Unlocking NOx Reduction Pathways in CO-Assisted NO Reduction over Ultra-Low Metal Content Catalysts Supported on Ceria-Zirconia

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Significance and Relevance

In order to gain detailed information on the mechanistic aspects involved in the CO-assisted NO reduction with the final purpose of avoiding the utilization of PGMs (Platinum Group Metals), which are featured by very high prices and very fluctuating, a fundamental study has been carried out with ultra-low metal contents as active phases (Cu, Ag and Co, as well as Pt taken as benchmark), supported onto ceria-zirconia, by combining the evaluation of the catalytic activity carried out by micro-reactor studies and the surface characterization in the course of the reaction by *operando* FT-IR analysis. Some pathways involved in the N-formation products were clarified related to the impact of the nature of the active phase used.

Automotive and stationary emission control and Fundamental advances in understanding catalysis.
Short Oral.

Introduction and Motivations

Modern three-way catalysts (TWCs) for aftertreatment systems are remarkably effective for removing nitrogen oxides (NOx), carbon monoxide (CO) and hydrocarbons (HC) from gasoline vehicles. However, the most efficient last-generation gasoline combustion engines, that can significantly increase fuel efficiency, and hence, producing lower exhaust temperatures resulting from these power gains, are being revealed as a significant challenge towards current emissions control catalysts. On the other hand, commercial TWCs have been traditionally developed with formulations composed of platinum group metals (PGMs) supported on durable inorganic oxides. PGMs, as well known, are very active components towards the pollutants removal but featured by a very high and fluctuating cost[1]. In this context, the need of developing more inexpensive and efficient catalysts which can operate at the required lower temperatures is essential. In this work, several ceria-zirconia based catalysts with ultra-low metal contents have been prepared, characterised and tested for the model reaction (CO-assisted NO reduction), in the presence and the absence of O_2, in order to understand in a comprehensive way all the possible routes that are taking place during this reaction by quantifying all the reaction products, thus evaluating the corresponding N- and O-mass balances. *Operando* FT-IR experiments were also conducted providing a complementary overview of the involved processes under selected cases. All the pathways to form the N-reduction products are explored and tried to be explained on the basis of the catalysts' formulations. These whole findings may provide a basis for designing more active and selective catalysts.

Materials and Methods

$Ce_{0.8}Zr_{0.2}O_2$ support was synthesised by means of the conventional coprecipitation method in alkaline media. The catalysts were prepared by IWI of the support with the corresponding metal precursors' solutions, loading different percentages in weight with the aim to reach the same molar composition in metals (for Cu 0.20 wt.%, for Co 0.19 wt.%, for Ag 0.34 wt.%, and for Pt 0.61 wt.%, respectively). The solids obtained were calcined for 1 h at 500°C. The catalysts synthesised were characterized in terms of textural and structural properties (N_2 adsorption at -196°C, XRD, XPS, H_2-TPR and Raman spectroscopy). The oxygen storage capacity (OSC) was also evaluated at 150°C for all the samples by a TG-MS equipment[2]. Catalytic activity was performed in a wide temperature range (TPR from 40°C up to 500°C) by using 86 mg of the sample mixed with 86 mg of quartz. For all the catalytic tests, the gas flow was fixed at 170 ml/min (GHSV of 90000 h^{-1}). All the catalysts were pre-treated using 5% O_2/He for 20 min at 500°C. Catalytic activity was analysed under: 1000 ppm CO/He; 1000 ppm NO/1000 ppm CO/He; 200 ppm NO/400 ppm O_2/1000 ppm CO/He. The same experimental procedure and protocol adopted for micro-reactor experiments was used in the *operando* FT-IR reactor cell.

Results and Discussion

Figure 1 depicts the corresponding product profiles of the CO-assisted NO reduction, as a function of temperature, for two representative catalysts (Pt0.6CZ and Cu0.2CZ). Both catalysts present a notable activity towards CO oxidation/NO reduction but with remarkable differences. The curves exhibit complex profiles, (especially for the case of Cu-catalyst), suggesting the possible co-existence of several reaction routes and their intrinsic complexity. By a detailed inspection of the corresponding mass balances versus temperature (not shown), the CO_2 emission profiles and the N-products emission profiles, estimated from the contribution of N_2, (main N-product), N_2O and NH_3, (suggested to be a secondary product due to the reaction of H_2, whose presence can be accounted for the well-known WGS reaction, with NO) are almost completely overlapped. This indicates a "coupled" process of CO oxidation/NO reduction, where CO_2 and N_2 (86% of selectivity) are the main reaction products. Conversely, the whole routes taking place during the CO-assisted NO reduction are much more complicated for Cu0.2CZ. At low temperatures, some events related to the fast reduction of generated surface nitrites by CO seem to occur (confirmed by *operando* studies). After this, the catalytic performance might proceed in sequential steps where CO molecules attack to the catalyst's surface, producing CO_2 and oxygen vacancies (this is consistent with CO-TPR profiles for this catalyst). Subsequently, NO molecules interact with the oxygen vacancies (by electronic transfer processes), thus generating N_2O as first product, and, subsequently, N_2. This sequential product generation is congruent with the proposed mechanism and far from that of Pt (whose onset temperatures for N_2O and N_2 are coincident), and relevant populations of $Pt^{\delta+}$-carbonyls and isocyanate species were identified as main intermediate. O-emission balance, but interestingly N-balance are fulfilled (N_2 selectivity 68%). However, the NO reduction is not coupled with the CO conversion, since CO oxidation proceeds first and, subsequently, the NO reduction, which seems to be conditioned by the oxygen vacancy population ("freshly created"), which is highly promoted by copper supported on CZ.

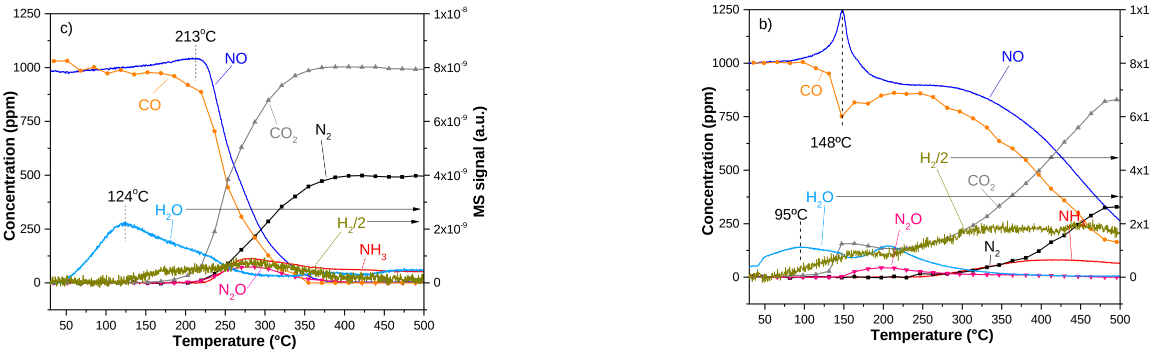

Figure 1. Evolution of reactants and products during the CO+NO reaction: a) Pt0.6CZ and b) Cu0.2CZ.

References

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