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Unexpected stability of CuO/Cryptomelane catalyst under Preferential Oxidation of CO reaction conditions in the presence of CO_2 and H_2O

A. Davó-Quiñonero*, D. Lozano-Castelló, A. Bueno-López

MCMA group, Inorganic Chemistry Department, University of Alicante, Carretera San Vicente s/n. E03080, Alicante, Spain

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ABSTRACT

The catalytic activity of CuO/Cryptomelane for the preferential oxidation of CO in H_2-rich streams has been studied in the absence and presence of H_2O and CO_2, paying special attention to the catalyst stability and to changes on its physical-chemical properties under CO-PROX reaction conditions.

For fresh CuO/cryptomelane catalyst, the presence of CO_2 and/or H_2O in the CO-PROX feed partially inhibits CO oxidation due to chemisorption of H_2O and CO_2 on the catalyst. H_2O chemisorption on CuO/Cryptomelane is stronger than CO_2 chemisorption, and simultaneous CO_2 and H_2O adsorption has a synergetic effect that enhances co-adsorption and significantly hinders CO oxidation.

On the contrary, the presence of $CO_2 + H_2O$ in the CO-PROX reaction mixture has a positive effect in the CuO/Cryptomelane stability upon several consecutive reaction cycles in the 25–200 °C range. XRD showed that chemisorbed $CO_2 + H_2O$ species partially prevent the catalyst deactivation due to cryptomelane reduction to hausmannite (Mn_3O_4) under the strongly reductive environment of the CO-PROX reaction, and H_2-TPR and Raman spectroscopy characterisation support that the cryptomelane structure is less damaged under CO-PROX conditions in the presence of CO_2 and H_2O than in the absence of these species. Therefore, interestingly under $CO_2 + H_2O$ environment (realistic CO-PROX conditions) CuO/Cryptomelane catalyst performs an improved catalytic activity.

1. Introduction

The PReferential OXidation of CO (CO-PROX) reaction is an efficient strategy to remove the residual CO content in H_2-rich streams produced by steam reforming of hydrocarbons coming from the water-gas shift reactor. This methodology permits utilisation of proton exchange membrane (PEM) fuel cells with current H_2-production technologies to provide stationary and portable power [1,2]. Basically, CO-PROX is a competitive process in which a stoichiometric content of O_2 is supplied to the gas mixture, and an appropriate catalyst should accelerate selectively CO oxidation to CO_2 with, ideally, no H_2 consumption [3].

Previous research done into this subject has agreed to claim the CuO/CeO_2 and derivate catalysts as promising materials to overcome the challenging requirements towards CO-PROX reaction in terms of activity and selectivity. Nevertheless, this catalyst is based in a rare-earth metal oxide and, thus, coming from resources involved in a serious environmental, political and social problematic associated to their extraction, purification and use. [4]. Although novel procedures are being investigated to reduce the mining processes by promoting the sustainable recycling of these materials, their availability and supply in extended use are still unclear and polemic matters. So, despite the properties of rare-earth elements are being unique, they should be gradually substituted if alternative materials are found to perform similarly for certain applications, such as catalysis.

In this particular context, manganese oxides result highly interesting given their abundance and variety, low cost, environmental compatibility and non-toxicity [5]. They have traditionally been combined to copper, forming the hopcalite catalyst ($CuMn_2O_4$), which has been used since World War I as an effective CO oxidation catalyst in masks and respiratory protection [6,7]. Its catalytic activity has been related to the existence of flexible valences Cu^{+}/Cu^{2+} and Mn^{3+}/Mn^{4+} in permanent equilibrium and to its low crystallinity [6]. However, it is still a subject of research to discern which is the role of each species in the catalytic steps, and how to control and prevent the severe deactivation process that occurs during reaction.

Among the wide range of manganese oxides, the cryptomelane-based oxide ($K_xMn_8O_{16}$) has been pointed out as a promising material for catalysis applications [8]. This material consists in an open tunnelled network formed by double chains of corner-sharing

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* Corresponding author.
E-mail address: arantxa.davo@ua.es (A. Davó-Quiñonero).

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MnO_6 octahedra (2 × 2), which gives rise to its typical denomination as Octahedral Molecular Sieve 2 × 2 (OMS-2). The channel size is 0.46 × 0.46 nm, where interstitial potassium species and water ions are hosted, compensating the charge imbalance generated into the mixed valence of manganese, typically around 3.8 by the presence of Mn^{4+}, Mn^{3+} and minor Mn^{2+} [9].

Particularly, cryptomelane has been thoroughly studied as a catalyst for oxidation reactions and has demonstrated an excellent activity, which has been related to its high oxygen mobility and its redox properties [10,11]. As well, the modification of cryptomelane with transition and noble metals has been reported to produce improvements on its catalytic activity when Co [12,13], Ce [14,15], Cu [16–18], Ag [19–21] or Au [14,22] among others were incorporated. From all of them, the best results were obtained when copper was the doping element, associated to the strong Cu-Mn interaction and synergistic effect on the reducibility [12,13].

On the other hand, deposition of finely dispersed CuO nanoparticles on cryptomelane surface has also been reported to be positive for CO oxidation [23]. Following this approach, in our previous study we tested a CuO/Cryptomelane catalyst in CO-PROX reaction with a $CO + H_2 + O_2$ gas mixture, and an exceptional performance was found [24]. However, its catalytic activity lowered in successive cycles of reaction, despite regeneration steps were conducted between cycles. Such deactivation was associated to partial collapse of cryptomelane structure produced by potassium segregation and copper sintering under CO-PROX reaction conditions. Despite this loss of activity, the remaining activity of CuO/Cryptomelane catalyst showed a good potential for CO-PROX oxidation under the reaction conditions of that study.

The effect of CO_2 and H_2O in the CO-PROX reaction feed in the activity, selectivity and stability of CuO/Cryptomelane was not evaluated in our previous study [24], and it is known the detrimental effect of these inhibitors in many CO-PROX catalysts, such as CuO/Ceria [25]. The study from Hernández et al. [16] was pioneer in undergoing CO-PROX real conditions using Cryptomelane. These authors evaluated the activity of Cu-modified cryptomelane for CO-PROX reaction with the addition of CO_2, H_2O and $CO_2 + H_2O$ in the reaction mixture, concluding that CO_2 partially inhibits the activity while H_2O inhibits or enhances the activity depending on the reaction temperature. The inhibiting effect of CO_2 and H_2O was attributed to the blockage of CO chemisorption sites while the positive effect of H_2O above a critical temperature was explained appealing to the thermodynamics of parallel reactions that could take place in presence of water, such as the Reverse Water Gas Shift reaction [26], and to the formation of labile intermediates of fast desorption by means of the surface hydroxyl groups. As far as we know, the stability of CuO/Cryptomelane catalysts under CO-PROX reaction conditions including CO_2 and H_2O in the reaction mixture has not been studied so far, and this is a critical issue for the potential application of this promising catalysts in real devices. Therefore, the goal of this study is to analyse the stability of CuO/Cryptomelane catalyst under realistic CO-PROX conditions including CO_2, H_2O and $CO_2 + H_2O$ in the gas mixture, not only paying attention to the effect of these species on the chemical processes occurring under reaction conditions but also to changes on the physical-chemical properties of the catalyst in consecutive reaction tests.

2. Experimental details

2.1. Catalysts preparation

Synthetic cryptomelane was prepared using the previously described reflux method [27]. To this end, 11 g of manganese (II) acetate were dissolved in 40 g of water and the pH of the solution was fixed at 5 using glacial acetic acid. Then, the solution was heated and maintained at the boiling temperature under reflux for 30 min. After that, a solution of 6.5 g of potassium permanganate dissolved in 150 ml of water was added, and the mixture was kept under reflux by vigorous stirring for 24 h. The solid was filtered, washed with distilled water until neutral pH and dried at 120 °C overnight. Finally, the sample was calcined in air at 450 °C for 2 h using a heating ramp of 5 °C/min.

The CuO/Cryptomelane catalyst was prepared with 5 wt.% of copper by incipient wetness impregnation of cryptomelane with a copper(II) nitrate trihydrate (Panreac) water solution. The impregnated solid was dried at 110 °C overnight and calcined in air at 400 °C for 5 h using a heating ramp of 5 °C/min.

2.2. CO-PROX catalytic tests

To perform CO-PROX experiments, 150 mg of CuO/Cryptomelane were placed in a U-shaped reactor with 16 mm inner diameter and the gas mixture of 2% CO, 2% O_2, 30% H_2 and He balance was fed to the reactor. The O_2 excess with regard to CO was $\lambda = 2$ (being $\lambda = 1$ for stoichiometric CO-O_2 conditions). The catalytic tests were performed using a heating rate of 2 °C/min from 25 to 200 °C and a total gas flow rate of 100 ml/min that was set by means of Mass Flow Controllers (Bronkhorst). The exhaust gases were analysed by gas chromatography in an Agilent Technologies 6890N device equipped with a CTRI column operating at 80 °C and a TCD detector.

In order to study the effect of CO_2 and H_2O in the CO-PROX catalytic activity of the prepared CuO/Cryptomelane, different catalytic tests were performed adding 9% CO_2 or 5% H_2O or 9% CO_2 + 5% H_2O to the reactant gas mixture. CO_2 was fed to the gas mixture using an additional mass flow controller and H_2O was introduced in the gas mixture passing the gas stream through a gas saturator at 33 °C.

Consecutive catalytic cycles were performed with the same parcel of catalyst under each gas mixture in order to evaluate the stability of the catalyst. After the first run, the reactor was cooled down to room temperature under He atmosphere and a new catalytic cycle was conduced, repeating the experimental conditions of each series for four consecutive runs.

2.3. Temperature programmed experiments

In order to study the chemical adsorption of CO_2 and H_2O on CuO/Cryptomelane catalysts, temperature programmed desorption (TPD) experiments were performed. 80 mg of catalyst were placed in a tubular quartz reactor and were pretreated at 400 °C for 30 min in a 100 ml/min flow of Ar. Then, a saturation step with the selected gas was carried out, which consisted of heating the catalyst at 150 °C and keeping that temperature for 1 h under 100 ml/min of 10% CO_2/Ar (for CO_2-TPD), 5% H_2O/Ar (for H_2O-TPD) or 10% CO_2 + 5%H_2O/Ar (for $CO_2 + H_2O$-TPD). After that, the gas mixture was switched to Ar, and once the CO_2 and H_2O signals reached the baseline, the reactor was heated up to 650 °C following a ramp of 10 °C/min in 100 ml/min of Ar. The outlet gases were analysed with a mass spectrometer (Pfeiffer Vacuum, model OmniStar).

Experiments of temperature programmed reduction with H_2 (H_2-TPR) were performed using a Micromeritics Pulse ChemiSorb 2705 device. 40 mg of catalyst were placed in a U-shaped reactor and the temperature was increased from room temperature up to 900 °C with a heating rate of 10 °C/min in 40 ml/min of 5% H_2 in Ar. The TCD signal was calibrated using a CuO pattern provided by the manufacturer of the equipment.