

N₂O catalytic decomposition over various spinel-type oxides

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Abstract

Various spinel-type catalysts AB₂O₄ (where A = Mg, Ca, Mn, Co, Ni, Cu, Cr, Fe, Zn and B = Cr, Fe, Co) were prepared and characterized by XRD, BET, TEM and FESEM-EDS. The performance of these catalysts towards the decomposition of N₂O to N₂ and O₂ was evaluated in a temperature programmed reaction (TPR) apparatus in the absence and the presence of oxygen. Spinel-type oxides containing Co at the B site were found to provide the best activity. The half conversion temperature of nitrous oxide over the MgCo₂O₄ catalyst was 440 °C and 470 °C in the absence and presence of oxygen, respectively (GHSV = 80,000 h⁻¹).

On the grounds of temperature programmed oxygen desorption (TPD) analyses as well as of reactive runs, the prevalent activity of the MgCo₂O₄ catalyst could be explained by its higher concentration of suprafacial, weakly chemisorbed oxygen species, whose related vacancies contribute actively to nitrous oxide catalytic decomposition. This indicates the way for the development of new, more active catalysts, possibly capable of delivering at low temperatures amounts of these oxygen species even higher than those characteristic of MgCo₂O₄.

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1. Introduction

Nitrous oxide (N₂O) is a compound that during the last decade has been recognized as a potential contributor to the destruction of the ozone in the stratosphere and acknowledged as a relatively strong greenhouse gas [1,2]. The continuous increase of its concentration, both due to natural and anthropogenic sources (adipic acid production, nitric acid production, fossil fuels, biomass burning) and longer atmospheric residence time (150 years), entails the need of developing efficient catalysts for its decomposition (into nitrogen and oxygen). The catalytic decomposition of N₂O has been intensively studied over several catalysts [3–6]. However, the catalytic activity towards decomposition of nitrous oxide would be significantly affected by various gases that coexist in real exhaust or flue gases. For instance, the presence of excess oxygen is one of the causes for catalyst inhibition [5].

In recent years, spinel-type oxides based on 3d transition metals have been the subject of increasing fundamental and applied research because of their catalytic properties [7,8].

Spinel-type oxides are represented by the chemical formula AB₂O₄, in which A ions are generally divalent cations occupying tetrahedral sites and B ions are trivalent cations in octahedral sites; this is the structure of most chromites.

For certain spinel structures the cations may shift between the A and B sites. This may result in the general formula B(AB)₃O₄: A and half of B in the octahedral sites, half of B in the tetrahedral sites. This is actually the structure of most of ferrites. To further add complexity, a mixed spinel structure is also possible, with wide variation in composition. The most general formula of mixed spinels can therefore be (A_{1-x}B_x)(A_xB_{2-x})O₄.

Our current research efforts are aimed at the development of catalytic systems based on spinel-type oxides because of their good stability and intrinsic catalytic activity. The work here presented concerns the synthesis, characterization, catalytic activity test and reaction mechanism assessment of a series of Co spinels, whose performance towards N₂O decomposition, evaluated both in presence and in absence of oxygen, is compared with that of other spinels (ferrites and chromites). Some conclusions are then drawn concerning either the role of each single constituting element on the activity of the most promising catalyst (MgCo₂O₄), or its reaction mechanism, thereby pointing out the way to the development of new, more active catalysts.

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2. Experimental

2.1. Catalyst preparation and characterization

A series of spinel catalysts were prepared via a highly exothermic and self-sustaining reaction, the so-called “*solution combustion synthesis*” method (SCS) [9]. Particularly, a concentrated aqueous solution of various precursors (metal nitrates and urea) was located in an oven at 600 °C for a few minutes in a crucible, so as to ignite the very fast reaction. Under these conditions nucleation of metal oxide crystals is induced, their growth is limited and nanosized grains can be obtained.

The catalyst was then ground in a ball mill at room temperature. X-ray diffraction (PW 1710 Philips diffractometer) was used to check the achievement of the spinel oxides structure. The specific surface area of the prepared catalyst was evaluated using a Micrometrics ASAP 2010 BET analyser. Direct observation of the nanosized spinels crystals was performed by transmission electron microscopy (TEM—Philips CM 30 T). A field emission scanning electron microscope (FESEM—Leo 50/50 VP with Gemini column) was used to analyse the microstructure of the catalysts crystal aggregates.

2.2. Catalyst activity measurements

The activity of the prepared catalysts was analysed by temperature programmed reaction (TPR), according to a standard operating procedure: a gas mixture (5000 ppm N₂O; 0 or 5 vol.% O₂, He = balance) was fed at the constant rate of 100 ml min^{−1} via a set of mass flow controllers to the catalytic fixed-bed micro reactor enclosed in a quartz tube placed in an electric oven. The tubular quartz reactor was loaded with 50 mg of catalyst and 200 mg of silica pellets (0.3–0.7 mm in size); this inert material was adopted to reduce the specific pressure drop across the reactor.

The W/F of the gases through the catalytic bed was about 5×10^{-4} g min/Nml (GHSV = 80000 h^{−1}). The reaction temperature was controlled through a PID-regulated oven and varied from room temperature to 700 °C at a 5 °C min^{−1} rate. The outlet gas composition was monitored through a NO/N₂O NDIR (ABB) and a NO/NO₂ chemiluminescence analysers (Eco Physics), as well as through a quadrupole detector (Baltzer Quadstar 422), as a function of the bed temperature. The temperature corresponding to half N₂O conversion (T_{50}) was taken as an index of the activity of each tested catalyst: the lower the T_{50} value, the more active the catalyst. The runs were repeated three times, and the average T_{50} value was assumed for each catalyst. The maximum variation between the three T_{50} values never exceeded 20 °C. To fully examine the catalytic effect of the spinels, blank nitrous oxide decomposition runs in the absence of any catalyst and in the presence of only SiO₂ were also carried out. Activity runs with different gas hourly space velocity (GHSV) were also performed on the best catalyst.

Some further analyses were carried out on some selected spinel catalysts in a Temperature Programmed Desorption/

Reduction/Oxidation (TPD/R/O) analyser, equipped with a thermal conductivity (TCD) detector (TPD/R/O 1100 Thermoquest). The catalysts were purged with He and then saturated with O₂ at room temperature; right away, they were heated up to 1100 °C and the O₂ desorbed during heating was detected by the TCD detector [9]. X-ray diffraction was once again used on the catalysts, which underwent TPD analysis, to check whether the spinel structure had been retained or not, and to check for the possible appearance of new phases.

3. Results and discussion

The characterization results regarding all the catalysts prepared are listed in Table 1. BET specific surface area (SSA) values ranging between 5 and 80 m²/g and T_{50} refers to the temperature of the half conversion of nitrous oxide in presence and absence of oxygen. All spinel samples were found to be well crystallized by XRD analysis, here not reported for the sake of brevity. No secondary phases could be detected by this technique (X-ray diffraction has a $\pm 4\%$ sensitivity). Fig. 1a shows a FESEM picture of MgCo₂O₄ spinel catalyst produced via SCS. Its microstructure appears foamy. During solution combustion synthesis, the decomposition/combustion of reacting precursors generates a large amount of gaseous products in a very short period of time, which leads to a spongy catalyst morphology. Fig. 1b shows a TEM picture of the same catalyst. It refers to the catalyst that showed the highest activity among those prepared. By employing this direct observation technique, values of the catalyst grain size of 5–75 nm could be estimated for the different catalysts. The spinel crystals range is perfectly in line with the BET specific surface areas measured. It is indeed easy to calculate that the above range size should correspond approximately to specific surface areas in the range 5–90 m²/g, once the average density of the catalyst particles is assumed to be 6500 kg/m³ and an average value for the spinels tested and a

Table 1
Collection of results of catalyst characterization tests concerning BET specific surface area and catalytic activity

Catalyst	BET area (m ² /g)	T_{50} without O ₂ (°C)	T_{50} with O ₂ (°C)
No catalyst	–	905	990
MgCr ₂ O ₄	80.8	625	715
CaCr ₂ O ₄	39.5	780	>800
MnCr ₂ O ₄	37.1	645	725
CoCr ₂ O ₄	59.0	550	685
NiCr ₂ O ₄	52.3	630	725
CuCr ₂ O ₄	14.2	630	745
MgFe ₂ O ₄	34.0	525	540
CoFe ₂ O ₄	10.2	580	600
CuFe ₂ O ₄	8.8	575	650
MgCo ₂ O ₄	52.3	440	470
CrCo ₂ O ₄	42.5	568	630
MnCo ₂ O ₄	9.6	650	735
FeCo ₂ O ₄	5.9	600	675
CoCo ₂ O ₄	7.8	475	510
NiCo ₂ O ₄	5.0	505	545
CuCo ₂ O ₄	3.6	700	>800
ZnCo ₂ O ₄	10.1	475	500

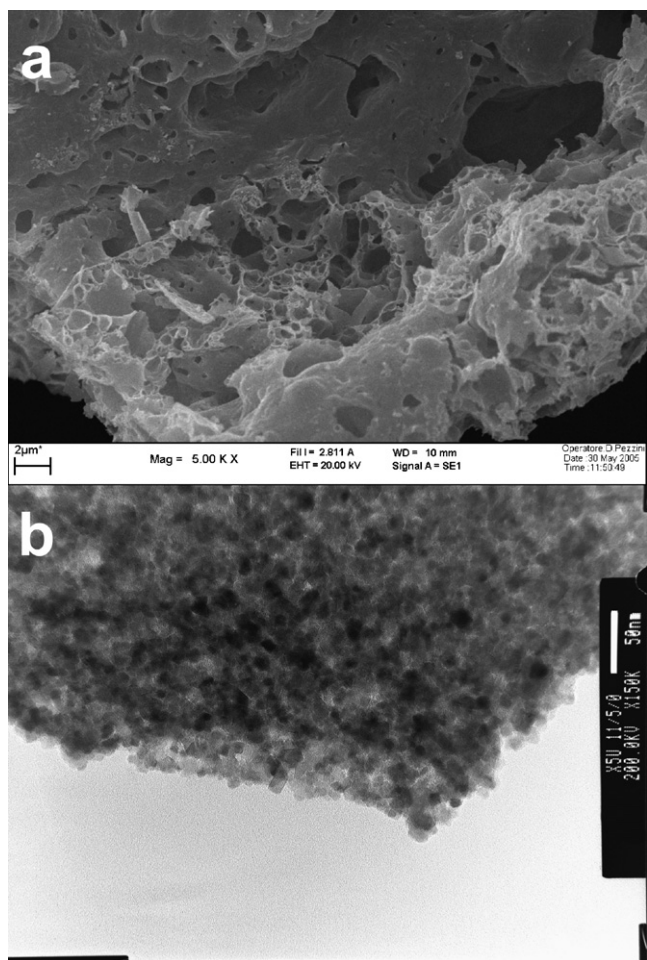


Fig. 1. Electron microscopy results concerning the MgCo_2O_4 catalyst: (a) FESEM view of the catalyst microstructure (b). TEM micrograph of the catalyst crystals.

spherical shape for the particles themselves. This slight discrepancy between measured and calculated is likely to be ascribed to the fact that spinel crystals are not spherical.

The SCS technique was adopted to obtain extremely pure spinels with a good specific surface area despite the absence of any carrier (Al_2O_3 , CeO_2 , La_2O_3 , etc). This allowed a deeper investigation of the mechanistic aspects of the N_2O catalytic decomposition over the active phase alone with no interference or synergic effects of the carrier. The latter will likely have to be adopted in the final application in an industrial reactor to maximise the specific amount of active sites. Comparing the activity results concerning all the investigated catalysts (Table 1), in line with literature information [7,10], the cobaltites showed the highest catalytic activity even if it may not result exclusively from the effect of the B site metal. The T_{50} of chromites and ferrites are always higher than 500°C whereas only three cobaltites showed T_{50} values lower than 500°C . For this reason a deeper investigation was carried out only on these three catalysts.

All catalysts guarantee much lower T_{50} values than the ones related to non-catalytic reduction (905 and 990°C in presence and absence of oxygen, respectively). Fig. 2 compares the catalytic decomposition of N_2O in the absence and in the presence of oxygen on the three best catalysts. Decomposition runs in the absence of any catalyst and in the presence of only inert SiO_2 were also reported. The catalytic reduction of N_2O to N_2 and O_2 in the absence of oxygen becomes appreciable from 400°C with the total conversion occurring in the range 500 – 650°C . When oxygen is present in the feed stream, the T_{50} shift is rather small ($<35^\circ\text{C}$).

It is generally accepted that surface vacant sites are responsible for nitrous oxide decomposition [5,11,12]. The decomposition of nitrous oxide mainly proceeds with three steps: (1) decomposition of N_2O into N_2 owing to the presence

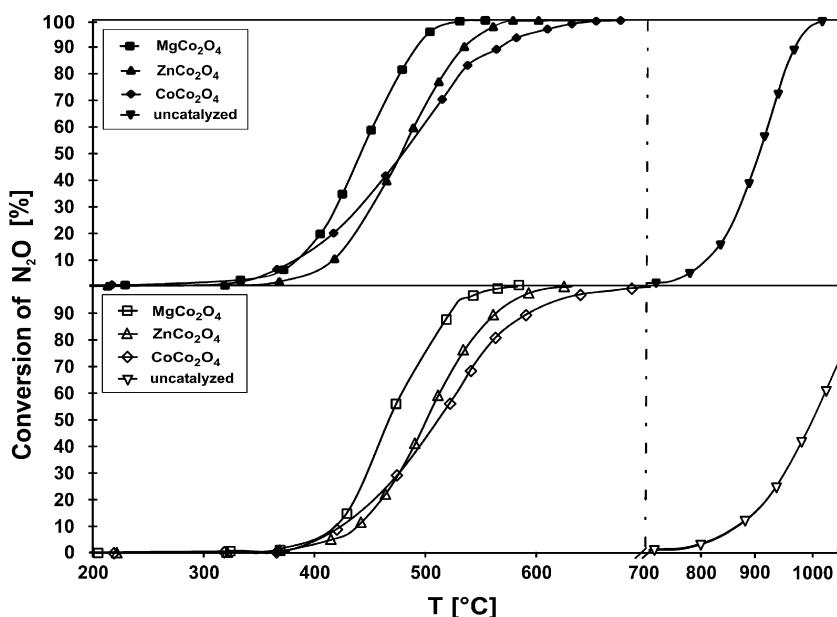


Fig. 2. Results of the catalytic activity runs— N_2O conversion to N_2 and O_2 over the three best catalysts in different feed compositions: solid symbols 5000 ppm N_2O , 0 vol.% O_2 , He = balance; open symbols 5000 ppm N_2O , 5 vol.% O_2 , He = balance.

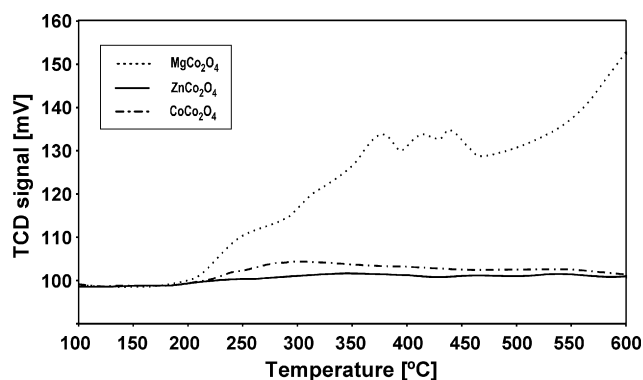


Fig. 3. Results of oxygen temperature-programmed desorption (TPD) tests on the three best catalysts.

of a vacant site ($[\]-M$) and adsorbed surface oxygen ($O-M$), desorption of this surface oxygen by combination with another oxygen atom as O_2 to gas phase (2) or by direct reaction with another N_2O molecule (3). Steps (1) and (3) may be irreversible, while (2) is reversible.



If the BET area values reported in Table 1 are now considered, it is worth underlining that spinels with quite high values of specific surface area can be obtained. The value related to $MgCo_2O_4$ is higher than those of the other two cobaltites, which helps to explain its superior activity compared to $ZnCo_2O_4$ and $CoCo_2O_4$. Taking into consideration the mechanistic aspects above reported, the main reasons for this superior activity may thus lie either in the presence of surface vacancies if the step (1) is considered or in a significantly higher specific surface concentration of active oxygen species compared to the other ones if the step (3) is considered. As declared earlier, temperature programmed desorption (TPD) of oxygen was carried out to better clarify these points. In particular, Fig. 3 shows the results obtained during oxygen TPD runs that were quite helpful in elucidating the behavior of

catalysts towards nitrous oxide decomposition. As thoroughly discussed in a previous paper of ours [13], perovskites can desorb two different types of oxygen species by increasing the temperature: a low temperature species, named α or *suprafacial*, desorbed in the 300–600 °C range, and a high-temperature one, named β or *intrafacial*, desorbed above about 600 °C. As far as *suprafacial* oxygen is concerned, the same behavior was observed for spinels. If attention is focused on the temperature range below 600 °C (inside the α oxygen region), where the most active spinels tested displayed their best nitrous oxide decomposition activities (see the conversion curves in Fig. 2), Fig. 3 shows oxygen desorption capability in this temperature range of the three most active spinels ($MgCo_2O_4$, $ZnCo_2O_4$, $CoCo_2O_4$). The amount of oxygen desorbed is negligible for the $ZnCo_2O_4$ (O_2 desorbed = 3.5 $\mu\text{mol/g}$), a little bit higher for $CoCo_2O_4$ (O_2 desorbed = 11.1 $\mu\text{mol/g}$) and increases dramatically considering the $MgCo_2O_4$ (O_2 desorbed = 60.9 $\mu\text{mol/g}$) catalyst. This trend is in good, even if just qualitative, agreement with the N_2O decomposition activity. The higher the oxygen desorption capability, the higher the N_2O decomposition activity. The effect is though far from being linear. The reason of this different behavior should lie in the different A sites, and particularly in the different ionic radius of the three atoms ($Mg^{++} = 0.57$, $Co^{++} = 0.58$ and $Zn^{++} = 0.60$ Å) and in a consequent increased distortion of the spinel structure. The amount of released α oxygen (and the corresponding temperature range), i.e. the capability to form surface vacancies, seems to be the governing parameter for the catalytic activity. This is also in agreement with the step (1) of the reaction mechanisms above reported. Moreover the partial inhibition by gaseous oxygen indicates that the active sites for nitrous oxide decomposition and oxygen adsorption/desorption sites should be basically the same. The presence of oxygen inhibits the reverse reaction of the step (2) giving a larger amount of adsorbed surface oxygen ($M-O$). This also indicates that reaction (1) is more likely to be the governing one, since reaction (3) should even be boosted by the presence of oxygen. Finally, the effect of different gas space velocities on the catalytic performance of $MgCo_2O_4$ was assessed. The results in Fig. 4 show that the conversion curve shifted to lower temperature at lower space velocity. The T_{50} values are 440 °C,

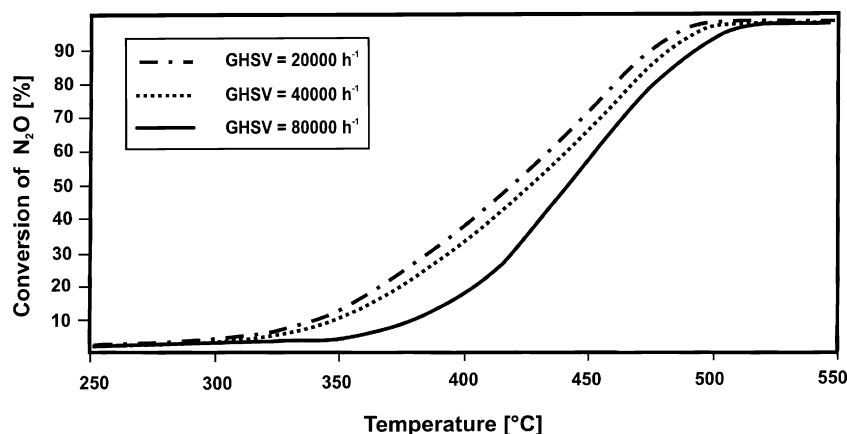


Fig. 4. Gas space velocity effect on the catalytic performance of the $MgCo_2O_4$ catalyst (5000 ppm N_2O ; 0 vol.% O_2 , He = balance).

426 °C and 418 °C at the space velocity of 80,000 h⁻¹, 40,000 h⁻¹ and 20,000 h⁻¹, respectively.

4. Conclusions

Several spinel-type oxide catalysts have been developed for the catalytic decomposition of N₂O to N₂ and O₂ in the absence and in the presence of oxygen. The innovative *solution combustion synthesis* technique was adopted successfully because it was possible to produce in an easy and low-cost “one shot” way catalysts with a rather high surface area and pureness. The same technique could be used to deposit the catalyst on ceramic carriers with a very high surface area. The present results demonstrated that the catalytic activity of the prepared spinel oxides essentially depends mostly on the B site metal. In our studies, the catalysts hosting cobalt at the B site presented the best behavior in the decomposition of N₂O. Particularly, MgCo₂O₄ showed the best performance, also taking into account the inhibitory effect of oxygen; the conversion of N₂O reached 50% at 440 °C and 470 °C in the absence and presence of oxygen, respectively. The MgCo₂O₄ spinel-type oxide exhibited the highest activity as a consequence of its greater capability to form surface vacancies, which was pointed out as the key player in the nitrous oxide catalytic decomposition.

Studies are now in progress to better elucidate the role of A and B sites on the catalytic activity achieved, to optimise the

catalyst preparation routes for the sake of maximising the surface area of the catalysts as well as to evaluate the inhibitory effect of water (steam) and CO₂ (that are generally present in real conditions) and the catalyst stability. Further improvements of the catalytic activity are expected to be attained by these means. Moreover a detailed kinetic analysis of all the catalysts prepared will be carried out to better clarify the structure–activity relationship of this type of catalysts.

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