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DEEP OXIDATION OF CHLORINATED VOLATILE ORGANIC COMPOUNDS OVER MANGANESE-BASED PEROVSKITE CATALYSTS

A. De Paoli and A.A. Barresi

V-19/V-22

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Deep Oxidation of Chlorinated Volatile Organic Compounds over Manganese-based Perovskite Catalysts

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ABSTRACT

The activity and stability of several La-Mn-O perovskites in the catalytic combustion of chlorinated compounds has been investigated, monitoring the variation of activity and selectivity with time on stream. Trieline in dry and moistened air has been used as test compound. Experimental data evidenced a partially reversible deactivation of the catalysts, which can be described by a power law type equation.

INTRODUCTION

Perovskite oxides with general formula ABO_3, where A represents a lanthanide and/or alkaline earth and B a transition metal ion, are intensively investigated as combustion catalysts. Relatively recent is the interest raised by these oxides for their potential application in the catalytic combustion of chlorinated volatile organic compounds. Previous studies [1-4] showed the good potentiality of these structures, which in addition to the relatively good activity and the possibility of adsorbing and/or desorbing large amounts of oxygen, show a better resistance to poisoning and chlorine deactivating action compared to other metal oxide catalysts. In particular, manganese-containing perovskites seemed the most promising.

In order to use these catalysts for the treatment of industrial emissions, it is necessary to improve both their activity and their durability. Previous work [5, 6] showed that it is possible to increase the activity of the fresh La-Mn-O perovskite catalysts forcing a variation in the oxidation number of a fraction of the Mn cations. $LaMnO_3$ is a perovskite that can accept structural underoccupation on the A as well as on the B-sites up to a certain amount, thus altering the A:B ratio; non-stoichiometric compounds ($La_{\varepsilon}Mn_{\varepsilon'}O_3$, with ε or $\varepsilon' = 0.9$; for which the perovskitic structure is maintained) have been considered. As an alternative, trivalent metal Mn can be partially substituted by a divalent cation; the Mn-perovskite allows a large substitution of the B-site cations with magnesium ($0 \leq x \leq 0.5$), and this substitution is accompanied by a correspondent change in the oxidation state, from Mn(III) to Mn(IV): $LaMn_{0.6}Mg_{0.4}O_3$ seems to be the most active of the series and has been considered here.

In this work the stability of the previous catalysts for prolonged time on stream has been investigated, comparing the catalytic activity and selectivity of fresh and aged catalysts and monitoring its variation with time on stream; the influence of water vapour on both activity and stability has been studied. The recover of catalytic activity following a thermal oxidative treatment has been also investigated.

EXPERIMENTAL

The La-Mn perovskite samples were prepared by thermal low-temperature decomposition of La and Mn nitrates. All the samples are monophasic if examined by X-ray diffraction. The specific surface was determined by the BET method. Catalytic tests were carried out in a steady state tubular microreactor, in the temperature range between 250 and 500°C; 0.5 or 1 gram of catalyst formed in 250 – 425 μm was used in all the runs. In the ageing test, the perovskites were kept on stream for more than 100 hours, at 350°C, in moistened or dry air, monitoring the concentration of CO, CO_2 and of the products of uncomplete combustion. 1,1,2-trichloroethene in air (500 ppm by volume) was used as test compound, fed at 6 Nl/h

flow rate. For the experiments with moistened air, the gases were saturated with water at 20°C. Further details concerning the catalyst preparation, characterisation and the experimental set-up can be found elsewhere [5, 6].

RESULTS AND DISCUSSION

Activity and stability of non-stoichiometric $LaMnO_3$

The most active catalyst in trieline combustion was $La_{0.9}MnO_3$, with a T_{50} (the temperature at which a 50% destruction of the main pollutant) of about 375°C, compared with T_{50} of 425°C for $LaMnO_3$; the $LaMn_{0.9}O_3$ activity resulted to be equivalent, or even poorer, than that of the stoichiometric perovskite (see Fig.1). The specific surface area was about 5 m^2/g for the stoichiometric, increases to 6 m^2/g in case of La/Mn=0.9 and to 6.6 m^2/g for La/Mn=1.11. The selectivity towards CO_2 was significantly higher for both the non-stoichiometric compounds: $La_{0.9}MnO_3$ > $LaMn_{0.9}O_3$ > $LaMnO_3$. Considering the formation of products of incomplete combustion (PICs), it is interesting to note that over $La_{0.9}MnO_3$ larger quantities of tetrachloroethene and free chlorine were detected. The presence of water vapour in the mixture increases the conversion, the selectivity towards the formation of CO_2 and reduces the amount of PICs, for all of the catalysts tested in this work. Similar results were observed in previous works [5-7].

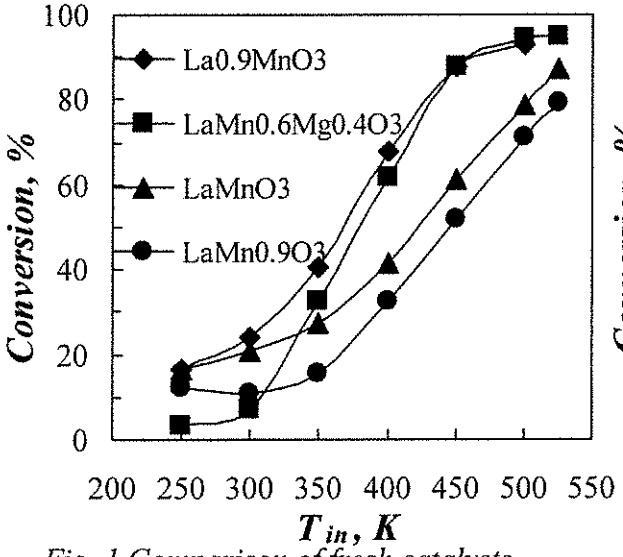

Fig. 1 Comparison of fresh catalysts. Conversion of trieline, 500 ppmV, in moistened air.

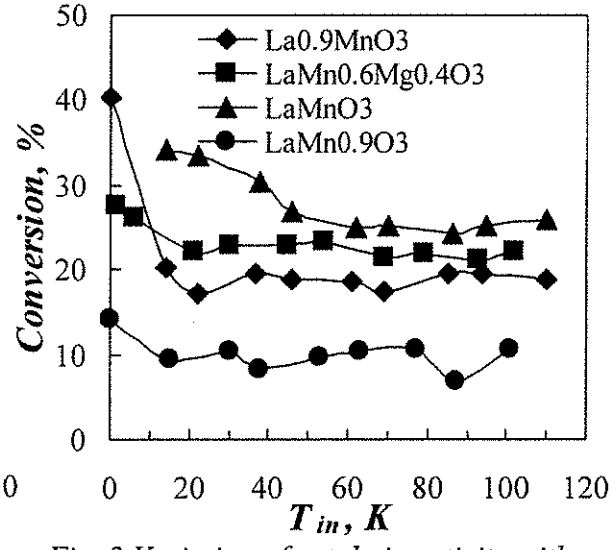

Fig. 2 Variation of catalytic activity with time on stream at 350°C. Trieline, 500 ppmV in moistened air; space velocity, 4800 h^{-1}.

All the catalysts showed a variation of the activity with time on stream, but the rate and degree of deactivation was different, as can be seen in Fig. 2. In the initial period a marked decrease was observed, especially for the $La_{0.9}MnO_3$; this catalyst, that was the most active initially, lost most of its activity after only 15-20 hours on stream, and once aged gave performances poorer than the stoichiometric perovskite. A nearly constant activity was showed by the other catalysts. The selectivity towards CO and chlorine formation increases slightly with time on stream, and seems correlated with the decrease of the catalytic activity; the selectivity toward PICs (tetracloroethene is the most abundant) does not change significantly. The ageing test was repeated for the stoichiometric perovskite, which resulted to be the most active for prolonged time on stream, with dry feed gases. The conversion was always significantly lower than in presence of water vapour, but it is interesting to note that

the variation with the time on stream was much more limited and very uniform.

Activity and stability of the Mg-substituted perovskite

The partial substitution increases the activity and the selectivity towards CO_2 (decreasing that toward CO) at higher temperatures (> 340°C). The temperature required for 50% conversion trieline over $LaMn_{0.6}Mg_{0.4}O_3$ was 375°C compared with T_{50} of 425°C for $LaMnO_3$ (Fig.1); the substitution with magnesium also improves the surface area, as showed in previous work [5]: it is about 10 m^2/g for the substituted catalyst, only 5 m^2/g for the stoichiometric one. The selectivity towards PIC and chlorine formation is the same for both catalysts. The variation of the conversion degree as a function of time on stream at 350°C is shown in Fig. 2. Also in this case an initial faster deactivation occurs, but after an initial period of about to 20 hours on stream a nearly constant conversion degree was reached, quite close to that observed over stoichiometric $LaMnO_3$. As in the previous case, the aged catalyst shows an higher selectivity toward chlorine, while the formation of PICs (tetrachloroethene and tetrachloromethane) is about constant.

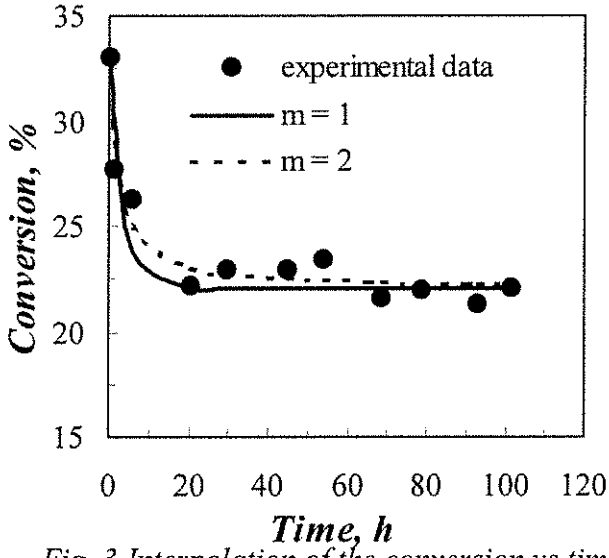

Fig. 3 Interpolation of the conversion vs time curve with the GPLE model. Trieline, 500 ppm, in moistened air, over $LaMn_{0.6}Mg_{0.4}O_3$

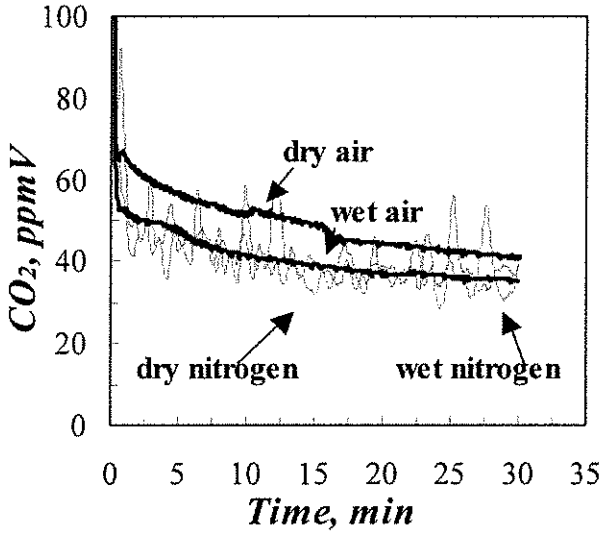

Fig. 4 CO_2 production during regeneration of $LaMnO_3$, with air and nitrogen in dry and wet conditions. T=600°C

Deactivation and regeneration

As can be seen in Fig. 2, each catalyst shows a different deactivation rate, which is also dependent on the operating conditions (the presence of water is very important). Anyway it is generally possible to describe the observed behaviour using a general power law expression (GPLE) as proposed by Fluentes [8]:

$$\frac{\partial\left(X/X_0\right)}{\partial t} = k_d \cdot \left(\frac{X}{X_0} - \frac{X_\infty}{X_0}\right)^m \qquad (1)$$

X_0 and X_∞ are the initial and limit value of conversion, k_d the kinetic constant and m the order of the deactivation process. The value of the parameters have been determined by fitting; an example is shown in Fig. 3.

A set of experiments was carried out to investigate the regeneration of the catalysts, in a stream of dry or moistened air (without chlorinated VOC); some experiments were also

carried out in absence of oxygen. The temperature of 600°C was selected for regeneration, after some preliminary experiments, and the CO and CO_2 production during the regeneration was continuously measured (see Fig. 4). The results suggest that a fast reversible deactivation occurs, caused probably by the interaction of hydrocarbon and chlorine with the catalysts; it is overimposed on a slow irreversible deactivation. In fact, nearly the same initial catalytic activity was measured after the regeneration in moistened air, during which the oxidation of the organic compounds, adsorbed on the catalytic surface during the combustion of trieline, takes place; CO_2 is the most abundant product. It is interesting to observe that during regeneration with dry air large oscillations in the production rate of CO_2 occur; this is typical of non-steady state phenomena. Some regeneration was obtained also in a stream of nitrogen; probably in this case the lattice oxygen is responsible for oxidating the adsorbed carbon species.

This mechanism is also supported by the results of the analysis carried out on the aged catalyst. While thermodynamic considerations suggest that at temperatures lower than 1000°C no decomposition of the perovskite phase should occur, the EDS analyses showed that the percentage of chlorine atoms over the total Mn+La atoms is very low (1-2%), while no significant variation of the cation ratio occurs, thus ruling out selective loss of metal.

CONCLUSIONS

The surface area and catalytic activity of La-Mn perovskites can be significantly improved by the partial substitution of the manganese and by altering the La/Mn ratio. These compounds show interesting catalytic properties in the destruction of chlorinated VOCs, namely good activity and selectivity towards products of complete combustion and higher stability than simple oxides. The total oxidation of trieline is connected with a partial reversible deactivation of the catalyst, probably caused by adsorption of hydrocarbon derived species on the catalyst.

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