



Sour water–gas shift reaction over Pt/CeZrO₂ catalysts



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ABSTRACT

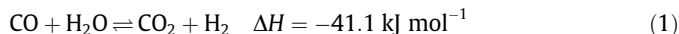
The influence of H₂S on the performance of platinum catalysts for the water–gas shift reaction was investigated. Platinum catalysts supported on different oxides (γ -Al₂O₃, ZrO₂, CeO₂, Ce_{0.75}Zr_{0.25}O₂, and Ce_{0.25}Zr_{0.75}O₂) were tested under industrial conditions in the absence and presence of H₂S. Pt/CeO₂ showed higher initial catalytic activity than Pt/Al₂O₃, but exhibited some deactivation and low recovery of catalytic activity when subjected to contaminated conditions, due to the formation of sulfur species on the ceria surface. Zirconia addition to CeO₂ was beneficial to increase sulfur tolerance and preserve high activity. The deactivation ratios for Pt/CeZrO₂ catalysts were very close and recovery ratios were 100%, indicating that for these catalysts the deactivation is reversible, which can be related to less interaction between H₂S and these supports.

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1. Introduction

The gasification of heavy residue oil is an interesting alternative way to obtain a low-cost syngas that can be applied to produce hydrogen and other compounds. The integration of a gasification system to heavy oil conversion improves the refinery margin. The need to use heavy oil as refinery feedstock leads to the formation of low-value liquid residues and coke. There is currently a lack of market for these products, and their conversion to lighter products is economically beneficial [1–3].

However, the H₂/CO ratio of the syngas produced by gasification is low. Thus, the water–gas shift reaction (WGS) is employed to adjust the H₂/CO ratio [2,4] for the production of hydrogen and other products. The WGS is a key step for many processes that require hydrogen [5]. This process consists in the catalytic reaction between carbon monoxide, contained in the syngas, and steam [6]:



The catalyst of choice for this reaction is dependent on the temperature. For the high-temperature WGS (HTS), in the 310–450 °C range, iron- and chromium oxide-based catalysts are employed. These catalysts also contain stabilizers and promoters such as magnesium, aluminum, and zinc oxides to avoid iron sintering [7]. In the 200–250 °C range, low-temperature WGS (LTS) catalysts based on copper supported on zinc oxide and alumina are used [8].

In the search for more advantageous catalysts for the WGS, several studies with noble metal catalysts have been reported

[9–21]. The use of noble metal catalysts is related to their capability of being stable in an oxidizing atmosphere. Copper-based catalysts are generally more active than noble metal-based catalysts, but they are unstable in the presence of oxidizing gases. Thus, there is interest in developing more active noble metal catalysts or more stable copper catalysts [22].

The syngas produced from gasification can contain high concentrations of sulfur [1,2,23] that can act as a poison for classical WGS catalysts, such as Fe–Cr and Cu–Zn [20,24]. Cu–Zn based catalysts are permanently damaged and need to be replaced if exposed to sulfur. Fe–Cr catalysts are still active, but less efficient [25,26]. To prevent catalyst deactivation by sulfur and avoid the desulfurization step, reducing energy costs, various studies of different catalysts in the presence of sulfur have been conducted [14,27–29].

Noble metal catalysts are an attractive alternative for the sour WGS, since they are more active than Fe–Cr and generally more tolerant to sulfur poisoning [20]. Some authors noted a certain tolerance of platinum catalysts in the presence of sulfur, which has been explained by the low stability of sulfur–platinum bonds [18,20,24].

Platinum catalysts (0.38–2%) supported on ceria were employed in the HTS (300–350 °C) with and without 20 ppm of H₂S. When the temperature and platinum content increased, the prejudicial effect of H₂S on CO conversion was less pronounced. After 300 h of reaction, the authors verified a decrease of 20% in the ceria surface area. The decrease of surface area and surface hydroxyl groups was associated with the formation of surface sulfates by H₂S adsorption on the support, leading to lower catalytic activity [20].

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A series of platinum and platinum–rhenium catalysts were tested and showed good performance in the absence of sulfur, but when a low sulfur content was added to the stream, from 0.1 to 5 ppm, the Pt–Re catalysts deactivated rapidly and irreversibly. For platinum catalysts, the adverse effects were proportional to the sulfur content in the stream: when sulfur was removed there was catalytic activity recovery, indicating that catalyst deactivation was reversible [30].

Xue et al. [18] performed a comparative study of sulfur tolerance between commercial Cu–Zn, Co–Cr, and Fe–Cr catalysts and Pt/ZrO₂. These catalysts were exposed to different H₂S concentrations (50, 200, and 1000 ppm). For Pt/ZrO₂, there was a decrease in CO conversion as H₂S concentration increased, ranging from 44% under sulfur-free conditions to 25%, 14%, and 12%. However, when sulfur was removed from the reaction mixture, the catalytic activity was recovered and the same initial conversion of 44% was achieved. Cu–Zn, Co–Cr, and Fe–Cr catalysts were deactivated due to the presence of H₂S. This deactivation was irreversible for the first two catalysts but reversible for Fe–Cr.

The authors also investigated the interaction between H₂S and the catalysts, observing that there was no reaction between H₂S and zirconia. A bond between H₂S and Pt occurred, forming H₂ and PtS, which blocked platinum surface sites and could explain the deactivation observed in the presence of sulfur [18].

CeZrO₂ mixed oxides have been used as supports for noble metal catalysts because they provide improved redox properties and mechanical strength. Inclusion of zirconia in ceria lattices improves oxygen storage capacity, due to higher oxygen mobility in the formed solid solution [31,32]. Because of these properties, CeZrO₂ supported catalysts have shown, in some conditions, higher activity than when pure CeO₂ or ZrO₂ are used as supports [17,19,33,34]. Despite the better performance of these oxides, there is a lack of publications about the performance of CeZrO₂-supported noble metal catalysts under sour WGS conditions.

Liu et al. [35] applied core–shell structured catalysts, Pt@CeO₂ and Pt@Ce_{0.67}Zr_{0.33}O₂, to the WGS, with the feed gas simulating a pure and sour syngas in a temperature range of 300–400 °C. Both catalysts achieve high activity under sulfur-free conditions with no methanation parallel reaction. Under this clean condition, Pt@CeO₂ showed better CO conversion than Pt@Ce_{0.67}Zr_{0.33}O₂, which was attributed to the size of the pores, which were relatively large and improved the passage of gas molecules to interact with platinum. However, under sour conditions, Pt@Ce_{0.67}Zr_{0.33}O₂ showed better activity, indicating more sulfur tolerance than Pt@CeO₂. A stability test over Pt@Ce_{0.67}Zr_{0.33}O₂ evidenced recovery of catalytic activity after the removal of H₂S.

As platinum catalysts were suitable for the WGS, showing some tolerance and/or good recovery when exposed to sulfur [18,20,24,30,35], and there is a lack of recent publications about Pt/Ce_xZr_{1-x}O₂ under sour WGS conditions, in this paper we investigate the behavior of platinum-catalyst-supported different oxides (Al₂O₃, CeO₂, ZrO₂, Ce_{0.75}Zr_{0.25}O₂, and Ce_{0.25}Zr_{0.75}O₂) under near-WGS industrial conditions in the absence and presence of H₂S.

2. Experimental

2.1. Catalyst preparation

The supports γ -Al₂O₃, ZrO₂, and CeO₂ were obtained by calcination of boehmite (Sasol), Zr(OH)₄ (Sigma–Aldrich), and (NH₄)₂Ce(NO₃)₆ (Fluka), respectively. Boehmite was calcined at 500 °C for 2 h (10 °C/min), while Zr(OH)₄ and (NH₄)₂Ce(NO₃)₆ were calcined at 800 °C for 1 h (5 °C/min).

Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.25}Zr_{0.75}O₂ were obtained from ZrO(NO₃)₂·6H₂O (Vetec) and (NH₄)₂Ce(NO₃)₆ (Fluka) by co-precipitation.

Aqueous solutions of cerium(IV) ammonium nitrate and zirconium nitrate were prepared with compositions of 75 mol.% CeO₂/25 mol.% ZrO₂ and 25 mol.% CeO₂/75 mol.% ZrO₂. Then an excess of ammonium hydroxide (Carlo Erba) was added as a precipitation agent to co-precipitate ceria and zirconium hydroxides. The precipitate was washed with deionized water, dried at 120 °C overnight, and calcined at 800 °C (5 °C/min) for 1 h.

2.2. Catalyst characterization

Surface areas were determined by the BET method from N₂ adsorption isotherms recorded at 77 K using an ASAP-2020 apparatus (Micromeritics). Prior to the measurements, the samples were dried for 4 h at 250 °C and degassed under vacuum for 2 h at 250 °C.

X-ray diffraction (XRD) was performed using a Rigaku Miniflex II diffractometer. XRD patterns were collected in the range of 10–90° (2 θ) with a step size of 0.05° and a time acquisition of 1 s/step.

Platinum dispersion was measured by H₂ and CO chemisorption at 35 °C in a Micromeritics ASAP 2010 instrument. The pretreatment of the samples consisted of drying in He at 150 °C for 30 min. Then the samples were evacuated at 150 °C for 60 min, followed by reduction with H₂ at 500 °C for 2 h. After that, the samples were evacuated for 60 min at the reduction temperature to remove any residual H₂ before being cooled under vacuum to 35 °C for analysis [36]. Pt dispersion was calculated using irreversible chemisorption uptakes.

Oxygen storage capacity (OSC) measurements were performed in a quartz microreactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). Prior to OSC analysis, the samples (300 mg each) were reduced under 30 mL/min of H₂ at 500 °C (10 °C/min) for 1 h. After the reduction procedure, the samples were heated to 800 °C (5 °C/min) in flowing He (50 mL/min) in order to clean their surfaces. Then the samples were cooled to 450 °C, which was the analysis temperature. A 5% O₂/He mixture was passed through the catalyst to verify the oxygen consumption, while the composition of the reactor effluent was measured by monitoring the oxygen signal ($m/z = 32$) with the mass spectrometer [37,38].

Temperature-programmed desorption of CO₂ (CO₂ TPD) experiments were performed with a fixed bed quartz reactor coupled to a mass spectrometer (Pfeiffer Prisma). The samples (350 mg) were dried at 150 °C (10 °C/min) for 30 min in a He flow of 30 mL/min, reduced in 30 mL/min of H₂ at 500 °C (10 °C/min) for 1 h, and then purged with He (30 mL/min) at the reduction temperature for 1 h. The samples were cooled to 30 °C under He and then 5% of CO₂ was added to the feed (keeping the total flow of 30 mL/min). The adsorption process followed four steps for 30 min each: (1) first CO₂ adsorption, (2) cleaning step with He, (3) second CO₂ adsorption, and (4) final cleaning with He. After these steps, thermal desorption was initiated by heating the sample to 1000 °C (10 °C/min) in a He flow and basic acid sites were quantified from desorbed CO₂ ($m/z = 44$) after TPD analysis.

Diffuse reflectance Fourier-transformed infrared spectroscopy (DRIFTS) experiments were carried out in a Bruker Vertex 70 spectrophotometer equipped with a LN-MCT detector, using a reflectance accessory (DRP-XXX, Harrick) containing a reaction chamber (HVC-DRP-4, Harrick) and ZnSe windows. The samples were previously reduced ex situ under H₂ flow at 500 °C for 1 h and passivated by 5% O₂/He. Prior to the adsorption experiments, the passivated samples were dried in situ at 120 °C under He flow, reduced under H₂ flow (30 mL/min) at 300 °C for 1 h, and purged under He at the reduction temperature for 1 h. Then background interferograms were collected under He flow at 300, 200, 100, and 40 °C. After the background interferogram was collected at 40 °C, the samples were exposed to a 5% CO/He flow for 15 min. After purging with He at 40 °C, interferograms were taken at the

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