ABSTRACT:

Role of the Zeolite Support in Water-Gas Shift Pathways over MoS_2 Catalysts under Operando Conditions

F. Dalena[1], J. Aguesse[1], A. Amedlous[1], Svetlana Mintova[1]*
[1]Laboratoire Catalyse et Spectrochimie (LCS) Normandie Univ, ENSICAEN, UNICAEN, CNRS, 14000 Caen, France

The water–gas shift (WGS) reaction over MoS_2 catalysts is commonly described as a redox process involving CO oxidation by water [1]. However, under water-rich conditions, the local organization of confined water can strongly influence reaction pathways [2]. Here, we investigate how zeolite supports modulate WGS chemistry by controlling the structure and reactivity of confined water.MoS_2 catalysts supported on ZSM-5 in its protonic (H-ZSM-5) and sodium (Na-ZSM-5) forms were used as a model system, preserving identical topology and comparable Mo loading while isolating the effect of the chemical environment. Operando FTIR combined with gas-phase analysis reveals that the nature of the compensating cation governs both transient behavior and steady-state reactivity.

On Na-ZSM-5, water is stabilized as molecular species coordinated to Na+ cations, leading to higher CO conversion and a WGS-dominated carbon distribution. In contrast, H-ZSM-5 promotes structured hydrogen-bonded networks and hydronium-like species (H3O+), which correlate with lower CO conversion and enhanced carbonyl sulfide (COS) formation, indicating a diversion toward sulfur-mediated pathways.Operando analysis shows that WGS proceeds through competing mechanisms involving COS formation and hydrolysis, with the balance between productive and parasitic pathways governed by the local water microenvironment.

These results demonstrate that catalytic performance is governed by water organization rather than total uptake, highlighting the role of confined water in directing reaction mechanisms.

[1] W. Zhao, F. Maugé, J. Chen, L. Oliviero, *Chem. Eng. J.*, **455**, 140575 (2023)
[2] Q. Liu, J. A. van Bokhoven, *Chem. Soc. Rev.*, **53**, 3065 (2024)