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# The effect of metal type on the sulfur tolerance of catalysts supported on niobia for sour water-gas shift reaction

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## ABSTRACT

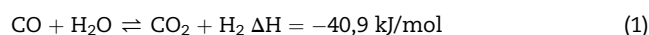
Hydrogen production via water-gas shift (WGS) reaction using heavy oil residues as syngas source is an attractive way to improve refinery margin. However, this low cost syngas may present significant concentration of sulfur, leading to poisoning of usual WGS catalysts. Searching for sulfur tolerant catalysts, the performance of niobia supported platinum, gold and copper catalysts was evaluated under near-industrial conditions, in the absence and presence of H<sub>2</sub>S. Cu/Nb<sub>2</sub>O<sub>5</sub> catalyst was inactive, even under clean conditions. Au/Nb<sub>2</sub>O<sub>5</sub> presented higher activity and complete deactivation when exposed to sulfur, but recovered its catalytic activity with the removal of H<sub>2</sub>S from the reaction mixture, indicating a reversible deactivation. Pt/Nb<sub>2</sub>O<sub>5</sub> catalyst was the most suitable among the catalysts evaluated to be used in sour conditions, not deactivating when exposed to 50 ppm and 1000 ppm of H<sub>2</sub>S.

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## Introduction

The growing interest in clean technologies and renewable sources of energy makes hydrogen a promising energy carrier. However, a huge amount of hydrogen produced nowadays comes from fossil fuels, such as heavy oil [1–3]. Therefore, gasification of residues from heavy oil as a way of producing hydrogen is an interesting alternative for refineries. Nevertheless, besides hydrogen, carbon monoxide is also produced,

so there is a need to adjust the CO/H<sub>2</sub> ratio through the water-gas shift reaction (WGS) [3–5].



Traditionally, the reaction occurs in two stages in order to optimize the conversion of carbon monoxide. The first stage takes place in high temperature (320–450 °C), using a Fe/Cr/Cu catalyst, while the second one happens in low temperature (200–250 °C), using typical CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst [6].

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Besides increasing the amount of hydrogen produced, another important aspect of reducing the CO/H<sub>2</sub> molar ratio is related to the catalysts employed in reaction systems containing carbon monoxide, such as methanol synthesis and PEM fuel cells, since they have a decrease in their activity or completely deactivate in the presence of CO [7].

Sulfur compounds, such as hydrogen sulfide, can be found in large amount in oil and coal, and, despite the use of desulfurization pre-treatment, H<sub>2</sub>S can still be present in the syngas due to the incomplete removal of sulfur [8,9].

In this context, sulfur poisoning is one of the main problems associated to the industrial application of water gas shift reaction and the development of sulfur resistant catalysts has become a relevant issue.

Nowadays, cobalt-molybdenum sulfide catalysts supported on alumina are used for sour gas-water shift reaction. However, these catalysts are dependent on the sulfur concentration contained in the feed to remain active, as well as on the concentration of sulfur present in the sulfidation source to exhibit activity [5,10].

De la Osa and coworkers [5] evaluated the influence of the amount of sulfur on activation of a high temperature industrial WGS catalyst. The sulfidation step was carried out at 210 °C varying the sulfur content from 42 ppm to 94 ppm of H<sub>2</sub>S, by exposing the commercial catalyst to a mixture of 90/10v/v% (H<sub>2</sub>S/N<sub>2</sub>)/H<sub>2</sub>. The exposing time change of 16 h–36 h, according to desired content of sulfur. Significant CO conversion became apparent after activation with 94 ppm of sulfur which is the maximum level recommended by commercial specifications. There was not any formation of active sulfide species for lower amounts of sulfur.

Some studies reported that concentrations of H<sub>2</sub>S above 300 ppm in the syngas are necessary to keep the activity of Co–Mo catalyst [10,11]. Hla et al. [12] verified the effect of varying H<sub>2</sub>S content in the feed on the performance of a Co–Mo based sour shift catalyst. The catalyst reactivity was significantly improved by the presence of sulfur and it was very poor when the concentration of H<sub>2</sub>S in the syngas was lower than 500 ppm. It was found that this sour shift catalyst presented better performance than a commercial HTS catalyst only when sulfur content in the syngas was kept above 1000 ppm.

Unconventional catalysts for WGS reaction, like perovskites, were also applied under sour condition. The use of La<sub>0.7</sub>Ce<sub>0.2</sub>FeO<sub>3</sub> was investigated aiming at the production of hydrogen from simulated coal-derived syngas. The WGS reaction was carried out at 600 °C and the perovskite performance was compared to the commercial catalysts, Fe/Cr and Co/Mo. La<sub>0.7</sub>Ce<sub>0.2</sub>FeO<sub>3</sub> showed higher activity at 600 °C than the traditional shift catalysts at 450 °C. The catalyst activity decreased with increasing concentrations of H<sub>2</sub>S up to 1100 ppm. However, the observed deactivation was reversible and even with the activity loss, it still remained higher than the activity obtained over Fe/Cr and Co/Mo catalysts.

Modifications in the composition of Mo based catalysts were investigated in order to find more active catalytic systems for WGS reaction. Sasaki et al. [13] reported that the sour shift Ni/Mo/TiO<sub>2</sub> catalyst was reactive at low temperature conditions, with reaction starting at temperature lower than

200 °C. The performance of this catalyst was compared to Co/Mo/Al<sub>2</sub>O<sub>3</sub>-MgO catalyst and evaluated in a bench-scale reaction apparatus using industrial coal gasification gas feed. The catalyst needed a sulfiding pretreatment with H<sub>2</sub>S (3 vol%)/H<sub>2</sub> (7 vol%) to be activated. The results of catalytic activity measurements evidenced the amount of Ni/Mo/TiO<sub>2</sub> catalyst could be decreased to 1/5 that of Co/Mo/Al<sub>2</sub>O<sub>3</sub>-MgO catalyst for the same conversion.

The study by Mi et al. [14] evaluated the use of niobium as a dopant for catalysts composed of Co and Mo supported on mixed Mg–Al oxide. The catalysts were first sulfided in a mixture of H<sub>2</sub>S/H<sub>2</sub> at 250 °C for 2 h, and then the catalytic test was performed in different temperatures, from 200 °C to 450 °C. The CoMo catalysts supported in MgAl decorated by Nb showed better activity for the WGS reaction than niobium-free catalyst and the conversion of CO grew with the increase of niobium content, obtaining the greater conversion with CoMo/Nb(5%)MgAl. The presence of niobium in the catalyst affected the sulfidation of the molybdenum species, lowering the apparent sulfidation activation energy of Mo species, and contributing to a greater dispersion of MoS<sub>2</sub>, which provided more active sites for the reaction.

Niobium oxide is not an usual component in WGS catalysts and it has been mainly used as a promoter. For example, Lin et al. [15] prepared a series of copper catalysts supported on ceria modified with different quantities of Nb<sub>2</sub>O<sub>5</sub> (0, 1, 5, 10 wt %) by parallel co-precipitation method. The experiment was performed under 10% CO, 60% H<sub>2</sub>, 8% CO<sub>2</sub> and balance N<sub>2</sub> feed gas in a temperature range between 200 °C and 400 °C. The introduction of niobium enhanced the performance of the CuO/CeO<sub>2</sub> catalyst and the one with 1% of niobium oxide presented the greatest improvement. However, increasing the niobium content, the performance of the catalysts decreased. The enhancement in the catalysts performance was attributed to the substitution of Nb<sup>5+</sup> with Ce<sup>4+</sup>, resulting in the variation of crystal structure, reduction and surface properties of the CuO/CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> catalysts [15].

Zhang et al. [16] investigated the effect of the introduction of Nb<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> to Au/Fe<sub>2</sub>O<sub>3</sub> applied to water-gas shift reaction under hydrogen-rich conditions. They evaluated 8%Au/Fe<sub>2</sub>O<sub>3</sub> catalysts promoted with ZrO<sub>2</sub> only (10 wt %) and Nb<sub>2</sub>O<sub>5</sub> only (10 wt %), denoted as AuFZ and AuFN, respectively, and also promoted with both oxides, with a fixed amount of ZrO<sub>2</sub> (10 wt %), and 1, 3, 5, 8 or 10 wt% of Nb<sub>2</sub>O<sub>5</sub> (AuFZN1, AuFZN3, AuFZN5, AuFZN8 e AuFZN10, respectively). The promoted catalysts were more active than 8%Au/Fe<sub>2</sub>O<sub>3</sub> and, among them, AuFZN10 presented the highest CO conversion and stability. The introduction of ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> enhanced the Fe<sub>2</sub>O<sub>3</sub> surface area, Au dispersion and lead to a small magnetite crystallite size [16].

In a recent study in our laboratory [17], we have achieved interesting results when niobia was applied as support for platinum catalyst. Pt/Nb<sub>2</sub>O<sub>5</sub> catalyst has not deactivated in the presence of 50 ppm of H<sub>2</sub>S during 2.5 h time on stream. Here, we further investigate the sulfur tolerance presented by Pt/Nb<sub>2</sub>O<sub>5</sub> and compare the catalyst performance with Cu/Nb<sub>2</sub>O<sub>5</sub> and Au/Nb<sub>2</sub>O<sub>5</sub> catalysts, evaluating the effect of the supported metal on sulfur tolerance and catalytic activity.

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