

ELECTRICAL AND CATALYTIC PROPERTIES OF SOME OXIDES WITH THE
FLUORITE OR PYROCHLORE STRUCTURE

PART 2 : CATALYTIC OXIDATION OF CARBON MONOXIDE

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ABSTRACT

The catalytic properties of mixed oxides with the fluorite or pyrochlore structure were investigated using CO oxidation. The presence of ions with a variable valence state, the size of the ions and especially the extent of pyrochlore ordering affect kinetic behaviour and activity of the investigated materials.

1 INTRODUCTION

The intended application of pyrochlore oxides as an electrocatalytically active electrode material requires a detailed description of the parameters, influencing electrical and catalytic properties. The structure and electrical properties of lanthanide titanates and neodymium zirconates with various levels of dopant ions (Bi^{3+} and Ce^{4+} , respectively) have been reported in part 1, together with arguments leading to this investigation.

A study on the activity and kinetics in an oxidation reaction is reported in this paper with the aim to collect information on the transfer of charge and of oxygen species to and from the surface. That knowledge can be used then to study the effect of electrical fields on redox reactions and to select more suitable materials.

Oxidation of carbon monoxide was chosen as a relatively uncomplicated test reaction. Other investigations on CO oxidation, using lanthanide oxides and fluorite oxides [1,2,3] indicated or demonstrated the use of lattice oxygen in the reaction. With temperature programmed reduction it is possible to acquire information on the extraction of oxygen from the crystal lattice [4]. Therefore the reducibility has been tested by TPR measurements as an additional means of characterization.

2 EXPERIMENTAL

2.1 Catalyst preparation

Calcined powders of titanates and zirconates were obtained as described in part 1. Zirconate powders were subjected to heat treatments in order to achieve an increase in the degree of pyrochlore ordering, as defined in part 1. Heat treatments were: 4 hours at 1050 °C, 5 hours at 1350 °C and 5 hours at 1500 °C.

All powders were pressed isostatically at 400 MPa, and after grinding the 0.3-0.6 mm. size fraction was used in the catalytic experiments. The BET surface areas of the powders, determined by Ar adsorption, do not vary strongly.

2.2 CO oxidation

Catalytic experiments were performed in a continuous flow microreactor with a fixed bed, consisting of a mixture of either 0.3 or 0.6 g of catalyst with an equal amount of quartz grains of the same mesh, thus avoiding possible hot spots.

Gas flow amounted 1 ml.sec⁻¹ (0.15 MPa, 20 °C), consisting of a mixture of 1-10% CO, 1-10% O₂, and either He or N₂ as inert carrier gas. The conversion was determined by gas chromatography, or by titration of the CO₂ formed.

For the zirconate materials the measurements were performed both at low (4%) and high conversion (40%), and the kinetic parameters were found to agree within experimental error. Titanates were measured only up to 20-30% conversion, due to the low catalytic activity of these materials. At high temperatures a correction for the conversion in the empty reactor was applied.

2.3 Temperature programmed reduction

The experiments have been performed in an apparatus described elsewhere [4]. In every experiment 300 mg of fresh catalyst was used and a continuous flow of 9% H₂ in Ar was passed over. Temperature was then increased linear in time up to 900 °C.

Further experimental conditions were: 10 ml.min⁻¹ of H₂/Ar mixture and heating rate 16° C.min⁻¹.

3 RESULTS

3.1 CO oxidation

The catalytic behaviour has been characterized using the kinetic equation:

$$r = k_0 \exp(-E_A/RT) [\text{CO}]^n [\text{O}_2]^m \dots\dots\dots (1)$$

r - specific reaction rate (moles.sec⁻¹.m⁻²). k_0 - pre-exponential constant, E_A - activation energy (kJ.mole⁻¹), n and m - reaction order in CO and O₂, respectively.

Since reaction orders vary appreciably from one material to another, it is not possible to characterize the catalysts by k_0 and E_A , as is usually done. Therefore the specific reaction rates are compared at a chosen temperature, pressure and gas composition. For this purpose the following reactor entry conditions have been chosen: 450 °C, 0.15 MPa, and 2.5% CO, 6% O₂ (NTP).

3.1.1 Titanates

Table 1 records the catalytic parameters of equation (1) for the pyrochlore titanates. The specific reaction rates show, that Tb₂Ti₂O₇ performs best of the undoped lanthanide titanates, while Eu₂Ti₂O₇ is rather inactive. Considering, that Tb³⁺ fairly easily becomes 4+, while Eu³⁺ transforms readily into Eu²⁺ [5], the preliminary conclusion may be drawn, that catalytic activity is related either to type of electronic conductivity or to the presence of cations, which can adopt a higher valence state in the surface layer of the catalyst.

Table 1 Catalytic data of pyrochlore titanates in CO oxidation

COMPOSITION	S_{BET} ($m^2 \cdot g^{-1}$)	n	m	$\ln k_o$	E_A ($kJ \cdot mole^{-1}$)	r_{450} ($mole \cdot s^{-1} \cdot m^{-2}$)
$Y_2Ti_2O_7$	5.5	0.95	0.15	2.1	77	$7.4 \cdot 10^{-9}$
$Eu_2Ti_2O_7$	4.7	0.85	0.00	5.1	90	97
$Tb_2Ti_2O_7$	6.7	0.45	0.10	5.8	86	3700
$Er_2Ti_2O_7$	4.6	0.85	0.20	4.7	88	26
$(Y_{0.8}Bi_{0.2})_2Ti_2O_7$	10.6	0.85	0.00	4.5	73	910
$(Y_{0.6}Bi_{0.4})_2Ti_2O_7$	8.8	0.85	0.05	6.0	74	2400
$(Tb_{0.6}Bi_{0.4})_2Ti_2O_7$	6.6	0.85	0.05	6.6	76	3100

Furthermore the presence of Bi^{3+} on the lanthanide sites dominates the catalytic behaviour completely, and strongly promotes the activity of inert materials. Particularly remarkable is the case of $Tb_2Ti_2O_7$; in this case the bismuth-doped material exhibits the same overall activity as the undoped material, but the kinetics of the reaction differ completely from the original kinetic behaviour, and now resembles closely that of the bismuth-doped $Y_2Ti_2O_7$.

3.1.2 Zirconates

The zirconate materials have been measured for varying Ce content and temperature treatments, resulting in a differing degree of pyrochlore ordering, as defined in part 1. As can be seen in table 2, this results in profound diffe-

Table 2 Catalytic data of zirconates $Nd_2(Zr_{1-x}Ce_x)_2O_7$ in CO oxidation.

TREATMENT	group	x	S_{BET} ($m^2 \cdot g^{-1}$)	% pyr	n	m	$\ln k_o$	E_A ($kJ \cdot mole^{-1}$)	r_{450} ($mole \cdot s^{-1} \cdot m^{-2}$)
1050°C, 4 hr	A	0	14	< 10	0.4	0.3	7.4	86	$63 \cdot 10^{-9}$
	A	5	18	< 10	0.8	0.2	10.2	75	76
	A	10	20	< 10	0.6	0.3	8.7	75	84
	A	20	15	< 10	0.6	0.3	10.6	85	96
1350°C, 5 hr	B	0	7	68	-0.3	0.4	3.3	100	550
	B	5	10	66	-0.4	0.7	7.3	102	1600
	C	10	11	64	0.0	0.5	10.5	94	7300
	A	20	7	25	0.8	0.1	11.4	85	190
1500°C, 5 hr	B	0	4	90	-0.3	0.9	5.9	92	35
	B	5	1	85	-0.4	0.8	10.0	108	2300
	C	10	2	82	-0.1	0.5	6.6	93	350
	C	20	3	76	-0.1	0.5	8.5	95	1700

rences in catalytic behaviour and activity of the materials $\text{Nd}_2(\text{Zr}_{1-x}\text{Ce}_x)_2\text{O}_7$.

Because literature [1, 22, 23] suggest CO_2 to have an inhibiting effect, the reaction order in CO_2 was determined for the 5% Ce material, temperature treatments 1050 and 1500 °C. These materials showed the order -0.2 and -0.1 respectively.

By inspection of table 2, three groups, each with a characteristic kinetic behaviour can be distinguished.

- Group A, with low structural order. The percentage pyrochlore does not exceed 25%. Kinetic features are a high order in CO (0.4-0.8) and a low order in O_2 (0.1-0.3).

Two groups, B and C, with higher structural order:

- In group B, with 0 and 5% Ce substitution, a negative order in CO (-0.3 - -0.4) and a high reaction order in O_2 (0.4-0.9) is observed.

- Group C, having a Ce content of 10 and 20%, exhibits an order in CO of about zero (-0.1 - 0.0) and the reaction order in O_2 is 0.5.

A higher degree of ordering generally gives an increase in activity; however, increasing the ordering towards to fully ordered pyrochlore structure seems to extinguish partly the initially beneficial effect.

The effect of increasing Ce substitution on catalytic activity within a given group is positive.

3.2 Temperature programmed reduction

The titanates gave in TPR experiments no measurable reduction in the temperature region covered.

In fig. 1 the TPR profiles of calcined (1050 °C) and heat treated zirconates (1500 °C) are presented. Relevant parameters are the temperature of maximum re-

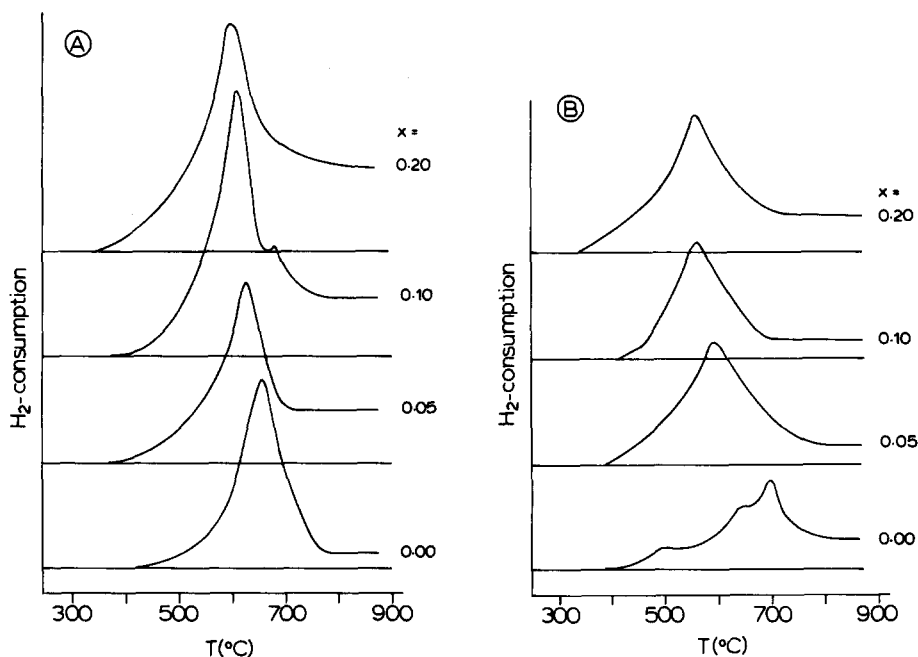


Fig. 1 TPR profiles of calcined (A) and heat treated (B) powders $\text{Nd}_2(\text{Zr}_{1-x}\text{Ce}_x)_2\text{O}_7$

duction rate T_R and the total amount of H_2 consumed, these parameters being a measure of ease of reduction and the amount of oxygen available from the catalyst, respectively. For unordered materials the amount of oxygen removed is approximately 1%, and for pyrochlores 0.5% of the total bulk oxygen content.

In all materials introduction of Ce progressively lowers T_R , and thus facilitates reduction. Also ordered zirconates are always more easily reduced, compared at the same Ce content. It is felt, however, that the degree of reduction of the catalyst at T_R is not very representative for our experimental conditions in CO oxidation, and so trends observed in T_R may not necessarily have general validity. A more realistic parameter would be the starting temperature of reduction

For the influence of Ce here the same trend is observed: Introduction of Ce lowers the starting temperature. No such influence of ordering is observed now - the starting temperatures stay approximately the same. However, the amount of oxygen removed, expressed as the fraction of oxygen in one surface plane (e.g. the stable [110] surface plane [23]) confirms qualitatively the trend in T_R . On unordered materials approximately 30% of the oxygen ions in the surface layer is removed after the TPR experiment, and on pyrochlore materials this fraction amounts to 150% of one surface layer.

Conclusions are now, that introduction of Ce lowers the starting temperature of surface reduction, and that the ordered lattice enables a much higher degree of surface reduction at the same reducing conditions. These conclusions are in agreement with the experimental results in CO oxidation: A positive influence of Ce substitution on activity in all materials, while the pyrochlores exhibited a completely different catalytic behaviour.

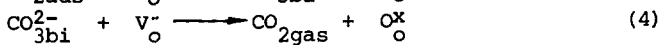
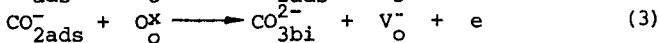
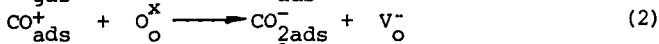
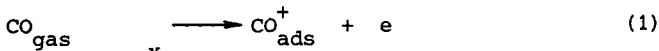
4 DISCUSSION

The behaviour of the investigated materials will be discussed, using a rather detailed mechanism, since the simple reduction-oxidation mechanism [7], which has been found suitable for CO oxidation on rare earth oxides and on fluorite oxides [1,2,6] can not explain satisfactorily the experimentally found kinetics. Especially the negative order in CO on some of the ordered materials conflicts with the assumption of independent adsorption sites for CO and O_2 in the simple model, and reveals the need of additional information on adsorption processes and surface intermediates of the reactants CO and O_2 .

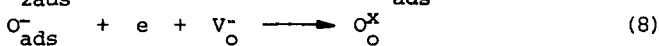
Several studies on the nature of adsorbed species, appearing after CO adsorption on various oxide materials have been published, using techniques such as IR spectroscopy, ESR and XPS. Many authors proposed or proved the existence of a positively charged CO^+ species on the surface of oxides such as MgO, ThO_2 and spinel ferrites at temperatures up to 250 °C [14-17]. Photocatalytic oxidation studies on ZnO indicate that the formation of this adsorbed entity must proceed via hole capture by the CO molecule [18], which could explain in our investigations the much higher activity of $Tb_2Ti_2O_7$, due to the presence of Tb^{4+} .

ESR and IR studies on ThO_2 [16,19,21] revealed the subsequent formation of a carboxylate CO_2^- species, in which lattice oxygen ions were incorporated. The same surface complex was reported for CO_2 adsorption on UO_2 [20]; the CO_2^- complex is stable up to 350 °C [19,20]. Further, on several oxides the formation of more or less stable mono- and bidentate carbonates is reported [15,21-23], where again lattice oxygen ions were proposed as the source of oxygen; the carboxylate CO_2^- may be an intermediate complex in the reaction [21]. The bidentate carbonate is less stable than the monodentate form [24], and decomposes first. Decomposition temperatures mentioned are 200-350 °C [21-23].

The decomposition temperatures for the various possible surface complexes (200-350 °C) are in the range in which all investigated materials started the oxidation. Using this information the reduction sequence may now be represented by:



The reoxidation must also be split up into more stages, and may be written as [2,25,26]:



Especially in step (1) the presence of holes, recombining with the electron, seems to be essential.

4.1 Titanates

The occurrence of both a reaction order in CO and O₂ for lanthanide titanates (table 1) implies reaction (2) or (3) to be rate controlling. In other words, the reduction step is slow, as n is high and m is low. This is in agreement with TPR results, where no reducibility could be observed.

As mentioned earlier, the distinct influence of the lanthanide ion is related either to p-type conductivity or to the presence of ions which can adopt a higher valence state. In the model we can associate this influence with CO adsorption on or near the lanthanide ion, since the CO molecule captures a hole, while adsorbing on the surface (step (1)). In table 4 this relation is illustrated somewhat more quantitatively: The reaction order in CO decreases as more lanthanide ions in the 4+ state can be present. The ionization potential E° for Y³⁺ has not been reported [5], but since Y³⁺ has a noble gas configuration, the value of E° will exceed those of the lanthanide ions.

COMPOSITION	n	m	E° (V)	r _{Ln³⁺} (Å)
Y ₂ Ti ₂ O ₇	0.95	0.15	-	1.019
Eu ₂ Ti ₂ O ₇	0.85	0.00	-6.4	1.066
Er ₂ Ti ₂ O ₇	0.85	0.20	-6.1	1.004
Tb ₂ Ti ₂ O ₇	0.45	0.10	-3.3	1.040

Table 4 Comparison of kinetic parameters n, m with E° for Ln³⁺ → Ln⁴⁺ + e [5] and ionic radius [8]

Further a relation between the reaction order in O₂ and the size of the lanthanide ion can be noticed: The smaller the ion, the higher m. This relation of m with a simple geometrical factor indicates an influence of the lattice structure on oxygen supply, as can be expected when lattice oxygen ions are used in the oxidation.

A smaller A ion in pyrochlores $A_2B_2O_6O'$ causes an increased distortion of the BO_6 octahedra, which leads to an increase in the oxygen position parameter X_{48f} , as defined by Knop [9]. Theoretical calculations, performed by Pannetier on pyrochlores $A_2B_2O_6O'$ [10], show that this increase in X_{48f} results in a less negative electrostatic energy of the B_2O_6 sublattice, while the energy of the A_2O' sublattice remains unaffected. Then the increasing order in O_2 at smaller Ln^{3+} ionic radius may be caused by an easier release of lattice oxygen ions, assuming that reoxidation is not grossly affected. This relation supports the proposed use of lattice oxygen ions for the oxidation of CO.

Some remarks on the influence of Bi^{3+} substitution can be made. The similarity in CO oxidation of doped $Y_2Ti_2O_7$ and $Tb_2Ti_2O_7$, in spite of the large differences in behaviour of the undoped materials, could be explained satisfactorily by a surface enrichment in Bi^{3+} beyond the bulk composition. Substantial enrichment of the surface with Bi in Bi-doped compounds has been shown previously in doped zirconia [11] and in doped scheelites [12]. The improvement of oxygen transfer, ascribed to Bi^{3+} ions [13], is reflected in the very low order in O_2 , indicating a fast reoxidation of the surface of Bi^{3+} -doped titanates.

4.2 Zirconates

The great differences in reactivity and kinetics between the three groups can be attributed mainly to the different degrees in ordering, showing the high sensitivity of the catalytic reaction to the crystal structure of the catalyst. This is probably related to the different geometrical arrangement of the adsorption sites, resulting from the ordering of cations, anion vacancies and the two non-equivalent oxygen ion species in the pyrochlore structure. According to the TPR measurements the ordered structure of the same chemical composition is easier reduced, which explains the higher activity and different kinetics of the groups B and C. There are indications however, that a full ordering is not necessary for optimum activity (see table 2); at this stage the reason for this apparent maximum in activity at intermediate degree of ordering is not clear, and is subject of further investigation.

In the low-ordered group A the reduction step (2) or (3) seems to be mainly rate controlling, judged by the high order in CO. Introducing Ce raises the activity, in accordance with TPR results.

The ordered group B (0-5% Ce) exhibits a completely different behaviour. The high order in O_2 , running towards unity in highly ordered materials indicates O_2 adsorption to be the slowest process, one of the steps (5)-(7) being mainly rate determining. Further, the negative order in CO implies, that the adsorption processes of CO and O_2 hinder each other. Apparently occupation of the CO adsorption site blocks the O_2 adsorption site, which means that they are identical or very close neighbours.

The behaviour of group C (10-20% Ce) can be interpreted as reoxidation step (8) controlling fully the rate of oxidation, since the value of m is 0.5, and stays so on increasing ordering.

The shift of the rate controlling process from reduction to reoxidation, going from group A to B and C is again in qualitative agreement with the TPR measurements, as ordered materials showed a deeper degree of reduction.

The mutual interference of CO and O_2 adsorption on the zirconate pyrochlore group B suggests adsorption of these gases on closely neighbouring, or even identical sites. For oxygen this site will be a surface anion vacancy, the normal and logical O_2 adsorption site [2,6,26,28]. Both vacancies and metal ions have been proposed as a CO adsorption site [14,21,22]; considering the immediate vicinity of metal and oxygen ion positions, steric hinderance of the O_2 adsorption process by the surface complex formed after CO adsorption can be rationalized. This implies, that the surface complex is relatively stable on group B zirconates, whereas it is less stable on group C zirconates. Since the groups B

and C differ in their Ce content (0-5% and 10-20% Ce substitution, respectively), this difference in stability may be related to the type of electronic conductivity: $\text{Nd}_2\text{Zr}_2\text{O}_7$ (group B) is a p-type electronic conductor [27], while $\text{Nd}_2(\text{Zr}_{0.8}\text{Ce}_{0.2})_2\text{O}_7$ (group C) probably has n-type electronic conductivity (see part I).

This explanation is supported by CO_2 adsorption experiments on n- and p-type UO_2 [20]. On p-type UO_2 the surface complex CO_2^- was formed, which was very stable; it could be removed only partially by outgassing at 350 °C. Further there was some evidence for (less stable) mono- or bidentate carbonates. On n-type however, no detectable surface complex was formed.

Thus it seems acceptable to expect the same to occur after CO adsorption on p- and n-type $\text{Nd}_2(\text{Zr}_{1-x}\text{Ce}_x)_2\text{O}_7$. Once formed on p-type material, the stable CO_2^- complex apparently blocks the surface anion vacancies for reoxidation, which is expressed in the negative order in CO and the order one in O_2 for group B pyrochlores. On group C pyrochlores then, any surface complex formed immediately decomposes, and does not interfere with the reoxidation. Possibly, on these materials the CO_2^- complex formed in reaction step (2) desorbs directly, injecting an electron and thus avoiding the carbonate route. Thus, in group C the highest specific oxidation rates are to be expected.

It would now, however, be premature to ascribe the good performance of group C solely to the type of electronic conductivity. If we remember, that adsorption of CO proceeds with hole capture by the CO molecule, and now it appears that direct desorption of CO_2 is accompanied by electron donation of the CO_2^- complex, the high activity of group C can very well be explained by the presence of two different redox couples: A couple such as $\text{Nd}^{3+}/\text{Nd}^{4+}$ with a rather high ionization potential, providing holes, and a couple such as $\text{Ce}^{3+}/\text{Ce}^{4+}$ with a low ionization potential as electron acceptor. Therefore further developments might be sought in pyrochlore oxides in which these kinds of redox couples are present.

5 CONCLUSIONS

It was established, that numerous factors determine the activity of mixed oxides with the pyrochlore composition $\text{A}_2\text{B}_2\text{O}_7$ in the oxidation of CO. The oxidation reaction proceeds with the use of lattice oxygen ions; reducibility of the catalyst, as measured by TPR, is therefore an important and useful parameter in the interpretation of the catalytic behaviour.

In lanthanide pyrochlores the choice of the B^{4+} ion mainly determines the distortion of the BO_6 octahedra, and thus the stability and reducibility of the crystal lattice; this is the cause of the difference in behaviour between the titanates and zirconates. Adsorption of CO involves hole capture, and therefore the choice of the A ion is also of crucial importance.

Another important parameter is the degree of ordering of the mixed oxide. Increasing the ordering leads to increased reducibility and activity; it appeared however, that complete ordering is not necessary for maximum activity. The reason for this is not clear, and will be further investigated.

On titanate pyrochlores the reduction of the surface was rate determining in CO oxidation. Insertion of Bi^{3+} on the A site strongly influences the catalytic behaviour, but with positive effects on activity only in an inert matrix.

Zirconate pyrochlores are generally more active in oxidation, compared with titanates. This is related to their higher reducibility, shifting the rate controlling process from reduction on the titanate pyrochlores to reoxidation on the zirconate pyrochlores. On zirconate pyrochlores with low Ce content the reoxidation of the surface is apparently hindered by a stable intermediate surface complex, whereas no influence of CO is observed on ordered materials with higher percentage Ce substitution. At the present stage we cannot yet descri-

minate unambiguously whether the change in behaviour above an apparent threshold of Ce substitution is due to a change in type of electronic conductivity or merely to the introduction of a new type of redox couple. It seems worthwhile to continue investigations on this point.

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