

Tackling the Problem of Sulfur Poisoning of Perovskite Catalysts for Natural Gas Combustion

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Abstract— $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts ($x=0-0.25$, $y=0-17$) were prepared, characterized (XRD, BET, SEM-EDS, TEM, FTIR, chemical and atomic absorption analyses), tested for high-temperature methane combustion and aged in presence of SO_2 to investigate sulfur effect on catalytic activity. Different roles of manganese and chromium in the perovskite structure have been assessed: (i) manganese improves the activity of catalysts in the fresh state, whereas chromium worsens it; (ii) owing to its basic nature, manganese makes perovskites more prone to adsorb SO_2 and so less resistant to sulfur poisoning, whereas chromium, owing to its acidic nature, has opposite effects; (iii) the partial solubility of chromium oxide in basic media renders Cr-catalyst regeneration by NH_3 leaching less effective. MgO promotes catalytic activity of fresh $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts and slows down sulfur poisoning of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalysts only.

Key words: $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$, $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$, Perovskite, Methane Catalytic Combustion, Sulfur Poisoning

INTRODUCTION

Catalytic combustion for energy production purposes has received considerable attention during the past decades because it represents the most effective strategy to significantly reduce pollutants (HC , CO and NO_x), produced during homogeneous combustion, and to improve oxidation efficiency [Trimm, 1984; Pfefferle and Pfefferle, 1987; Zwinkels et al., 1993].

Industrial applications, however, have been limited, so far, to diffusive-type catalytic heaters, because the other promising applications (gas turbines [Garten et al., 1997] and premixed catalytic burners for heat generation purposes [Ceri et al., 2000]) require very strict properties of catalytic materials. The development of innovative and reliable technology would make catalytic combustion widely acceptable. Our current research efforts are addressed to developing cost-effective catalysts for application in premixed natural gas catalytic burners for domestic boilers [Ceri et al., 2001] and in the treatment of the exhaust gases of compressed natural gas cars (CNG), characterized by the presence of significant unconverted methane concentrations (having a 35-fold higher greenhouse potential than CO_2) [Farrauto and Heck, 1999]. Low ignition temperature, high-temperature resistance (up to $1,300^\circ\text{C}$), long-term stability and good resistance to poisoning agents such as sulfur compounds (either present in natural gas ground reservoirs or introduced as odorants) are the required properties of combustion catalysts suitable for both applications.

Perovskite-type mixed oxides can meet these requirements, owing to their low cost, thermo-chemical stability at comparatively high temperatures ($900-1,100^\circ\text{C}$), and good catalytic activity [Arai et al., 1986; Klvana et al., 1994; Collongue et al., 1991]. Perovskites have

the ABO_3 stoichiometry (where A is generally a rare-earth-metal cation in the +3 oxidation state and B is a transition-metal cation in the same valence state) and the number of different perovskites available from various preparation techniques is quite large owing to both the variety of A and B metals that can enter the perovskite structure and the possibility to substitute partially both A and B [Ciambelli et al., 2000; Saracco et al., 1999].

Perovskite catalysts, however, are sensitive to sulfur compounds. For this reason, they failed to become practical as automotive catalysts, as sulfur is often present in relatively high concentrations in the combustion products of automotive fuels [Wan, 1993] but they are promising in the field of natural gas combustion because much more resistant to the low levels of sulfur compounds (about 10 ppm) present in ground reservoirs or added on purpose to commercial natural gas [Klvana, 1997].

Previous studies on the effect of sulfur on the catalytic activity of $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ perovskites [Rosso et al., 2001a] showed drastic catalyst deactivation after a 200 ppmv SO_2 exposure at 800°C for 24 hours because of sulfates formation. The introduction of magnesium oxide in $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3 \cdot y \text{ MgO}$ catalysts [Rosso et al., 2001b] improved sulfur resistance, because MgO represented the preferential adsorption site for the SO_2 molecules: deactivation of such catalysts was appreciable only after 32 days of exposure to 200 ppmv SO_2 at 800°C (accelerated ageing conditions). It can be expected that the use of a more acidic element than Mn, as chromium, in the above perovskite could improve the catalyst stability towards sulfur poisoning. On the basis of previous studies on the $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_3$ perovskites ($x=0-0.5$) [Saracco et al., 1996], chromium was introduced in perovskite structure as partial or complete substitution of manganese ($\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3$, ($x=0-0.5$)) and sulfur resistance of the resulting system was evaluated. In this paper our efforts to improve sulfur resistance of perovskite catalysts for natural combustion were summarized and discussed comparing 0.5 Mg-substituted

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manganites, chromites and the bridging family, $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3$, with or without the MgO promoter.

EXPERIMENTAL

1. Catalyst Preparation

A series of catalysts of the perovskite type $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3$ ($x=0, 0.25, 0.5$) with different excess of MgO compared to the stoichiometric value (perovskite-MgO excess ratios: 25/75 wt%, 50/50 wt% and 75/25 wt%, corresponding to 1/17, 1/6 and 1/2 molecular ratios, respectively) was prepared via a modified version of the so called "citrate method" described in Rosso et al., 2001a, b.

Calcination was performed in calm air at 900 °C for 8 hours for all $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ catalysts and for MgO-free $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3$ catalysts. Calcination was performed at 1,000 °C for 3 hours for MgO-rich $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3$ catalysts, in order to avoid, for the Cr-containing materials, the formation of less active phases, containing Cr^{6+} compounds such as La_2CrO_6 [Saracco et al., 1996] which are formed at lower calcination temperatures and times. Pure MgO was prepared with the same experimental procedure and calcinated at 900 °C for 8 hours.

2. Catalyst Ageing Tests

Different samples of $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ powdered catalysts were treated at 800 °C for 1, 2, 4, 8, 16 and 32 days in a controlled-atmosphere oven. As previously done [Rosso et al., 2001a, b] a flow of air with 200 ppmv of SO_2 was forced to pass at a rate of $20 \text{ Ncm}^3 \text{ min}^{-1}$ over 1 g of powdered material located in a porcelain combustion boat.

A high SO_2 level (about 20 times higher than that corresponding to odorants usually added to commercial natural gas) was chosen in order to accelerate the ageing effect. Fractions of the SO_2 -treated catalysts were used for characterization, catalytic activity tests and catalyst regeneration studies.

3. Fresh/Aged Catalyst Characterization

Chemical analysis (dissolution in acid+atomic absorption) was performed by a Perkin Elmer 1100B atomic absorption spectrometer on each catalyst to confirm that the amount of the various elements of interest (La, Mn, Cr, Mg) was consistent with the nominal content.

XRD analyses (Philips XPert apparatus equipped with a monochromator for Cu $K\alpha$ radiation) were performed on all fresh catalysts (to check the formation of crystallized perovskite and MgO phases) and on the aged ones (to check the possible formation of new phases).

The specific surface area was measured by the BET method using N_2 on all fresh $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ catalysts (Micromeritics ASAP 2010 M apparatus). BET measurements were also performed on 32 aged catalysts to assess the influence of SO_2 poisoning on the specific surface area.

Transmission electron microscopy (TEM, Philips EM 400 apparatus) was performed on the different powdered perovskites to investigate their microstructure. Scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) (Philips 515 SEM equipped with EDAX 9900 EDS) were performed to investigate the morphology as well as the elemental composition and distribution of all the catalysts. Since the morphological analysis (SEM) needs gold

metallization of the sample and the X-ray emission (EDS) of gold overlaps those of other elements of interest (e.g. sulfur), simultaneous EDS and SEM measurements on the same sample were not possible.

Infrared spectroscopy spectra (Bruker Equinox 55 FTIR, equipped with MCT detector) were recorded in the transmittance mode on samples pelletized or deposited on silicon wafer of fresh and 32-days-aged $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ powders, after degassing in vacuum at room temperature for 30 min.

4. Catalytic Activity Screening Tests

Catalytic activity tests were performed on fresh, aged and regenerated (see section 2.5) catalysts in the experimental apparatus and according to the procedures described in detail in Saracco et al. [1999]. After 30 min stay at 800 °C in air flow as a common pre-treatment, a gas flow rate of $50 \text{ Ncm}^3 \text{ min}^{-1}$ (composition: $\text{CH}_4=2\%$, $\text{O}_2=18\%$, $\text{He}=\text{balance}$) was fed to a fixed-bed of 0.5 g of catalyst particles. Such pellets were obtained by pressing at 125 MPa the perovskite powders into tablets, which were then crushed and sieved to obtain 0.2-0.5 mm pellets. The fixed bed was enclosed in a quartz tube (I.D.: 4 mm) and sandwiched between two quartz-wool layers. The reactor was placed in a PID-regulated oven and a K-type thermocouple was inserted into the packed bed.

After the pretreatment, the reactor temperature was lowered at a 3°C min^{-1} rate from 800 °C down to 300 °C, meanwhile analyzing the outlet CO_2 concentration (the only detectable carbon oxidation product) through an NDIR analyser (Hartmann & Braun URAS 10E) in order to determine methane conversion. Typical sigma-shaped curves were obtained for methane conversion versus temperature. Twin runs were performed on two different samples of the same catalytic material and the results were then averaged. The deviation between the conversions measured at the same temperature in the twin runs was always less than 10%. No significant hysteresis was observed for these curves, with the catalytic tests performed upward (from 300 to 800 °C) after the downward standard run. The half-conversion temperature (T_{50}) was regarded as an index of the catalytic activity.

5. Catalyst Regeneration

$\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ and $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ catalysts, aged in SO_2 atmosphere for 32 days, were regenerated by leaching with either distilled water or an aqueous NH_3 solution (2.5% v/v), according to the procedure described in Rosso et al., [2001a]: 1 g of each catalyst was washed with 60 cm^3 of the leachant at room temperature in a stirred beaker; the powder was then filtered on a paper filter and dried in an oven at 120 °C.

The leachates obtained during catalyst regeneration were acidified by adding a diluted aqueous HCl solution. Cations and soluble sulfur were detected in the leaching medium by atomic absorption.

RESULTS AND DISCUSSION

The calcination step in the catalyst preparation was performed at the lowest temperatures yielding the desired phases in a well crystallized form, so as to obtain specific surface areas as high as possible. Whereas all the $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ catalysts crystallize after 8 hours at 900 °C, the Cr-containing catalysts show a different behavior: MgO-free perovskites crystallize after 8 hours at 900 °C, but MgO-rich perovskites crystallization needs 3 hours at 1,000 °C.

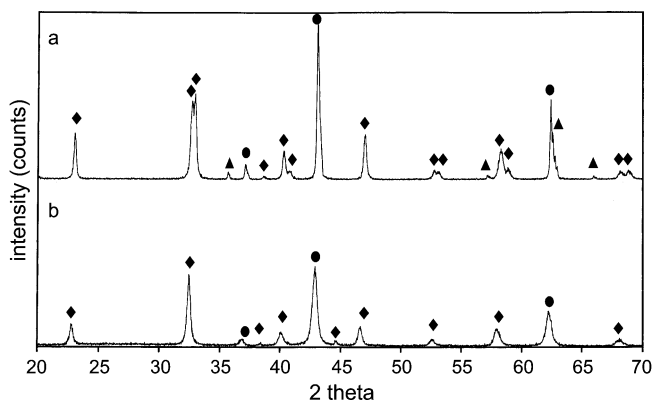


Fig. 1. X-ray diffraction patterns of: a) fresh $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst calcinated for 8 hours at 900°C ; b) fresh $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst calcinated for 3 hours at $1,000^\circ\text{C}$. Legend: (◆) perovskite; (●) MgO , (▲) Mg_6MnO_8 .

For Cr-containing catalysts, an excess of magnesium oxide slows down the perovskite crystallization process, so that a higher calcination temperature is required.

Performing these calcinations, the typical ABO_3 structure was formed in all cases, showing well-defined orthorhombic diffraction

lines (JCPDS card 33-0701) for Cr and Cr/Mn-containing species and well-defined rhombohedral diffraction lines (JCPDS card 32-0484) for Mn/Mg-containing species. The diffraction peaks of MgO (JCPDS card 45-0946) were clearly seen in all diffraction patterns of MgO -rich catalysts and their intensity rises with the increasing of the MgO excess in the catalysts (from 25% to 75%, respectively). Weak diffraction peaks attributable to La_2CrO_6 phase (JCPDS card 26-0817) were present only in the $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ spectrum while the spectra of all the MgO -rich Mn/Mg-containing catalysts show weak diffraction peaks of the Mg_6MnO_8 phase (JCPDS card 19-0766). The diffraction patterns of fresh $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ and $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ are shown, as an example, in Fig. 1a and Fig. 1b, respectively.

The data of specific surface area of all fresh catalysts are listed in Table 1. MgO -free catalysts have a specific surface area of $6\text{--}14 \text{ m}^2 \text{ g}^{-1}$, which rises by increasing the MgO excess up to $37\text{--}40 \text{ m}^2 \text{ g}^{-1}$ for all MgO -richest catalysts. In spite of the higher calcination temperature required for MgO -rich Cr-containing catalysts, their specific surface area rises by increasing the MgO excess and the BET data of all the MgO -richest catalysts are comparable, so confirming the textural promoting effect of MgO , already observed [Sarracco et al., 1999; Rosso et al., 2001b].

Fig. 2 shows, as an example, TEM micrographs of $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ (Fig. 2a) and $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ (Fig. 2b) catalysts. The per-

Table 1. Specific surface area (BET, $\text{m}^2 \text{ g}^{-1}$) and methane half-conversion temperatures (T_{50} , $^\circ\text{C}$) of fresh $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ perovskites. BET and T_{50} values of MgO are: $34.5 \text{ m}^2 \text{ g}^{-1}$ and 582°C , respectively

y MgO	$\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$		$\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$		$\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$	
	BET [$\text{m}^2 \text{ g}^{-1}$]	T_{50} [$^\circ\text{C}$]	BET [$\text{m}^2 \text{ g}^{-1}$]	T_{50} [$^\circ\text{C}$]	BET [$\text{m}^2 \text{ g}^{-1}$]	T_{50} [$^\circ\text{C}$]
0	7.0 ⁽¹⁾	455 ⁽¹⁾	6.1	577	14.4	506
2	32.8 ⁽²⁾	489 ⁽²⁾	13.6	552	-	-
6	20.8 ⁽²⁾	468 ⁽²⁾	24.2	545	-	-
17	40.3 ⁽²⁾	498 ⁽²⁾	36.9	529	38.0	532

⁽¹⁾ Rosso et al. [2001a]

⁽²⁾ Rosso et al. [2001b]

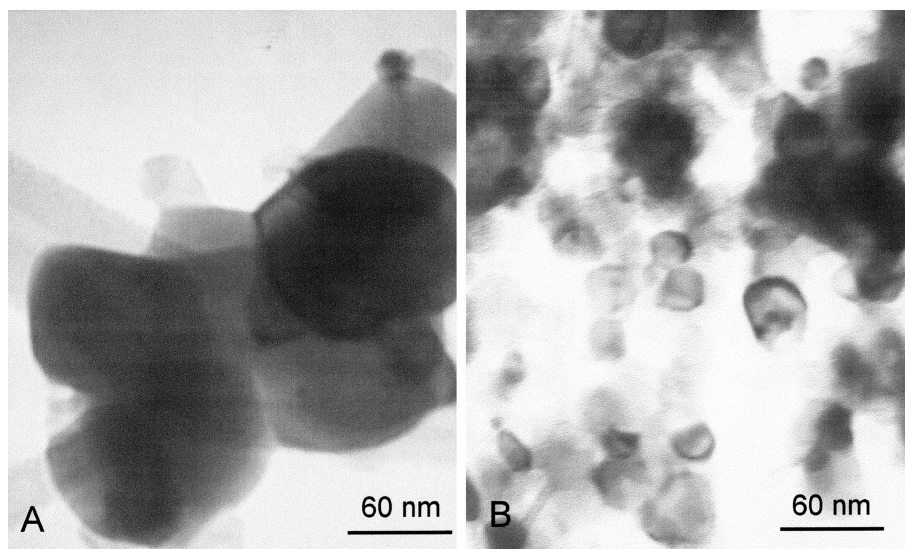


Fig. 2. TEM micrographs of fresh catalysts (280,000 $\times$): A) $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$; B) $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$.

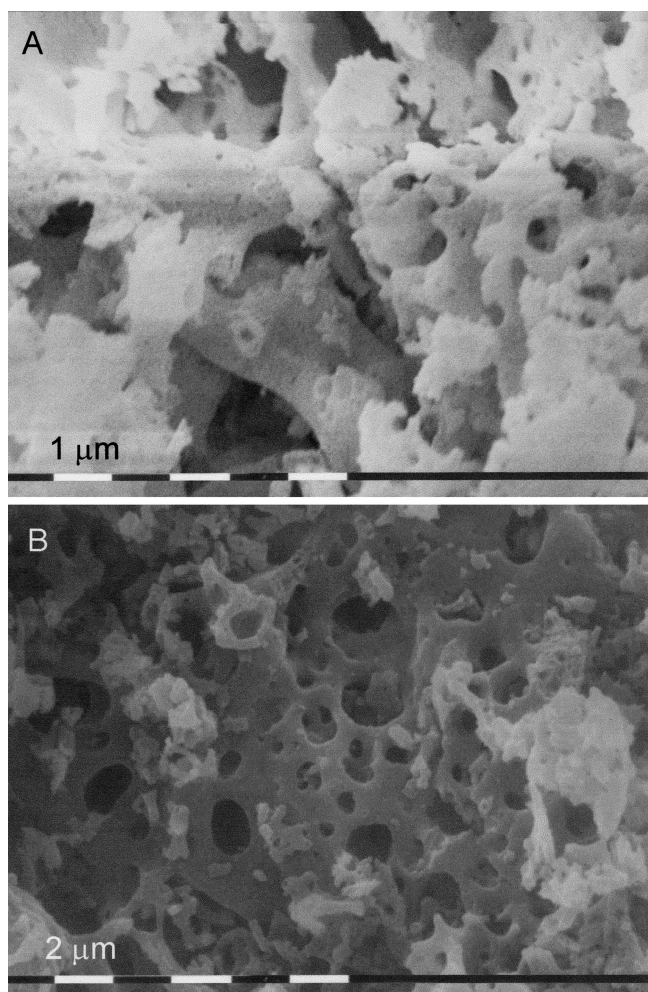


Fig. 3. SEM micrographs of fresh catalysts: B) $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 6 \text{ MgO}$ (10,000 $\times$); A) $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ (5,000 $\times$).

ovskite crystal size is about 90–120 nm in MgO-free catalyst (Fig. 2a) and about 30 nm in MgO-richest one (Fig. 2b), where the dark perovskite crystals are surrounded by light-grey MgO ones. The co-crystallization with MgO brings about the reduction of the average perovskite crystal size, in good agreement with BET data. Catalyst morphology is shown, as an example, in Fig. 3. SEM micrographs of fresh $\text{LaMg}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 6 \text{ MgO}$ (Fig. 3a) and $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ (Fig. 3b) catalysts show a spongy microstructure for both catalysts.

For the catalytic activity of fresh catalysts (Table 1), the results are as follows:

(1) the partial substitution of Cr with Mn in the perovskite structure improves the catalytic activity. That of $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ perovskite is close to that of MgO ($T_{50}=577^\circ\text{C}$ and 582°C , respectively); the half-conversion temperature of $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3$ perovskite is definitively lower ($T_{50}=506^\circ\text{C}$); and that of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3$ perovskite is the lowest ($T_{50}=455^\circ\text{C}$). The presence of Mn brings about a progressive improvement of catalytic activity. This is not surprising as it is already known that in the absence of Mg, Mn-containing catalysts are more active than Cr-containing ones [Seiyama, 1992]; in the present case, because the Cr/Mg and Mn/Mg

substitutions force a fraction of either manganese or chromium to shift to the IV oxidation state [Saracco et al., 1996, 1999], it can be stated that the Mn^{4+} species has an activity higher than that of the Cr^{4+} ones.

(2) MgO has a promoting effect on the catalytic activity of $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts. The higher specific surface area of MgO-rich perovskites is favorable in terms of increase of the specific number of active sites and of an improvement of catalytic activity.

(3) MgO does not have a promoting effect on the catalytic activity of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalysts. The large gain in the specific surface area obtained by introducing MgO seems not to have a direct positive effect on the catalytic activity. The observed decrease of catalytic activity could be caused (i) by the progressive dilution of the perovskite active phase due to increasing the MgO content ($y=2, 6, 17$), (ii) by the very strict mixture between MgO and perovskite crystals, observed in TEM micrographs (Fig. 2b), that, as already proposed [Saracco et al., 1999], could hamper the reacting gases from reaching the active catalyst surface. These effects are not important for $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts probably because the catalytic activity of $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ perovskite is close to that of MgO, so that the increase of the specific surface area is the prevailing factor.

Sulfur poisoning of the catalysts brings about no consistent structural modifications on the catalysts, as no new peaks are observed in the XRD spectra of all the aged catalysts.

BET data obtained on 32-day-aged catalysts show that MgO-free perovskites with low BET values in the fresh state do not change their specific surface area: from 7.0 to $7.2 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3$ perovskite and from 6.1 to $5.9 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ perovskite. MgO-richest perovskites with highest BET data in the fresh state, instead, lose after the same exposure some specific surface area: from 40.3 to $28.5 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst, from 36.9 to $30 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst and from 38 to $27 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst. A pure thermal effect in the absence of SO_2 was evaluated on the specific surface area of MgO: it diminishes from 34.5 to $19.6 \text{ m}^2 \text{ g}^{-1}$ after 16 days at 800°C [Rosso et al., 2001b]. The decrease of specific surface area observed on all 32-days-aged MgO-richest catalysts can be due to both sulfur presence and thermal effects; the high BET data kept after ageing, however, confirm the effectiveness of MgO as a textural promoter.

The effect of SO_2 exposure for progressively longer contact times at 800°C on the catalytic activity of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts is shown in Fig. 4a and b, respectively.

Mn-containing catalysts (Fig. 4a), more active in the fresh state, show a drastic deactivation after only 1 day of SO_2 exposure for the MgO-free catalyst and a comparable deactivation after about 4, 16 and 32 days for the catalyst with 25 wt%, 50 wt% and 75 wt% of MgO excess, respectively. In MgO-free catalysts, perovskite phase deactivates rapidly, because of the basic nature of elements such as La, Mg and Mn which are very prone to adsorb acidic species like SO_2 . MgO-rich catalysts deactivate more slowly and the higher is the MgO content, the slower is the deactivation rate, because of the presence of the basic MgO, which preferentially adsorbs sulfur and thus allows the perovskite active sites to avoid sulfur poisoning for

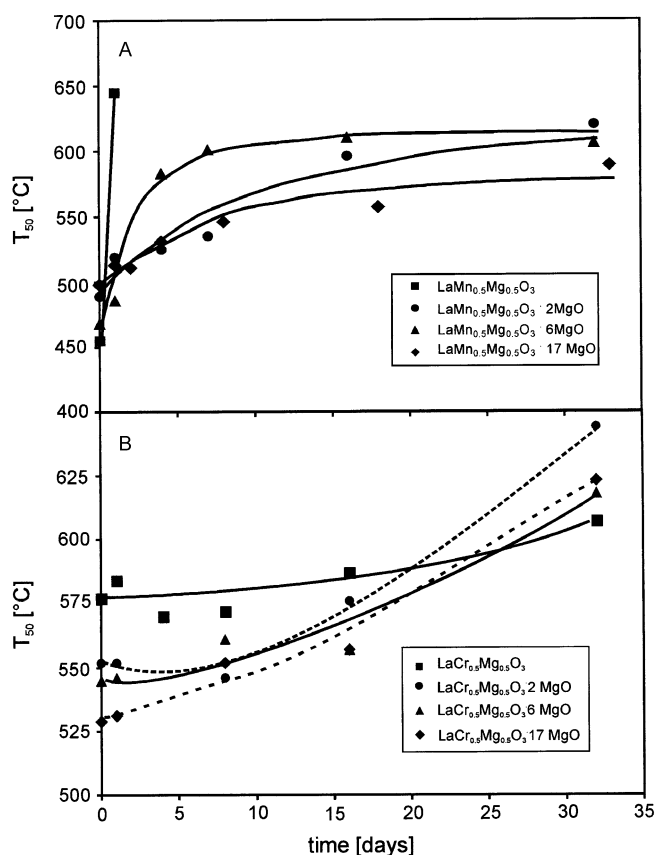


Fig. 4. Methane half conversion temperatures (T_{50} , °C) of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ (A) and $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ catalysts (B) vs. exposure time to 200 ppmv SO_2 at 800 °C.

a longer time. MgO actually furnishes preferential adsorption sites for SO_2 molecules [Wan, 1993], as confirmed by the use of MgO derivatives as SO_x adsorbents in catalytic cracking units [Bertolacini, 1991]. However, after prolonged exposure to SO_2 , the active sites of the perovskite phase are also involved in sulfur poisoning, so that the catalytic activity is depressed.

Cr-containing catalysts (Fig. 4b), instead, show a quite different behavior. If the $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ catalyst, within the $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ series, shows the best catalytic activity in the fresh state, the MgO-free $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ catalyst preserves, among the catalysts tested, its starting catalytic activity after 32 days of SO_2 exposure at 800 °C. The MgO-rich catalysts, in fact, show a negligible deactivation up to 16 days of SO_2 exposure, but their catalytic activity decreases after 32 days. Again, MgO furnishes preferential adsorption sites for SO_2 molecules, as for $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ catalysts. EDS analysis reveals a significant presence of sulfur on each 32-day-aged catalyst (from 0.9–1 wt% for $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3$ catalysts to 1.3 wt% for $\text{LaMg}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ perovskite and up to 1.7–1.8 wt% for $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ ones) but the amount of sulfur detected on all MgO-richest 32-days-aged catalysts is about twice the amount of sulfur detected on 32-days-aged MgO-free catalysts (this fact alone is not conclusive, as it could be due to the higher specific surface area of the former).

Evidence of sulfates formation on MgO phase of all MgO-richest 32-days-aged catalysts is given by FTIR spectra. Fig. 5 reports, as an example, the spectra of fresh and 32-days-aged $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot$

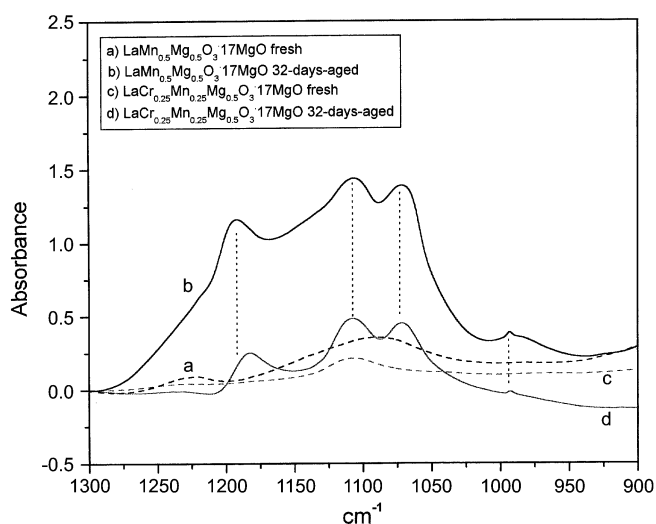


Fig. 5. FTIR absorbance spectra in the 1,300–800 cm^{-1} region (corresponding to the modes of sulfates) of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ catalyst in: a) fresh state; b) aged for 32 days at 800 °C in 200 ppmv SO_2 atmosphere and of $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ catalyst in: c) fresh state; d) aged for 32 days at 800 °C in 200 ppmv SO_2 atmosphere.

17 MgO (curve a and b) and $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$ catalysts (curve c and d) in the sulfate region. The spectra of 32-aged samples (curve b and d) show four bands at about 1,181, 1,106, 1,071 and 993 cm^{-1} that can be assigned to bulk SO_4^{2-} ions in C_{2v} symmetry [Bensitel et al. 1989; Rosso et al., 2001b]. It is important to underline that the difference in the intensity between the two spectra is due to the different experimental procedure followed to prepare the samples (pelletization for $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$, curve b and deposition for $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{MgO}$, curve d) and not, necessarily, to different amounts of sulfates on the two catalysts.

The negative extent of sulfates formed on MgO phase on the catalytic activity of aged Cr-containing catalysts can be explained considering a shielding effect that sulfate species formed on the MgO phase might have on the perovskite surface. Considering that the perovskite crystals are embedded into the MgO matrix, it is well possible that the steric hindrance of sulfate species formed on the MgO phase prevents the reacting gases from reaching the perovskite active sites and causes a consequent decrease of the catalytic activity. After prolonged exposure to SO_2 , however, perovskite active sites can be directly involved in sulfur poisoning, so the shielding effect of sulfates formed on MgO together with the direct deactivation of perovskite active sites are responsible of each catalyst deactivation (Mn-containing catalysts, too).

In contrast, the MgO-free $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ catalyst, thanks to the acidic nature of chromium which is less prone than manganese to sulfur adsorption, shows a higher resistance to sulfur poisoning.

At last, Cr/Mn-containing catalysts (Fig. 6), although crystallize in the same orthorhombic perovskite phase of $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{MgO}$ catalysts, show a behavior similar to the Mn-containing catalysts. Thanks to the Mn presence, MgO-free $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3$ catalyst is more active than $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ one in the fresh state, but it deactivates drastically after only one day exposure to SO_2 . $\text{LaCr}_{0.25}$

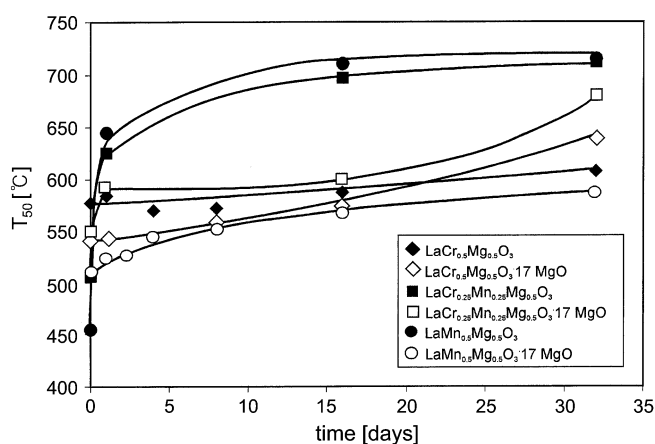


Fig. 6. Methane half conversion temperatures (T_{50} , °C) of $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$, $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$, $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3$, $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ and $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3$, $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalysts vs. exposure time to 200 ppmv SO_2 at 800 °C.

$\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst, instead, deactivates more slowly than the corresponding MgO-free ones, thanks to the protecting role of MgO against sulfur poisoning.

From the comparison among the different catalyst families (Fig. 6), $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalyst keeps the best catalytic activity after 32 days of SO_2 exposure, although it gets worse at about 90 °C, thanks to its highest starting catalytic activity. $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ catalyst, instead, shows a little worse catalytic activity after 32 days of SO_2 exposure, although its starting catalytic activity is the lowest,

thanks to its worsening of only 30 °C.

On the basis of the expertise derived from previous works on $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ catalysts [Rosso et al., 2001a], catalyst regeneration was performed by washing with either water or an aqueous NH_3 solution (Table 2). Surprisingly, the extent of regeneration of Cr-containing catalysts is somehow better using the water leaching, whereas both water and ammonia leaching are effective for Mn-containing catalyst regeneration. A previous comparison on $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ perovskites between the washing with water or with aqueous NH_3 solution [Rosso et al., 2001a] demonstrated that ammonia leaching was more effective in restoring the catalytic activity of the catalysts. Assuming that metal sulfate $[\text{M}_2(\text{SO}_4)_n]$ dissolution by water is based on the following mechanism [Rosso et al., 2001a]:



It is evident that the NH_4OH leaching should be more effective because it shifts the equilibrium to the right side. Then the formation of the metal hydroxide, which turns into metal oxide at high temperature, allows preserving the original composition of the perovskite.

Atomic absorption data listed in Table 3 show the presence of chromium, magnesium and sulfur in both water and NH_3 leachate for all the Cr-containing catalysts, and magnesium and sulfur for the Mn-containing catalysts (manganese was absent, while lanthanum was not detected because of its high detection limit (25 $\mu\text{g}/\text{ml}$)). The sulfur amounts are much larger than the magnesium and the chromium ones, which allows the original composition of catalyst to be substantially preserved. The NH_3 leaching dissolves more

Table 2. Methane half-conversion temperatures. (T_{50} , °C) of fresh, 32-days-aged and washed $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ perovskites

y MgO	$\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$		$\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$		$\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$	
	0	17	0	17	0	17
fresh	577	529	506	532	455 ⁽¹⁾	498 ⁽²⁾
32-days-aged	607	623	724	687	645 ^{(1)*}	589 ⁽²⁾
washed (NH_3)	605	588	554	532	458 ⁽¹⁾	514 ⁽²⁾
washed (H_2O)	585	566	505	532	462 ⁽¹⁾	515 ⁽²⁾

*1-day-aged

⁽¹⁾ Rosso et al. [2001a]

⁽²⁾ Rosso et al. [2001b]

Table 3. Atomic absorption data (mg element/g catalyst) on the leachate obtained on the 32-days-aged $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ perovskites by aqueous NH_3 and water leaching

y MgO		$\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$		$\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$		$\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$	
		0	17	0	17	0	17
Cr	(NH_3)	0.46	0.13	0.23	0.05	-	-
	(H_2O)	0.35	0.11	0.18	0.03	-	-
Mg	(NH_3)	0.14	0.58	0.03	0.21	0.13 ^{(1)*}	0.50
	(H_2O)	0.62	2.3	0.15	1.1	0.53 ^{(1)*}	1.5
S	(NH_3)	32	58	38	67	6.4 ^{(1)*}	62
	(H_2O)	18	34	25	40	3.7 ^{(1)*}	38

*analysis performed on the leachate obtained on 1-day-aged catalyst.

⁽¹⁾ Rosso et al. [2001a]

sulfur and less magnesium than the water leaching, confirming at least for MgSO_4 the shift to the right side of Eq. (1), as observed for $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ catalysts [Rosso et al., 2001a]. However, it dissolves more chromium than the water leaching. Chromium oxide is probably partially dissolved by ammonia with formation of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complexes [Pascal, 1959] that were actually noticed to provide the solution with a yellow color. This fact could explain the poorer effectiveness of ammonia leaching on the regeneration of $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ catalysts. Only $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts and $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ one, the catalyst with the lowest chromium content among the Cr-containing ones recover, in fact, completely their starting catalytic activity also with ammonia leaching.

The slow deactivation by sulfur poisoning and the complete regenerability to the original high catalytic activity by water or NH_3 leaching make the catalyst performance of $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$ (or $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$, for its comparable behavior) promising for application purposes. However, the $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$ catalyst, even if less active in the fresh state, seems to be perhaps preferable for its highest stability and resistance to sulfur poisoning in order to assure stable performance and durability to catalytic reactors (e.g. catalytic burners [Ceri et al., 2001]).

CONCLUSIONS

$\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ and $\text{LaCr}_{0.5-x}\text{Mn}_x\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts have been prepared, characterized, tested for high-temperature methane catalytic combustion. Ageing in presence of SO_2 was also accomplished to investigate the effect of sulfur on their catalytic activity.

Experimental results demonstrate different roles of manganese and chromium in the perovskite structure: (i) in the fresh state the presence of manganese increases the activity of the catalysts, whereas the presence of chromium lowers it; (ii) the basic nature of manganese makes the perovskites more prone to adsorb SO_2 , and so less resistant to sulfur poisoning, whereas the acidic nature of chromium has an opposite effect; (iii) the partial solubility of chromium oxide in ammoniac media makes the leaching with aqueous NH_3 solution not very effective to catalyst regeneration compared to Mn-containing catalysts [Rosso et al., 2001a].

MgO has a protecting role against sulfur poisoning of Mn and Cr/Mn-containing catalysts, which becomes consistent only after 32 days of SO_2 ageing. Concerning $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts, MgO has a promoting effect on their catalytic activity in the fresh state, but, representing a preferential adsorption site for the SO_2 molecules, its presence has a negative extent on the catalytic activity of the $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot y \text{ MgO}$ catalysts aged for 32 days in SO_2 laden atmospheres, because of the shielding effect of sulfates formed on it.

Therefore, $\text{LaMn}_{0.5}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$, or at least the catalyst with the lowest Cr-content, $\text{LaCr}_{0.25}\text{Mn}_{0.25}\text{Mg}_{0.5}\text{O}_3 \cdot 17 \text{ MgO}$, result is promising for application purposes thanks to the slow deactivation by sulfur poisoning and the complete regenerability to their original high catalytic activity by water or NH_3 leaching. On the other hand, the catalyst with the highest Cr-content, $\text{LaCr}_{0.5}\text{Mg}_{0.5}\text{O}_3$, although less active in the fresh state, seems to assure a more stable performance because it shows the highest stability and resistance to sul-

fur poisoning and does not require regeneration leaching. This is a non-negligible feature for practical application in industrial catalytic reactors (e.g., catalytic burners, catalytic converters for gas turbines, and so on) where long-term stability is an important prerequisite.

REFERENCES

- Arai, H., Yamada, T., Eguchi, K. and Seiyama, T., "Catalytic Combustion of Methane over Various Perovskite-type Oxides," *Appl. Catal.*, **26**, 265 (1986).
- Bensitel, M., Waqif, M., Saur, O. and Lavalley, J. C., "The Structure of Sulfate Species on Magnesium Oxide," *J. Phys. Chem.*, **93**, 6581 (1989).
- Bertolacini, R. G., Hirschberg, E. H. M. and Modica, F. J., US 4381991 Patent, Standard Oil (1991).
- Ceri, I., Saracco, G., Geobaldo, F. and Specchia, V., "Development of a Methane Premixed Catalytic Burner for Household Applications," *Ind. Eng. Chem. Res.*, **39**, 24 (2000).
- Ceri, I., Saracco, G., Specchia, V. and Trimis, D., "Improved-Performance Knitted Fibre Mats as Supports for Pre-Mixed Natural Gas Catalytic Combustion," *Chem. Eng. J.*, **82**, 73 (2001).
- Ciambelli, P., Cimino, S., De Rossi, S., Lisi, L., Minelli, G., Porta, P. and Russo, G., "A FeO_3 (A=La, Nd, Sm) and $\text{LaFe}_{1-x}\text{Mg}_x\text{O}_3$ Perovskites as Methane Combustion and CO Oxidation Catalysts: Structural, Redox and Catalytic Properties," *Appl. Catal. B*, **757**, 1 (2000).
- Collongue, B., Garbowski, E. and Primet, M., "Catalytic Combustion of Methane over Bulk and Supported LaCrO_3 Perovskites," *J. Chem. Soc. Faraday Trans.*, **87**, 2493 (1991).
- Farrauto, R. J. and Heck, R. M., "Catalytic Converters: State of the Art and Perspectives," *Catal. Today*, **51**, 351 (1999).
- Garten, R. L., Dalla Betta, R. A. and Schlatter, J. C., "Catalytic Combustion," Handbook of Heterogeneous Catalysis, Ertl, G., Knözinger, H., Weitkamp, J., eds., VCH, Weinheim (1997).
- Klvana, D., Kirchnerova, J., Gauthier, P., Delval, J. and Chaouki, J., "Preparation of Supported $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$ Perovskite Catalysts and Their Performance in Methane and Odorized Natural Gas Combustion," *Can. J. Chem. Eng.*, **75**, 509 (1997).
- Klvana, D., Vaillancourt, J., Kirchnerova, J. and Chaouki, J., "Combustion of Methane over $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$ and $\text{La}_{0.4}\text{Sr}_{0.6}\text{Fe}_{0.4}\text{Co}_{0.6}\text{O}_3$ Prepared by Freeze-drying," *Appl. Catal. A*, **109**, 181 (1994).
- Pascal, P., "Nouveau Traité de Chimie Minérale," Masson, Paris, vol. 14 (1959).
- Pfefferle, L. D. and Pfefferle, W. C., "Catalysis in Combustion," *Catal. Rev.-Sci. Eng.*, **26**, 219 (1987).
- Rosso, I., Garrone, E., Geobaldo, F., Onida, B., Saracco, G. and Specchia, V., "Sulphur Poisoning of $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3$ Catalysts for Natural Gas Combustion," *Appl. Catal. B*, **30**, 61 (2001a).
- Rosso, I., Garrone, E., Geobaldo, F., Onida, B., Saracco, G. and Specchia, V., "Sulphur Poisoning of $\text{LaMn}_{1-x}\text{Mg}_x\text{O}_3 \cdot y\text{MgO}$ Catalysts for Methane Combustion," *Appl. Catal. B*, **34**, 29 (2001b).
- Saracco, G., Geobaldo, F. and Baldi, G., "Methane Combustion on Mg-doped LaMnO_3 Perovskite Catalysts," *Appl. Catal. B*, **20**, 277 (1999).
- Saracco, G., Scibilia, G., Iannibello, A. and Baldi, G., "Methane Combustion on Mg-doped LaCrO_3 Perovskite Catalysts," *Appl. Catal. B*, **8**, 229 (1996).

- Seiyama, T., "Total Oxidation of Hydrocarbons on Perovskite Oxides," *Catal. Rev.-Sci. Eng.*, **34**, 281 (1992).
- Trimm, D. L., "Catalytic Combustion," *Appl. Catal.*, **7**, 249 (1984).
- Wan, L., "Poisoning of Perovskite Oxides by Sulphur Dioxide," Properties and Applications of Perovskite-Type Oxides, Tejuca L. G., Fierro, J. L. G. (Eds.), Dekker, New York (1993).
- Zwinkels, M. F. M., Järås, S. G. and Govin Menon, P., "Catalytic Materials for High Temperature Combustion," *Catal. Rev.-Sci. Eng.*, **35**, 319 (1993).