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Catalysis Today 33 (1997) 239–249

CATALYSIS TODAY

Transition metal mixed oxides as combustion catalysts: preparation, characterization and activity mechanisms

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Abstract

A number of transition metal mixed oxides with spinel-type, corundum-type and perovskite-type structures have been prepared and characterized. Attempts have been made to improve their morphological properties and their stability. Some of them have been tested in the catalytic combustion of methane, CO and H_2 (perovskites), of propane and of phenantrene. FT-IR experiments allowed to obtain a quite complete picture of the mechanism of catalytic combustion of C3 organic compounds on spinel-type oxides $MgCr_2O_4$ and Co_3O_4. Nucleophilic oxygen species (lattice oxygen) is thought to be involved in both partial and total oxidation.

Keywords: Transition metal mixed oxides; Combustion catalysts; Preparation; Characterization; Activity mechanisms

1. Introduction

Transition metal oxides represent a prominent class of partial oxidation catalysts [1,2]. However, materials belonging to this class are also active in catalytic total oxidation processes aimed at the limiting of air pollution, which often is carried out on the more expensive noble metal-based catalysts [3]. On the other hand, total oxidation limits selectivity in partial oxidation processes. Thus, investigations on the mechanism of catalytic combustion on transition metal oxides can be useful not only to obtain criteria in order to increase selectivity in partial oxidation but also to develop new lower cost materials for catalytic combustion.

Materials for high-temperature combustion of hydrocarbons like methane and natural gas need exceptionally high chemical and morphological stability at temperatures of the order on 1500°C [4]. Less stringent requirements are needed for VOC abatement technologies operating at lower temperatures [5]. In either case, catalytic materials should be refractory to sintering and surface area loss as well as to volatilization of the active phase.

Previous studies report that the spinel Co_3O_4 is the most active in catalytic combustion among binary oxides [6,7]. However, Co_3O_4 is not stable at high temperatures [8]. Other spinel-type materials like the chromites $CoCr_2O_4$, $CuCr_2O_4$, $ZnCr_2O_4$ and $MgCr_2O_4$ are also very active and rather stable [9,10], spinel-type aluminates like $CoAl_2O_4$ and $NiAl_2O_4$ have also been considered [4,8]. On the other hand, also the pure sesquioxides with the corundum-type structure, α-Cr_2O_3 and α-Fe_2O_3 are active in combustion catalysis [6,7]. However, in the recent research

PII S0920-5861(96)00112-5

perovskite-like materials of the type $LaMO_3$ are also reported as very promising [11–14], due to their high activity and stability at high temperatures.

In order to have more data on the activity of transition metal-based oxides in combustion catalysis we undertook a research program aimed at the systematic investigation of materials with different composition and crystal structure and at the understanding of the nature of the mechanisms involved in total oxidation. As a first step of this program, a number of mixed oxides with different well-characterized structures have been prepared by conventional and unconventional methods and their morphological stability has been investigated. In parallel, test procedures for the evaluation of the catalytic combustion activity of these materials in different conditions (methane and synthesis gas combustion, light gaseous hydrocarbon combustion, solid hydrocarbon combustion) have been set up. Thirdly, mechanistic studies on light alkane combustion have been undertaken on spinel-type mixed oxides. In the present paper we review some already published results and we also summarize some preliminary data on the different aspects of this work. The aim is giving an idea of the present progress extent of our research program.

2. Experimental

Transition-metal mixed oxides have been prepared by two main procedures: (i) classical coprecipitation/calcination procedures starting from metal nitrates and/or alkoxides; (ii) preparation based on the supercritical drying of gels prepared from organic metal complexes (alkoxides, acetylacetonates or acetates). Details on these preparation methods can be found in [15] and [16], respectively.

Gas-phase catalytic combustion experiments have been performed in flow reactors operating below the lower explosion limits using HC/air and /or $HC/O_2/He$ mixtures. The product analyses were done by gas chromatography. Catalytic combustion tests of solid hydrocarbons have also been performed in a DTA apparatus using phenantrene as the hydrocarbon. In this case, the activity in catalytic combustion was evaluated from the temperature at which the heat is evolved by combustion in a temperature program 10 K/min in air.

FT-IR spectra were recorded with a Nicolet Magna 750 instrument, using conventional IR cells connected with evacuation-gas manipulation apparatus. The powder was pressed into self-supporting disks, calcined in air at 773 K for 1 h and outgassed at 773 K for 20 min before adsorption experiments. Liquid adsorbates and phenantrene were from Carlo Erba (Milano, Italy) while gases were purchased from SIO (Milano, Italy).

3. Results and discussion

3.1. Catalysts preparation and structural and morphological characterization

As already said, a first part of this work concerns the set up of preparation procedures of different mixed metal oxides with well-defined structure and morphology. Materials belonging to three different structure types have been prepared and investigated so far. They are (i) spinel-type materials; (ii) corundum-type materials; (iii) perovskite type materials. The properties of spinel-type and corundum-type materials are summarized in Table 1. The properties of perovskite-like materials can be found in Table 2. Spinel-type and corundum-type metal oxides can be obtained with very high phase purity while perovskite-type mixed oxides often contain impurities like La-oxycarbonates. A main limit of these materials concerns their morphological stability. In fact, they tend to sinter at temperature as low as 700 to 800°C.

Mixing transition metal oxides with non transition metal oxides creates higher surface areas and stability. However, this also results in dilut-

Table 1
Surface areas and phase compositions of spinel-type and corundum-type catalytic combustion materials

Composition	Preparation	As prepared		First calcination			Second calcination		
		S (m^2/g)	XRD phase	T_{calc} (K)	S (m^2/g)	XRD phase	T_{calc} (K)	S (m^2/g)	XRD phase
$NiAl_2O_4$	coprecipitation		amorphous				1073	133	inverted spinel
$Ni_2Al_2O_5$	coprecipitation		hydroxycarbonate				1073	120	spinel + NiO
$CoAl_2O_4$	coprecipitation		hydroxycarbonate	673	105	normal spinel	1073	40	normal spinel
Co_3O_4	commercial	13	normal spinel						
$CoCr_2O_4$	coprecipitation		amorphous	673	59	normal spinel			
$Co_2Cr_2O_5$	coprecipitation		amorphous	673	101	normal spinel			
$MgCr_2O_4$	aerogel	250	amorphous	573	180	amorphous	973	53	normal spinel
Cr_2O_3	aerogel	85	amorphous	573	45	eskolaite α-Cr_2O_3			
$ZnFe_2O_4$	aerogel	62	partly inverted spinel	773	27	normal spinel	1073	4	normal spinel
$Mg_2Fe_2O_4$	aerogel	43	spinel + hydroxycarb.	773	83	spinel	1073	90	spinel
$MgFe_2O_4$	aerogel	117	inverted spinel	773	56	inverted spinel	1073	10	inverted spinel
$Mg_2Fe_{10}O_{17}$	aerogel	98	spinel	773	100	spinel + α-Fe_2O_3	1073		
Fe_2O_3	aerogel	22	hematite α-Fe_2O_3	573	21	hematite α-Fe_2O_3	973	10	hematite α-Fe_2O_3
Cr_2O_3	precipitation	18	amorphous	673	24	eskolaite α-Cr_2O_3	1173	11	eskolaite α-Cr_2O_3
$Fe_4Cr_2O_9$	coprecipitation	42	amorphous	673	18	α-$(Fe,Cr)_2O_3$ sol. sol.			
$FeCrO_3$	coprecipitation	101	am + oxyhydroxide	673	51	α-$FeCrO_3$			
$Fe_2Cr_4O_9$	coprecipitation	80	am + oxyhydroxide	673	90	α-$(Fe,Cr)_2O_3$ sol. sol.			
Fe_2O_3	precipitation	86	α-FeOOH	673	102	hematite α-Fe_2O_3	1073	10	hematite α-Fe_2O_3
Fe_2O_3	precipitation	119	amorphous	673	43	hematite α-Fe_2O_3	1173	8	hematite α-Fe_2O_3
$Fe_{18}Al_2O_{30}$	coprecipitation	303	amorphous	673	66	α-$(Fe,Al)_2O_3$ sol. sol.	1173	21	α-$(Fe,Al)_2O_3$ sol. sol.
$Fe_4Al_2O_9$	coprecipitation	239	amorphous	673	173	γ-$(Fe,Al)_2O_3$ + α	1173	32	α-Fe_2O_3 + α-Al_2O_3 [b]
$FeAlO_3$	coprecipitation	257	amorphous	673	191	γ-$FeAlO_3$	1173	39	α-Fe_2O_3 + α-Al_2O_3 [b]
$Fe_2Al_4O_9$	coprecipitation	233	amorphous	673	193	γ-$(Fe,Al)_2O_3$	1173	39	α-Fe_2O_3 + α-Al_2O_3 [b]
$FeAl_{19}O_{30}$	precipitation	250	mixed hydroxides	673	204	γ-$(Fe,Al)_2O_3$	1173	5	α-$(Al,Fe)_2O_3$ sol. sol.
$Cr_4Al_2O_9$	coprecipitation		cryst. hydroxycarbonate	673	195	α-$(Cr,Al)_2O_3$ + am	1173	45	α-Cr_2O_3 + α-Al_2O_3 [b]
$CrAlO_3$	coprecipitation		cryst. hydroxycarbonate	673	326	am + α-$(Cr,Al)_2O_3$	1173	63	α-Cr_2O_3 + α-Al_2O_3 [b]
$Cr_2Al_4O_9$	coprecipitation		cryst. hydroxycarbonate	673	345	amorphous	1173	78	α-Cr_2O_3 + α-Al_2O_3 [b]

[a] sol. sol. = solid solution.

[b] Mixture of two solid solutions.

ing the active species in non-active matrices, so that lower catalytic activities can result. However, this effect does not seem to be very important for perovskites like $La_xSr_{1-x}Mn_xZr_{1-x}O_{3+\delta}$, whose catalytic activity in methane combustion is similar to that of $LaMnO_3$ also for $x = 0.1$.

3.2. Catalytic activity tests

Transition metal mixed oxides can play a role in different types of catalytic combustion technologies. The combustion of solid hydrocarbons, like, e.g. phenantrene, is relevant with respect to technologies aimed at the purification of waste gases from soot and unburnt carbonaceous solid materials, like for example in the case of Diesel engines exhaust gases. DTA tests in catalytic combustion of solid phenantrene were performed using some Fe- and Cr-containing materials (Table 3). They show that Cr_2O_3 is more active that Fe_2O_3 or their solid solutions, and that mixing Fe_2O_3 with MgO (giving rise to Mg-ferrite spinels) or with alumina (giving rise to biphasic materials) decreases the catalytic activity, so shifting markedly to higher temperatures the combustion of phenantrene.

The high-temperature combustion of methane, natural gas and syngas are of relevance with respect to the development of new technologies aimed at the production of energy with low NO_x emission. The catalysts of the perovskite type structure were found to be very active in the catalytic combustion of methane, according to literature data [11–17]. Moreover, they were found to be active in the oxidation of CO, hydrogen and their mixtures [17]. The temperature at which the methane conversion rises 50% with 1% CH_4 in air is 545°C for $LaCoO_3$ and $LaFeO_3$, while it is slightly higher (580°C) for $LaMnO_3$.

Table 3
Temperature at which the maximum heat evolution by phenantrene combustion is found in DTA experiments

Composition	Preparation	T (°C)
$Mg_2Fe_2O_5$	aerogel	410
$MgFe_2O_4$	aerogel	390
γ-Fe_2O_3	commercial	370
α-Fe_2O_3	aerogel	355
α-Fe_2O_3	precipitated	355
$Fe_4Cr_2O_9$	coprecipitated	340
$FeCrO_3$	coprecipitated	330
$Fe_2Cr_4O_9$	coprecipitated	325
α-Cr_2O_3	precipitated	320

Attempts to improve morphological stability of these materials have been done by preparing solid solutions of these perovskites with ceramic materials having the same structure but being apparently more resistant to sintering. In effect ceramic materials like $SrTiO_3$ and $SrTi_{1-x}Zr_xO_3$ solid solutions can be prepared with surface areas exceeding 100 m^2/g and retain areas higher than 20 m^2/g after calcination at 800°C.

Table 2
Surface areas and phase compositions of perovskite-type catalytic combustion materials

Composition	Preparation	As prepared	First calcination			Second calcination		
		XRD phase	T_c (K)	S (m^2/g)	XRD phase	T_c (K)	S (m^2/g)	XRD phase [a]
$LaCoO_3$	coprecipitation	amorphous	773		amorphous	973	8	HP (La_2CO_5)
$LaMnO_3$	coprecipitation	amorphous	773		amorphous	973	7	HP
$LaFeO_3$	coprecipitation	amorphous	773		amorphous	973	10	OP (La_2O_3)
$LaFeO_3$	coprecipitation II	amorphous	773	18	OP + La_2O_3 + γ-Fe_2O_3	973	12	OP (La_2O_3)
$LaFeO_3$	aerogel	amorphous	773	44	OP	973	19	OP
$LaCrO_3$	coprecipitation	amorphous	773		amorphous	973	4	OP + La_2CrO_6
$LaCrO_3$	aerogel	amorphous	773	12	amorphous	973	6	OP + La_2CrO_6
$La_{0.25}Sr_{0.75}Mn_{0.25}Zr_{0.25}O_3$	coprecipitation	amorphous	973	7	OP + La_2CO_5	1473	2	OP

[a] OP = orthorhombic perovskite (S.G. Pnma); HP = hexagonal perovskite (S.G. R$\bar{3}$c).

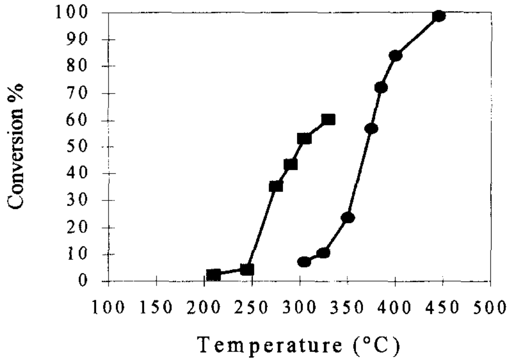


Fig. 1. Conversion of propane in oxygen (O_2:HC = 5:1) on Co_3O_4 (■) and on $MgCr_2O_4$ (●).

These materials can dissolve $LaMnO_3$ in amounts of the order of 20% mol/mol and their area stability after calcination is better than for the pure lanthanum metallates. The catalytic activity is not significantly decreased by diluting the active metallate in the inactive matrix.

The catalytic combustion of C3 hydrocarbons and oxygenates have been investigated as test reactions for a better understanding of the mechanisms involved in the catalytic destruction of volatile organic compounds (VOC abatement). We undertook this work by studying p-type semiconductor spinels, like $MgCr_2O_4$ and Co_3O_4. In Fig. 1 the light-off curves of propane measured over these catalysts are compared. Conversion of propane is definitely higher over Co_3O_4 than over $MgCr_2O_4$ at least at low temperature. In the conditions used here (propane:oxygen:helium ratio 2:10:88 vol/vol, flow rate 500 cc/min; catalyst weight 0.25 g for Co_3O_4, 0.1 g for $MgCr_2O_4$) 50% propane conversion is obtained near 365°C on $MgCr_2O_4$ and near 290°C on Co_3O_4. The different catalyst weights used in the two experiments have been chosen in order to have comparable catalyst surface in contact with the gas phase. In fact, the surface area of $MgCr_2O_4$ (53 m^2/g is more than 2.5 times that of Co_3O_4 (15 m^2/g). So, it is evident that Co oxide is definitely more active than $MgCr_2O_4$ in oxidizing propane at least at low temperatures. In both cases, oxidation is essentially total, CO_x being the main products and traces of oxygenates being only observed at very low conversions over $MgCr_2O_4$.

Fig. 1 shows that the catalytic activities of these spinel-type mixed oxides in propane combustion are comparable or even higher than those of perovskite-type compounds involving the same transition metals like, e.g. $LaCoO_3$ [11] and $LaCrO_3$.

To have indication on the mechanisms of catalytic combustion we also studied the oxidation of other C3 compounds over these catalysts. The curves relative to the oxidation of isopropanol and acetone over both catalysts are compared in Fig. 2. Again Co_3O_4 is more active than $MgCr_2O_4$ in converting both isopropanol and acetone. The corresponding curves are shifted to lower frequencies of nearly 50°C passing from Mg-chromite to cobalt oxide. In Fig. 2 the selectivities to acetone upon isopropanol oxidation are also reported. It is evident that both materials, in spite of being essen-

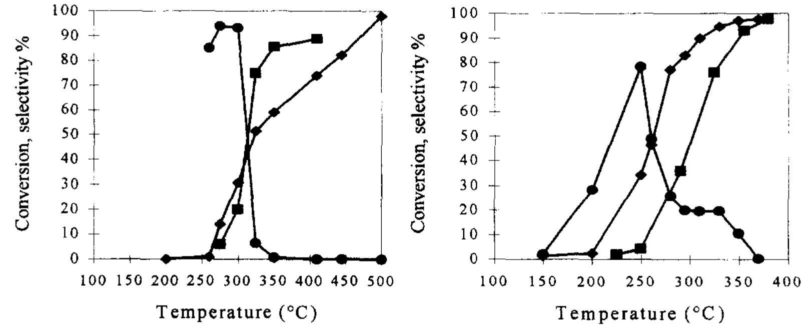


Fig. 2. Isopropanol conversion (♦), acetone selectivity upon isopropanol oxidation (●) and acetone conversion (■) over $MgCr_2O_4$ (left) and Co_3O_4 (right).

tially non-selective total oxidation catalysts, show high selectivities in converting isopropanol to acetone with maximum yields of the order of 30%. Selectivity to acetone from propanol falls down in both cases at the temperatures where conversion in acetone oxidation to CO_x starts. So, it is evident that acetone is an intermediate in isopropanol total oxidation, in both cases.

In the temperature range 200–300°C in contact with the same oxygen partial pressure, the oxidation of propane on Co_3O_4 is almost totally unselective while the conversion of isopropanol is rather highly selective to acetone. The same occurs for the $MgCr_2O_4$ in the range 250–380°C. Although the reaction temperature can be locally altered by the heat evolved during the oxidation reaction, it seems likely that the splitting 'selective versus unselective' oxidation is essentially associated to the nature of the reactant substrate more than to the nature of the active oxygen species [2].

3.3. Mechanistic studies

In order to define the mechanism of catalytic combustion of Volatile Organic Compounds over spinel type transition metal oxides catalysts, we approached the problem using FT-IR spectroscopy. In Fig. 3 the spectra of the adsorbed species arising from the contact of acetone gas with Co_3O_{4+x} (oxidized Co_3O_4) and further heat treatment are reported. Molecularly adsorbed acetone is characterized by the $\nu C=O$ band at 1715 cm^{-1} and by the νCCC band at 1230 cm^{-1}. Upon heating under outgassing these bands progressively decrease, first due to acetone desorption (25–100°C) but later, new bands appear due to adsorbed decomposition products arising from acetone oxidation. These

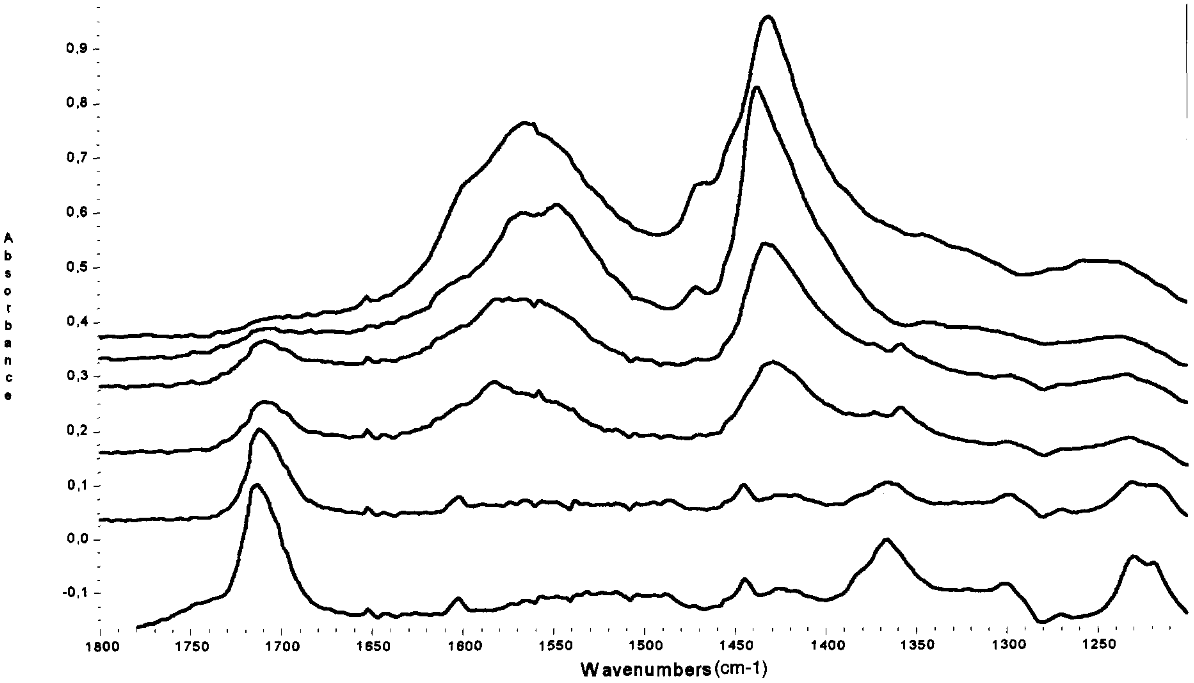


Fig. 3. FT-IR spectra of the adsorbed species arising from acetone interaction with Co_3O_{4+x} and further treatment at (from bottom to top) 300 K, 373 K, 423 K, 473 K, 523 K, 573 K.

bands are in the region 1600–1530 cm^{-1}(ν_{as} COO^-), at 1430 cm^{-1} (ν_{sym} COO^-) and at 1355 cm^{-1} (weak, δCH_3) and are typical of acetate species. The bands of acetone have completely disappeared only at 300°C while those of acetates disappear completely just above this temperature.

The spectra in Fig. 3 can be discussed in parallel with the conversion curve relative to acetone oxidation, in Fig. 2. Acetone is adsorbed as such over the catalyst surface without any trace of transformation, up to near 150°C, i.e. when conversion of acetone starts. The bands of adsorbed acetone decrease progressively in the range 150–300°C, because in these conditions oxidation rate increases rapidly. In the range 150–300°C the bands of acetate species, that are surface intermediates in acetone oxidation, are detectable strong while, above 300°C, when conversion of acetone approaches to be complete, they cannot be observed more.

Analogous experiments show that 2-propanol adsorption at r.t. on Co_3O_{4+x} gives rise to alcoholates, mainly characterized by the νC–O/νC–C bands at 1163 and 1130 and 1090 cm^{-1} (Fig. 4). These species have already almost disappeared at 100°C when adsorbed acetone is observed, mainly characterized by the $\nu C=O$ band at 1710 cm^{-1}. At 150°C the bands of acetate species are already predominant although acetone can be found up to 250°C, when it starts to leave the surface, and high selectivities are found. The bands of acetates, that are intermediates in acetone oxidation, grow in the range 150–300°C, when acetone oxidation becomes fast, and later disappear when only CO_x are produced.

Analogous FT-IR experiments of isopropanol and acetone adsorption have been performed on $MgCr_2O_{4+x}$ (i.e. preoxidized $MgCr_2O_4$) and have been reported previously [18]. With both systems a good agreement is obtained between

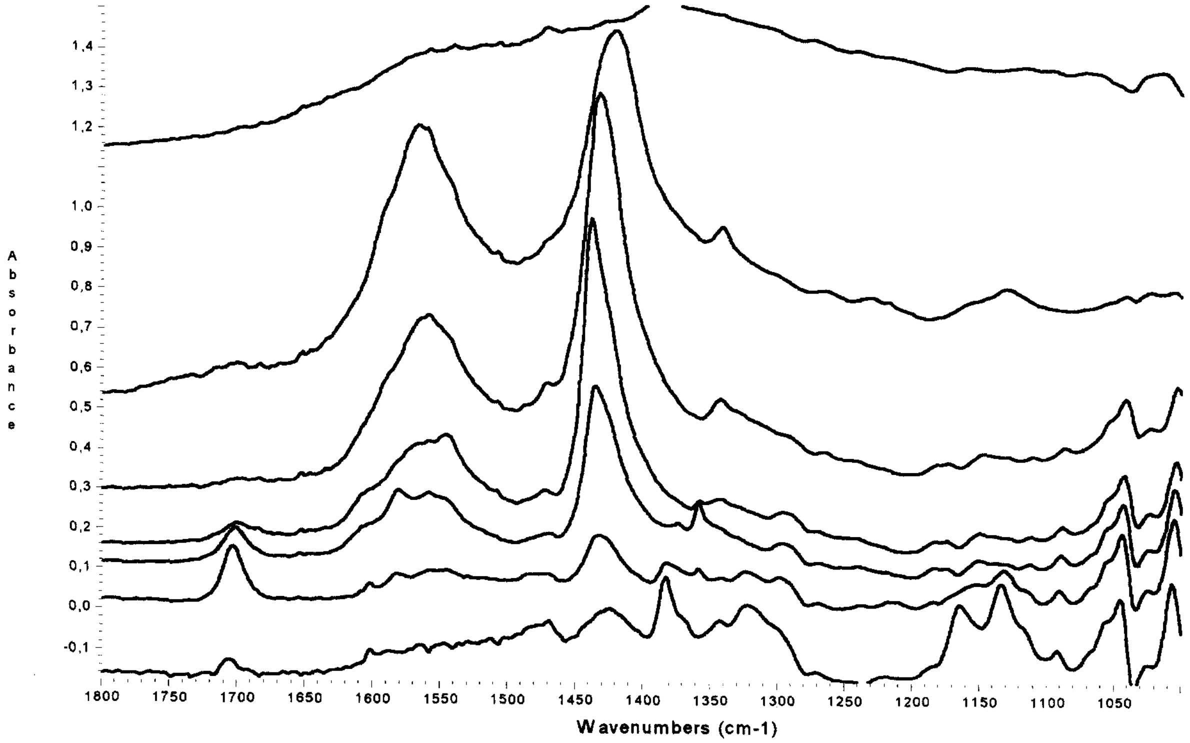


Fig. 4. FT-IR spectra of the adsorbed species arising from 2-propanol interaction with Co_3O_{4+x} and further treatment at (from bottom to top) 300 K, 373 K, 423 K, 473 K, 523 K, 573 K, and 623 K.

FT-IR and flow reactor catalytic experiments, performed using the same catalytic materials and in closely corresponding conditions. Over both surfaces it seems quite evident that the sequence adsorbed isopropoxides → adsorbed acetone → adsorbed acetates → gas-phase CO_x occurs upon isopropanol total and partial oxidation. As described in detail elsewhere [19,20], the oxidized surface of Co_3O_{4+x} is covered by trivalent Co ions and excess oxide ions. Electrons can easily be promoted from the O2p valence band to the Co3d conduction band, or to acceptor levels giving rise to the typical p-type semiconducting behavior of this solid. This results in the appearance of a broad absorption extended to the entire IR spectral range. This absorption disappears upon oxidation of organic molecules at the expense of excess oxygen. However, the oxidized organic species are always those expected to be formed by nucleophilic oxygen species, while oxidation products typically formed by electrophilic oxygen species are not found at all. For this reason, we believe that the active oxygen species are, in the case of both partial and total oxidation, nucleophilic lattice oxygen species. This is just the same conclusion we reached previously concerning the oxidation and combustion of several hydrocarbons and oxygenates on $MgCr_2O_{4+x}$ [18,21], where the active oxygen species are oxide ions bonded to hexavalent (or pentavalent) chromium (chromates). The complex of these data seem to allow a quite complete picture on the mechanism of catalytic combustion of oxygenate organic compounds on transition metal oxides (Scheme 1).

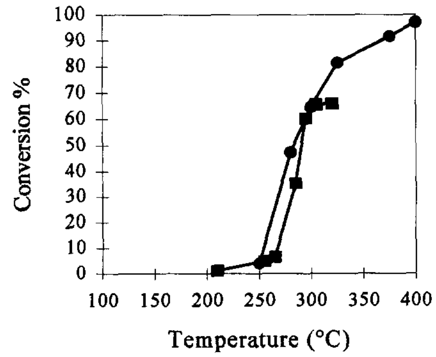
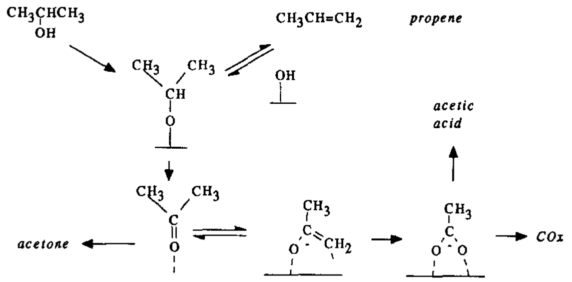


Fig. 5. Conversion of propene in oxygen (O_2:HC = 5:1) on Co_3O_4 (■) and on $MgCr_2O_4$ (●).



Scheme 1. Mechanism of isopropanol partial and total oxidation over $MgCr_2O_4$ and Co_3O_4.

The above pictured mechanism is also relevant in relation to the combustion of propane, at least over the $MgCr_2O_4$ catalyst. In fact, acetone is produced also by propane activation over this catalyst, as shown in Fig. 6, so that it is a common intermediate in the combustion of propane and isopropanol. On the other hand, the oxidation of more reactive hydrocarbons, like propene and isobutane, allowed us to conclude that on $MgCr_2O_4$ C–H activation occurs through the formation of alcoxides. So, we believe that iso-epoxides are actually the earliest intermediates in the oxidation of propane, although they cannot be detected because they form in a temperature range where they are very fast further oxidized to acetone.

The oxidation of propane over Co_3O_4 is a more complex story. FT-IR experiments (Fig. 6) show the formation of multiple absorption, certainly due to several different species. In the spectrum, the bands of acrylate species are certainly present. However, other bands, likely due to both acetates and propionates, are also evident. This indicates that propane is activated both at C2 and at C1 over Co_3O_4 [20]. The comparison of the curves relative to propane (Fig. 1) and acetone (Fig. 2) combustion on Co_3O_4, shows that at low temperatures (below 300°C) they are almost coincident. At higher temperatures, acetone conversion is by far higher

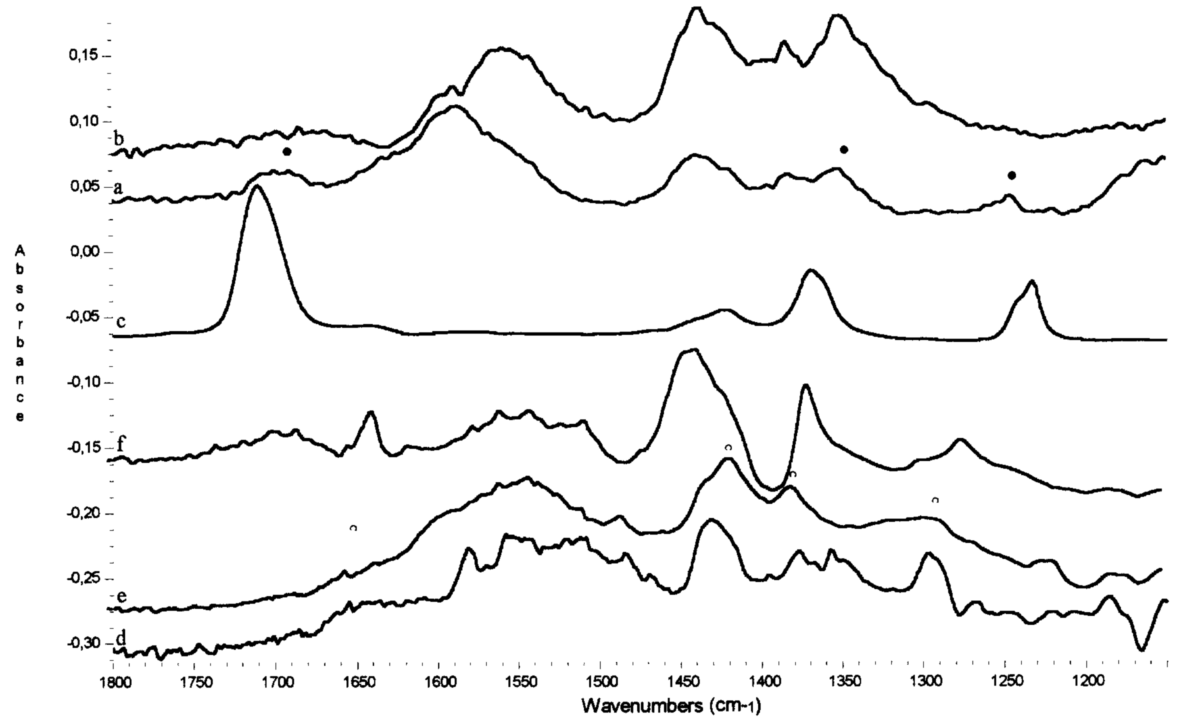
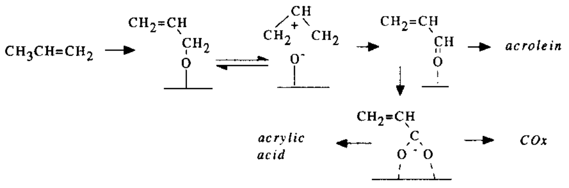


Fig. 6. FT-IR spectra of the adsorbed species arising from propane oxidation over $MgCr_2O_4$ at 423 K (a), 523 K (b) and spectrum of acetone adsorbed at room temperature (c), (●) bands due to adsorbed acetone; FT-IR spectra of the adsorbed species arising from propane oxidation over Co_3O_4 at 373 K (d), 473 K (e) and spectrum of the acrylate species arising from acrylic acid adsorption over Co_3O_4 at room temperature (f), (o) bands due to adsorbed acrylate species.

than propane conversion. It is possible to suppose that at lower temperatures the rate determining step in both cases is the combustion of the last common intermediate, the acetate species, while at higher temperature the rate determining step is, in the case of propane oxidation, the first C–H bond breaking. In fact, acetates over Co_3O_4 become unstable just above 300°C (see Fig. 4).

FT-IR studies show that on both Co_3O_4 and $MgCr_2O_4$ propene is activated almost exclusively at the allylic position and burns via allyloxy species → acrolein → acrylates [19,20]. The two catalysts appear to not differ significantly with respect to their catalytic activity in the oxidation of propene (Fig. 5), although traces of acrolein as a product are only found over $MgCr_2O_4$. In fact, Co_3O_4 seems to be not more active than $MgCr_2O_4$ in the oxidation of propene and acrolein, in contrast to what appears for propane and isopropanol. The curves relative to the conversion of propene and acrolein are almost coincident on both catalysts. Only at higher temperatures the conversion of acrolein is definitely higher than that of propene. This supports the hypothesis that, at low temperatures, the rate



Scheme 2. Mechanism of propene oxidation over $MgCr_2O_4$ and Co_3O_4.

is determined by the combustion of the common intermediate acrylate species.

The difference between $MgCr_2O_4$ and Co_3O_4, where the latter is definitely more active than the former in the oxidation of propane but not in that of propene (at low temperatures) parallels the behavior of acetate and acrylate species over them. In fact acetates, intermediates in propane catalytic combustion, are definitely more stable on $MgCr_2O_4$ (where they burn above 400°C) than on Co_3O_4, where they burn already below 300°C. On the contrary, acrylate species appear to be as stable on Co_3O_4 as on $MgCr_2O_4$: over both surfaces they burn just below 300°C (Scheme 2).

These data and their interpretation appear to strongly support the idea that combustion of hydrocarbons occurs through the overoxidation of oxygenated adsorbed species produced by partial oxidation.

4. Conclusions

This paper summarizes some partial results of research programs, performed mainly in the frame of Ph.D. theses still under development. At this stage the following preliminary conclusions can be drawn.

1. Conventional coprecipitation and supercritical drying techniques allow the successful preparation of transition metal mixed oxides with the spinel, corundum and perovskite-type structures.
2. These materials are active in the catalytic combustion of hydrocarbons and oxygenated organic compounds.
3. The morphological stabilities of these materials appear to be hardly sufficient for catalytic combustion at high temperature, but could allow low-temperature processes like VOC abatement technologies.
4. The catalytic combustion of light hydrocarbons and of oxygenated organic compounds seems to occur through the successive overoxidation of adsorbed partial oxidation products.
5. The oxidation of propene occurs over both Co_3O_4 and $MgCr_2O_4$ catalysts through the allylic oxidation way, via allyloxy-species, acrolein and adsorbed acrylates.
6. The oxidation of propane over $MgCr_2O_4$ involves intermediates activated at C2 (acetates, acetone and, very probably, 2-propoxy-groups), while on Co_3O_4 activation at C1 (via propanoates) and the allylic oxidation way via propene seem also to occur.
7. Catalytic combustion likely occurs at the expense of high-valency cations and nucleophilic oxide ions, as for partial oxidation.
8. It can be hypothesized that the rate of oxidation of the carboxylate intermediates (acetates for propane and acrylates for propene) can influence the reaction rate at low temperature.

Acknowledgements

The authors acknowledge NATO and MURST (Rome) for partial support for this research.

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