

Comparative In Situ DRIFTS-MS Study of ^{12}CO and ^{13}CO TPR on CuO/CeO₂ Catalyst

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Introduction

Catalysts of copper oxide dispersed on ceria are highly active for several reactions involving CO such as preferential CO oxidation (CO PROX), water gas shift (WGS) reaction and CO oxidation while they are more interesting from an economical point of view than those based on dispersed noble metals typically employed for these processes [1,2]. In this respect, it is important to study the nature of the interaction of CO with CuO/CeO₂ and one of the methods typically employed for this purpose is temperature programmed reaction employing CO as reductant (CO-TPR) [3]. There are however many uncertainties during interpretation of redox processes responsible of features detected in the classical CO-TPR runs performed over this type of catalysts. In order to get more precise information in this sense, on the basis of analysis of the evolutions of mainly carbonyls or carbonates formed during the course of the TPR runs, a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell has been used as reactor and the corresponding spectra have been simultaneously recorded. In turn, TPR of ^{12}CO has been compared with that of ^{13}CO to achieve a complete analysis of carbonyls and carbonate-type species formed during the course of the run. Furthermore, complementary temperature programmed oxidation (TPO) performed subsequently to the ^{13}CO -TPR run and carbonyl-carbonates stability tests done by means of temperature programmed desorption (TPD) runs, with simultaneous DRIFTS recording, have been employed to help in the interpretations of the various spectroscopic or CO-TPR features detected.

Materials and Methods

CeO₂ support was prepared by reverse microemulsion method, whose details can be found elsewhere [1,2]. Final calcination under air at 500 °C gave rise to nanostructured CeO₂ (ca. 7 nm average crystal size) [1]. The supported CuO catalyst was prepared by incipient wetness impregnation of CeO₂ support using an aqueous solution of Cu(NO₃)₂·3H₂O. The resulting material was dried overnight at 110 °C and subsequently calcined under air at 500 °C for 2h yielding a catalyst with $S_{\text{BET}} = 107 \text{ m}^2\text{g}^{-1}$. Main characteristics of the catalyst at structural, morphological and electronic levels, on the basis of XRD, Raman, HRTEM-XEDS and XPS were reported elsewhere [1].

TPR experiments employing ^{12}CO and ^{13}CO (from Spectra Gases Inc., having a small portion of $^{13}\text{C}^{18}\text{O}$) as reductant (CO-TPR) were performed with a Pfeiffer Omnistar mass spectrometer (MS). A DRIFTS cell (Harrick) fitted with CaF₂ windows and a heating cartridge that allowed samples to be heated to 500 °C was employed as reactor. Prior to the CO-TPR run, the sample was calcined under 20% O₂/He for 1 h at 500 °C and TPR was performed with 5% CO/He using a ramp of 10 °C min⁻¹ and a flow of 50 cm³ min⁻¹. In situ DRIFTS analysis of the samples was carried out using a Bruker Equinox 55 FTIR spectrometer fitted with an MCT detector. At the end of the CO-TPR runs, the samples were cooled under He to room temperature (25 °C) and further tests employing CO as probe molecule under flow conditions

at room temperature followed by heating under He using a 5 °C min⁻¹ ramp (TPD run) were performed to check carbonyls/carbonates stabilities. Additional TPO-DRIFTS runs under 5% O₂/He were also done on the catalyst subsequently to the CO-TPR run in some cases.

Results and Discussion

DRIFTS of carbonyl region shows mainly a sharp peak at 2108 cm⁻¹ at room temperature that could be assigned to Cu⁺- ^{12}CO species, on the basis of thermal stability tests. Residual peaks at 2094 and 2060 cm⁻¹ that could be assigned to carbonyl species adsorbed on metallic Cu particles are also detected. All of them show expected shifts in homologous experiments done with ^{13}CO (double $^{13}\text{C}^{16}\text{O}$ - and $^{13}\text{C}^{18}\text{O}$ -derived contributions being detected). Additionally, there is a signature of a small peak at ca. 2120 cm⁻¹ which did not shift the position during ^{13}CO TPR. This peak could accordingly be assigned to forbidden electronic transition ($^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) of Ce³⁺ [4,5]. Appearance of these features already upon first contact with CO at room temperature is shown to follow from a reduction process that is correlated with CO consumption produced during reactant equilibration prior to starting the CO-TPR ramp and which involve also generation of carbonate-type species on the ceria support. MS analysis shows two low temperature peaks at 150 and 225 °C corresponding to different well dispersed CuO and a peak at 325 °C that could be attributed to reduction of bulk CuO [3] or the existence of parallel WGS (involving CO interaction with hydroxyls) [2] or Boudouard reactions. The presence of different types of dispersed copper oxide entities is in agreement with previous EPR and Ar⁻-sputtering XPS analyses [1], while subsequent TPO run indicates that carbon deposition during the CO-TPR test must be only residual, on the basis of simultaneous analysis of changes produced in the carbonate-type species along with MS monitoring of $^{13}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ evolutions. In definitive, the combined ^{12}CO - ^{13}CO temperature programmed tests with simultaneous DRIFTS analysis allow achieving a complete attribution of CO-TPR features, serving as a significant basis for this important analytical tool.

Significance

Catalysts based on combinations between copper and ceria are promising for substitution of noble metal catalysts for reactions involving CO as reactant for industrial processes of high relevancy in Energy and Environment areas. The work deals with a study of CO interaction with a catalyst of the mentioned type, aiming to achieve fundamental understanding that could lead to optimization of their catalytic properties within the mentioned challenging field.

References

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