Catalysis Science & Technology

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/catalysis

CREATED USING THE RSC REPORT TEMPLATE (VER. 3.1) - SEE WWW.RSC.ORG/ELECTRONICFILES FOR DETAILS

3 Multipurpose composite $MnCeO_x$ catalysts for environmental applications

Francesco Arena

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

The pressing need to preserve the state of the environment and of natural resources imposes a global technological effort aimed at turning the current "money-making" industrial policies into a *sustainable development* pattern. This *green revolution* entails a big scientific effort for developing handy and economic technologies for decontamination of gas and liquid wastes, improving the quality of air and water, clean industrial manufacturing, and renewable energy supply. In this context the composite $MnCeO_x$ system represents a viable alternative to highly-cost noble metals for a variety of environmental catalytic applications like the detoxification treatment of industrial wastewater; the abatement of pollutants in gas exhausts; and bio-fuel and fine-chemicals synthesis manufacture.

1 Introduction

Forced by the unprecedented population growth and economic development in place, new efficient solutions are required to minimize the impact of human activities on the state of the environment and natural resources [1]. Beside to an efficient use of energy, water, and raw materials, the accomplishment of a true *sustainable development* pattern relies on the easy accessibility of environmental safeguard and remediation processes, *Green Chemistry* synthesis technologies, and renewable energy supply, free of carbon dioxide and, more generally, of noxious emissions [1]. Despite many environmental safeguard catalytic technologies are already available; a widespread use of costly noble-metal catalysts negatively affects their economics on small and large scale. Indeed, almost all the pollutants abatement processes, both in gas and liquid phases, drive total oxidation reactions in presence of noble-metal catalysts [2] that, beside to high costs, have serious stability problems because of various deactivation phenomena harnessing their lifetime like fouling, coking, sintering, and poisoning. Hence, most of the attempts to improve the efficiency and accessibility of *environmental remediation* and *Green Chemistry* processes direct the attention onto catalyst formulations including abundant and low-costly *transition* and *rare-earth* metal oxides instead of noble-metals. Although a high variability of targets and operating conditions hinders the assessment of general requirements of oxide-based environmental catalysts; high mobility and availability of oxygen species due to easy surface electron-transfer processes are essential to drive the mineralization of organic compounds [2], while abundance and reactivity of the surface hydroxyl population are further key-features shaping the catalytic functionality of oxide systems [3]. Then, easy redox activity under mild conditions, surface amphoteric behaviour, promoting both adsorption and acid-base catalytic functionality, and good chemical stability render the $MnCeO_x$ composite catalyst a suitable alternative to supported noble-metals for environmental applications in both

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

liquid [4-26] and gas phase [27-55]. Indeed, after the pioneering work of Imamura *et al.* who first synthesized by the co-precipitation method MnO_x-CeO_2 catalysts for the wet air oxidation (CWAO) of ammonia [4], many attempts to improve their reactivity pattern were made by the design of new synthesis routes promoting the interaction strength of the oxide phases [15-17,22,23,35,40,49,50,56-61]. In fact, the co-precipitation technique generally leads to a mixture of "bulky" oxide particles in a weak interaction" because of very different precipitation kinetics of the cationic precursors; while in addition to much larger surface area, synergistic effects at atomic/molecular scale confer to *nanostructured* systems very peculiar physico-chemical properties that can strongly promote the redox and acid-base catalytic functionalities [62]. Therefore, the described synthesis routes adopted different strategies to promote a quasi-molecular dispersion of the oxide phases like the "spatial confinement" effect (*nanocasting*) [13,16,17], the simultaneous "redox-precipitation" of the oxide phases (*redox-precipitation*) [15,25,35,56-61] and the "surfactant-assisted" co-precipitation [22,36].

1.1 Advances on Synthesis Routes

In 2007 Abecassis-Wolfovich *et al.* described a method of preparation of *nanocasted* $MnCeO_x$ composites by "confinement" of metal oxide precursors into the pores of mesostructured, high surface area, silica matrices (SBA-15, MCM-41) [13,16]. A water-methanol solution of Mn(II) and Ce (III) ions is mixed with acetic acid, the SBA-15 matrix, and propylene oxide; the solid is separated by filtration and left under saturated pressure of methanol for intrapore gelation, dried under vacuum and further calcined in air (350-500-700°C). The composite $MnCeO_x$ catalyst, obtained by dissolution of the silica scaffold in NaOH solution, consists of crystalline nanodomains (d, 2-3 nm) of Mn_2O_3 and CeO_2 phases, with surface area of 300 m^2/g and a high CWAO performance toward 2,4,6-trichlorophenol [13] and aniline [17]. Likewise, Alarco and Talbot exploited the *confinement effect* using carbon black as scaffold and an anionic surfactant, to attain *nanosized* $MnCeO_x$ composites active in the detoxification of Bayer liquors [22]. While a surfactant-assisted co-precipitation leading to high surface area MnO_x-CeO_2 catalysts (160-240 m^2/g) has been recently proposed by Zou *et al.* for the total oxidation of CO and C_3H_8 [36].
Meanwhile Arena and coworkers synthesised *nanostructured* $MnCeO_x$ catalysts by an alternative procedure involving redox reactions (*redox-precipitation*) between $KMnO_4$ and Ce(III)-Mn(II) precursors [15,25,57,58]

$$\begin{cases} MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 \Downarrow + 4HO^- & (1) \\ Mn^{2+} + 4HO^- \rightarrow MnO_2 \Downarrow + 2e^- + 2H_2O & (2) \\ Ce^{3+} + 4HO^- \rightarrow CeO_2 \Downarrow + e^- + 2H_2O & (3). \end{cases}$$

The above redox reactions between oxidant and reducing precursors forces a simultaneous generation of the oxide phases favouring the aggregation of the "nascent" MnO_x and CeO_2 domains into homogeneously sized ($d \approx 20$ nm) spherical oxide clusters [49,56,57]. Characterised by a completely amorphous architecture resistant to calcination treatments in the range of 100-500°C [63], this structural pattern discloses a peculiar random arrangement of the oxide moieties hindering the development of any "long-range" crystalline order [15,24,25,56-59].

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

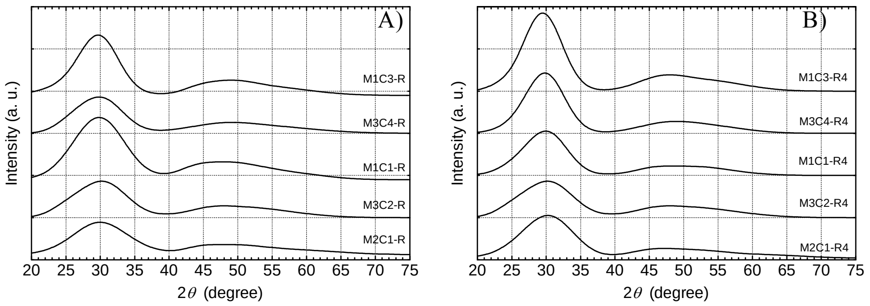

Fig. 1 XRD patterns of dried (A) and calcined (B) $MnCeO_x$ catalysts with different Mn/Ce atomic ratio (*reprinted with permission from ref. 56. Copyright (2007) American Chemical Society*).

These structural characteristics, which are independent of catalyst composition, along with the straight formation of the oxide phases, avoiding the need of calcination treatment for catalyst stabilization [19,56], are evident from the XRD patterns of the dried and calcined samples shown in Fig. 1 [49,56,57,63]. Such an arrangement of the oxide components leads to larger surface area and active phase exposure than both co-precipitation [11] and combustion routes [32], while an unprecedented surface Mn-enrichment is probed by surface atomic Mn/Ce ratios larger than bulk ones in a wide composition range (Fig. 2A) [49,56,57]. In turn, the superior active phase dispersion increases the oxidation state of surface manganese ions [49,64] explaining the much higher reducibility of the redox-precipitated catalyst (Fig. 2B) that reflects in a stronger oxidation activity at low temperature in comparison to co-precipitated one [15,19,34,49]. In addition to a high reproducibility and control of the catalyst structure and texture [49,56,57], the method allows further tuning the physico-chemical and catalytic properties by variation of synthesis parameters like pH [25], thermal treatment or type of the precipitating base [19]. The peculiarity of the redox-precipitation technique has been recently exploited to synthesize a nanostructured bulk MnO_x system very active in the water oxidation process [65].

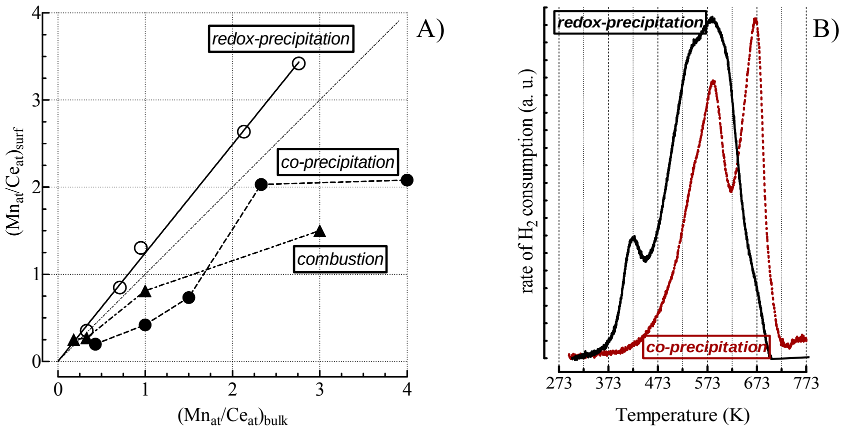

Fig. 2 (A) Surface (XPS) *vs.* bulk composition (XRF) of "redox-precipitated" [*ref. 49*], "co-precipitated" [*ref. 11*], and "combustion" [*ref. 32*] $MnCeO_x$ catalysts. (B) Temperature Programmed Reduction (TPR) profiles of redox-precipitated and co-precipitated (Mn_{at}/Ce_{at}, 1) catalysts (*reprinted with permission from ref. 15. Copyright (2007) American Chemical Society*).

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

This resulted one of the most active and stable manganese oxide-based catalysts reported to date for the water oxidation, although consisting mostly of the generally inactive *pyrolusite* phase [65].
This rush toward an improved catalyst efficiency is mostly pressed by the great practical concern for applications in wastewater and gas streams purification treatments, though recent studies document the suitability of the composite $MnCeO_x$ catalyst also for "green" chemical synthesis [58,59] and biofuels manufacture processes [60,61].

2 Wastewater purification

Since more than two decades the issue of wastewater detoxification has become a topic of major concern pressed by a constantly growing world population and the consequent development of agriculture and industry, already accounting for more than 90% of the global freshwater consumptions [66]. This implies continuous water resources depletion and huge releases to the environment, while ca 1 billion people globally lack access to safe water supplies and ca 2.6 billion are without access to basic sanitation, particularly in the least developed regions of Asia, Central and South America, and Africa [66]. Considering that clean-water accessibility would prevent almost one-tenth of diseases worldwide, improvement of the quality of drinking water and reduction of water contamination are very challenging issues worthy of ca $57 billion global business in 2011, increasing at a 10.4% annual growth rate to exceed $93 billion in 2016 [67].
In addition to the consolidate biological treatment, alternative wastewater purification technologies like adsorption, advanced oxidation (AOP's), and combustion processes are suitable only for small-scale applications because of high costs and complexity [5,6,68-70]. Then operational versatility and good efficiency in the abatement of various industrial pollutants press a big scientific and technological concern on heterogeneous CWAO processes, though the main drawback still remains the lack of cheap, robust and efficient oxide-based catalysts [68-70]. In this context, the $MnCeO_x$ system shows a performance even better than homogeneous Cu^{2+} [5,6,21,24] and noble-metal catalysts [7,24] in the CWAO of several polluting substrates. However, assuming the same *free-radical* path of homogeneous systems, the role of the $MnCeO_x$ catalyst was related to a promoting effect on the process of radicals generation arguing thus a *surface-assisted* heterogeneous-homogeneous mechanism [4-6,21,68-70]. Whereas, forthcoming studies of the CWAO of phenol highlighted a fundamental role of surface adsorption on the reactivity pattern of the $MnCeO_x$ catalysts inferring, rather, the occurrence of a typical Langmuir-Hinshelwood (L-H) mechanism [8-15,24,26]. In fact kinetic and mechanistic evidences in the homogeneous and heterogeneous CWAO of phenol indicated the occurrence of different reaction paths [21] fixed by very different phenol-TOC (total organic carbon) conversion relationships, shown in Fig. 3 [24]. This documents the high selectivity of the heterogeneous $MnCeO_x$ and Pt/CeO_2 catalysts, yielding a contemporary abatement of phenol and TOC by *surface adsorption* with minor release of by-products, while the exponential trend of the TOC-phenol conversion of the homogeneous systems stresses the unselective behavior pattern and the active role of reaction intermediates on the radical-chain propagation of the *autocatalytic free-radical path* [21,24].

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

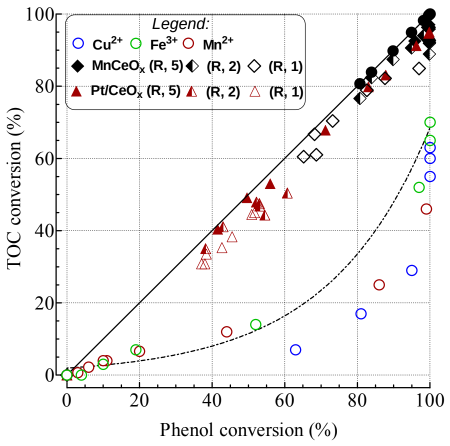

Fig. 3 TOC-phenol conversion relationships (150°C) for homogeneous (Cu^{2+}, Fe^{3+}, Mn^{2+}) and heterogeneous Pt/CeO_2 and $MnCeO_x$ catalysts at various catalyst-to-phenol weight ratios (R) (*reprinted from ref. 24, Copyright (2012), with permission from Elsevier*).

Hence, despite a comparatively lower mineralization rate fixes the surface oxidation of adsorbed C-species as the *rate determining step* (*r.d.s.*) of the heterogeneous CWAO process [7-15,19-21], on the whole the $MnCeO_x$ catalyst ensures a much better conversion-selectivity pattern than homogeneous catalysts [4,21,23,24,68-70]. In fact, at the end of nineties Larachi's group carried out a systematic research activity on the CWAO of phenol by co-precipitated MnO_x-CeO_2 catalysts [7-11], finding out that the composite Mn/Ce (7/3) oxide exhibits a better performance than 1% Pt/Al_2O_3 catalyst in the range of 80-130°C [7]. Despite a much greater efficiency in the removal of substrate and TOC, a moderate selectivity toward mineralization of the adsorbed species into CO_2 and H_2O was found to be the major drawback determining the formation of deactivating carbonaceous deposits [7-11]. To improve the mineralization efficiency, reducing at the same time the accumulation of C-deposits, they explored the effects of Pt and/or Ag promoters, both ensuring an improved mineralization selectivity and maintenance of higher activity at very mild (110°C) conditions, which was ascribed to a marked improvement of the catalyst reducibility [8]. Later they claimed that K-doping enhances to much higher extent the resistance to fouling of the $MnCeO_x$ catalyst (Mn_{at}/Ce_{at}, 1/1) [9,10], although it retains a similar reduction behavior as the non-promoted catalyst [10].

Abecassis-Wolfovich *et al.* reported similar results for a co-precipitated $MnCeO_x$ catalyst in terms of phenol adsorption capacity and deactivation pattern (80-130°C), stressing a minor influence of K, Cs, Pt, and Ru promoters thereon [12]. However, they found that an oxidative treatment at $T<300$°C restored the activity that kept unchanged during four reaction cycles; then, exploiting the favorable adsorption-oxidation characteristics of the $MnCeO_x$ system, they proposed a cyclic adsorption-regeneration process for the treatment of phenol-containing waste streams [12].

A typical co-precipitated $MnCeO_x$ catalyst shows also a better activity than 5% Pt/Al_2O_3 in the CWAO of lactose (170°C), though the addition of Pt renders the system more selective toward mineralization, with lower production of side products [18].

Catalysis Science & Technology Accepted Manuscript

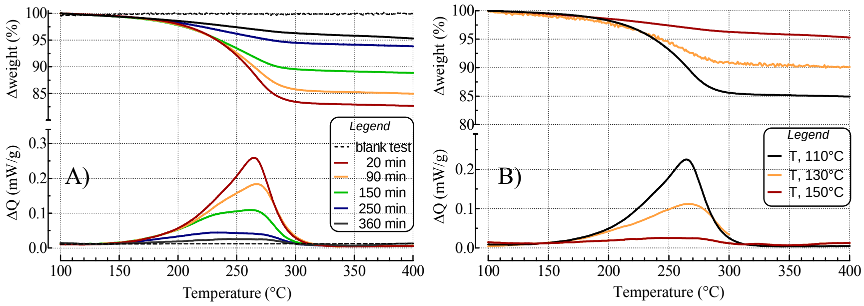

Fig. 4 TGA-DSC data of the "used" catalyst samples in the CWAO of phenol at 150°C after different reaction time (A) and at different temperature (110-150°C) after 6h of reaction time (B) (*adapted from ref. 26, Copyright (2014), with permission from Elsevier*).

Arguing the potential for catalyst improvement by increasing the "amount of metal and oxygen ions at the surface, bulk density, surface area, interface, and redox ability", Abecassis-Wolfovich *et al.* devised the *nanocasting* strategy to enhance the efficiency of the $MnCeO_x$ composite [13,16,17]. Despite a conversion rate of the 2,4,6,-trichlorophenol (120°C) similar to a reference co-precipitated system, the *nanocasted* catalyst attains a TOC conversion of 94% in comparison to only 14% of the latter one [13]. The same is efficient in the CWAO of aniline (100-140°C) though a relevant Mn leaching due to the complexation ability of the substrate at basic pH, which is suppressed by acidification of the reacting solution [17].

Arena *et al.* earlier carried out systematic studies on the effects of the Mn/Ce ratio (3/4-1/1), calcination temperature (400-1000°C), K and Pd-doping on the structure and redox properties of co-precipitated catalysts, providing evidence of the strong relationship between physico-chemical features and activity in the CWAO of phenol (100-110°C) [14,15]. In particular, a direct relationship between reducibility and extent of phenol mineralization, and the occurrence of the catalyst reduction and adsorbed-phenol oxidation in a same temperature window confirmed that the mineralization activity of $MnCeO_x$ catalysts depends on the "surface oxygen mobility" [15]. Supported by TGA-DSC characterization data of "fresh" and "used" catalysts, documenting the ongoing mineralization of the adsorbed substrate with time and temperature (Fig. 4), all these evidences match the occurrence of a typical heterogeneous L-H path with surface oxidation as *r.d.s.* [14,15,24,26]. Hence, high catalyst *surface area* and *reducibility* were fixed as main targets of catalyst design for improving adsorption (conversion) and mineralization (selectivity) functionality, respectively; the latter is also responsible of undesired side reactions leading to *intermediates release* and *C-deposits* buildup (Fig. 5) [8-15,19,21,24,26].

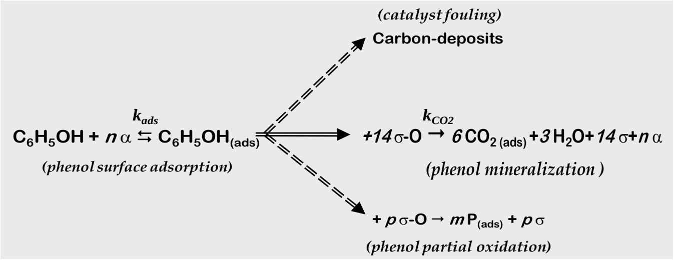

Fig. 5 Simplified reaction mechanism of the heterogeneous CWAO of phenol (*reprinted from ref. 21, Copyright (2010), with permission from Elsevier*).

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

Then, a typical redox-precipitated system shows a CWAO performance better than co-precipitated [15,19,25] and 5% Pt/CeO_2 [24] catalysts in terms of adsorption capacity, TOC removal and kinetics of phenol conversion and mineralization (Fig. 5) [25,26]. In addition, a "model" redox-precipitated catalyst (Mn_{at}/Ce_{at}) shows a good activity in the CWAO of refractory C1-C2 organic acids [26], generally found as residual reaction intermediates of the oxidative abatement of heavier organic compounds [4-15,19,21,26,68-70]. Despite the different adsorption mechanism of acidic substrates depending on electrostatic interactions with surface acidic sites (E_{ads}, 81±5 kJ/mol), at variance of the apolar phenol molecule whose small energetic barrier (E_{ads}, 16±4 kJ/mol) has been related to physical adsorption, the $MnCeO_x$ catalyst drives the abatement of formic and acetic acids by an analogous L-H mechanism, with a higher efficiency than supported noble-metals under more severe conditions [26].

Zheng also documented the efficiency of a co-precipitated MnCe oxide catalyst in the CWAO of a pharmaceutical wastewater (220°C), attaining an activity higher than a homogeneous Cu salt with a 94% COD removal and without appreciable loss in activity [23]. Moreover, a recent patent application claims that *surfactant-assisted* co-precipitated catalysts are active in the CWAO of Bayer liquors [22], while redox-precipitated catalysts have been recently employed also in the CWAO of p-cumaric acid and oil-mill wastewater [71].

Finally, another remarkable instance of application to the wastewater treatment relies in the use of a co-precipitated $MnCeO_x$ catalyst for improving the efficiency of ozonation of phenolic acids; for a catalyst load of 10 g/L it was observed a strong promoting effect on the process efficiency, consisting in a marked reduction of time for the complete removal of noxious compounds and an extent of TOC removal (74%) much higher than single ozonation (24%) [20].

3 Gas-exhausts treatment

In addition to wastewater treatments, $MnCeO_x$ catalysts have been also successfully applied in a variety of environmental gas-phase processes, included the oxidative abatement of VOC and CO, soots, and Hg vapors, and the selective catalytic reduction of NO_x (SCR). However, structural stabilizers or chemical promoters are frequently used to improve activity, selectivity, and/or stability.

For instance, Tang *et al.* combined the intrinsic oxidation strength of the composite MnO_x-CeO_2 with the superior oxygen-activation functionality of Ag [30] and Pt [31], obtaining very active catalysts in the oxidative abatement of formaldehyde for indoor applications. From a systematic study of catalyst composition they found an optimum Mn/Ce atomic ratio of one ensuring the largest surface exposure, the easiest reducibility and the highest HCHO oxidation activity [31]. They ascribed the positive influence of ceria to structural and electronic effects, although a surface activity rising monotonically with the Mn/Ce ratio denoted minor changes in the intrinsic functionality of the active MnO_x phase [31]. The addition of Ag enhances considerably the reactivity of the $MnCeO_x$ system at low temperature (50-80°C), though the prevalent effect of the promoter is evident from the higher reactivity of the Ag/MnO_x system [30]. Moreover, a Pt/MnO_x-CeO_2 catalyst shows a much better activity driving the complete conversion of HCHO to CO_2 at 25°C under very low contact time, and with high stability, although the effect is related to "Cl-free" Pt precursors, avoiding the incorporation of Cl ions onto the catalyst structure [31].

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

Unpromoted MnO_x-CeO_2 catalysts were used in the oxidative abatement of volatile organic compounds (VOC) like ethanol, ethyl acetate, and toluene [32]. The synthesis by the combustion method led to low surface area (38-50 m^2/g) catalysts, with crystalline oxide phases and a surface Mn availability comparable with that of co-precipitated systems (Fig. 2A); an optimum Mn/Ce atomic ratio of one ensures the best activity allowing a full conversion of all the substrates between 170 (ethanol) and 250°C (toluene, ethyl acetate) [32]. Liao *et al.* found a comparable total toluene oxidation activity using a nanorod-structured $Mn_{0.85}Ce_{0.15}O_x$ sample obtained by a hydrothermal synthesis route, pointing also out direct relationships between the oxidation activity and the mobility of lattice oxygen [48]. Li *et al.* showed that high surface area (180-200 m^2/g) co-precipitated $MnCeO_x$ catalysts exhibit a higher activity in the oxidative abatement of ethyl acetate, with a complete conversion being recorded at 200°C; despite a surface area decrease, zirconia addition ($Mn_{0.4}Ce_{0.45}Zr_{0.15}O_x$) improves activity and thermal stability of the system [37]. Dai *et al.* addressed the effect of La addition on the chlorobenzene catalytic combustion activity of $MnCeO_x$ catalysts prepared via a complexation method [45]. Ascribing the high reactivity of the system to the formation of a $MnCeO_x$ solid solution, they found that La enhances dispersion, activity, and stability favoring the full combustion of chlorobenzene at 200°C and stable operations during 16 hours at 350°C.

According to the finding that higher accessibility and oxidation state enhance the redox activity of surface Mn sites, promoting activity and stability in the oxidation of CO (20-150°C) [34,49], redox-precipitated MnO_x-CeO_2 catalysts (Mn_{at}/Ce_{at}, 1-2) were found to be fairly more active than co-precipitated ones also in the oxidative abatement of o-xylene [35]. On the other hand, Zou *et al.* prepared a series of high surface area mesoporous MnO_x-CeO_2 catalysts by a *surfactant-assisted precipitation* method, finding that a Mn/Ce atomic ratio close to 1 (4/6) ensures the best surface area (215 m^2/g), active phase availability, and redox properties, resulting in the best catalytic activity for both CO and C_3H_8 oxidation [36]. The addition of a small amount of Pd greatly enhances the CO oxidation activity due to the acceleration of oxygen activation and transfer via spillover, while the negligible effects on propane oxidation were ascribed to a different reaction mechanism [36].

Using an alumina support, a recent study reports a significant improvement in the reactivity of the $MnCeO_x$ system for NO decomposition, CO oxidation and CO+NO interaction, as result of better dispersion and lower average oxidation state [54]. Likewise Lin *et al.* found that the introduction of the alumina support degrades the soot oxidation activity of the fresh catalyst, while it helps maintaining higher surface area and MnO_x dispersion than unsupported MnO_x-CeO_2 mixed oxide after aging at 800°C, improving NO-to-NO_2 and NO_2-soot oxidation activity below 350°C [55].

This preludes to another major environmental application of $MnCeO_x$ catalysts that is the reductive abatement of NO_x, major source of air pollution causing photo-chemical smog, acid rains, ozone depletion and greenhouse effect [27-29,39-42,50-53]. The abatement of NO_x from stationary sources is currently carried out upstream of the desulfurization process by selective reduction with ammonia (SCR) at 300-400°C using V_2O_5/TiO_2 catalysts, while hydrocarbons and CO serve as reductants in automotive converters [43]. However, the discovery of catalysts active below 200°C (LT-SCR) would allow a major technological breakthrough with location of the SCR unit downstream of desulfurizer and electrostatic precipitator to avoid re-heating of flue gas and catalyst dust deposition [27,28].

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

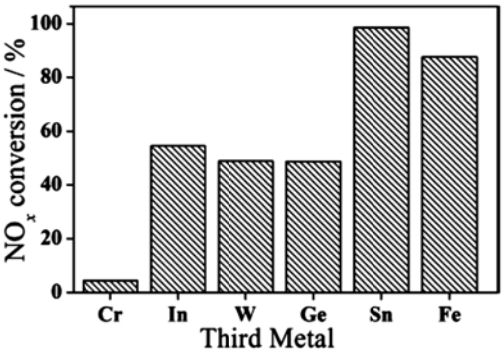

Fig. 6 NO_x conversion at 80°C on MnO_x−CeO_2 catalysts modified by different metal oxide promoters (*reprinted with permission from ref. 53. Copyright (2013) American Chemical Society*).

The peculiar adsorption and redox characteristics also account for the high LT-SCR activity of MnO_x-CeO_2 systems. Indeed, Qi and Tang first investigated the influence of the preparation method finding an optimum composition for manganese molar fraction of 0.4 and a higher LT-SCR activity of the catalyst prepared via the citric acid method rather than co-precipitation or impregnation [27]. Paralleling the development of surface area, the best catalyst gives a full NO conversion at T>120°C and high space velocity with negligible effects of the H_2O-SO_2 co-feeding [27]. In agreement with a non-competitive adsorption of NH_3 and NO_x species [29], 0^{th}- and 1^{st}- kinetic orders were taken as evidences of an Eley-Rideal (E-R) path involving adsorbed ammonia and gas-phase NO, respectively [27]. Further, studying the effects of various promoters on the reactivity of the co-precipitated MnO_x-CeO_2 system the same authors found that the addition of Fe and Zr increases the NO conversion activity and the N_2 selectivity without N_2O formation below 150°C, while Pr and Cu have negative effects on activity or N_2 selectivity respectively [28]. Adopting a surfactant-template preparation method Liu *et al.* recorded a better activity in comparison to co-precipitated catalysts that was related to higher surface area and better MnO_x dispersion [51]. In particular, Mn/Ce atomic ratios higher than 0.5 ensure nearly 100% NO_x conversion in the range of 100-200°C, while surfactant-template catalysts also show a better tolerance to H_2O-SO_2 species than co-precipitated one [51]. After documenting a positive influence of Sn-addition on activity, selectivity, and SO_2-resistance of the MnO_x-CeO_2 catalyst (80-230°C) [41], Chang *et al.* compared the effects of various promoters (i.e., Cr, In, W, Ge, Sn, Fe), confirming that the addition of Sn leads to the highest activity increase, while the Cr-modified catalyst showed nearly no activity (Fig. 6) [53]. Attributing the promoting effect of Sn to a higher surface acidity favoring ammonia adsorption, they report an optimum formulation including Sn, Mn, and Ce in an atomic ratio of 1/4/5. Recent papers claim significant catalyst improvement also by the addition of structural promoters like carbon nanotubes (CNTs) used to enhance the dispersion and the LT-SCR (100-200°C) activity of $MnCeO_x$ catalysts [50,52]. The positive effect of carriers on the active phase dispersion explains the excellent activity recorded also using an activated-carbon-honeycomb as support [42], while Fan *et al.* prepared TiO_2/CNTs supported $MnCeO_x$ catalysts very active in a reactor configuration similar to a real SCR situation (120-250°C) [39].

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

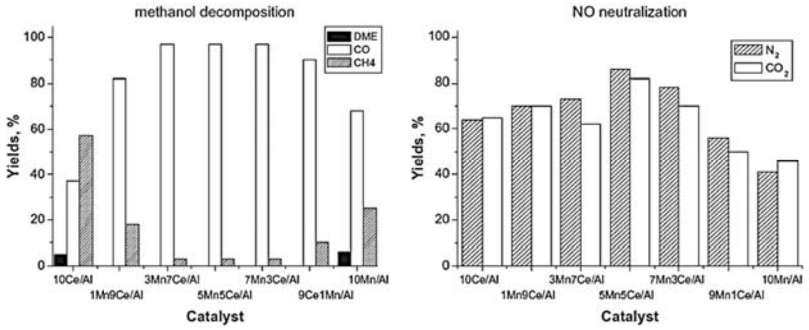

Fig. 7 Activity of the alumina supported MnO_x-CeO_2 catalysts at 350°C in the decomposition of methanol (left) and reduction of NO with CO (right) in dependence of the Mn/Ce atomic ratio (*reprinted from ref. 43, Copyright (2013), with permission from Elsevier*).

Spassova *et al.* synthesized alumina-supported $MnCeO_x$ (10%) catalysts for the SCR of NO with methanol, as a method for removing the NO_x from the automotive gas-exhausts; an optimum Mn/Ce atomic ratio of ca 1 ensures the highest activity in both methanol decomposition and NO SCR reactions above 350°C (Fig. 7), temperatures of the exhausted gases from vehicles and some stationary stations [43]. On the other hand, Hong *et al.* report that BaO/$MnCeO_x$ catalysts with a Mn/Ce atomic ratio of 0.3 are active in the direct decomposition of NO to N_2 in the range of 600-800°C [38]. The formation of a Ce-Mn(x) solid solution by incorporation of Mn^{2+} ions into the fluorite lattice leads to an increase in the concentration of oxygen vacancies, enhancing the NO decomposition functionality of the system. The limited amount of Mn^{2+} cations that can dissolve into the cerianite structure, substituting Ce^{4+} ions and leading to the formation of structural O-vacancies in the host CeO_2 lattice [72], allows the amount of oxygen vacancies decreasing with the Mn loading explaining the highest activity of the BaO/$Mn_{0.25}Ce_{0.75}O_x$ system [38].

In addition to VOC and NO_x, mercury emissions from coal-fired boilers constitute a very serious environmental threat because of persistence, long-range mobility in the atmosphere, bio-accumulation in aquatic ecosystems and neurotoxic effect on human health [46,47]. However, to facilitate its removal from flue gases in scrubbers a preliminary (catalytic) oxidation step is needed to convert it into water-soluble species. Then, Li *et al.* investigated the Hg oxidation activity of a TiO_2 supported MnO_x-CeO_2 catalyst with Mn/Ce atomic ratio of 0.4 and MnO_2-CeO_2/TiO_2 mass ratio of 1 [46,47]; under flue gas and SCR flue gas conditions the catalyst showed a good activity increasing in the range of 120-250°C, but decreasing drastically at 300°C due to significant Hg desorption [47]. This excellent performance has been attributed to the high concentration of Mn^{4+} sites and the presence of Ce^{3+} driving a surface L-H reaction path between adsorbed Hg and reactive oxygen species [47], also explaining the influence of the various flue gas components on activity [46]. In particular, HCl acts as a promoter favoring the Hg^0 oxidation by its complexation ability, while the competitive adsorption explains the inhibition of SO_2, NO and H_2O on Hg oxidation kinetics (Fig. 8) [46]. Moreover, even if ammonia reduces the oxidation activity competing with Hg for the active sites and/or consuming the surface oxygen species responsible for the Hg oxidation, a full recovery in activity has been observed after stopping the ammonia feed [46].

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

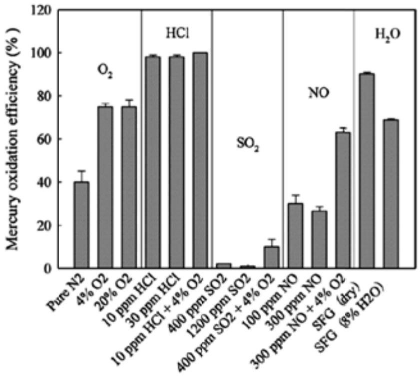

Fig. 8 Effect of individual flue gas components on Hg oxidation at 200°C (*reprinted from ref. 47, Copyright (2012), with permission from Elsevier*).

4 Scouting applications in Biofuels and Fine Chemicals syntheses

Further emerging applications of $MnCeO_x$ catalysts concern the manufacture of biofuels [60,61] and the *green* synthesis of fine chemicals [58,59]; indeed, because of their enhanced acid-base and redox functionalities, redox-precipitated $MnCeO_x$ catalysts are quite active under mild reaction conditions in the transesterification of triacylglycerides to fatty methylesters (biodiesel) [60,61] and the selective oxidation of aromatic alcohols with molecular oxygen [58,59], respectively.

Comparing the reactivity of redox-precipitated $MnCeO_x$ samples with that of various solid acid catalysts in the transesterification reaction of sunflower oil with methanol (65-200°C), Cannilla *et al.* found that the former are considerably more active, especially at temperatures lower than 120°C. In fact, methylesters yields higher than 90% were obtained operating at 140°C and at low catalyst/oil mass ratio (1/100) without any appreciable catalyst deactivation phenomena [60]. Moreover, a specific activity rising with the Mn loading (Fig. 9) has been ascribed to the high dispersion of the active MnO_x phase and the incorporation of progressively increasing amounts of K^+ ions enhancing the concentration of medium-strong basic sites, responsible of methanol activation [60,61].

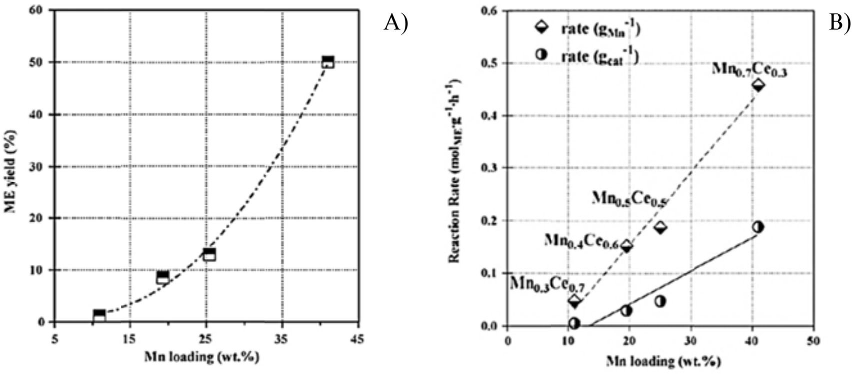

Fig. 9 (A) Methylesters (ME) yield as a function of Mn loading; (B) Rate of ME formation under kinetic regime (*reprinted from ref. 60, Copyright (2010), with permission from Elsevier*).

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

CREATED USING THE RSC REPORT TEMPLATE (VER. 3.1) - SEE WWW.RSC.ORG/ELECTRONICFILES FOR DETAILS

In fact, forthcoming FTIR spectroscopic evidences of adsorbed methanol revealed that the peculiar reactivity of the $MnCeO_x$ system depends on its surface amphoteric behaviour, as medium-strong basic sites are decisive for the activation of methanol molecule while triacylglycerides molecules are activated on Lewis acid sites, according to a dual-site L-H reaction path [61].

The first example of fine chemicals manufacture by the "green" selective oxidation of aromatic alcohols using $MnCeO_x$ catalysts has been documented by Qinghu *et al.* [58]. They synthesized by the redox-precipitation method a series of $MnCeO_x$ catalysts with different Mn/Ce molar ratios for the selective oxidation of various aromatic alcohols with oxygen to the corresponding aldehydes or ketones, using toluene as solvent; a Mn/Ce ratio of 10 ensures the highest benzyl alcohol oxidation rate, with a conversion of 97% at 100°C after 1h, a total benzaldehyde selectivity (>98%), and without appreciable loss of activity during six reaction runs. An even higher activity was recorded for more "electron-rich" substrates such as the α-methyl benzyl alcohol. Also in this case the authors argued that the key active component for the O_2 activation was the coexistence of multiple high oxidation states of Mn ions (e.g.,+3/+4), while CeO_2 played an important role by increasing surface area, promoting the reduction and the surface oxygen replenishment capacity of the active MnO_x phase [49,58,59].

Recently, Chen *et al.* synthesised crystalline and amorphous $MnCeO_x$ systems by co-precipitation and redox-precipitation methods respectively, which were used as support to produce Pd/$MnCeO_x$ catalysts very active in the *green* selective oxidation of benzyl alcohol in absence of solvent (T, 160°C) [59]. Despite a good accessibility of the Pd active phase and a high surface concentration of Pd^0 explain the high initial reaction rate of the crystalline $MnCeO_x$-supported catalyst, the amorphous $MnCeO_x$ support enhances the catalyst stability due to the "mutual promotion between redox properties and oxygen mobility" [59].

5 Conclusions

A great scientific and technological effort is in place worldwide for accomplishing a green industrial revolution fulfilling the guidelines of a Sustainable Development pattern. In this context Catalysis is destined to play a pivotal role by providing low-costly *environmental safeguard-remediation* processes and *clean manufacture* technologies based on catalyst formulations alternative to noble-metal systems.

High redox activity, surface amphoteric behaviour, and good chemical stability render the $MnCeO_x$ composite catalyst a suitable substitute of supported noble-metals for environmental applications in both liquid and gas phase. Documenting the most recent and important applications of the $MnCeO_x$ composites in a variety of environmental-related processes, this perspective would offer a systematic background for further advances toward the development of low-costly, multipurpose, and environmental-friendly catalysts.

References

[a] *Dept. of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, Viale F. Stagno D'Alcontres 31, 98166 S. Agata, Messina, Italy. Fax: +39 090 391518; Tel: +39 090 393134; E-mail: Francesco.Arena@unime.it*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 I.S. Yunus Harwin, A. Kurniawan, D. Adityawarman, A. Indarto, Environ. Technol. Rev., 2012, 1, 136.
2 A. Bielański, J. Haber, in: *Oxygen in Catalysis*, Marcel Dekker, Inc., N.Y., 1991.
3 G. Busca, *Physical Chemistry Chemical Physics*, 1999, **1**, 723.
4 S. Imamura, A. Doi, N.S. Ishida, *Ind. Eng. Chem. Prod. Res. Dev.*, 1985, **24**, 75.
5 Imamura, S., in *Catalysis by Ceria and Related Materials* (A. Trovarelli, Ed.), Imperial College Press, London, UK, 2002, **14**, 431.
6 Y.I. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res., 1998, **37**, 309.
7 S. Hamoudi, F. Larachi, A. Sayari, J. Catal. 1998, **177**, 247.
8 S. Hamoudi, A. Sayari, K. Belkacemi, L. Bonneviot, F. Larachi, Catal. Today, 2000, **62**, 379.
9 S.T. Hussain, A. Sayari, F. Larachi, J. Catal., 2001, **201**, 153.
10 S.T. Hussain, A. Sayari, F. Larachi, Appl. Catal. B: Environ., 2001, **34**, 1.
11 H. Chen, A. Sayari, A. Adnot, F. Larachi, Appl. Catal. B: Environ., 2001, **32**, 195.
12 M. Abecassis-Wolfovich, M.V. Landau, A. Brenner, M. Herskowitz, Ind. Eng, Chem. Res., 2004, **43**, 5089.
13 M. Abecassis-Wolfovich, M.V. Landau, A. Brenner, M. Herskowitz, J. Catal., 2007, **247**, 201,
14 F. Arena, A. Parmaliana, G. Triunfio, Stud. Surf. Sci. Catal., 2007, **172**, 489.
15 F. Arena, J. Negro, A. Parmaliana, L. Spadaro, G. Trunfio, Ind. Eng. Chem. Res., 2007, **46**, 6724.
16 M. Landau, M. Herskowitz, M. Abecassis-Wolfovich, “Manganese oxide-cerium oxide composite”, WO 2007069238 (A1), June 2007.
17 R. Levi, M. Milman, M.V. Landau, A. Brenner, M. Herskowits, Environ. Sci. Technol., 2008, **42**, 5165.
18 Y.N. Chia, M.P. Latusek, J.H. Holles, Ind. Eng. Chem. Res., 2008, **47**, 4049.
19 F. Arena, G. Trunfio, J. Negro, L. Spadaro, Appl. Catal. B: Environ., 2008, **85**, 40.
20 R.C. Martins, R.M. Quinta-Rerreira, Appl. Catal. B: Environ., 2009, **90**, 268.
21 F. Arena, C. Italiano, A. Raneri, C. Saja, Appl. Catal. B: Environ., 2010, **99**, 321.
22 J.A. Alarco, P. Cade Talbot, “Removing organic impurities from Bayer process liquors”, WO 2010105305 (A1), Sept. 2010.
23 Y. Zheng, Proceeding of the 2011 International Symposium on Water Resources and Environment Protection 2 (ISWREP2001), 2011, 1316.
24 F. Arena, C. Italiano, L. Spadaro, Appl. Catal. B: Environ., 2012, **115-116**, 336.
25 F. Arena, L. Spadaro, “Nano-structured composite materials based on compositions of manganese and cerium, usable as oxidation catalysts and/or molecular adsorbers”, WO 2012168957 (A1), Dec. 2012.
26 F.Arena, C. Italiano, G. Drago Ferrante, G., Trunfio, L. Spadaro, Appl. Catal. B: Environ., 2014, **144**, 292.
27 G. Qi, R.T. Yang, J. Catal., 2003, **217**, 434.
28 G. Qi, R.T. Yang, R. Chang, Appl. Catal. B: Environ., 2004, **51**, 93.
29 F. Eigemann, M. Maciejewski, A. Baiker, Appl. Catal. B: Environ., 2006, **62**, 311.
30 X. Tang, J. Chen, Y. Li, Y. Li, Y. Xu, W. Shen, Chem. Eng. J., 2006, **118**, 119.
31 X. Tang, J. Chen, X. Huang, Y. Xu, W. Shen., Appl. Catal. B: Environ., 2008, **81**, 115.
32 D. Delimaris, T. Ioannides, Appl. Catal. B: Environ., 2008, **84**, 303. 46.
33 Y. Hanaki, J. Ito, K. Masuda, “Oxidation catalyst composition and PM oxidation catalyst”, WO 2008130010 (A1), Oct. 2008.
34 F. Arena, G. Trunfio, J. Negro, C. Saja, A. Raneri, L. Spadaro, Sud. Surf. Sci. Catal., 2010, **175**, 493.
35 Y. Wu, Y. Zhang, M. Liu, Z. Ma, Catal. Today, 2010, 153, 170.
36 Z.-Q. Zou, M. Meng, Y.-Q. Zha, J. Phys. Chem. C, 2010, **114**, 468.
37 X. Li, J. Wang, C. Liao, H. Cao, Y. Chen, M. Gong, J. Natur. Gas Chem., 2011, **20**, 623.
38 W.-J. Hong, S. Iwamoto, S. Hosokawa, K. Wada, H. Kanai, M. Inooue, J. Catal., 2011, **277**, 208.
39 X. Fan, F. Qiu, H. Yang, W. Tian, T. Hou, X. Zhang, Catal. Comm., 2011, **12**, 1298.
40 A. Princivalle, P. Vernoux, A. Hadjar, C. Guizard “Use of an nox-reducing catalyst system based on a mixed cerium oxide”, WO 2011157964 (A1), Dec. 2011.
41 H. Chang, J. Li, X. Chen, L. Ma, S. Yang, J.W. Schwank, J. Hao, Catal. Comm, 2012, **27**, 54.
42 Y. Wang, C. Ge, L. Zhan, C. Li, W. Qiao, L. Ling, Ind. Eng. Chem. Res., 2012, **51**, 11667.

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript

43 I. Spassova, T. Tsonctcheva, N. Velinchova, M. Khristova, D. Nihtianova, J. Coll. Interface Sci., 2012, **374**, 267.
44 Y. Wu, Y. Zhang, M. Liu, Z. Ma, Catal. Today, 2012, **153**,170.
45 Y. Dai, X. Wang, Q. Dai, D. Li, Appl. Catal. B: Environ., 2012, **111-112**, 141.
46 H. Li, C.-Y. Wu, Y. Li, Y. Zhao, J. Zhang, J. Hazard. Mater., 2012, **243**, 117.
47 H. Li, C.-Y. Wu, Y. Li, J. Zhang, Appl. Catal. B: Environ., 2012, **111-112**, 381.
48 Y. Liao, M. Fu, L. Chen, J. Wu, B. Huang, D. Ye, Catal. Today, 2013, **216**, 220.
49 F. Arena, G. Trunfio, B. Fazio, J. Negro, L. Spadaro, J. Phys. Chem. C, 2009, **113**, 2822.
50 L. Li, W. Lishan, P. Siwei, W. Zhengle, H. Bichun, Chin. J. Catal., 2013, **34**, 1087.
51 Z. Liu, Y. Yi, S. Zhang, T. Zhu, J. Zhu, J. Wang, Catal. Today, 2013, **216**, 76.
52 X. Wang, Y. Zheng, J. Lin, Catal. Comm., 2013, **37**, 96.
53 H. Chang, X. Chen, J. Li, L. Ma, C. Wang, C. Liu, J.W. Schwank, J. Hao, Environ. Sci. Technol., 2013, **47**, 5294.
54 N. Drenchev, I. Spassova, E. Ivanova, M. Khristova, K. Hadjiivanov, Appl. Catal. B: Environ., 2013, **138-139**, 362.
55 F. Lin, X. Wu, S. Liu, D. Weng, Y. Huang, Chem. Eng. J., 2013, **226**, 105.
56 F.Arena, G. Trunfio, J. Negro, B. Fazio, L. Spadaro, Chem. Mater., 2007, **19**, 2269.
57 F. Arena, G. Trunfio, J. Negro, L. Spadaro, Mater. Res. Bull., 2008, **43**, 539.
58 T. Qinghu, W. Chengming, H. Xiaona, Y. Yanhui, Chin. J. Catal., 2009, **30**, 207.
59 Y. Chen, H. Zheng, Z. Guo, C. Zhou, C. Wang, A. Borgna, Y. Yang, J. Catal., 2011, **283**, 34.
60 C. Cannilla, G.Bonura, E. Rombi, F. Arena, F. Frusteri, Appl. Catal. A: General, 2010, 382, 158.
61 C. Cannilla, G. Bonura, F. Arena, E. Rombi, F. Frusteri, Catal. Today, 2012, 195, 32.
62 C. Burda, X.B. Chen, R. Narayanan, M. El-Sayed, Chem. Rev., 2005, 105, 1025.
63 B. Fazio, L. Spadaro, G. Trunfio, J. Negro, F. Arena, J. Raman Spectrosc., 2011, **42**, 1583.
64 F. Arena, T. Torre, C. Raimondo, A. Parmaliana, Phys. Chem. Chem. Phys., 2001, **3**, 1911.
65 M. Fekete, R.K. Hocking, S.L.Y. Chang, C. Italiano, A.F. Patti, F. Arena, L. Spiccia, Energy Environ. Sci., 2013, 6, 2222.
66 Progress on Drinking-Water and Sanitation: 2012 Update, UNICEF & World Health Organization (WHO).
67 J. Wilson, BCC Research Report "Water and Wastewater Treatment Technologies: Global Markets", Report code ENV008B, Feb. 2012.
68 F. Luck, Catal. Today, 1999, 53, 81.
69 S.K. Bhargava, J. Tardio, J. Prasad, K. Foger, D.B. Akolekar, S.C. Grocott, Ind. Eng. Chem. Res., 2006, 45, 1221.
70 G. Busca, S. Berardinelli, C. Resini, L. Arrighi, J. Hazard. Mater., 2008, 160, 265.
71 F. Arena, D. Lombardo, G. Drago Ferrante, C. Italiano, L. Spadaro, G. Trunfio, Desalin. Water Treat., 2013, xx, xx (doi: 10.1080/19443994.2013.867412).
72 D. García Pintos, A. Juan, B. Irigoyen, J. Phys. Chem. C, 2013, **117**, 18063.

This journal is © The Royal Society of Chemistry [year]

Catalysis Science & Technology Accepted Manuscript