Enhancement of catalytic activity of perovskite-based catalysts in TWC by Cu and Ca doping and optimisation of the surface composition

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Introduction

Automotive exhaust gas treatment by 3-way catalysis (TWC) is expensive due to high loadings of noble metals in the catalytic converter. Fe-based perovskites, $LaFeO_3$, on the other hand, are non-toxic, thermally stable and low-cost. However, activity of such catalysts is generally lower compared to toxic Co-based perovskites [1]. Furthermore, Lanthanum enrichment at the surface is generally observed [2].

In the present study, we will present the improvement of catalytic activity of non-toxic, low-cost Fe-based perovskites by doping in A- and B-site, $LaFe_{1-x}Cu_xO_3$ and $La_{1-x}Ca_xFe_{1-x}Cu_xO_3$, and by optimisation of the surface composition, Lanthanum-deficient perovskite solids, to enhance the redox properties for DeNOx reactions.

Materials and Methods

The perovskite catalysts were prepared by conventional citrate method and finally calcined at 600 °C. BET, H_2-TPR, Raman spectroscopy, XRD and XPS characterisations were investigated before and after catalytic measurements. NO_x and reductants concentrations were measured during temperature-programmed reactions in a fixed bed continuous-flow reactor at GHSV=60,000 mL.g^{-1}.h^{-1} from 110°C to 500°C under stoichiometric, lean, and rich conditions. Complex realistic feed streams consisted of 0.1% NO, 15 % CO_2, 10 % H_2O, CO (0.5 %; 0.7 %; 0.9 %), CH_4 (150 ppm; 225 ppm; 300 ppm), C_3H_6 (300 ppm; 450 ppm; 600 ppm), C_3H_8 (150 ppm; 225 ppm; 300 ppm), O_2 (0.935 %; 0.777 %; 0.609 %), and H_2 (0.167 %; 0.233 %; 0.3 %) under lean, stoichiometric and rich conditions respectively).

Results and Discussion

The partial substitution of $LaFeO_3$ with Cu and Ca was observed from XRD patterns with characteristic peaks of orthorhombic perovskite structure. Surface compositions as well as reducibility of solids were strongly influenced by Cu substitution whereas Fe element prevented the decomposition of the structure in reducing atmosphere.

The conversions of CO, NO and propene during temperature-programmed reactions are presented in **Figure 1** for the series of perovskite-based catalysts. Temperatures corresponding

Table 1: Temperatures of 50 % conversion of CO (stoichiometric) and NO (rich) and surface properties of the low-cost Fe-based perovskite catalysts.

	T_{50} CO	T_{50} NO	atom. Fe/La ratio (XPS)	S. S. A. (m²/g)
$LaFeO_3$	492 °C	*460 °C* (T_{25})	0.41	9.5
$La_{0.7}FeO_3$	382 °C	494 °C	1.47	31.9
$LaFe_{0.9}Cu_{0.1}O_3$	305 °C	489 °C	0.42	18.4
$LaFe_{0.8}Cu_{0.2}O_3$	294 °C	*501 °C* (T_{25})	0.40	13.8
$La_{0.9}Ca_{0.1}Fe_{0.9}Cu_{0.1}O_3$	288 °C	478 °C	n. a.	21.4
$La_{0.8}Ca_{0.2}Fe_{0.8}Cu_{0.2}O_3$	279 °C	469 °C	n. a.	24.0

n.a.-not available

to 50 % conversion of CO under stoichiometric conditions and NO under rich conditions as well as their surface properties are reported in **Table 1**. The reference catalyst $LaFeO_3$ exhibited poor catalytic performances. By contrast, a significant enhancement of CO and NO conversion is observed for the La-deficient sample, $La_{0.7}FeO_3$. This enhancement is related to higher Fe surface concentration previously evidenced by XPS measurements.

The partial substitution of La and Fe by Ca and Cu was used to develop the catalytic performances (**Figure 1**). Copper addition led to a CO activation at much lower temperature of around 300 °C whereas NO and propene were converted above 400-450 °C. Replacing part of the La by Ca led to even higher activities, with light-off conversion curves shifting more than 200 °C for CO oxidation as compared to the reference, $LaFeO_3$. Propene oxidation is enhanced for $La_{1-x}Ca_xFe_{1-x}Cu_xO_3$ perovskites (x = 0.1, 0.2) and $La_{0.7}FeO_3$ catalysts. Return tests and post-test analysis by XRD confirm the stability of the perovskite structure in the presence of steam which was assigned to the presence of Fe.
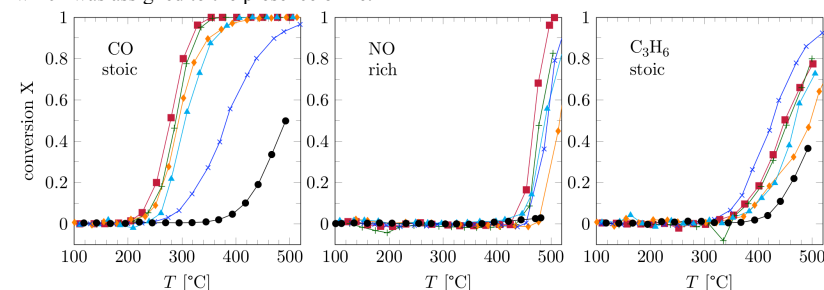

Figure 1: CO, NO, and C_3H_6 conversions of Fe-based perovskite catalysts under stoichiometric and rich conditions: $LaFeO_3$ (●), $La_{0.7}FeO_3$ (✗), $LaFe_{0.9}Cu_{0.1}O_3$ (▲), $LaFe_{0.8}Cu_{0.2}O_3$ (♦), $La_{0.9}Ca_{0.1}Fe_{0.9}Cu_{0.1}O_3$ (+), $La_{0.8}Ca_{0.2}Fe_{0.8}Cu_{0.2}O_3$ (■).

The development of CO oxidation at low temperature is very interesting since CO is known to strongly adsorb on noble metal and further inhibit NO reduction to N_2 at low temperature. The combination of Cu and Ca doping and surface composition optimisation will also be investigated. Furthermore, the impregnation with low loading of noble metal for the promotion of NO+C_3H_6 reaction will be implemented.

Significance

Fe-based perovskites are low-cost alternatives to partly replace noble metals in conventional 3-way catalysts. Surface composition optimisation strongly enhances the catalytic activity of the perovskite by increasing the accessibility of the active sites. Cu and Ca doping further increases the catalytic activity especially CO oxidation which can avoid CO inhibition on noble metals. Combination of partial substitution, non-stoichiometric formulation and low loading with noble metals allows promising catalytic performances in 3-way catalysis.

References

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