WS_2 catalysts for ultra-deep HDS: IR/CO characterization for quantification of active sites and effect of citric acid addition.

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Ultra-deep Hydrodesulfurization (HDS)

The increasing demand for low sulfur fuels puts pressure on the development of more active HDS catalysts. Intensive attention has been paid to Mo catalysts and less work has been devoted to the W-based catalysts, although these catalysts, with a high hydrogenation potential, are a promising option for deep HDS.

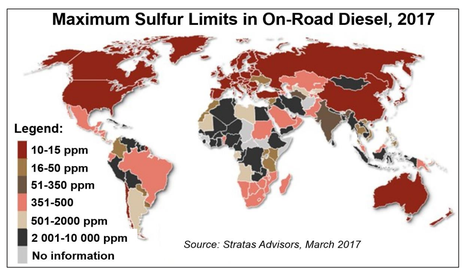


Fig. 1 . Maximum sulfur limits in on-road Diesel, 2016.

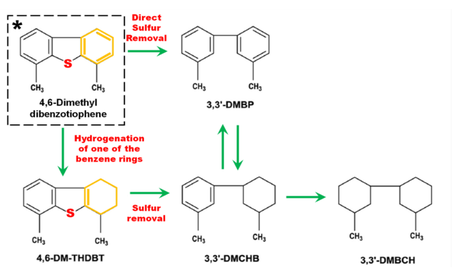


Fig. 2. Pathways of HDS of DBT reaction.

A better understanding of the nature of the active phases is of prime importance. However, the chemical properties of W-based catalysts are poorly understood in comparison with the Mo-based catalysts.

MoS_2 structure detected by IR/CO [1-4]

MoS_2 slab present two types of edges with different terminations. Recently, parallel between IR/CO spectroscopy on sulfided Mo/Al_2O_3 and DFT calculation provides evidence that the IR/CO signal can discriminate between the M- and S-edges of supported MoS_2 phase.[3,4]

Fig. 3. Low temperature IR/CO spectra of Mo/Al_2O_3 after sulfidation at 623 K. Samples prepared with different CA concentration.

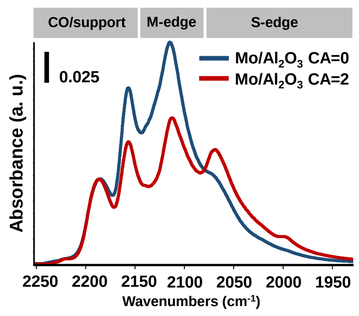


Fig. 4. Slab morphology according to the M-edge/S-edge ratio when CA conc. Is varied.

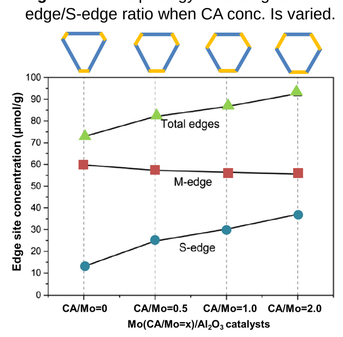
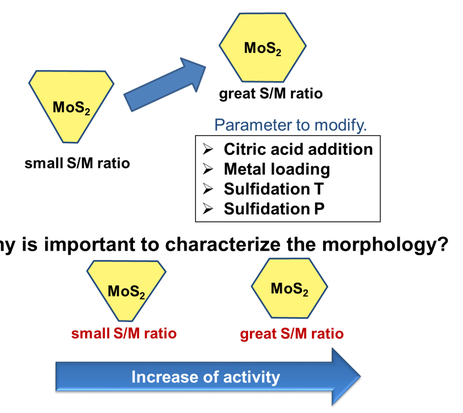


Fig. 5. Parameters involved on MoS_2 morphology.



MoS_2 morphology is strongly influenced by MoS_2− Al_2O_3 interactions under the same sulfidation temperature and that these can be altered by the addition of a chelant agent.

Experimental

Catalyst preparation

W/Al_2O_3 catalysts with different amounts of citric acid (CA) and different W loading were prepared by a one-step pore volume impregnation method. The catalysts were dried at 383 K for 16 h to keep the chelating agent in its initial form.
the W/Al_2O_3 catalysts prepared with citric acid are denoted as $W(CA/W = x)/Al_2O_3$.
x = 0, 1, 2. W content was varied from 0.85 W to 3.3 atoms/nm^2.

IR/CO Characterization

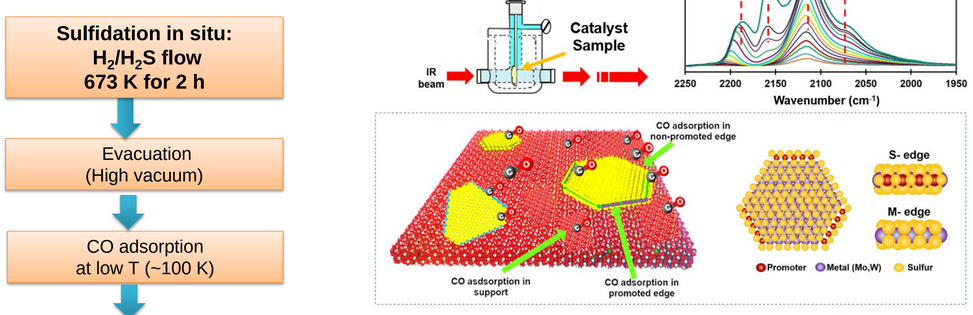
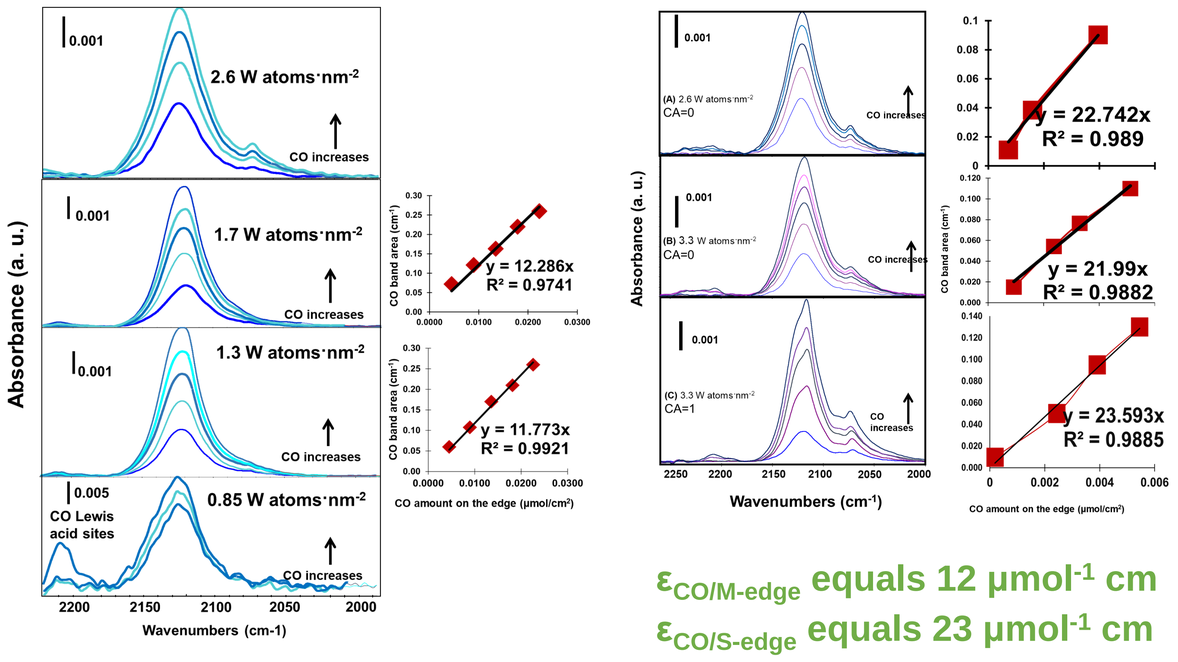


Fig. 6. low temperature *In situ* IR/CO cell; CO adsorption on exposed edges on MS_2 slab.

CO molar extinction coefficient $\varepsilon_{CO/M\text{-}edge}$ and $\varepsilon_{CO/S\text{-}edge}$.

For determination of molar extinction coefficient of CO adsorbed on S-edge ($\varepsilon_{CO/S\text{-}edge}$), the ratio between M-edge and S-edge bands has to be modified through the addition of citric acid. the first step was to select carefully the W catalysts for calculation of the CO molar extinction coefficient $\varepsilon_{CO/M\text{-}edge}$ and $\varepsilon_{CO/S\text{-}edge}$.



$\varepsilon_{CO/M\text{-}edge}$ equals 12 µmol^{-1} cm
$\varepsilon_{CO/S\text{-}edge}$ equals 23 µmol^{-1} cm

Fig. 9. IR spectra of the first CO doses adsorbed on W/Al_2O_3 at different metal loadings.

IR Spectroscopic Evidence of WS_2 Morphology Change with Sulfidation Temperature and citric acid addition.

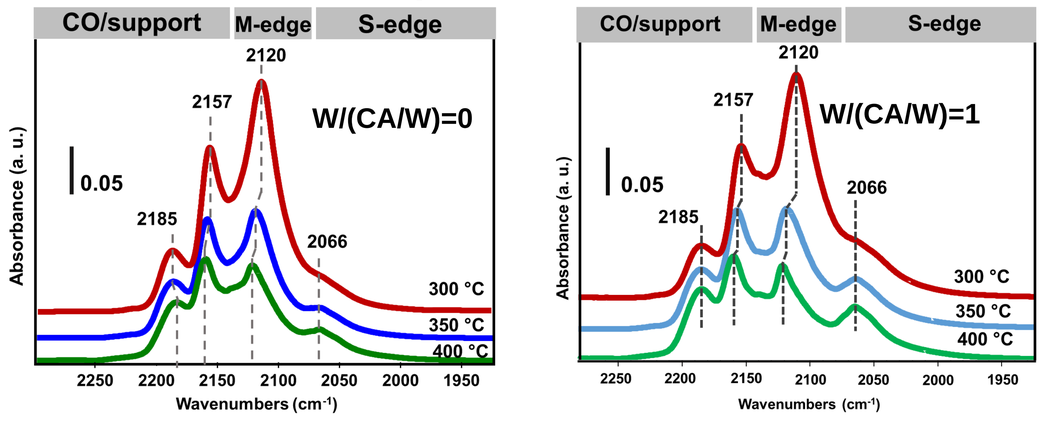


Fig. 7. IR spectra of CO adsorbed (133 Pa at equilibrium, 100 K) on W/Al_2O_3 catalyst sulfided with 10% H_2S/H_2 at different temperatures.

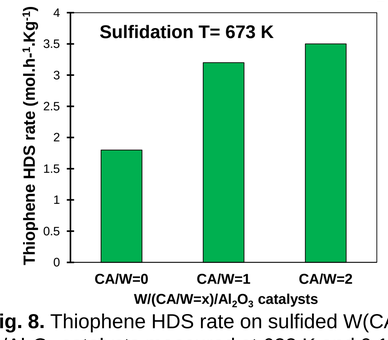


Fig. 8. Thiophene HDS rate on sulfided $W(CA/W = x)/Al_2O_3$ catalysts measured at 623 K and 0.1 MPa.

- ✓ The IR/CO data indicate that the truncation degree (ratio of S-edge/M-edge) of WS_2 slabs gradually increases with sulfidation temperature and citric acid addition.
- ✓ These results are in agreement with the ones of Mo based catalysts.
- ✓ The increase of S-edge/W-edge ratio leads to an increase in HDS activity.

Conclusions

Low-temperature (IR/CO) was used to depict the WS_2 morphology change with sulfidation temperature on W/Al_2O_3 and $W(CA)/Al_2O_3$ catalysts. Within a HDS sulfidation temperature range (573 to 623 K), it is found that the WS_2 phase on the W/Al_2O_3 and $W(CA)/Al_2O_3$ catalyst exposes both the M-edge and S-edge, and ratio of the Sedge/ M-edge steadily increases with sulfidation temperature, indicating that the WS_2 slab becomes more heavily truncated. For the first time molar extinction coeficients associated to M-edge and S-edge were successfully determined.

Perspectives

Proof by DFT calculations on the WS_2 system.
Density Functional Theory (DFT) calculations are envisaged in order to verify the CO bands attributions according to the sulfidation temperatures for the nonpromoted WS_2 system examined here. In the same line, a comparison between our experimental results and the DFT calculations for stable morphologies will help to verify and proof the results obtained by IR/CO. This, along with quantification of W-edge and S-edge concentrations will provide reliable information that describes the WS_2 systems closely to real operating conditions.

References
[1] J. Chen, E. Dominguez, L. Oliviero, F. Maugé. J. Catal. 332 (2015) 77–82.
[2] J. Chen, F. Maugé, J. El Fallah, L. Oliviero, J. of Catal. 320 (2014) 170–179.
[3] J. Chen, V. Labruyere, F. Maugé, A Quoineaud, A. Hugon, L. Oliviero, J. Phys Chem C. 118, 51 (2015) 30039-30044.
[4] J. Chen, L. Oliviero, X. Portier, F. Maugé, RSC Advances, 5 (2015) 81038-81044.