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Remarkable Enhancement of O_2 Activation on Yttrium-Stabilized Zirconia Surface in a Dual Catalyst Bed

*Mélissandre Richard, Fabien Can, Daniel Duprez, Sonia Gil, Anne Giroir-Fendler, and Nicolas Bion**

Abstract: *Yttrium-stabilized zirconia (YSZ) has been extensively studied as an electrolyte material for solid oxide fuel cells (SOFC) but its performance in heterogeneous catalysis is also the object of a growing number of publications. In both applications, oxygen activation on the YSZ surface remains the step that hinders utilization at moderate temperature. It was demonstrated by oxygen isotope exchange that a dual catalyst bed system consisting of two successive $LaMnO_3$ and YSZ beds without intimate contact drastically enhances oxygen activation on the YSZ surface at 698 K. It can be concluded that $LaMnO_3$ activates the triplet ground-state of molecular oxygen into a low-lying singlet state, thereby facilitating the activation of the O_2 molecule on the YSZ oxygen vacancy sites. This phenomenon is shown to improve the catalytic activity of the $LaMnO_3$-Pd/YSZ system for the partial oxidation of methane.*

A drastic increase in the global demand for natural gas is expected in the coming decades and its transformation into more easily transportable fuels such as Fischer–Tropsch products[1] or chemicals like methanol is required.[2] The conversion of methane to synthesis gas is a promising way to yield liquid products and therefore solve the difficulty of its transportation. From the work of Liander et al. in 1929,[3] a well known method for producing synthesis gas is the catalytic partial oxidation of methane (CPOM). Several reviews have reported the catalytic performances of noble-metal, transition-metal, and mixed-oxide catalysts.[4] Two general mechanisms have been suggested. These involve consecutive total oxidation and reforming reactions,[5] or a direct partial oxidation reaction.[6] In recent works, yttrium-stabilized zirconia (YSZ) has appeared as a promising catalyst.[7] Whatever the reaction pathway, the catalytic partial oxidation of methane proceeds through a Mars van Krevelen route that involves the lattice oxygen of the YSZ catalyst.[6b,7d] Perovskite solids also constitute interesting materials in terms of redox properties and oxygen mobility,[8] and good catalytic performance in the catalytic partial oxidation of methane has been reported for such materials.[9] In this work, we studied oxygen activation and mobility on a dual catalyst bed composed of $LaMnO_3$ perovskite and 8 mol% yttrium-stabilized zirconia (YSZ) by applying an oxygen isotope exchange technique, a well known technique for reactions of oxygen isotopes with metal-oxide supported systems.[10] We specifically investigated heterolytic oxygen exchange, in which $^{18}O_2$ is scrambled with the "lattice" oxygen species of the catalyst. We performed similar experiments on a dual catalyst bed and on isolated YSZ and $LaMnO_3$. The different catalytic formulations were then investigated in the catalytic partial oxidation of methane to check whether the remarkable behavior observed over the dual catalyst bed system regarding oxygen activation and lattice oxygen diffusion resulted in an improvement in catalytic activity.

In a first set of experiments, we studied the behavior of isolated $LaMnO_3$ and YSZ by using temperature-programmed oxygen isotope exchange (TPOIE). The results are shown in the Figure 1, in which it can be seen that the decrease in the $^{18}O_2$ partial pressure in the system started at 533 K on $LaMnO_3$, while it occurred at 773 K on the YSZ sample. Simultaneously an increase of the $^{18}O^{16}O$ partial

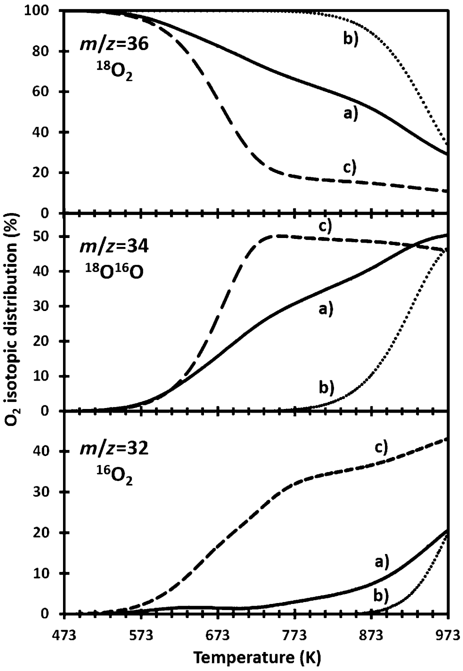

Figure 1. Changes in the isotopic oxygen distribution during TPOIE experiments over a) $LaMnO_3$ (solid line), b) YSZ (dotted line), and c) a dual $LaMnO_3$-YSZ bed (dashed line).

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[*] M. Richard, Dr. F. Can, Dr. D. Duprez, Dr. N. Bion
University of Poitiers, CNRS, UMR 7285, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP)
4 rue Michel Brunet—TSA 51106–86073 Cedex 9 (France)
E-mail: nicolas.bion@univ-poitiers.fr

Dr. S. Gil, Prof. Dr. A. Giroir-Fendler
Université Lyon 1, CNRS, UMR 5256, Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON)
2 avenue Albert Einstein, 69626 Villeurbanne (France)

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pressure is observed. This result indicates that on both solids, the exchange proceeds through a heterolytic mechanism involving a single lattice oxygen atom ($^{18}O_{2(g)} + ^{16}O_{(s)} \rightarrow ^{16}O^{18}O_{(g)} + ^{18}O_{(s)}$; denoted hereafter as simple exchange) as already reported for $LaMnO_3$-type perovskite,[11] Y_2O_3, ZrO_2, and YSZ oxides.[7d,12] The high activity of $LaMnO_3$ is related to the existence of two oxidation states for the manganese, which can shift between Mn^{4+} and Mn^{3+}.[11] The enhanced ionic conductivity of YSZ is not related to the redox couple of the yttrium and zirconium cations, which are considered to be irreducible, but results from the presence of oxygen vacancies created by the doping of zirconia with lower valence Y^{3+} ions. For YSZ, the exchange between molecular oxygen and lattice atoms remains a process that requires high temperature since equilibrium is not achieved even at 973 K. To construct the dual catalyst bed, we introduced into the reactor the same amounts of solids as used previously: 13.3 mg and 20 mg for $LaMnO_3$ and YSZ, respectively, which corresponds to 40 wt% $LaMnO_3$ and 60 wt% YSZ (justification for the composition is given in the Supporting Information, Figure S2). In the closed recycle setup of the exchange technique, the circulating isotopic oxygen flow first meets $LaMnO_3$, which is placed upstream YSZ. Contrasting with the expected results, the changes in the isotope distribution (Figure 1c) show a considerable enhancement of the exchanged atom fraction. Indeed, with the dual catalyst bed, the equilibrium of the ^{18}O fraction between the gas phase and the solid, which indicates the end of the exchange process, is reached at 773 K, which is the temperature at which the exchange started on YSZ alone. Note that the exchange activity of the dual catalyst bed was observed to start at 533 K, which is the starting temperature on $LaMnO_3$ alone.

The drastic improvement in the exchange activity is characterized by the modification of the isotopic distribution since $^{16}O_2$ is first observed in the gas phase. This result indicates that the enhancement of activity in oxygen exchange results either from two successive simple exchange reactions or from a heterolytic mechanism with two O atoms ($^{18}O_{2(g)} + ^{16}O_{(s)} \ldots ^{16}O_{(s)} \rightarrow ^{16}O_{2(g)} + ^{18}O_{(s)}$; denoted as multiple exchange).

To assess the importance of yttrium doping in the occurrence of this remarkable phenomenon, a similar experiment was undertaken in which pure ZrO_2 or pure Y_2O_3 were substituted for YSZ. The isotopic distribution shown in Figure S3 clearly illustrates the absence of a synergetic effect in these cases. We only detected a small improvement above 700 K for Y_2O_3 and above 800 K for ZrO_2 owing to the expected cumulative exchange activities of the $LaMnO_3$ and ZrO_2, or $LaMnO_3$ and Y_2O_3 materials.

To ascertain whether the contact between the two catalyst beds is a key element in the enhancement of $^{16}O_2$ production, TPOIE experiments were undertaken by separating the $LaMnO_3$ and YSZ either with a quartz wool plug (less than 1 cm separation) or by a 4 cm gap. Note that the temperature was always identical for the two beds. Figure S4 shows that the $LaMnO_3$/YSZ contact is not necessary to observe the phenomenon, although increasing the space between the two catalytic beds progressively inhibits the enhancement of the exchange activity.

Table 1: Numbers of total and exchanged oxygen atoms for each catalytic formulation during TPOIE experiments.

Samples mixture	N_O (10^{20} atoms g^{-1})[a]	N_e (10^{20} atoms g^{-1})[b]		
		698 K	773 K	973 K
40% $LaMnO_3$ + SiC[c]	29.9	5.3	8.1	17.8
60% YSZ + SiC	57.2	0.0	0.1	17.0
40%$LaMnO_3$ + 60% YSZ	87.1	20.9	27.4	28.8

[a] Total number of O atoms per gram of mixture based on the stoichiometry $LaMnO_3$ for the perovskite and 8 mol%Y_2O_3-ZrO_2 for the yttrium-stabilized zirconia. [b] Number of exchanged O atoms normalized per gram of mixture. [c] SiC = Silicon Carbide.

A quantification of the amount of oxygen exchanged with each catalytic formulation is presented in the Table 1. The results clearly show the synergetic effect of the dual catalyst bed in terms of number of atoms exchanged. If we consider that the behavior of the perovskite remains the same when isolated or in the dual bed, one can determine that at 698 K, 15.6×10^{20} O atoms from YSZ are exchanged, which corresponds to 27% of the O atoms present in the YSZ phase, while there is no oxygen exchange when YSZ is tested alone. At 773 K, the temperature at which the exchange starts on YSZ alone, almost 34% of the O atoms of the YSZ are exchanged. At higher temperatures, the value stagnates for the dual bed system because an equilibrium between the fraction of ^{18}O in the gas phase and in the solid is reached.

In the dual bed system, the characteristics of both $LaMnO_3$ and YSZ solids are unchanged compared to isolated samples in terms of composition and structural and morphological properties. The remarkable enhancement of the oxygen activity cannot therefore be ascribed to a difference in the nature of the surface active sites as reported by Chao et al., who enriched the Y concentration of the YSZ surface layers by atomic layer deposition.[13] Our results clearly show that despite the similarity in the samples, the behavior of the YSZ solid drastically changes when perovskite is placed upstream. The presence of oxygen vacancies in the YSZ solid is crucial since the enhancement is not observed with pure ZrO_2. Finally, although the enhancement is also visible when the samples are slightly separated, it has been observed that increasing the space between the two beds inhibits the synergetic effect.

In a second set of experiments, the behavior of the dual $LaMnO_3$-YSZ bed was investigated in the catalytic partial oxidation of methane. A dual bed system has been already employed for this reaction by Lefferts et al.[7b,c] Their objective was to use a first YSZ bed in order to consume O_2 by complete oxidation while the second $LaCoO_3$ bed was active for the dry reforming. Through this approach, the deactivation effect produced by the exothermic combustion of methane in the transition metal catalyst could be avoided. In the present study, the aim was to investigate whether the remarkable oxygen exchange activity described above influences the catalytic activity. To prevent the activation of CH_4 as a limiting step without improving the O_2 activation process, YSZ was impregnated with 0.2 wt% of Pd on the surface (denoted hereafter as Pd/YSZ). It is worth mentioning that the presence of Pd did not modify the activity in terms of oxygen exchange either on the dual catalyst system or on the isolated Pd/YSZ samples (Figure S5). The catalytic partial oxidation of methane was performed at 698 K with labeled oxygen in the isotope exchange system ($CH_4/^{18}O_2 = 2:1$ molar ratio; same amounts of sample). Prior to the reaction, the samples were pretreated in situ under oxidizing conditions (see the Supporting Information). The results obtained on the dual $LaMnO_3$-Pd/YSZ bed are presented in Figure 2. Two steps are identifiable: 1) during the first 3 min, a rapid consumption of the CH_4 and O_2 was detected with a concomitant increase of the intensities of the signals for m/z 44, 46, 48, 30 and 28 (note that m/z signals corresponding to water are also detected); 2) after 3 min, the appearance of H_2 slightly before the total consumption of O_2 occurred with the simultaneous increase of the signals for m/z 28 and 30. The first step is clearly due to the complete oxidation of CH_4, which is confirmed to occur through a Mars van Krevelen mechanism since $C^{16}O_2$ is the first molecule to appear in the gas phase. The major part of the increase in the signals for m/z 28 and 30 is due to the mass fragments resulting from $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ ionization. The production of H_2 occurs in the second step with the simultaneous production of $C^{16}O$ (a small increase in $C^{18}O$ is also observed). These products are not a result of the dry reforming reaction since the CO_2 is not consumed. We propose two reactions to explain the hydrogen formation: steam reforming and direct partial oxidation of CH_4 with lattice oxygen atoms. The curve corresponding to 18 m/z shown in the Figure 2 does not allow validation of the former reaction. The latter reaction was observed when CH_4 was introduced alone at the same temperature on the dual-bed reactor in agreement with the results of Lefferts et al.[7d] Note that CH_4 decomposition can also produce H_2.

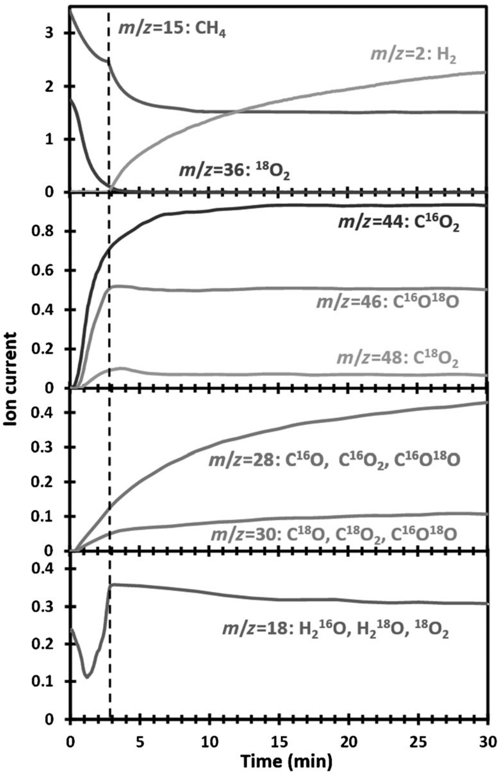

Figure 2. Changes in the m/z signal over time during CPOM reaction at 698 K over $LaMnO_3$-Pd/YSZ.

The same experiment was performed on Pd/YSZ, $LaMnO_3$, and dual $LaMnO_3$-YSZ bed systems (Figures S6, S7, and S8). A comparison between the catalytic formulations is given in Figure 3 on the basis of $^{18}O_2$ conversion and H_2 production. A difference in activity is evident in both steps. Complete oxidation is enhanced in the dual-bed systems, thus indicating that the beneficial effect observed in terms of oxygen exchange positively influences the oxidation activity. Furthermore, $C^{18}O_2$ is first observed on perovskite when tested alone, thus indicating that the reaction does not proceed through a Mars van Krevelen mechanism. H_2 production does not occur on the $LaMnO_3$ and dual $LaMnO_3$-YSZ bed systems, which means that the presence of Pd particles is crucial at this temperature to activate CH_4. Finally the production of H_2 occurs at 19 min on Pd/YSZ compared to 3 min for the $LaMnO_3$-Pd/YSZ combination.

Our study demonstrates that the simple exchange that occurs on the $LaMnO_3$ bed makes the O_2 molecules more reactive toward the surface of the second YSZ bed. This effect results in a dramatic enhancement of the oxygen exchange process with the YSZ structure, together with an improvement of the catalytic oxidation activity. However, the nature of the perovskite-induced activated oxygen molecule remains unclear. It appears that the ground state of the free oxygen molecule, which is a triplet state $^3\Sigma_g^-$ (denoted as $^3\Sigma_g^-O_2$) with two unpaired electrons in the degenerate π_g* antibonding orbital (π_g^x and π_g^y), is not an effective source in oxygen isotope exchange over the YSZ material below 773 K (Figure 1, curve b). By contrast, in the dual system, the fraction of exchanged atoms is enhanced. In contact with the first catalytic bed ($LaMnO_3$), a strong interaction with the surface is expected to split the π_g^x and π_g^y energy levels because of the anisotropic environment of the surface.[14] Consequently, the two electrons would pair up in the lower of the two states. This effect results in a low-lying electronically excited state of $^3\Sigma_g^-O_2$ (so called singlet oxygen, $^1\Delta_gO_2$),

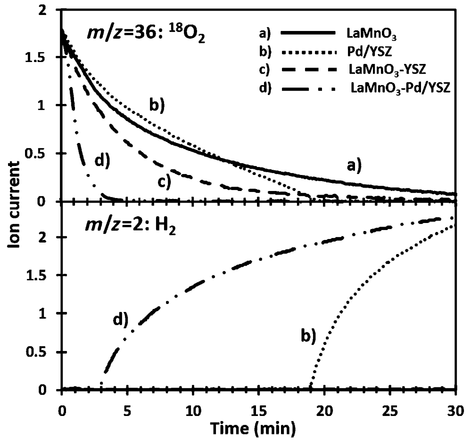

Figure 3. Evolution of $^{18}O_2$ ($m/z=36$) and H_2 ($m/z=2$) as a function of time during the CPOM reaction at 698 K over a) $LaMnO_3$, b) Pd/YSZ, c) $LaMnO_3$-YSZ, and d) $LaMnO_3$-Pd/YSZ.

with two electrons with opposite spins lying in the π_g* antibonding orbital. Thus, for adsorbed oxygen, the normal orbital degeneracy is removed and the singlet configuration may become the one with the lowest energy.[15] The resulting adsorbed species (${}^1\Delta_gO_{2(ads.)}$) can thereafter desorb in the first excited state (${}^1\Delta_gO_{2(gas)}$), since the transition to the triplet ground state is spin forbidden. Finally, the interaction between the ${}^1\Delta_gO_{2(gas)}$ species and the YSZ surface in the dual catalytic bed system is suspected to enhance the oxygen exchange activity (Figure 1, curve c).

Although the possibility that singlet oxygen could play a role in reactions at oxide surfaces was initially not considered seriously because the energy level is about 94.7 kJ above that of ground-state triplet oxygen (${}^3\Sigma_g^-O_2$), the generation of singlet oxygen from a gas–solid interface and its participation as an effective active source in heterogeneous catalytic reactions is now well accepted.[15a,16] This knowledge leads to the hypothesis that ${}^1\Delta_gO_2$ is formed on $LaMnO_3$ perovskite after exchange as expressed by Equation (1). The first excited state can thus be supposed as the

$$({}^3\Sigma_g^-)^{18}O_{2(gas)} + {}^{16}O_{(LaMnO3)} \rightarrow ({}^1\Delta_g)^{16}O^{18}O_{(gas)} + {}^{18}O_{(LaMnO3)} \qquad (1)$$

active O_2 species responsible of the remarkable exchange activities observed on YSZ placed downstream to $LaMnO_3$ sample as expressed in the Equation (2).

$$({}^1\Delta_g)^{16}O^{18}O_{(gas)} + {}^{16}O_{(YSZ)} \rightarrow ({}^3\Sigma_g^-)^{16}O_{2(gas)} + {}^{18}O_{(YSZ)} \qquad (2)$$

The lifetime of the ${}^1\Delta_gO_{2(gas)}$ species is also an important parameter to reinforce this hypothesis. Indeed, the lifetime observed in this work (ca. 7 ms; calculated on the basis of the results presented in Figure S4) is of a similar order of magnitude to those reported in the gas-phase media,[17] thus confirming the ${}^1\Delta_gO_2$ species as a likely active source that gives rise to the enhancement of O_2 activation on the oxygen vacancies of the YSZ surface (see the Supporting Information).

The crucial role that the oxygen vacancies generated in YSZ by Y_2O_3 doping play in the catalytic partial oxidation of methane has already been identified by several groups.[6b,7,18] In particular, the Y-induced surface oxygen vacancies were shown to activate the dissociative adsorption of O_2. These results led to strategies aiming at modifying the structural composition of YSZ samples to optimize the concentration of oxygen vacancies in the outermost surface of the solid, for instance, by atomic layer deposition.[13] Herein, we demonstrate that another strategy should be taken into account. The utilization of a reducible perovskite prior to the YSZ in the form of a dual catalyst bed enables a faster activation of the O_2 molecule on the YSZ surface, thereby resulting in a very active catalytic system for the oxidation of refractory molecules at moderate temperatures. This discovery opens avenues to explore new combinations of perovskite-based catalysts with surface-engineered yttrium-stabilized zirconia to produce efficient and industry-compatible catalytic systems for syngas production. These results may also enable a lowering of the operating temperature of the SOFC system.

Experimental Section

$LaMnO_3$ perovskite, with 35 $m^2 g^{-1}$ BET surface area, was prepared by the citrate route (see the X-ray diffraction pattern in Figure S1). The 8 mol% Y_2O_3-stabilized ZrO_2 (YSZ) material, supplied by TOSOH, has a BET surface area of 13 $m^2 g^{-1}$. For the Pd/YSZ material, Pd was added by wet impregnation. For further experimental details, see the Supporting Information.

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