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The utilization of ceria in industrial catalysis

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Abstract

The main applications of cerium dioxide in industrial catalysis are reviewed, with particular attention to the role played by ceria. The main uses of CeO_2 are connected to depollution of noxious compounds from gaseous streams originating from industrial productions and from automobiles (de-SO_x in FCC processes; treatment of emissions from spark-ignited and diesel engines), although ceria is also a key component of catalyst formulation for the dehydrogenation of ethylbenzene to styrene. Recent advances in the application of ceria for the removal of organic compound from wastewater through oxidation (catalytic wet oxidation CWO) are also reviewed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: CeO_2; Ceria; Cerium dioxide; TWC; FCC; Catalytic wet oxidation; Combustion; Diesel; Ethylbenzene; Styrene; $DeSO_x$; $DeNO_x$

1. Introduction

Rare earth oxides have been widely investigated in catalysis as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts. The most significant of the oxides of rare earth elements in industrial catalysis is certainly CeO_2. Ceria has an important role in two of the most important commercial catalytic processes in terms of economic relevance and tonnage: three-way catalysis (TWC) and fluid catalytic cracking (FCC). The importance of CeO_2 in catalysis is also demonstrated by the number of industrial and academic publications which have appeared on the topic over the last few years, Fig. 1. This indicates that there are several emerging applications or processes for which cerium oxide is currently being actively investigated. Specifically, CeO_2 has potential uses for the removal of soot from diesel engine exhaust [1], for the removal of organics from wastewaters (catalytic wet oxidation) [2], as an additive for combustion catalysts and processes and [3], in fuel cell technology [4]. In addition to these applications, much effort has been dedicated recently to studying the role of ceria in well-established industrial processes such as FCC, TWCs and ethylbenzene dehydrogenation, where CeO_2 is a key component in catalyst formulation [5]. A detailed analysis of publications in the year 1997 reveals that about 50% of contributions deal with the use of ceria-based compounds in the treatment of emissions from mobile and stationary sources, and that the majority of articles deal with the application of ceria in TWCs and novel technologies for the treatment of emissions from diesel and spark-ignited internal combustion engines, Fig. 2. This also explains the increase in the number of patent applications between 1984 and 1992, when more stringent environmental legislation came into

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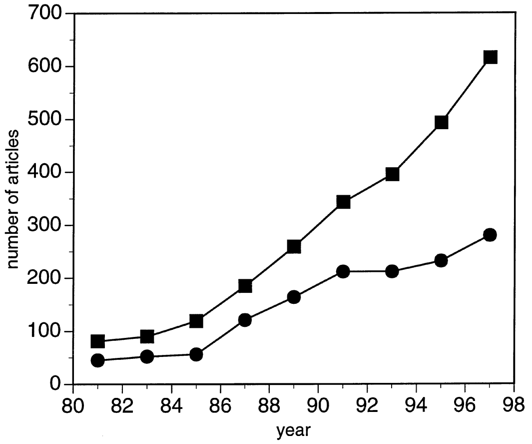


Fig. 1. Number of publications on CeO_2-based materials in catalysis: (■) open literature, (●) patents (Source: Chem. Abstr.).

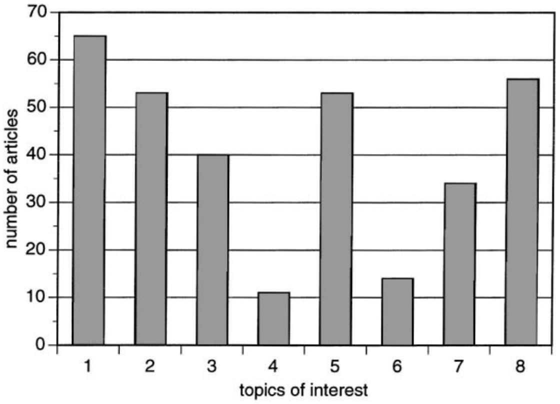


Fig. 2. Number of scientific articles (not patents) published in 1997 on ceria and related materials in different areas of catalysis: 1 (TWC), 2 (flue gas treatment), 3 (oxidation), 4 (treatment of diesel exhaust), 5 (catalyst characterization), 6 (electrocatalysis), 7 (hydrogenation), 8 (others), (Source: Chem. Abstr.).

force in all the industrialized countries. It was during this period that the CeO_2-based $MgAl_2O_4$ spinel catalyst for SO_x removal and novel CeO_2-based catalysts for auto-exhaust treatment were first developed [6–9]. In this paper, we shall review the main industrial processes as well as some potential applications which use CeO_2 as a key ingredient in catalyst formulations. Our description, which does not claim to be exhaustive, will focus mainly on the assessment of the role of ceria in these applications and the identification of some common points that link the various utilizations.

2. Treatment of gaseous emissions

As we have mentioned above, the main uses of ceria are in the depollution of noxious compounds from gaseous streams originating either from stationary or mobile sources. In these applications and related studies, CeO_2 is seldom used alone but it is often employed in combination with other oxides or in conjunction with active metals (generally noble metals) and thermally stable supports. Therefore, strictly speaking, ceria may function either as a structural/electronic promoter or as a co-catalyst, depending on the type of application, but not as a true catalyst, although the amount of cerium oxide which is used in certain catalyst formulations may easily exceed 20–30 wt%.

The main reason why CeO_2 alone is of comparatively little interest as a support or catalyst is its textural stability, which is not high enough to meet the requirements of several gas-phase catalytic applications such as FCC and TWCs. The surface area of CeO_2 generally drops to a few square meters per gram at around 1000–1100 K, depending on preparation procedure and type of treatment [10], although a high degree of textural stability can be obtained by doping and modifying the preparation procedure [11]. Another factor which discourages the use of pure ceria is its cost, which is higher than that of more common supports like Al_2O_3 and SiO_2. Much effort has therefore been directed in recent years to finding catalyst formulations which can enhance the thermal stability of ceria without diminishing its special features, such as its redox/oxidation properties and its high oxygen mobility. The main catalyst formulations studied contain ceria spread over a thermally stable support or thoroughly mixed with other oxides in mixed-oxide formulations. In both cases, noble metals can be used to improve catalyst activity. Catalysts of this type are those currently used in the de-SO_x process from FCC units and in the treatment of auto-exhaust, as we will describe in Sections 2.1 and 2.2.

2.1. Catalytic removal of SO_x

It is very well known that sulfur oxides are precursors of acid rain and that their emission constitutes a global threat to the atmosphere. Environmental agencies have therefore regulated emissions of SO_2

and SO_3 and the limits are becoming increasingly severe. Approximately 5% of all SO_x emissions are from FCC units. In these, the amount of sulfur that is emitted is primarily a function of the sulfur in the feedstream and of conversion in the reactor. Nearly 40% of incoming sulfur remains in the liquid products and 50% is converted to H_2S which is then treated downstream in a Claus plant. The rest (<10%; the amount is highly dependent on feedstock composition) remains trapped in the coke which builds up on the catalyst. This sulfur is then oxidized to SO_3 in the catalyst regeneration step and it is this SO_2/SO_3 mixture that needs to be treated before release into the atmosphere. Desulfurization at this stage can be done by flue gas scrubbing, however, the addition of an SO_x adsorption/reduction additive to the main FCC catalyst formulation is a less costly option [12]. The function of this additive is to transform SO_x back to H_2S which can then be treated directly in the Claus plant.

A catalyst for this purpose should thus perform the following actions:

- oxidation of SO_2 to SO_3 during FCC catalyst regeneration;
- chemisorption of SO_3 and its storage as sulfate; and
- release of sulfate as H_2S (reduction step) in the FCC riser reactor.

The temperatures for the first and the second step, which are carried out in the catalyst regeneration section of the plant, are in excess of 973 K whereas the final step is carried out at around 820 K in the riser reactor. An ideal catalyst should have the following characteristics to be of interest for this reaction: (i) basic sites for adsorption of SO_2/SO_3; (ii) active centers for oxidation of SO_2 to SO_3 and (iii) redox properties for the reductive decomposition of sulfates to H_2S under reducing atmosphere.

One catalytic system which meets all these criteria is a ceria containing magnesium aluminate spinel-MgO solid solution of the type $CeO_2/MgAl_2O_4{\cdot}MgO$ [13]. Several modifications of the basic system have recently appeared containing V and Fe either deposited [14] or incorporated in the solid solution [15]. The role of ceria in this catalyst formulation derives from its basic/redox character. Ceria possesses sufficient oxidation activity to promote oxidation of SO_2 to SO_3 and its basic sites allow the adsorption of SO_2/SO_3 with formation of sulfates [16]. In addition, it must facilitate the reductive desorption of sulfates as hydrogen sulfide under reductive conditions. A possible scheme for the reaction is the following:

$$SO_2 + 0.5O_2 \rightleftarrows SO_3 \quad (1)$$

$$SO_3 + MO \rightleftarrows MSO_4 \quad (2)$$

$$MSO_4 + \text{red.} \rightleftarrows MO + H_2S + H_2O \quad \text{red.} = C_xH_y, H_2,$$
$$M = \text{sulfur storage component} \quad (3)$$

Cerium dioxide can contribute to all these steps. Its reducibility facilitates the oxidation of SO_2 to SO_3 under FCC regeneration conditions by reacting with SO_2 to give substoichiometric cerium oxide, which is then reoxidized by oxygen:

$$xSO_2 + CeO_2 \rightleftarrows xSO_3 + CeO_{2-x}$$

$$CeO_{2-x} + 0.5xO_2 \rightleftarrows CeO_2$$

The next step is the adsorption of SO_3. The best oxides for the storage of SO_3 are those that form stable metal sulfates following SO_3 adsorption. However, their stability should not be high enough to interfere with the desorption step. Strong bases which form stable sulfates (CaO, SrO, BaO, MgO) are not therefore suitable for this purpose. The best catalyst support for SO_3 adsorption is a solid solution of MgO and the aluminate spinel $MgAl_2O_4$. This has sufficient SO_3 adsorption capacity and facilitates removal of sulfates. Fig. 3 reports the effect of sulfation and desorption of sulfate over CeO_2/MgO and $CeO_2/Mg_2Al_2O_5$. It may be seen that although they exhibit a similar adsorption capacity (27% versus 23% by wt), with MgO about 27% of the adsorbed SO_3 still remains within the catalyst after reduction whereas in the case of $Mg_2Al_2O_5$ the catalyst is regenerated with 100% efficiency under H_2 [13]. Although the adsorption of SO_2 to give sulfates is a specific function carried out by $Mg_2Al_2O_5$, oxidative adsorption of SO_2 on ceria with a concomitant reduction of CeO_2 is possible. A comparison of thermodesorption traces of SO_2 followed by TPD and TG showed that although CeO_2 readily desorbs SO_2 (at temperatures lower than MgO), weight loss does not correspond to 100% SO_2 elimination, Fig. 4 [17]. This indicates that there is a thermal transformation of sulfite species into sulfate [16–18], a reaction that involves reduction

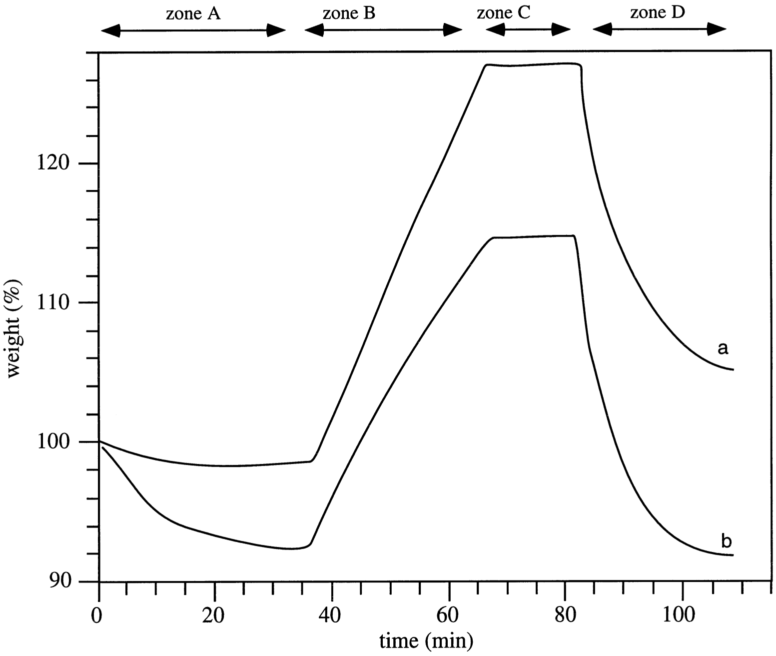


Fig. 3. TGA test of de-SO_x activity of CeO_2/MgO (a) and CeO_2/$Mg_2Al_2O_5$ (b) catalyst: zone A: heating under N_2 to 973 K; zone B: treatment under SO_2 (0.32%), O_2 (2%) and N_2 at 973 K; zone C: treatment under N_2 at 923 K; zone D: treatment under H_2 [13].

of CeO_2 with formation of oxygen vacancies. A correlation between the oxygen vacancies formed and the de-SO_2 activity of a CeO_2-supported $Mg_2Al_2O_5$ spinel has been recently found, showing that activity reaches a maximum as the amount of CeO_2 loaded onto the spinel increases, Fig. 5 [19]. This maximum, corresponding to optimum de-SO_2 activity, falls exactly in the region of monolayer CeO_2 dispersion when the cerium oxide content is in the range 7–10 wt%. In this region of optimum activity, a maximum number of oxygen vacancies was also detected by positron lifetime measurements.

CeO_2 is also an efficient catalyst for the reduction of sulfates to give H_2S (step 3 of the reaction scheme). A comparison of the efficiency of several metal oxides supported on Mg–La–Al–O oxide was carried out by

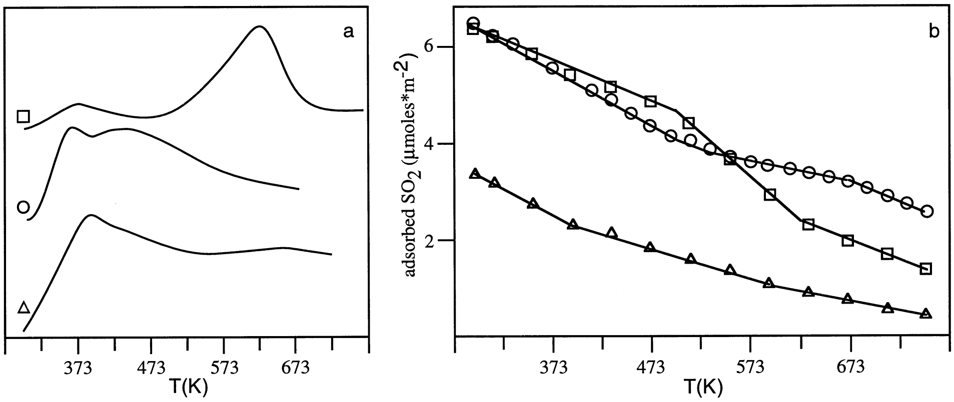


Fig. 4. TPD profiles of SO_2 desorbed from (△) $MgAl_2O_4$ (○) CeO_2 and (□) MgO and corresponding variation of SO_2 mass detected by TGA [17].

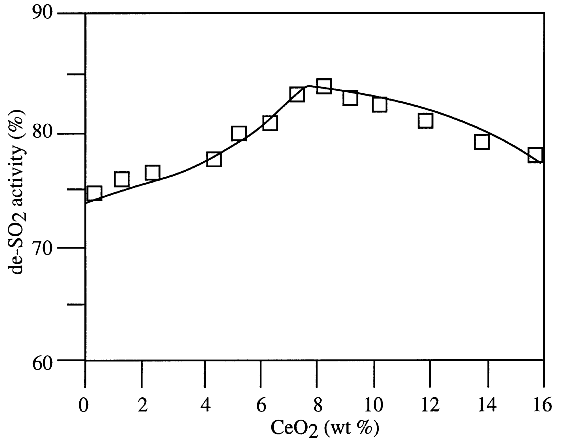


Fig. 5. De-SO_2 activity versus CeO_2 content in CeO_2-supported $Mg_2Al_2O_5$ [19].

studying TPR profiles under different reducing atmospheres [14]. It was demonstrated that reduction to H_2S of sulfated species adsorbed on ceria is fairly easily achieved by using propane as a reducing agent. Of the oxides tested, CeO_2 and V_2O_5 were the most active, both in terms of ignition temperature for H_2S formation and total H_2S released, Table 1 [14]. Decomposition of sulfates is therefore enhanced by oxides with a strong redox character, like CeO_2 and V_2O_5. It seems that the principal role of the metal oxide is to provide active hydrogen from hydrocarbons under conditions typical of FCC, facilitating the C–H bond cleavage. The rate-determining step is the direct reaction between SO_2 and hydrocarbons to give H_2S.

The direct reaction between SO_2 and hydrocarbons or CO to give sulfur catalyzed by ceria was also found to be of potential interest [20]. In this case the suggested mechanism implies the alternate reduction and oxidation of the catalyst through the formation of oxygen vacancies. High oxygen mobility in the catalyst is an important requirement facilitating oxygen transfer on the surface and from the bulk to the surface. This high mobility can be obtained through the doping of ceria lattice with transition and rare-earth metal oxides like Zr, Cu, La [20].

The use of catalyst compositions similar to those of FCC has also been reported to be effective for the treatment of tail gases (SO_2, CO, COS and CS_2) from a Claus plant [21]. In this case, tail gases are oxidatively adsorbed over the catalyst in one step and reductively desorbed with H_2 to give H_2S, which is recycled to the main Claus plant for further processing (see Scheme 1).

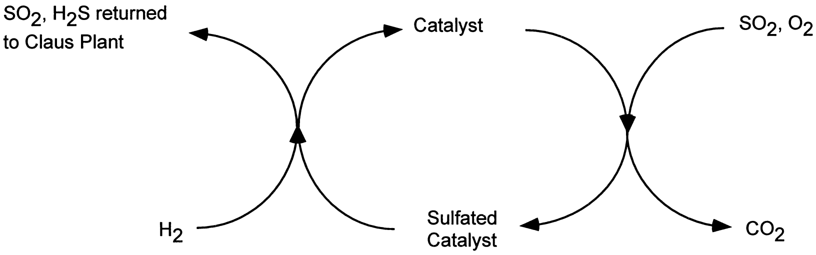
Under FCC conditions, ceria is also able to reduce NO_x emission originating from a cracking unit [22]. Here, the role of ceria is to provide oxygen vacancies for the reduction of NO to N_2. The ceria-containing material can be reduced by H_2 or hydrocarbons in the riser reactor and in the regenerator it serves as a reducing agent for NO. A substantial amount of reducing agent is also required in the regenerator to maintain the redox process of cerium between Ce^{3+} and Ce^{4+}. CO originating from incomplete combustion of coke can be used for this purpose and a direct inverse relationship exists between CO concentration in the regenerator and NO emitted by the cracking unit. Reduction of 300 ppm NO_x to 150 was observed.

2.2. *Treatment of exhaust from mobile sources*

The most important application of ceria in catalysis is certainly the treatment of exhaust gases (CO, NO, hydrocarbons) from spark-ignited internal combustion engines. It is not the intent of this review to fully describe the utilization of ceria in TWC as a number of papers have recently been published on the role of ceria in TWC technology [5,23]. However, a brief summary of the main features of ceria will be given.

Table 1
Performance of supported oxides in the reduction of sulfated samples by propane-TPR [14]

Catalyst	Loading (wt%)	Surface area (m^2/g)	Ignition temperature (K)	Total H_2S released (μmol)
Only support	–	151	873	118
V_2O_5	2.49	167	733	235
Cr_2O_3	2.14	193	853	212
Fe_2O_3	2.13	186	793	171
CeO_2	4.22	186	773	229



Scheme 1.

TWC catalyst formulation consists primarily of noble metals and metal oxides dispersed either on the surface of alumina pellets or on an alumina washcoat anchored to a monolithic ceramic substrate. It is very well-known that the main role of ceria in this complex mixture is to provide oxygen buffering capacity during the rich/lean oscillation of exhaust gases.

A typical closed-loop control system causes the air/fuel ratio (A/F) to cycle rapidly around the stoichiometric composition with a frequency of the order of 1 Hz. Under these conditions, the catalyst is exposed to constantly varying feedstream compositions going alternately from rich exhaust stoichiometry (deficient O_2) to lean stoichiometry (excess O_2). In this environment, ceria has the ability to donate its oxygen for the removal of CO and hydrocarbons (HC) during the oxygen-deficient portion of the cycle (reactions 4–6) while adsorbing and storing oxygen from O_2, NO and water during excursion into the lean part of the cycle (reactions 7–9). These reactions positively affect the conversion of the three major pollutants (CO, HC and NO) under conditions typically encountered in the normal operation of a three-way catalyst.

$$CeO_2 + xCO \rightarrow CeO_{2-x} + xCO_2 \tag{4}$$

$$CeO_2 + C_xH_y \rightarrow CeO_{2-(2x+0.5y)} + xCO_2 + 0.5yH_2O \tag{5}$$

$$CeO_2 + xH_2 \rightarrow CeO_{2-x} + xH_2O \tag{6}$$

$$CeO_{2-x} + xNO \rightarrow CeO_2 + 0.5xN_2 \tag{7}$$

$$CeO_{2-x} + xH_2O \rightarrow CeO_2 + xH_2 \tag{8}$$

$$CeO_{2-x} + 0.5xO_2 \rightarrow CeO_2 \tag{9}$$

This ability derives from the ease with which ceria can deviate from a stoichiometric format to give a continuum of oxygen deficient nonstoichiometric oxides CeO_{2-x}. If the atmospheric environment in which CeO_2 operates changing continuously from a net oxidizing to a net reducing composition, the oxidation state of cerium correspondingly shifts from +4 to +3, enhancing the conversion of CO and hydrocarbons during rich oscillations, and of NO during lean oscillations. This feature of ceria is called oxygen storage capacity [24,25] and its uniqueness derives from the kinetics and thermodynamics of the redox processes which allow a good fit of the extent and the rate of the redox processes on the ceria surface and the timescale of fluctuation of composition in the exhaust. This feature is enhanced if ceria is in contact with noble metals (such as Rh) which can help the transfer of oxygen from the bulk to the surface [26].

The major drawbacks of an oxygen storage system based on pure ceria relate to thermal resistance and low-temperature activity [27]. The severe conditions to which catalysts are subjected during operations (especially high-temperature aging) causes a loss of OSC due to sintering of the ceria particles which reduces the interaction of ceria with supported metals and does not allow the Ce to cycle between oxidation states. In addition, the poor low-temperature performance of the material does not enable ceria-only catalysts to meet the increasingly demanding standards required by legislation. This has forced researchers to seek new catalyst compositions with the aim of (i) increasing thermal stability and (ii) enhancing low-temperature redox performances. New catalyst composition involves the use of ceria doped with other rare-earth or transition metal oxides [28,29]. In this case the kinetics of oxygen transport is heavily modified and more efficient redox processes are permitted at much lower temperatures.

Although the main role of ceria is to supply and subtract oxygen, several other functions can be carried out by this material. One of its most relevant features is its high degree of synergetic interaction with noble metals (Pd, Pt, Rh), [5] which can lead to

1. the promotion of bulk and surface reduction with enhanced reactivity towards CO and NO,
2. an enhanced rate of exchange between oxygen from the bulk and reactants from the gas phase, and
3. an enhanced dispersion of the metal.

In addition, the metal/ceria system is able to modify the activity of the catalyst in WGSR and steam reforming reactions, both of which are important in TWC catalysis.

Ceria is also utilized in the treatment of emissions from diesel engines. Here, the problem is dealing with solid and liquid emissions since diesel engines are relatively clean for hydrocarbons and CO. Emissions can be controlled by placing a ceramic filter made of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) downstream to collect solid particles [30]. The filter must possess sufficient filtration efficiency to meet the requirements of legislation and should also have a high thermal shock resistance. In addition to filtration efficiency, the filter must control the pressure drop which builds up on deposition of solid particles. Solid particles must therefore be periodically eliminated by regeneration of the filter. Regeneration, however, requires temperatures that are higher than those encountered under normal driving conditions. There are therefore two approaches that can be adopted. The first is to increase the temperature of the exhaust gases or of the filter and the second is to lower the combustion temperature of soot in the filter to allow elimination at much lower temperatures. Catalytic additives in the diesel fuel or coated on the filter are an efficient way of lowering the combustion temperature of solid particulate and allowing on-site filter regeneration, Fig. 6 [31]. Cerium naphthenate and octoate alone or in combination with other organometallic additives containing Fe, Cu and Ca have been found to be effective in lowering the combustion temperature of soot. These are added in the fuel at a concentration of ca. 500–10 000 ppm metal by weight and during combustion the metal oxide is formed and deposited, along with carbon particles, in the filter. The mechanism of cerium's action can be described as combustion of solid particulate catalyzed by fragments of ceria which are formed in contact with soot. Cerium oxide is included in soot during its formation and it is therefore expected to be finely dispersed inside the particle. This will enable good contact between the catalyst (CeO_2) and the reagents (particulate) so that a high degree of conversion can be achieved. Fig. 7 illustrates the combustion efficiency of soot doped with CeO_2, a mixture obtained by adding organometallic cerium compounds to the fuel [1]. The ability of CeO_2, in comparison to other oxides, to lower the combustion temperature of soot [32] or of soluble organic fractions [33] emitted from diesel engines is well evidenced in Table 2, where ignition temperature and total amount reacted are indicated.

3. Treatment of liquid wastes

3.1. *Catalytic wet oxidation*

The use of ceria in environmental applications also involves aqueous phase in catalytic wet oxidation

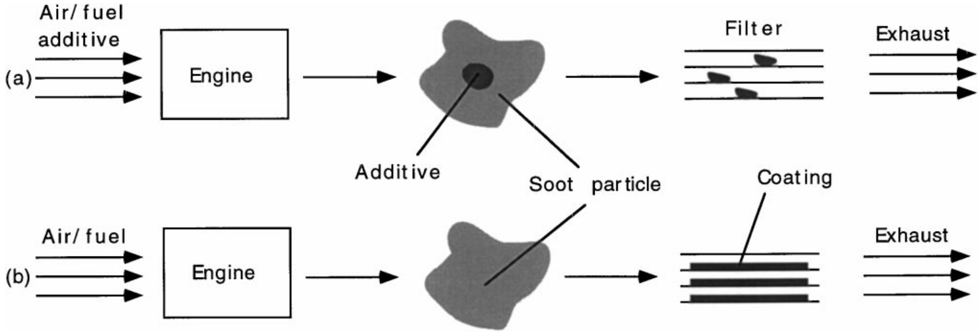


Fig. 6. Mechanism of regeneration of diesel particulate filter by lowering the soot ignition temperature: catalytic additives can be added in the fuel (a) or coated on the filter (b), [31].

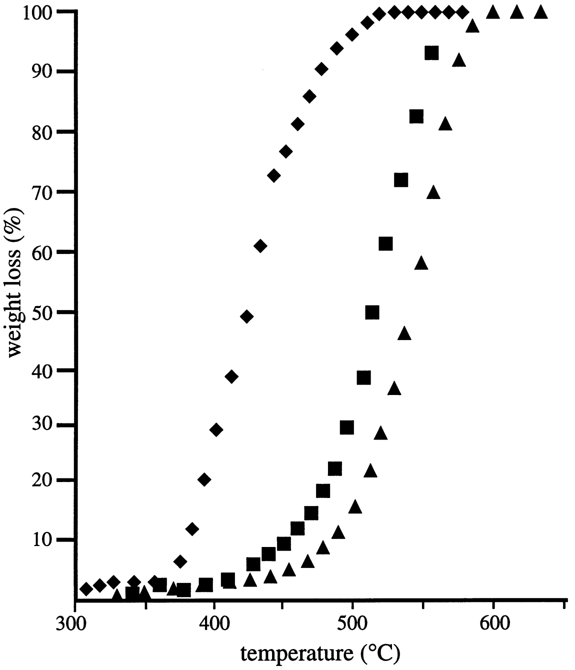


Fig. 7. Catalytic combustion of soot (weight loss %) versus temperature, at different contents of Ce: (▲) soot without Ce, (■) soot impregnated with 450 ppm of Ce, and (◆) with 3300 ppm of Ce [1].

(CWO), a destruction method applied to waste streams. The aim is catalytic abatement of organic pollutants present in wastewater to less toxic compounds that are then amenable to biological treatment for final purification. Catalytic wet oxidation is carried out at high oxygen pressure and high temperature to oxidize a significantly high concentration of organic compounds in aqueous phase [2].

Attention has been focused on ceria and related compounds because they are active both in the oxidation of lower carboxylic acids (especially acetic acid) and of ammonia [2,34]. The former are very refractory to oxidation and they are key compounds in the degradation of organic pollutants. Ammonia is one of the pollutants which cause eutrophication of the receiving water system. Moreover, because nitrogen atoms contained in various organic compounds are converted into ammonia during wet oxidation, a further treatment to remove ammonia is necessary even after the carbonaceous part of the organic pollutant has been removed.

Imamura et al. [35] first found the beneficial effect of CeO_2 addition on a Co_3O_4-BiO(OH) composite catalyst in the oxidation of ammonia; the activity was found to increase by a factor of 2 with the addition of ca. 10% wt. of CeO_2. Similar catalyst compositions containing Co_3O_4–CeO_2 and MnO_x–CeO_2 were also active in this reaction. Generally it was observed that mixed oxides had a higher activity than single components, particularly it was observed that Co_3O_4 and CeO_2 had no activity in this reaction under the same conditions. Therefore it was first suggested that the redox properties of the mixed oxide compositions are the main factors contributing to their activity.

Catalysts of similar composition containing oxides of manganese and cerium in the molar ratio (Mn/Ce:3/

Table 2
Combustion of soluble organic fraction over CeO_2-based catalysts followed by DTA [33]

Catalyst	SA (m^2/g)	Pt load (wt%)	DTA peak area	DTA onset temperature (K)
α-Al_2O_3	20	0	2.0	250
γ-Al_2O_3	150	0	10.5	230
γ-Al_2O_3	150	0.5	11.2	230
γ-Al_2O_3	150	5	21.1	145
Y_2O_3	40	0	6.0	190
TiO_2	47	0.015	10.5	190
Al_2O_3–SiO_2	–	0.015	8	266
SiO_2	220	0.06	5.7	260
CeO_2	140	0	21.7	135
CeO_2/Al_2O_3	80	0.015	15.8	151
CeO_2/Al_2O_3	145	0.015	22.4	150
CeO_2/TiO_2	93	0.015	21.2	151
CeO_2/Al_2O_3–SiO_2	–	0.015	20.1	151
CeO_2/SiO_2	180	0.06	20.5	160

1) were also tested in the oxidation of carboxylic acids [35], which is one of the rate-determining steps in the wet oxidation of various organic compounds, and in the oxidation of phenol in aqueous solution [36]. The results show that the catalyst is highly active, irrespective of the kind of reactant to be oxidized, suggesting that it will be effective for the treatment of wastewaters encountered under field conditions containing various selected representative compounds. Activity was also greater than that of commercial homogeneous copper-based catalysts [35].

Mn–Ce–O was also tested in the oxidation of a neutral compound in order to investigate the importance of interaction between catalyst and reactant without acid–base interactions. As shown in Fig. 8, the initial rate of TOC removal (r_i) rises in the oxidation of polyethylene glycol (PEG) as the cerium content is increased in the catalyst to reach a maximum value around a Ce content of 40–60 mol% and at the same time TOC removal increases to a maximum value at around 60 mol% of cerium. It is important to note that surface area reaches its maximum value with pure ceria, indicating that the promotion of activity is not due to an increase in the surface area of the catalyst.

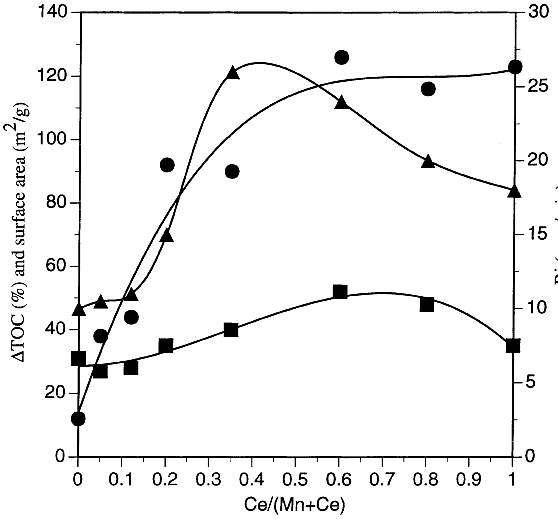


Fig. 8. Variation in total organic carbon (ΔTOC) (■), surface area (●) and initial rate of TOC decrease (▲) versus the composition of Mn–Ce–O composites [35] in the wet oxidation of polyethylene glycol.

The interaction of Mn and Ce in composite oxides heavily modifies the redox activity of manganese, increasing lattice oxygen lability. This is strongly dependent on the method of preparation and on catalyst composition. Temperature-programmed desorption of oxygen in Mn–Ce–O catalyst (50 mol% each component) indicated that the composite oxide desorbs lattice oxygen at lower temperatures than pure manganese oxide and that the amount of desorbed oxygen is higher than that obtained with the pure oxides [37]. Thermogravimetric results show significant modification of the behavior of Mn oxide when doped with a small amount of ceria compared with the pure oxide [38]. At high temperatures (over 750 K), Mn–Ce–O (Mn/Ce:95/5) shows a remarkable weight loss due to desorption of oxygen, which is not observed on the pure oxide. Moreover the valence state of Mn in doped material is higher than in pure Mn oxide in the low-temperature region. It thus seems that the role of cerium is dynamic. It provides oxygen to Mn at low temperatures, stabilizing the oxidation state at a value around 3.2, and withdraws oxygen at high temperatures, lowering the oxidation state of Mn to 2.7. This behavior is in contrast to that of that observed in pure manganese oxide, where the oxidation state changes from a value of 2.8 at low temperatures to a value of 3.1 at high temperatures. It appears that the redox properties of the catalyst are an important factor in controlling the activity. Fig. 9 summarizes the activity of Mn–Ce–O catalysts calcined at different

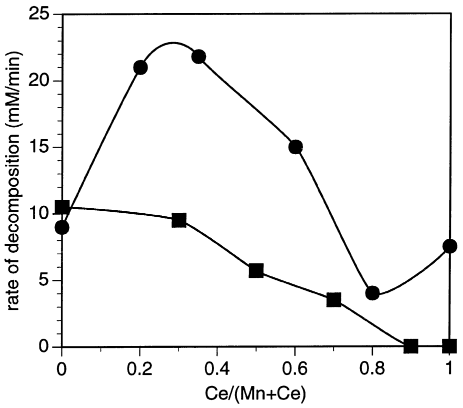


Fig. 9. Rate of decomposition of H_2O_2 catalyzed by Mn–Ce–O composites: initial rate versus composition for catalysts calcined at 623 K (●, 33) and at 773 K (■, 37).

temperatures in the decomposition of H_2O_2, which is a test reaction for redox properties. The activity of Mn–Ce–O calcined at lower temperature appears to correlate well with the redox properties of the catalysts whereas for samples calcined at higher temperatures the redox properties do not seem to be the main factor controlling the activity. This highlights that preparation procedure is another important problem in the use of mixed oxide compositions in this reaction. Preparation can affect activity for at least two reasons. The first is the difference in surface area between the single oxide and the mixed oxides and the other is the degree of homogeneity, which can be very different depending on the methodology used for catalyst preparation. This in turn can modify the degree of contact between domains belonging to single component and vary the degree of interaction.

The enhanced redox activity of mixed oxides was also applied to acetic acid oxidation by de Leitenburg et al. [40]. In this case, the activity of ceria was compared with that of ceria–zirconia solid solution (Ce/Zr:80/20) and ceria–zirconia doped with MnO_x and CuO (5 mol%). Ternary oxides showed the highest activity, although the surface areas were approximately the same for all catalysts. It was suggested that the presence of small amounts of copper and manganese promotes the low-temperature redox properties of ceria–zirconia solid solution and enhances its low-temperature oxidation ability. Another advantage of these systems is the very low level of catalyst leaching during reaction.

Mn/Ce catalysts have also been utilized recently in the supercritical water oxidation (SCWO) of phenol and ammonia [41,42]. Under these conditions, conversions of phenol and ammonia of 99% and 40% were attained at temperature 663 and 723 K and contact time 5 and 0.8 s. Exposure to the harsh SCWO environment (723 K, 28 MPa) caused a marked change in the texture, morphology and composition of the catalyst although catalyst leaching was minimal.

The use of noble metals can improve the oxidation activity of these systems [39,43–46]. Ru seems to be the most promising of several noble metals supported on ceria. Its activity in wet oxidation of polyethylene glycol is higher than that of Pt, Pd, Rh and Ir, and also superior to that of Mn–Ce–O composites [43]. However, activity is strongly dependent on the type of substrate used and in the oxidation of acetic acid Imamura et al. found Ru/CeO_2 inferior to Mn–Ce–O catalyst. The activity of Ru/CeO_2 in the oxidation of acetic acid is also strongly dependent on the textural properties of the CeO_2 support. Barbier et al. [46] have recently compared the behavior of Ru supported on various cerias and other oxides; see Table 3 for a summary of results on acetic acid. It turned out that ceria was the best support for this reaction and that the higher the surface area, the better the catalytic activity. This was not correlated to Ru dispersion (activity decreased as dispersion increased) but originated after reduction of the metal with some kind of metal/support interaction. It was observed that activity is also

Table 3
Wet oxidation of acetic acid catalyzed by ceria containing catalysts

Catalyst	SA (m^2/g)	Catalyst quantity	P (atm)	T (K)	Concentration (g/l)	Conversion (%)	Time (h)	Solvent (ml)	Reference
5%Ru/CeO_2	n.a.	12 mM	10	473	2	44.5	1	<270	43
MnO_2/CeO_2 (Mn/Ce:7/3)	95.6	20 mM	10	473	2	99.5	1	<270	35
5%Ru/CeO_2	125	1 g	38	473	5	82	1	250	46
2%Ru/CeO_2	140	1 g	38	473	5	53	1	250	46
1%Ru/CeO_2	145	1 g	38	473	5	23	1	250	46
5%Ru/CeO_2	40	1 g	38	473	5	13	1	250	46
CeO_2	67	1 g	30	463	2	14	7	100	40
CeO_2–ZrO_2 (Ce/Zr:8/2)	88	1 g	30	463	2	27	7	100	40
CeO_2–ZrO_2–CuO	78	1 g	30	463	2	90	7	100	40
CeO_2–ZrO_2–MnO_x	80	1 g	30	463	2	96	7	100	40

SA=surface area; catalyst quantity=amount of catalyst loaded; P=pressure; T=temperature; concentration=acetic acid concentration; conversion=% conversion; time=reaction time; solvent=amount of water used.

dependent on catalyst pretreatment and reduction was most effective in promoting catalytic activity. A combination of noble metals with mixed oxides ceria-containing supports enabled preparation of very active catalysts. Thus Ru supported on Mn–Ce–O composites at various compositions was found to be an excellent catalyst for the oxidation of model domestic waters [39]. The best support composition was not Mn/Ce:3/1 but one containing mainly cerium with a Mn/Ce:1/9 ratio. The higher activity was attributed to a preferential interaction of Ru with ceria.

Recently, the effect of ceria was tested in the oxidation of organic pollutants in industrial effluents [47]. The authors reported that ceria is effective in the promotion of activity of a conventional Pt/Al_2O_3 catalyst, but it was found to inhibit the activity of an Al_2O_3-supported Pd catalyst (Fig. 10). In both cases the dispersion of ceria and the metal (and therefore the degree of interaction between CeO_2 and Pd) was found to be an important factor influencing the activity, although the reason for the opposite action of ceria was not clearly evidenced. One possibility is that the high Pd–CeO_2 interaction could facilitate oxidation of Pd to give palladium–oxygen surface complexes, less active than Pd metal.

A few studies have carried out a more detailed kinetic investigation to obtain information on the mechanism of reaction and on the role played by ceria [35,46]. It seems that, at least for acetic acid oxidation, the mechanism is of a radical type involving the formation of reactive oxygen species of the type HO° or HO_2° originating from the reaction of superoxide radicals $O_2^{\circ-}$ with H^+ at low pH. Ceria can assist Ru in the formation of these radicals as it is known that interaction of ceria with oxygen can produce superoxide and peroxide species [48]. Generally speaking the role of a catalyst is that of enhancing the formation of alkoxy radicals (path 10), the decomposition of hydroperoxides (path 11) or the chain initiation (path 12):

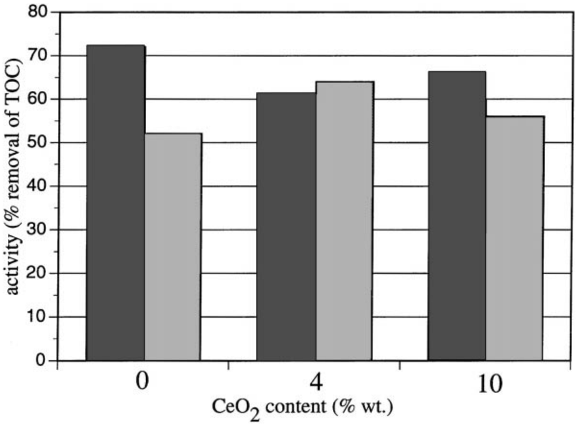


Fig. 10. Influence of Ce on the activity of a $M/CeO_2/Al_2O_3$ catalyst in the oxidation of oragnics in an effluent from a softwood Kraft Pulp Mill: M=Pd (blak bar), M=Pt (gray bar); $T=463$ K, $P=1.5$ MPa, $t=1$ h [47].

$$RH + Me^{(n+1)+} \rightarrow R^\circ + M^{n+} + H^+ \qquad (10)$$

$$ROOH + Me^{(n-1)+} \rightarrow RO^\circ + Me^{n+} + OH^- \qquad (11)$$

$$ROOH + Me^{n+} \rightarrow ROO^\circ + Me^{(n-1)+} + H^+ \qquad (12)$$

According to these mechanisms the ability of a catalyst could be correlated to the redox potential of the $Me^{n+}/Me^{(n-1)+}$ couple. In the presence of a noble metal an additional effect could originate from its ability to perform oxidative addition reaction.

Overall, it seems that ceria-based materials are promising systems for the catalytic depollution of water streams. The main features of these systems are:

1. stability under reaction conditions;
2. low catalyst leaching;
3. the possibility of varying the composition over an almost unlimited range; and
4. enhanced textural and redox properties at low temperatures.

However despite the increasing number of studies in this direction, research is generally focused exclusively on the assessment of catalytic behavior and kinetic modeling. Catalyst characterization under reaction conditions has not been adequately addressed, and in our opinion, needs to be investigated in the near future for a better understanding of catalysts of this type and their rational design.

4. Dehydrogenation of ethylbenzene to styrene

The dehydrogenation of ethylbenzene (EBDH) accounts for more than 90% of worldwide styrene production. The rest is obtained as a by-product in the epoxidation of propylene with ethylene hydroperoxide. The reversible conversion of EB to styrene and hydrogen:

$$C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CHCH_2 + H_2$$

is highly endothermic (ΔH=124.9 kJ mol^{-1}) and conversion is favored by low pressures and high temperatures (at 1050 K and 1 bar pressure the equilibrium conversion is 90%) [49]. Industrially, the reaction is carried out over potassium-promoted iron oxide at temperatures ranging from 820 to 923 K and pressures from sub-atmospheric to 2 atm, with a selectivity of about 90% in styrene at a conversion of 50–60%. Typically, by-products are benzene and toluene (1–2%) as well as traces of methane, ethylene and CO_2, owing to side reactions involved in the dehydrogenation process. The reaction is carried out in the presence of superheated steam, which furnishes the heat for the reaction. It has been found that steam does not participate in the reaction but its use increases the activity, selectivity, life-time and stability of the catalyst, allowing uninterrupted operation of commercial units for 1–2 years with a single catalyst charge [50]. For the conventional K–Fe catalyst (i.e. Nissan Girdler's catalyst: 60 wt% Fe_2O_3, 25 wt% K_2CO_3 and a few percent Cr_2O_3) a steady state is reached after the first 20 h of reaction where the conversion of EB increases gradually [51]. This effect indicates the formation of active phases under EBDH conditions, and several models for the active state of catalyst have been proposed in the literature [52–54]. All models point to the importance of the K–O–Fe^{3+} entity as the active center of catalysis. Muhler et al. [54,55], using several characterization techniques, suggested that the working catalyst is a metastable mixture of $KFeO_2$, $K_2Fe_{22}O_{34}$, and Fe_3O_4. They found that $KFeO_2$ is formed under EBDH conditions (850–870 K) from very finely dispersed, nonstoichiometric Fe_3O_4 (with an excess of Fe_2O_3) and $K_2Fe_{22}O_{34}$, which serves as a source of potassium.

In the latest generation of catalysts, various oxides of V, Ce, W, Li, Mg, Ca, Ti, Zr, Ni, and Co have been added to the K–Fe system to improve its activity and selectivity and to delay the deactivation of the catalyst. Although at present only a few basic studies have been carried out to understand the role of promoters, it has been suggested that they could influence the number, organization and nature of the reactive centers and contribute either to stabilizing the active phase or to accelerating its formation under reaction conditions [55].

It has been found that, of the various dopants, cerium oxide is particularly efficient in increasing the activity of K–Fe based catalysts [56] and many patents claim cerium oxide as a component of dehydrogenation catalysts [57–59]. Cerium oxide is added in percentages ranging from 5 to 60 wt% as carbonate, oxide, nitrate and hydroxide along with other promoters, such as NiO, CuO, CaO, MoO_3, Bi_2O_3, TiO_2 [60]. Currently it is used in many styrene plants. The SÜD CHEMIE catalyst Group sells the highly selective catalyst G64-C with 58 wt% Fe_2O_3, 23 wt% K_2CO_3, 5 wt% CeO_2 and 2.5 wt% MoO_3 [61]. These catalysts show improved activity compared to previous formulations and selectivity can also be implemented, thanks to the synergetic action of the components.

Despite the well-known positive effect of CeO_2 in the activity of K–Fe based dehydrogenation catalysts, few basic studies have been carried out to investigate its role in this reaction. At first glance, it appears that the role of ceria is not fully explained by its redox and oxidation features. Hirano [56], in a kinetic study, tried to elucidate the effects of molybdenum and cerium oxide promoters. It was found that the CeO_2-containing catalyst showed higher activity to styrene formation without reducing selectivity whereas the Mo-containing catalyst showed higher selectivity to styrene although activity decreased. It is noteworthy that the addition of Ce and Mo promoters to the Fe–K system enhanced both activity and selectivity, Table 4 [56]. The addition of cerium decreased the activation energy for styrene formation from 30 to 25.6 kcal mol^{-1} and catalyst activity was increased by higher concentrations of cerium oxide. Therefore cerium, which was suggested to exist as CeO_2 crystallites under the reaction conditions, contributed to an increase in the number of active sites and also to modifications of their nature. Hirano correlated the improved performance of the cerium oxide-doped catalyst to increased basicity of the catalyst surface, in accordance with a mechanism of dehydrogenation relying on basic sites [62]. One of the elementary steps of reaction should be a two proton abstraction process enabled by an Fe^{3+}/Fe^{2+} redox cycle. Such a reaction requires an ionic catalyst surface providing electrostatic fields that induce dipole moments in the che-

Table 4
Performance of Ce and Mo containing catalysts in the dehydrogenation of ethylbenzene [56]

Catalyst	Surface area (m^2/g)	Rate of styrene formation[a]	Selectivity to styrene (%)	Activation energy (kcal/mol)		
				Styrene	Benzene	Toluene
Fe–K	6.3	26.6	96.9	30.0	36.2	50.9
Fe–Ce–K	7.0	34.6	96.7	25.6	35.8	48.7
Fe–Mo–K	6.1	20.2	97.2	30.4	35.8	50.0
Fe-Mo–Ce–K	6.9	30.5	97.6	23.6	36.2	49.3

Reaction conditions: T=823–900 K; steam/EB molar ratio=11.8; composition: Fe_2O_3:ca.60–70 wt%, K_2CO_3:28 wt%, CeO_2:5 wt%, MoO_3=2.5 wt%.

[a] Mol g^{-1} min^{-1} $\times 10^5$ measured at 853 K.

misorbed organic species, so lowering the activation barrier for the dehydrogenation step. Cerium ions will enhance the polarization of the Fe–O bond and increase the basicity of this reaction center.

The nonoxidative dehydrogenation of ethylbenzene over iron catalysts can be classified as a typical base catalyzed model reaction [62]. The abstraction of β-hydrogen to form a π-adsorbed complex can be viewed as a combination of an acid–base and redox reaction:

$$R^- - H^+ + O^{2-} \rightarrow R^- + OH^- (\text{acid}-\text{base})$$

$$R^- + M^{n+} \rightarrow R^+ M^{(n-2)+} (\text{redox})$$

The acid–base reaction involves the lattice O^{2-}. In this mechanism the reduced Fe(II) cation could be reoxidized by migration of lattice oxygen from the cerium (IV) oxide which in turn is reoxidized by water. The ionization potentials (36.7 eV for Ce^{3+} and 30.5 eV for Fe^{2+}) and the electrode standard potentials ($Fe^{2+/3+}$, 0.77 V; $Ce^{3+/4+}$, 1.44 V), although representative of different operative conditions, are compatible with the oxidation of Fe^{2+} to Fe^{3+} by Ce^{4+}.

This mechanism hypothesis is similar to the one successfully applied to the ammoxidation of propylene to acrylonitrile over the multicomponent bismuth molybdate-based catalyst containing $Fe^{2+/3+}$, $Ce^{3+/4+}$ or $Cr^{2+/3+}$ as redox elements [63]. The key catalytic functions of these catalysts are:

1. an α-H abstraction site (Bi^{3+});
2. an alkene/ammonia-chemisorbing and oxygen/nitrogen insertion element (Mo^{6+}); and
3. a redox component ($Fe^{2+/3+}$, $Ce^{3+/4+}$ or $Cr^{2+/3+}$) having a reduction potential greater than that of the oxygen/nitrogen insertion element.

This reoxidation site provides a constant source of lattice oxygen to the active site as it becomes reduced through the ammoxidation cycle. In this way Bi–O–Mo sites are maintained in their active high oxidation state. The redox moieties are therefore capable of dioxygen dissociation, its reduction to lattice oxygen O^{2-} and incorporation of the latter into the catalyst matrix. For this mechanism to be operative, close contact between the different components of the catalysts must be obtained and it is necessary to develop a preparation methodology which leads to the dissolution of the redox element within the catalyst matrix. The methodology of preparation should also have a key role in the dehydrogenation of ethylbenzene, where the state and location of cerium may influence activity.

The possibility of cerium oxide acting as a source of oxygen for iron does not exclude that Ce^{4+} could act along with Fe^{3+} as an oxidation center for ethylbenzene, providing a more active catalyst site. In this case, ethylbenzene oxidation could involve both the Fe^{3+} and the Ce^{4+} ions at an Fe^{3+}–O–Ce^{4+} site through the same basic mechanism suggested for conventional catalysts. Alternatively, the cerium ion could be present as Ce^{3+}, giving the active site a bifunctional character: Fe^{3+} is the acid site while Ce^{3+} is the basic site. The copresence of Fe^{3+} and Ce^{3+} is likely, on the basis of the reduction potential of the $Fe^{2+/3+}$ and $Ce^{3+/4+}$ couples. Hirano [56] reported the presence of cerium as CeO_2 but the state of the catalyst was investigated on the used catalyst, not on the working catalyst. In a concerted mechanism close to that suggested by Wu et al. [64], the α-hydrogen of ethylbenzene attacks the acid site of catalyst (Fe^{3+}) while simultaneously the β-hydrogen attacks the basic

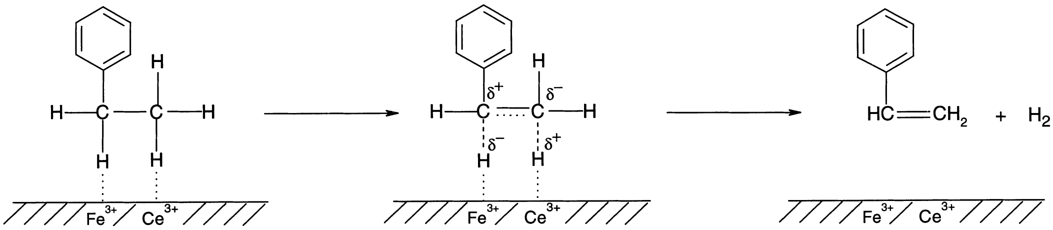


Fig. 11. A schematic representation of a concerted mechanism for the dehydrogenation of ethylbenzene catalyzed by Fe and Ce containing catalysts.

site (Ce^{3+}), as shown in Fig. 11. The positive charge on the α-carbon in the transition state could be stabilized by the aromatic ring.

Recently other studies characterizing the promoter action of cerium oxide have been published. A Mössbauer study [65] has shown that the incorporation of CeO_2 into the K–Fe system decreases the hyperfine magnetic fields of Fe^{3+} ions owing to the presence of Ce^{4+} ions in the neighborhood. Yixiang et al. [66], on the basis of XPS, TPR and X-ray diffraction studies, maintained that the interaction between CeO_2 and Fe_2O_3 results in the shift of the negative charge from Fe to Ce and enhances the antireduction ability of Fe_2O_3.

CeO_2 is also used as a component in new catalyst formulations for the oxidative dehydrogenation of paraffins and EB. Hagemeyer et al. [67] claim a redox process involving the dehydrogenation of ethylbenzene by contact with a catalyst containing a reducible metal oxide (Bi_2O_3, CeO_2) and Cr_2O_3 in the absence of oxygen and simultaneous reduction of the catalyst, followed by oxidation of reduced catalyst with an oxidizing agent.

Overall, it was found that cerium oxide has a positive effect on the nature of the sites. It enhances their stability, by hindering the reducibility of Fe^{3+} to Fe_3O_4, and improves their activity polarizing the Fe–O bond. Moreover if we consider the reduction potential of the Ce^{3+}/Ce^{4+} redox couple, cerium oxide may play an active role in the redox cycle involved in the dehydrogenation process. As cerium oxide is becoming one of the main promoters in industrial dehydrogenation catalysts for the production of styrene, it would be worthwhile focusing attention on understanding the chemistry, both at the preparation stage and during reaction, in which cerium oxide is involved.

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