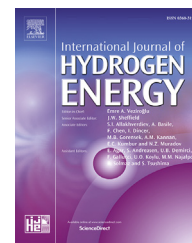




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Short Communication

Hydrogen production by water-gas shift reaction over Co-promoted MoS₂/Al₂O₃ catalyst: The intrinsic activities of Co-promoted and unprompted sites

Jianjun Chen ^{a,b}, Jincheng Zhang ^a, Jinxing Mi ^a,
Elizabeth Dominguez Garcia ^c, Yanning Cao ^a, Lilong Jiang ^{a,*},
Laetitia Olivier ^{c,**}, Françoise Maugé ^c

^a National Engineering Research Center of Chemical Fertilizer Catalyst, School of Chemical Engineering, Fuzhou University, Fujian, China

^b School of Environment, Tsinghua University, Beijing, China

^c Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, Caen, France

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ABSTRACT

Co-promoted MoS₂/Al₂O₃ is the industrial-widely used catalyst for hydrogen production by water-gas shift (WGS) reaction under sulfur-containing condition. Despite of the intensive physicochemical characterizations, the intrinsic activities of Co-promoted and unprompted sites on this catalyst are still unreported, mainly owing to the lack of quantification method of catalytic sulfide sites. With low temperature CO adsorption followed by IR spectroscopy, a distinguish technique developed by our group, this short communication reports the temperature-dependent TOFs (turnover frequencies) of these two sites, and reveals that Co-promoted site is intrinsically much more active than unprompted site at low temperatures, while these two sites are catalytically comparable at higher reaction temperatures. The catalytically different performances are related to the different apparent activation energies of WGS reaction on these two sites. This work fills in the long-standing gaps in hydrogen production by WGS reaction over sulfided CoMo/Al₂O₃ catalyst.

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Introduction

Hydrogen is known as an environmental-benign and sustainable energy for the future, the production of which is a world-wide topic for both academia and industry [1–4]. Various catalytic reactions have been developed for large-

scale H₂ manufacture in the past decades, among which is the water gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂) [5,6]. While the WGS catalysts such as Fe₂O₃-Cr₂O₃ and CuO-ZnO-Al₂O₃ deactivate quickly after contacting with sulfur-containing compounds, Co-promoted MoS₂/Al₂O₃ catalyst shows excellent activity in the presence of H₂S [7–9].

* Corresponding author.

** Corresponding author.

E-mail addresses: jl@fzu.edu.cn (L. Jiang), Laetitia.oliviero@ensicean.fr (L. Olivier).

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Due to the importance and wide applications of hydrogen, many studies were conducted on the Co-MoS₂/Al₂O₃ WGS catalysts [10–15]. Recent experimental and theoretical investigations [16–18] reveal that there are generally two type of active sites on the surface of Co-MoS₂/Al₂O₃ catalyst. One is the Co-promoted site, or the so-called CoMoS site, formed by the decoration of Co on the edge of MoS₂ nano-slabs; the other one is the MoS₂ edge site that is not occupied by cobalt, or the unprompted MoS₂ edge site. With low temperature (liquid nitrogen temperature) CO adsorption followed by in-situ IR spectroscopy (IR/CO), we well distinguished and quantified the Co-promoted and unprompted sites, and further compared the activities of these sites in hydrotreating reactions [19–25].

In this work, the intrinsic activities of Co-promoted and unprompted sites in WGS reaction are reported. For this purpose, a set of Co-MoS₂/Al₂O₃ catalysts with variable cobalt was prepared with impregnation method. The catalytic WGS rates over the series of Co-MoS₂/Al₂O₃ catalysts were tested, and IR/CO was employed to probe the concentrations of Co-promoted and unprompted sites. Based on the activity and IR/CO results, the temperature-dependent TOFs (turnover frequencies) of Co-promoted and unprompted sites in WGS reaction were calculated. The obtained TOFs were further discussed with the apparent activation energies on the two sites.

Experimental

Catalyst preparation

A series of oxidic CoMo/Al₂O₃ with variable Co loadings were prepared by one-step pore-volume impregnation. Impregnation solutions were made by dissolving ammonium heptamolybdate and variable amounts of cobalt nitrate in deionized water. After impregnation, the samples were aged for 24 h, followed by drying at 110 °C for 4 h and calcining at 500 °C for 4 h. The prepared catalysts were denoted as Co(x)Mo(9)/Al₂O₃, the values in brackets mean the weight percentage of Co and Mo, wherein x = 0, 1, 2, 3, respectively. All the reagents are AR grade. Detailed catalyst preparation can be found in [Supplementary information \(SI\)](#).

Catalyst activity tests

The catalytic WGS activity tests were conducted in a vertical fixed-bed micro-reactor. Prior to activity test, the oxidic catalysts were sulfided in a gas mixture of 10% H₂S/H₂ with the temperature raising from RT to 350 °C (3 °C/min) and maintaining at 350 °C for 2 h. The catalytic activity were measured under the following condition: temperature range 200–450 °C, feedstock composition 26 vol% CO, 54 vol% H₂ and 20 vol% CO₂, space velocity of 2000 h⁻¹, and water/gas molar ratio 1. Water was introduced into the reactor using a steam generator along with the gas flow. After a stabilization period at each temperature point, the CO concentration was measured using an on-line GC. The catalytic rate (r , μmol/(s·g_{cat.})) was calculated with the following equation.

$$r = X_{CO} \cdot F_{CO} / (22.4 \text{ L/mol} \cdot m_{cat.})$$

In the above equation, X_{CO} is the conversion of CO (%) which was controlled below 20%. F_{CO} is the flow of CO (μL/s) and $m_{cat.}$ (g) is the mass of the catalyst after sulfidation. X_{CO} was calculated as $X_{CO} = [(1 - V'_{CO}/V_{CO}) / (1 + V'_{CO})] \times 100\%$, in which V_{CO} and V'_{CO} are the inlet and outlet CO volume fraction (%), respectively.

Low temperature CO adsorption followed by in-situ IR spectroscopy (CO/IR)

The CO/IR experiments were performed on a special-designed IR cell (CellEX) in the Laboratoire Catalyse et Spectrochimie (LCS), France. CellEX consists of three parts for activation, transfer and IR characterization of the catalyst [26]. The catalyst pressed into a pellet was sulfided with the same procedure as activity test in the activation zone. The sulfided pellet was moved into the IR characterization part through transfer zone without air contamination. In the IR characterization zone, the catalyst was evacuated at 350 °C for 1 h and cooled down to RT under evacuation. After that the pellet was cooled down with liquid nitrogen and small doses of CO were introduced onto the surface of the pellet until 133 Pa CO at equilibrium was reached in the IR cell. An IR spectrum was collected after each dose of CO. The obtained spectra were normalized and carefully decomposed, after that the concentrations of CO adsorbing sites were calculated. The details of the CellEX was described in our early work [26], while the spectrum normalization/decomposition and site quantification was reported in our previous studies [19,22,25].

Results and discussion

Before activity test, the physicochemical properties of Co(x)Mo(9)/Al₂O₃ catalysts were investigated by a set of characterizations such as BET, HRTEM, H₂-TPR, Raman and UV–Vis spectroscopy. The results are well consisted with previous studies [27–34] and can be found in the [Supplementary information \(SI\)](#).

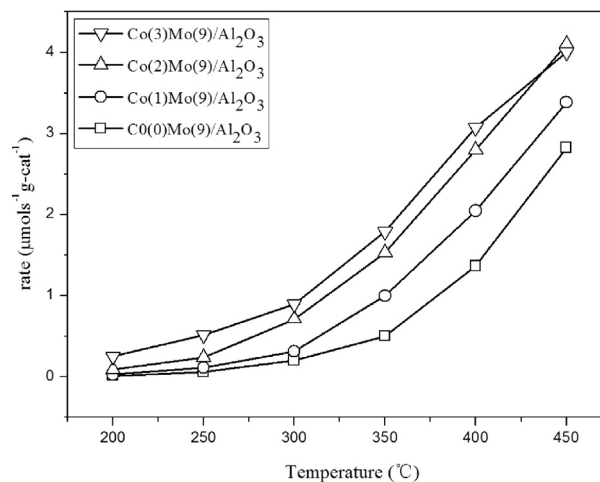


Fig. 1 – The water gas shift (WGS) activities over sulfided Co(x)Mo(9)/Al₂O₃ catalysts at different temperatures.

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