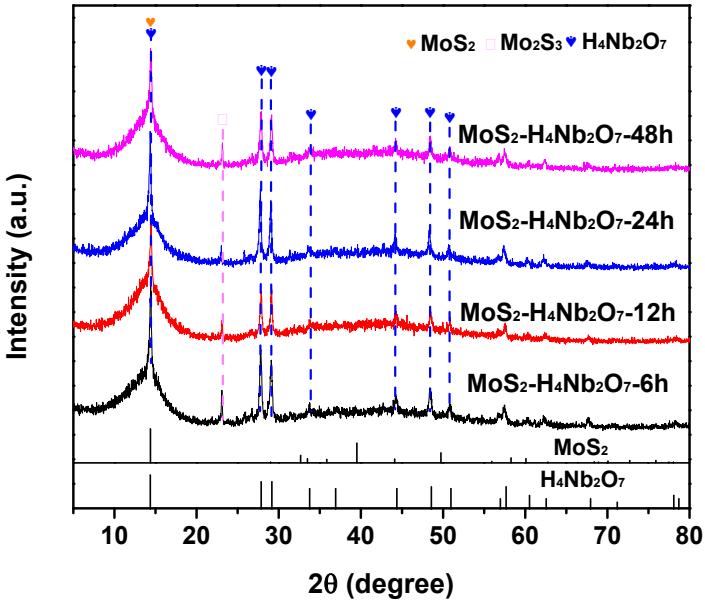


**Figure S2.** XRD spectra of the samples prepared under different hydrothermal time.

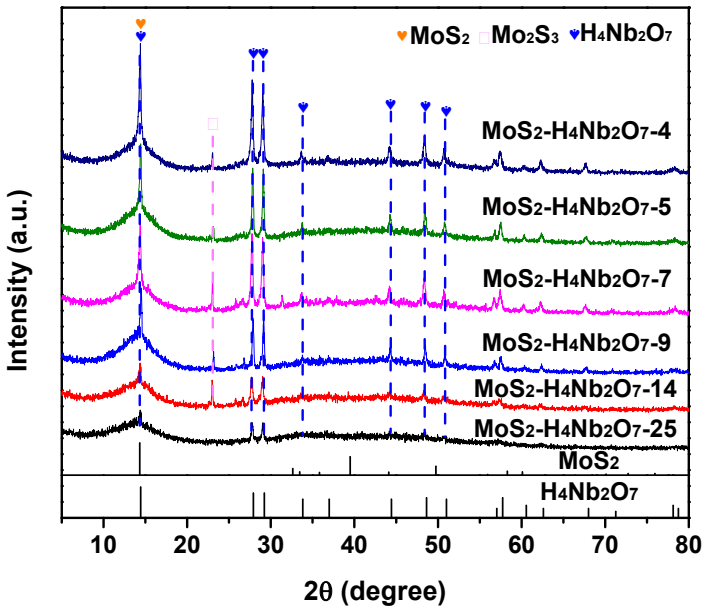


**Figure S3.** XRD spectra of the samples prepared under different Mo/Nb molar ratio.

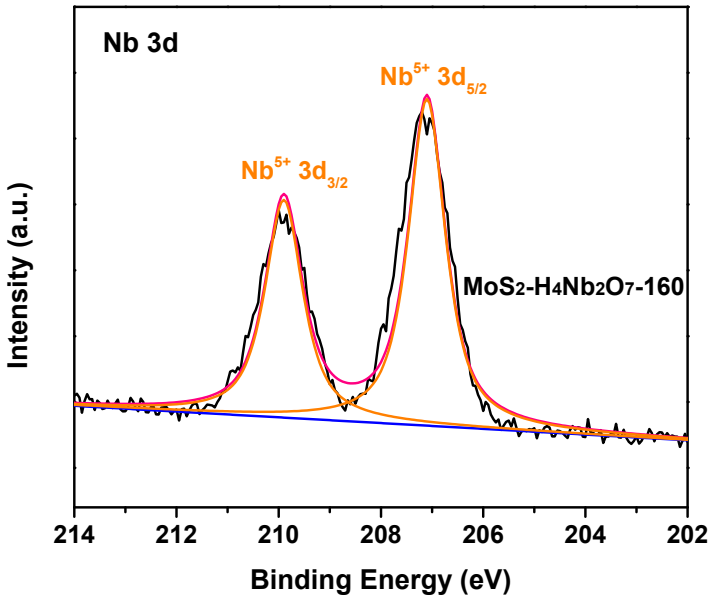


**Figure S4.** XPS spectrum of Nb 3d of the $MoS_2$-$H_4Nb_2O_7$-160 catalyst.

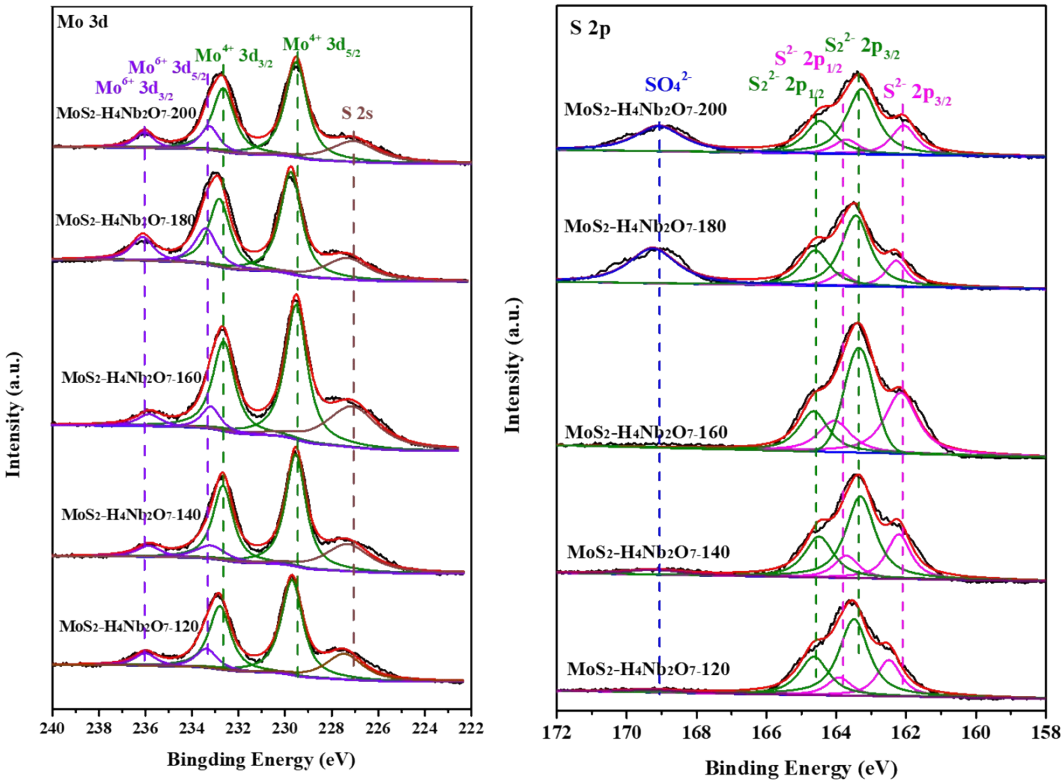


**Figure S5**. XPS spectra of (a) Mo 3d and (b) S 2p of $MoS_2$-$H_4Nb_2O_7$ catalysts.

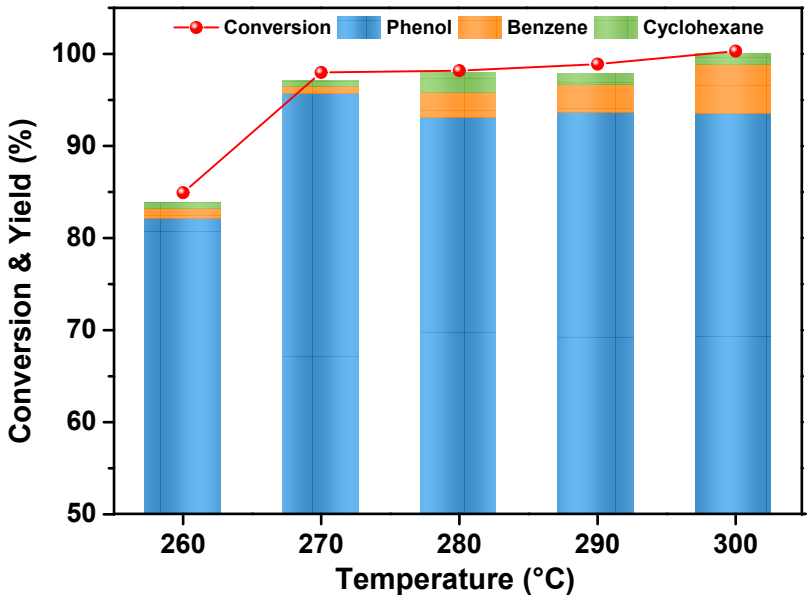


**Figure S6.** Effect of the reaction temperature in the conversion of anisole in the presence of $MoS_2$-$H_4Nb_2O_7$-160 catalyst (initial $H_2$ pressure was 3 MPa, reaction time was 4 h).

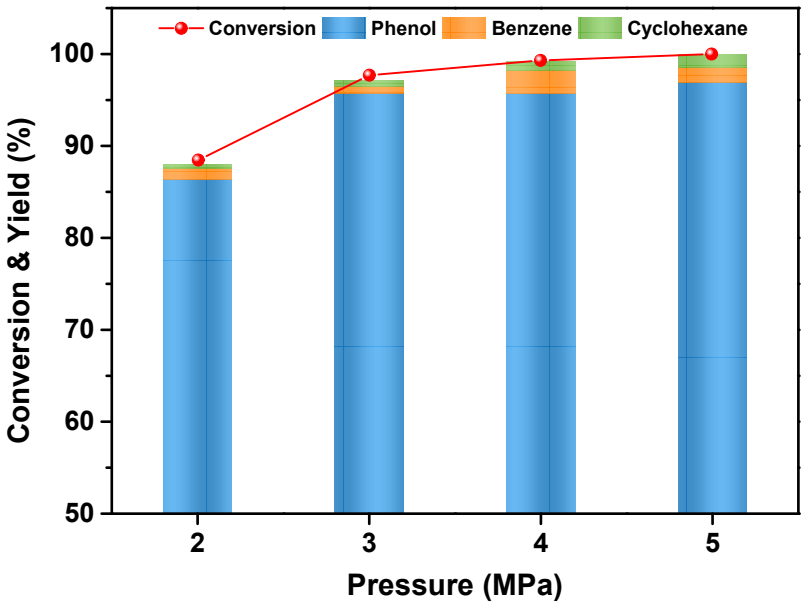


**Figure S7.** Effect of the initial $H_2$ pressure in the conversion of anisole in the presence of $MoS_2$-$H_4Nb_2O_7$-160 catalyst (reaction temperature was 270 °C, reaction time was 4h).

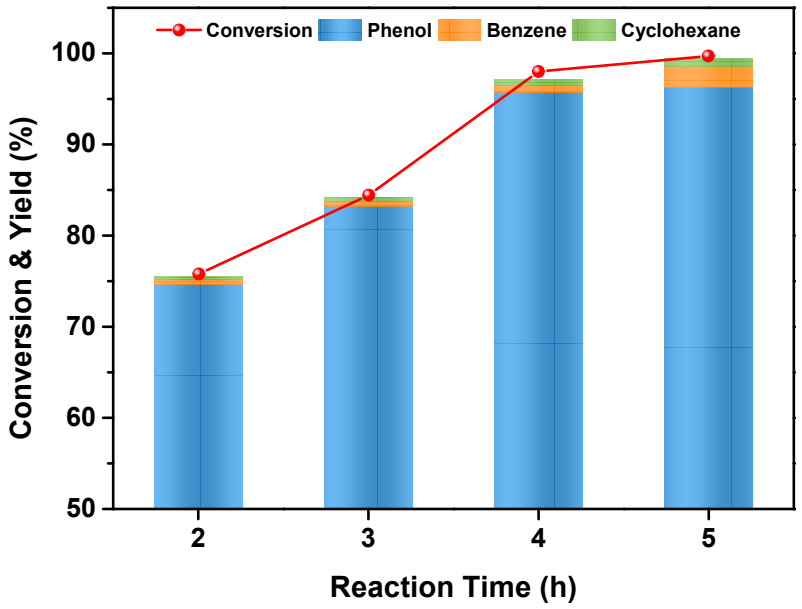


**Figure S8.** Effect of the reaction time in the conversion of anisole in the presence of $MoS_2$-$H_4Nb_2O_7$-160 catalyst (reaction temperature was 270 °C, initial $H_2$ pressure was 3 MPa).

## SECTION S2 SUPPLYMENTARY TABLES

**Table S1.** Demethylation of anisole to phenol results over different catalysts

| Catalyst | Reaction conditions | | | Results | | Ref. |
|---|---|---|---|---|---|---|
| | T (°C) | P (MPa) | t/TOS[b] (h) | Conv. (%) | Sel. (%) | |
| $Fe/SiO_2$ | 400 | 0.1 | 15[b] | 17.12 | 56 | 1 |
| Fe/Ni/HY | 350 | 4 | 1 | 94.02 | 37.56 | 2 |
| $Pd/NbOPO_4$ | 300 | 0.1 | 22[b] | 6.1 | 36.6 | 3 |
| Pt/HBeta | 400 | 0.1 | 0.5[b] | 96 | 33 | 4 |
| Pd@MIL-101 | 240 | 1 | 8 | 19 | 45.1 | 5 |
| PtZn/C | 325 | 2.75 | 1[b] | 30 | 66 | 6 |
| Ni/SBA-15 | 220 | 5 | 2 | 99.8 | 53.5 | 7 |
| RuNi/Al-SBA-15 | 400 | 0.1 | 24[b] | 10 | 99 | 8 |
| $Ni/Al_2O_3$-$SiO_2$ | 400 | 0.1 | 0.5[b] | 75.5 | 37.1 | 9 |
| Mo/CNTs | 450 | 0.8 | 3[b] | 75 | 90 | 10 |
| $CoMoS/Al_2O_3$ | 300 | 0.8 | 6[b] | 40 | 70 | 11 |
| Pt/Ni/Al-SBA-15 | 420 | 0.1 | 6 | 40 | 90 | 12 |
| $Mo@Pt/SiO_2–Al_2O_3$ | 450 | 0.1 | 1[b] | 87 | 65 | 13 |
| $Re\text{-}MoO_x/TiO_2$ | 300 | 5 | 4 | 10 | 65 | 14 |
| HY | 240 | 0.5[a] | 3 | 96.6 | 32.8 | 15 |
| $MoS_2$-$H_4Nb_2O_7$ | 270 | 3 | 4 | 97.7 | 98.0 | this work |

[a] $N_2$ was pumped in to provide initial pressure

**Table S2**. The morphology parameters of $MoS_2$ in different catalyst

| Catalyst | Slab Length (nm) | Stacking Number | $f_e$ | $f_c$ | $f_c/f_e$ |
|---|---|---|---|---|---|
| $MoS_2$ | 3.1 | 5.6 | 0.28 | 0.085 | 0.30 |
| $MoS_2$-$H_4Nb_2O_7$-160 | 2.4 | 4.6 | 0.32 | 0.141 | 0.44 |

**Table S3**. Products distribution over $MoS_2$ and $MoS_2$-$H_4Nb_2O_7$-160 catalysts at 300 °C

| Catalyst | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|
| | | Phenol | Benzene | Cyclohexane |
| $MoS_2$ | 99.7 | 88.2 | 10.4 | 2.1 |
| $MoS_2$-$H_4Nb_2O_7$-160 | 98.8 | 95.6 | 2.6 | 0.6 |

[a] Reaction conditions: 300 °C, 3 MPa, 3 h.

**Table S4**. Catalytic activity of $MoS_2$-$H_4Nb_2O_7$ prepared under different temperatures

| Catalyst | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|
| | | Phenol | Benzene | Cyclohexane |
| $MoS_2$-$H_4Nb_2O_7$-120 | 58.5 | 55.9 | 2.2 | 0.4 |
| $MoS_2$-$H_4Nb_2O_7$-140 | 84.4 | 74.5 | 3.9 | 1.1 |
| $MoS_2$-$H_4Nb_2O_7$-160 | 97.7 | 95.7 | 0.8 | 0.6 |
| $MoS_2$-$H_4Nb_2O_7$-180 | 94.9 | 88.9 | 5.4 | 0.6 |
| $MoS_2$-$H_4Nb_2O_7$-200 | 80.9 | 76.8 | 1.8 | 2.2 |

Reaction conditions: 270 °C, 3 MPa, 4 h.

**Table S5**. Catalytic activity of $MoS_2$ prepared under different temperatures

| Catalyst | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|
| | | Phenol | Benzene | Cyclohexane |
| $MoS_2$-120 | 56.5 | 52.5 | 2.3 | 0.3 |
| $MoS_2$-140 | 65.2 | 61.4 | 2.2 | 0.8 |
| $MoS_2$-160 | 68.9 | 67.8 | 0.7 | 0.4 |
| $MoS_2$-180 | 95.5 | 82.7 | 2.3 | 1.3 |
| $MoS_2$-200 | 95.7 | 83.3 | 6.7 | 1.4 |

Reaction conditions: 270 °C, 3 MPa, 4 h.

**Table S6.** Catalytic activity of $MoS_2$-$H_4Nb_2O_7$ prepared under different time

| Catalyst | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|
| | | Phenol | Benzene | Cyclohexane |
| $MoS_2$-$H_4Nb_2O_7$-6h | 87.0 | 67.3 | 3.2 | 1.3 |
| $MoS_2$-$H_4Nb_2O_7$-12h | 97.7 | 95.7 | 0.8 | 0.6 |
| $MoS_2$-$H_4Nb_2O_7$-24h | 97.3 | 90.8 | 3.8 | 1.1 |
| $MoS_2$-$H_4Nb_2O_7$-48h | 100.0 | 90.3 | 2.5 | 0.0 |

Reaction conditions: 270 °C, 3 MPa, 4 h.

**Table S7**. Catalytic activity of $MoS_2$-$H_4Nb_2O_7$ prepared at different Mo/Nb molar ratio.

| Catalyst | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|
| | | Phenol | Benzene | Cyclohexane |
| $MoS_2$-$H_4Nb_2O_7$-25 | 76.9 | 72.3 | 3.0 | 1.7 |
| $MoS_2$-$H_4Nb_2O_7$-14 | 89.4 | 86.0 | 1.1 | 2.3 |
| $MoS_2$-$H_4Nb_2O_7$-9 | 96.5 | 93.6 | 1.9 | 1.1 |
| $MoS_2$-$H_4Nb_2O_7$-7 | 97.7 | 95.7 | 0.8 | 0.6 |
| $MoS_2$-$H_4Nb_2O_7$-5 | 75.9 | 72.5 | 1.1 | 2.2 |
| $MoS_2$-$H_4Nb_2O_7$-4 | 62.0 | 60.2 | 0.9 | 0.9 |

Reaction conditions: 270 °C, 3 MPa, 4 h.

**Table S8**. Recyclability test of $MoS_2$-$H_4Nb_2O_7$-160 with $CS_2$ added in the reaction.

| Entry | Run | Conversion (%) | Yield (%) | | |
|---|---|---|---|---|---|
| | | | Phenol | Benzene | Cyclohexane |
| 1 | 1st | 98.7 | 94.7 | 3.7 | 0.2 |
| 2 | 2nd | 92.2 | 90.5 | 1.4 | 0.2 |
| 3 | 3rd | 88.9 | 85.9 | 1.4 | 0.3 |
| 4 | 4th | 88.4 | 83.9 | 0.8 | 0.2 |

Reaction conditions: 270 °C, 3 MPa, 4 h.

## SECTION S3 SYNTHESIS OF THE CATALYSTS

**Synthesis of $H_4Nb_2O_7$:** 0.2 g $Sn_2Nb_2O_7$ was dispersed in 48 mL deionized water, and then the mixture was transferred into a 100 mL Teflon-lined stainless autoclave. The pH value was adjusted to 0.9 by adding 12 mL hydrochloric acid into the mixed solution under stirring. The autoclave was sealed and heated in an oven at 160 °C for 12 h. When the reaction finished, $H_4Nb_2O_7$ was obtained by filtering, washing, and drying.

**Synthesis of $MoS_2$:** 0.92 g ammonium molybdate, and 1.2 g thiourea were dispersed into 48 mL deionized water, and then the mixture was transferred into a 100 mL Teflon-lined stainless autoclave. The pH value was adjusted to 0.9 by adding 12 mL hydrochloric acid into the mixed solution under stirring. The autoclave was sealed and heated in an oven at 160 °C for 12 h. After the hydrothermal reaction, $MoS_2$ was received by separation. $MoS_2$-X represented that the synthesis temperature was changed to X °C, while $MoS_2$-160 was written directly as $MoS_2$.

**Synthesis of $Sn_2Nb_2O_7$:** 0.8 g $Nb_2O_5$ was dispersed in 72 mL KOH solution (3 mol/L) and transferred into a 100 mL Teflon-lined stainless autoclave. After a hydrothermal process at 200°C for 12 h, 0.72 g $SnCl_2$ and 4.8 g urea were added into the solution obtained from the first step then nitrogen gas was entered to the bottom of the autoclave for 30 minutes to remove oxygen from the solution. Heated at 200 °C for 12 h, the products $Sn_2Nb_2O_7$ were obtained after filtration and washed and dried.

## SECTION S4 REFERENCES


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