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MoS2 catalysts for production of H2 through water gas shift reaction: Role of potassium on active edge sites and catalytic activity

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PURPOSE OF THE ABSTRACT

On the way towards non-carbonaceous energy, dihydrogen appears as a promising energy vector. In particular, efforts are focus on its production from biomass, a carbon-neutral and naturally abundant sustainable energy resource. The treatment of biomass either thermic or biologic leads to formation of so-called syngas (CO, H2). The water gas shift (WGS) reaction, which transforms CO and H2O in CO2 and H2, is then attracted renewed interest as the key process of maximum hydrogen production from the biomass-derived syngas1. However, conventional metal oxide catalysts for WGS reaction are easily deactivated by sulfur-containing impurities, which are generally present between 100 to 200 ppmv in syngas issued from biomass feedstocks. Establishing an energy-efficient and economical WGS catalytic process requires the development of high-performance and stable catalysts capable of adapting to the diversified qualities biomass feedstocks, especially for the issue of sulfur poisoning. For this issue, transition metal sulfides are considered good candidates. However, in order to tailor their composition and morphology, fundamental understanding of their activity in WGS is required.

In this work, we first apply the in situ low temperature adsorption of CO followed by IR spectroscopy (IR/CO) methodology on alumina-supported MoS2 catalysts presenting different sulfide slab morphology and after contacting them with CO and/or H2O doses. This approach shows for the first time that the two different edges exposed by MoS2 slabs, M-edge and S-edge sites, present different behavior towards the reactant CO and H2O. More precisely, it appears that the M-edge sites are sensitive to H2O through S/O exchange while the S-edge sites are reactive with CO which is transformed in COS. Next, following the WGS reaction in classical reactor and/or in operando IR cell, it appears that these two edge sites have also different activities and stabilities with time-on-stream. The M-edge sites partially deactivate during WGS reaction. Stepwise operando reaction study further reveals that on these M-edge sites, the formate mechanism preferentially occurs. On the S-edge sites, the WGS goes through a redox pathway involving COS as intermediate. This is the first time that such a modified redox pathway is identified.

From these structure-activity/stability results, our study further aims to explain the promoting effect of alkali metal on supported MoS2 water-gas shift (WGS) reaction2. The promotion of alkali metal has usually been linked to enhanced dispersion of the active phase, i.e. increase in active site concentration. However, our IR/CO results on K-MoS2/Al2O3 catalyst series, prepared by a one-step pore volume impregnation method, show that after potassium addition the concentration of accessible edge sites on MoS2 slabs is decreased. Thus, it appears that the increase in activity through K addition is rather linked to an increase in intrinsic activity of the edge sites. Accordingly, a downward shift of the v(CO/MoS2) wavenumber indicates that the presence of K increases the electron density of edge Mo atoms. This electronic effect affects the reactivity of both edge sites with CO through activation of terminal S atoms, leading to greater COS formation at low temperature (423 K). Additionally, little or even no formate species are observed on K-modified MoS2 catalysts during IR operando studies. If the increase in redox path activity appears clearly; stepwise reaction study is on the way to check if the formate route is either favored or totally limited by K addition.

In conclusion, this work that reveals the different reactivities of the two edges of the MoS2 slabs and their

modification by K addition, gives original and new perspectives towards the improvement of sulfide catalysts for production of H_2 through WGS reaction.

FIGURES

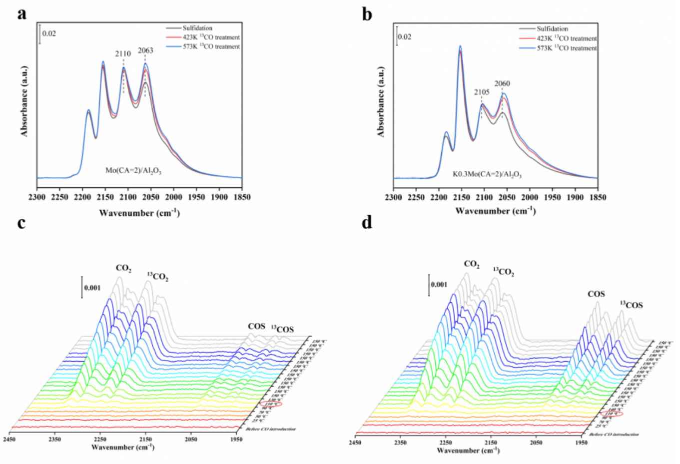

FIGURE 1

Investigation of the effect of K on S- and M- edge sites upon CO treatment

(a-b) CO/IR spectra at 133 Pa equilibrium on sulfided Mo(CA=2)/Al2O3 (a) and K0.3Mo(CA=2)/Al2O3 (b) catalysts before and after CO treatment. (c-d) Operando IR spectra of gas phase recorded during 423K CO treatment on sulfided Mo(CA=2)/Al2O3 (c) and K0.3Mo

FIGURE 2

KEYWORDS

CO adsorption | IR spectroscopy | Operando study | redox/formate mechanism

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