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Environmental catalysis for stationary applications

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Abstract

Recent findings in the selective catalytic reduction (SCR) of NO_x by ammonia and in the catalytic combustion (CC) for gas turbines are herein reviewed as major examples of environmental catalysis for stationary applications. Future opportunities for the $DeNO_x$ technology are represented not only by the development of SCR catalysts with optimised morphology, geometry and mechanical properties, but also by the combination of the present technology with selective and effective NH_3 oxidation catalysts. Some mechanistic and kinetic aspect of the SCR reaction are still open; in this respect, dynamic investigation has proven to be a highly informative approach of research.

Although important developments have been recently reported, the catalytic combustion for power application has not reached yet a commercialisation stage and additional tests at the pilot and full scale laboratory and field level have to be done to improve the reliability of the most promising system configurations and to better address the issues still open. The major research opportunities are also outlined. These include the enhancement of the Pd-catalyst activity in CH_4 combustion and the improvement of the dynamic response of Pd on fast temperature rise to reduce risks of runaway as well as the development of system configurations and catalyst designs able to operate with dual fuel combustors.

Keywords: Environmental catalysis; Selective catalytic reduction; Catalytic combustion

1. Introduction

The use of catalytic systems for pollution abatement has grown in the last decades from virtually non-existing to a multi-billion-dollar world-wide business due to the adoption of strict environmental regulations for both mobile and stationary sources.

In the case of stationary sources, the most important application was originally represented by VOC abatement from chemical processing plants and from a wide range of manufacturing processes [1]. These include can coating, automobile painting, semi-conductor manufacture, baking, printing, lithography, paper manufacture, textile manufacture, oil production, plastic production and many others. Catalytic oxidation of VOCs is now a well established technology; it has demonstrated a high level of efficiency at a cost which is competitive with other available technologies, such as thermal incineration, and will continue to play in the future a key role in cleaning up areas with unhealthy air quality. Recent developments in VOC abatement include: the use of adiabatic reactors with periodic flow reversal that allow for autothermal operation even in the case of process streams with low VOC concentration (<1 g/N m^3 corresponding to an adiabatic temperature rise of 10°C) [2], the use of a catalytic combustion unit downstream from a concentrator that is well suited for the abatement of VOC in streams with very high flow rates and very low

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pollutant concentrations [3], and the development of improved catalysts for the purification of waste gases containing chlorinated hydrocarbons [4].

The SCR of NO_x by NH_3 represents another important catalytic process that was introduced in the late 1970s for the control of NO_x emissions in stack gases from thermal power plants and other industrial facilities [5–7]. SCR systems are currently operating in Japan, Europe and Far East for a total capacity of about 150.000 MWe; this technology presently accounts for more than 90–95% of total $DeNO_x$ flue gas treatments in Europe and Japan. Although, the potential market for SCR in the US amounts to a few hundred thousands MWe, still SCR applications in the US are essentially confined to gas turbines (GTs) for a total capacity of slightly more than 5.000 MWe and are primarily located in California. This is because current federal NO_x emission limits are designed to be met essentially by combustion modifications. In addition to the most common power plant applications, the SCR technology has been proved and applied in the treatment of waste gases of industrial and municipal incinerators, of chemical industry (e.g. nitric acid plants, catalytic cracking units), and of glass, steel, and cement industries. The SCR technology is also used for the combined removal of NO_x and SO_x in thermal power plants and industrial boilers and for the abatement of NO_x and dioxins in incinerators. The SCR technology is recognised as the best available technology for NO_x abatement from stationary sources.

Another technology that has attracted much attention in the last decade is adiabatic lean-premixed catalytic combustion for gas turbines application. This novel technology has the potential to achieve ultra low emissions of NO_x, CO and unburned hydrocarbons (UHCs) from natural gas fired turbines without incurring in the capital and operating costs associated with the current practised technology based on steam injection or lean-premixed homogeneous combustion and SCR systems [8–11]. If commercialised, this technology will represent a real breakthrough and would dramatically alter the way industry generates power and abates emissions.

In this review, I will focus on SCR of NO_x by NH_3 and on catalytic combustion for GT applications.

In the first part of the paper, the recent and novel findings of SCR $DeNO_x$ing catalysis for stationary applications will be addressed. These involve: the physico-chemical and catalytic properties of metal oxide based catalysts, and especially of the V_2O_5–WO_3/TiO_2 and V_2O_5–MoO_3/TiO_2 catalysts that are most widely used in the industrial practice; the optimal design of SCR catalyst; the study of the $DeNO_x$ and the SO_2 oxidation reactions under transient conditions for reactor design and control purposes, and for a more demanding approach to the investigation of the mechanism and kinetics of the SCR process.

sIn the second part of the paper, first the different designs of the combustion systems for gas turbines will be presented and the results of pilot tests and field trials with retrofitted machines illustrated. Then, the open research problems in the area will be addressed, including the relevant physico-chemical and catalytic properties of highly active supported PdO and highly stable metal substituted hexaaluminate combustion catalysts, the use of fuels alternative to natural gas, and the use of mathematical models in the design and analysis of the catalytic combustion systems.

At the end of each section, an attempt will be made to identify the opportunities that can be envisaged, respectively, for NO_x removal catalysis from stationary sources, in spite of the fact that SCR appears a consolidated technology, and for catalytic combustion for GT applications, that if commercialised will indeed represent a breakthrough catalytic technology.

2. SCR of NO_x by NH_3

2.1. Relevant catalytic and physico-chemical properties of commercial catalysts

The SCR process is based on the reduction of NO_x with NH_3 into water and nitrogen according to the reaction

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

If SO_2 is present in the combustion gases it can be oxidised to SO_3, over the catalyst

$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3 \qquad (2)$$

Even very small SO_2 conversions to SO_3 are highly undesired because they cause deposition and accumulation of ammonium sulphate salts onto the catalyst (if the temperature of the catalyst is not high enough) and onto the air-pre-heater downstream from the catalytic reactor.

The DeNO$_x$ reaction is operated over commercial metal oxide SCR catalysts made of homogeneous mixtures of titanium dioxide, tungsten oxide (or molybdenum trioxide) and vanadium pentoxide [12–14]. TiO_2 in the anatase form is used as high surface area carrier to support the active components. Vanadia is responsible for the activity of the catalyst in the reduction of NO_x and also for the undesired oxidation of SO_2 to SO_3. Accordingly, the vanadia content is generally kept low and is reduced below 1% (w/w) in high sulphur applications. WO_3 (or MoO_3) is employed in larger amounts (10 and 6% (w/w) for WO_3 and MoO_3, respectively); they act as "chemical" and "structural" promoters by enlarging the temperature window of the SCR reaction, limiting the oxidation of SO_2, and improving the mechanical, structural, and morphological properties of the catalysts. Silico-aluminates and fibreglass are used as ceramic additives to improve the catalyst strength. The commercial SCR catalysts are employed in the form of honeycomb monoliths or plates because of the following main advantages over the packed bed arrangement: (i) lower pressure drop by two or three orders of magnitude, (ii) superior attrition resistance and lower tendency to fly ash plugging, (iii) comparable geometric surface areas per unit volume of catalytic reactor that must be maximised in the DeNO$_x$ process, where the reaction is confined only to a narrow outer shell due to the strong intraporous diffusional limitations.

The most important and critical requirement for commercial catalysts is to combine high activity in the DeNO$_x$ reaction and very low (almost negligible) activity in the oxidation of SO_2 to SO_3. As shown in Fig. 1, the rate constant for the reduction of NO_x by NH_3 depends almost linearly on the vanadia content, while the rate constant for the oxidation of SO_2 increases more than linearly with the loading of vanadia. This is consistent with the identification of the active sites for SO_2 oxidation as dimeric (or polymeric) vanadyl sulphates, in line also with the consolidated picture of the active sites in commercial sulphuric acid catalysts [15], as opposite to the active sites for NO_x reduction that are likely associated with isolated vanadyl species. Accordingly, high dispersion of surface vanadyls must be secured during the impregnation of tungsta–titania powders with the solution of vanadium salts. Indeed, this represents the most critical step in the preparation of SCR catalysts; if this step is not accomplished properly the activity of the catalyst in the SO_2 oxidation may increase up to one order of magnitude. FTIR and laser Raman data (see Fig. 2) have confirmed that monomeric vanadyls and wolframyls and polymeric W_xO_y groups are present in the samples with low vanadia loadings, that are apparently similar from the structural and vibrational point of view to those present on the surface

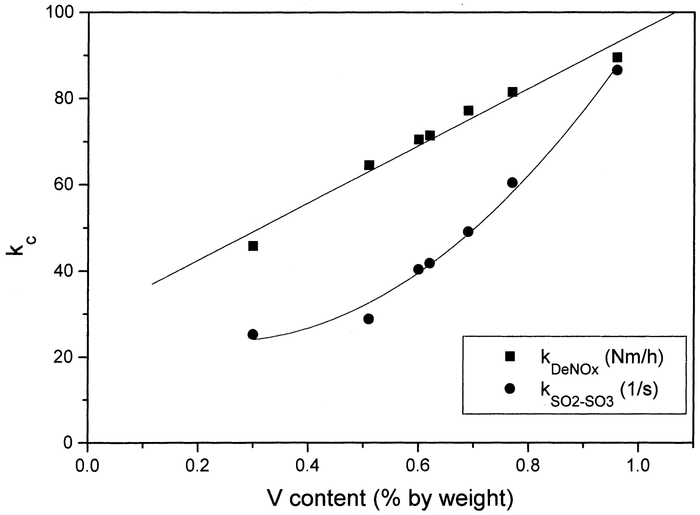

Fig. 1. Dependence of the intrinsic kinetic constants of DeNO$_x$ and SO_2 oxidation reactions on the catalyst vanadium content, $T = 350°C$.

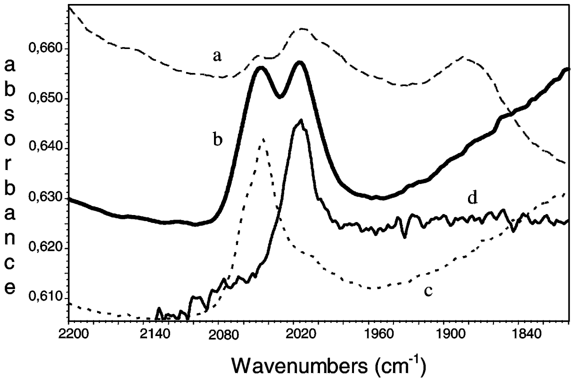

Fig. 2. FTIR spectra of (a) commercial SCR catalyst; (b) a model V_2O_5–WO_3/TiO_2 catalyst (V:W atomic ratio 1:1); (c) a model V_2O_5/TiO_2 catalyst; (d) a model WO_3/TiO_2 catalyst, after outgassing at 673 K.

of the binary oxide systems with comparable metal loadings [16–18]. On increasing the vanadia content polyvanadate species are also formed.

Concerning the steady state reactivity of the commercial SCR catalysts, it was found that the reactivity of the V and/or W oxide species in the V_2O_5–WO_3/TiO_2 ternary catalysts is significantly higher than that calculated from a simple additive model on the basis of the values of the TOFs for V and W in the binary V_2O_5/TiO_2 and WO_3/TiO_2 samples with the same metal oxide loadings [19–21]. This is shown in Fig. 3. TPSR/TPR experiments performed in the presence and in the absence of oxygen indicated that the ternary catalysts can be reduced at lower temperatures, due to the participation of labile oxygen atoms in the reaction, and can be re-oxidised more easily by gaseous oxygen. Accordingly the higher reactivity of the ternary catalysts with respect to the corresponding binary samples can be related to their superior redox properties. This was taken as an indication that a synergism between V and W oxide surface species operates in the ternary catalysts; the synergism has been ascribed to the electronic interaction between V and W and the TiO_2 support which has been evidenced by EPR, FTIR, FT-Raman and UV–Vis diffuse reflectance [16–21]. It has been speculated that W and V oxide centres, although vibrationally and chemically isolated, do interact electronically through the TiO_2 conduction band, due to the semi-conducting nature of titania and the similarity of the d levels of tungsten, vanadium and titanium oxides.

A detailed investigation performed over V_2O_5–MoO_3/TiO_2 (and MoO_3/TiO_2) samples has demonstrated that the same conclusions outlined above for the WO_3 based catalysts also apply to the MoO_3 containing catalysts, the difference being that these materials are more easily reduced [22,23].

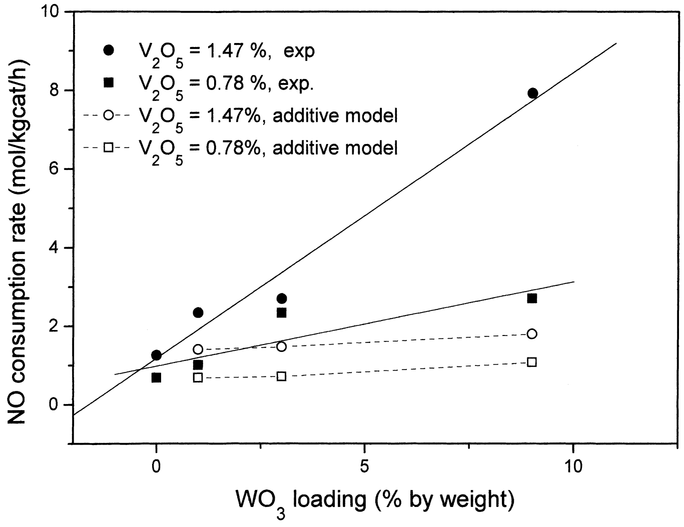

Fig. 3. Comparison between experimental (solid symbols) and calculated (open symbols) values of the rate of NO consumption over ternary catalysts, $T = 600$ K. Calculations refer to a simple additive model which sums up the contributions of the single components to the activity of the ternary catalyst, as estimated on the bases of the activity of binary catalysts and pure titania.

2.2. Importance of interphase and intraparticle limitations

In reality, the performances of the SCR reactor under industrial conditions are strongly influenced by intraparticle and external diffusion. The activity of $DeNO_x$ catalysts is quoted in the technical literature in terms of first order overall activity constant k_{NO} according to the following expression:

$$k_{NO} = -AV \ln(1 - x_{NO}) \qquad (3)$$

where x_{NO} represents the fractional conversion of NO_x and k_{NO} is given by

$$\frac{1}{k_{NO}} = \frac{1}{k_{app}} + \frac{1}{k_{mt}} \qquad (4)$$

where k_{app} is the apparent pseudo first-order rate constant for the surface chemical reaction and incorporates the influence of mass transfer in the catalyst pores, and k_{mt} represents the interphase gas–solid mass transfer coefficient.

The comparison of 1D and multidimensional models of the SCR reactors has proven that the rate of gas–solid mass transfer is affected by the geometry of the monolith channel and by the rate of the $DeNO_x$ reaction at the wall [24]. In the specific case of monoliths with square channels, which is most frequent in SCR applications, however, it has been shown that the latter dependence vanishes and the local Sherwood number can be estimated by the analogy with the Graez–Nusselt problem governing heat transfer in duct under laminar flow conditions with constant wall temperature. The analysis of intraphase mass transfer in SCR reactor in the literature has been based on the adoption of the Wakao–Smith random pore model [25] to describe NO and NH_3 diffusion inside the catalyst wall [26,27]. Solution of differential mass balances for diffusion and reaction in the intraporous region confirmed that the presence of steep internal concentration gradients of NO and NH_3 prevails under industrial conditions, resulting in extremely low effectiveness factors (below 0.1–0.2). Recently, the $DeNO_x$ SCR model has also been extended to incorporate the kinetics of SO_2 oxidation [28,29]. It has been shown that, opposite to the former reaction, the latter one occurs in a chemical regime due to its very low rate. Dedicated experiments and diagnostic calculations have indicated in fact that SO_2 oxidation involves the whole catalyst volume, and have confirmed the absence of external and intraporous gradients of SO_2 concentration. The model has been applied to study the influence of the morphology and of the wall thickness, with specific regard to the possibility of exploiting the observed inhibition of NH_3 on the rate of SO_2 oxidation [30] and the different control regimes for the $DeNO_x$ and SO_2 oxidation reactions in order to minimise the formation of SO_3. Fig. 4 shows that a strong reduction of the rate of SO_2 oxidation is predicted for NH_3/NO feed ration $\alpha > 1$, as expected; however no pore size distribution is able to induce an excess of NH_3 inside the catalyst to inhibit SO_2 oxidation under industrial conditions ($\alpha < 0.9$–0.95), since this is primarily controlled by the stoichiometric constraints. This analysis indicated that the optimal morphology of SCR catalysts consists of a large fraction of macropores to increase the effectiveness factor and that the optimal monolith catalysts have very thin walls (see Fig. 5a and b). These indication offer a challenge to develop innovative SCR catalysts, provided that they are combined with appropriate catalyst mechanical properties, since it is well documented that the crushing strength of the extruded honeycombs decreases markedly both by increasing the macroporosity of the materials and by reducing the catalyst wall thickness.

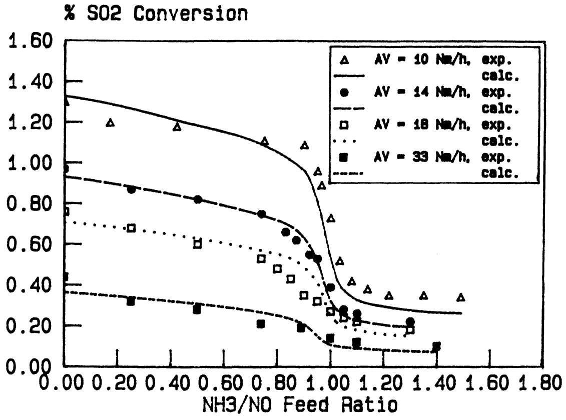

Fig. 4. Experimental and calculated effect of NH_3/NO feed ratio on SO_2 conversion for varying *AV*.

The model of the SCR reactor has also been used to simulate the behaviour of reactors in the presence of non-uniform NH_3/NO feed ratio across the duct. The calculated increments of catalyst volume required

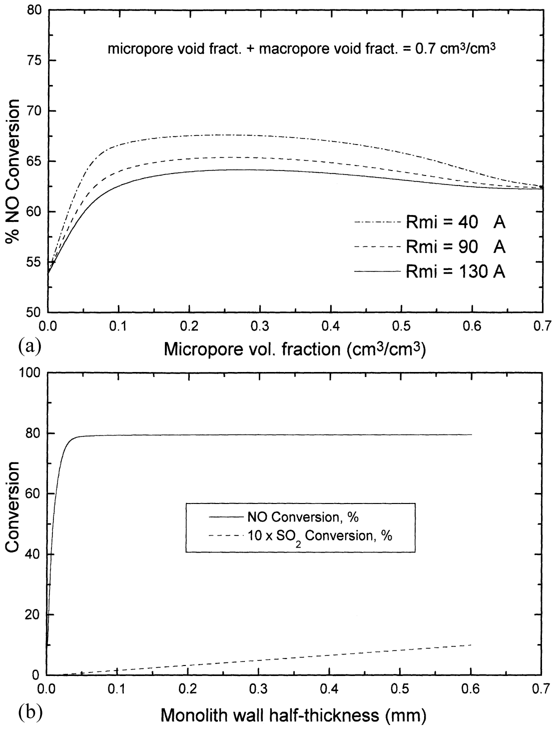

Fig. 5. (a) Effect of catalyst morphological properties on NO conversion, $T = 350°C$. (b) Effect of monolith wall thickness on NO and SO_2 conversion.

to secure NH_3 slip below the design value of 5 ppm increases markedly with the standard deviation σ of the normal distribution of α, and shows an asymptotic behaviour for a growing degree of discretisation of the normal distribution. This clearly indicates the necessity to avoid large stoichiometric deviations. The practical consequence is that the SCR process suffers from a limit in the maximum viable NO_x abatement efficiency. This limit can be overcome if the SCR systems are operated with high NH_3/NO feed ratio and selective NH_3 oxidation catalysts are developed and used to eliminate the NH_3 slip. This would guarantee high NO_x conversions along with low ammonia slips and in addition low SO_2 oxidation levels, due to the inhibiting effect of NH_3 on SO_2 oxidation.

2.3. *Dynamic investigation of SCR–DeNO$_x$ reactors*

SCR–DeNO$_x$ reactors are often involved in transient operations associated, e.g. with start-up, shutdown or load variations. This has stimulated in the last years a growing interest towards the study of the dynamics of SCR reactors [31–35] particularly in view of a possible development of predictive control systems of SCR plants able to avoid pollutants emission peaks during transient conditions. Also, the study of the dynamics of SCR catalysis over powder catalysts and under kinetic regime is highly demanding and in fact it could provide valuable mechanistic and kinetic information. The transient response method was adopted in the dynamic study, by applying perturbations to the reaction system (e.g. step or linear changes in the reactant concentration) and analysing the transient response [36–38]. The adsorption–desorption of the reactants was at first investigated, and then their surface reaction was addressed in the case of NO_x reduction.

The following main information were obtained from the dynamic study:

1. Conditioning of the catalyst is required to obtain significant and reproducible steady-state data both in the reduction of NO_x and in the oxidation of SO_2. Conditioning of the catalyst is associated with the build up of sulphates at the catalyst surface and proceeds until a steady state concentration of sulphates is reached due to the attainment of a dynamic equilibrium between the rate of SO_2 oxidation and SO_3 desorption–readsorption.
2. Formation of sulphates occurs first at or near the vanadyl sites, which explains the enhancement of the reactivity in the DeNO$_x$ reaction during conditioning, and later on at the titania and tungsta surface, which accounts for the longer characteristic times of conditioning for SO_2 oxidation.
3. When applying step changes in the operating variables much shorter response times were measured for both DeNO$_x$ reaction and SO_2 oxidation as compared to catalyst conditioning and are also associated with the modifications induced on the surface coverage of sulphates. The different time responses for NO_x reduction and SO_2 oxidation have been rationalised by considering that sulphation of vanadia and sulphation of vanadia, of titania and of tungsta are responsible for the transient phenomena in the two cases, respectively. In particular, the occurrence of fast variations in the outlet SO_3 concentration with overshoot in the case of stepwise temperature increase (as it may be observed in practice during a fast load change) has been quantitatively rationalised.

4. Surface heterogeneity must be considered to describe the kinetics of NH_3 adsorption–desorption, in line with the presence of isolated and polymeric V and W sites, of Ti sites, and of sulphated sites.
5. The rate of NO reaction is virtually independent from the ammonia surface coverage above a critical value. This is explained by assuming that a reservoir of adsorbed ammonia species, possibly associated with poorly active but most abundant W and Ti sites, are present on the catalyst surface and are available for the reaction which occurs on the reactive V sites through desorption followed by fast readsorption. Because of this and of the previous points the analysis of spectroscopic data aiming at identifying reactive ammonia surface species in the reaction should be done with caution [39–42].
6. A weak inhibiting effect of ammonia on the $DeNO_x$ reaction was observed at high ammonia surface coverages, in line with a previous literature indication [43]. This observation has not been incorporated so far in any mechanistic treatment of the $DeNO_x$ reaction however.
7. Water was found to inhibit the surface reaction but apparently not the adsorption of ammonia. This is at variance with the consolidated picture reported in the literature that water competes for adsorption with ammonia, thus inhibiting the surface reaction. A more direct participation of water in the mechanism of the $DeNO_x$ reaction must be suggested.
8. The analysis of the rate parameters estimated by fitting the dynamic data indicates that the rate of ammonia adsorption is comparable to the rate of surface reaction, whereas NH_3 desorption is much slower. Accordingly the assumption of equilibrated ammonia adsorption, that is usually present in the kinetic studies available in the literature, may be incorrect and specifically at temperatures exceeding 300°C.

In addition to provide valuable fundamental information on the mechanism and kinetics of the $DeNO_x$ reaction and of SO_2 oxidation, as outlined above, the study allowed to develop a complete dynamic model of the SCR reactions in monolith catalysts that is capable to predict NO_x reduction efficiency, NH_3 slip and SO_3 emission levels for changes in the operating conditions of industrial SCR reactors [44,45]. Besides the model computing times are consistent with its use in a predictive control system for optimised control of the off-gas emissions.

2.4. Open issues and future opportunities

In spite of the fact that the SCR $DeNO_x$ technology is well established and used worldwide, still the following opportunities can be envisaged for NO_x removal catalysis from stationary sources in the near future.

1. To improve the catalyst design in order to accomplish at the same time: a higher effectiveness factor for the $DeNO_x$ reaction, a lower activity in the oxidation of SO_2 and the fulfilment of the mechanical specifications.
2. To overcome the present limit on the viable NO_x reduction efficiency through the development and use of a selective and NH_3 oxidation catalyst.
3. To extend the present applicable temperature range of SCR catalysts towards lower and higher temperatures, both below 300°C down to 150–200°C and above 400°C up to 600°C. For instance, this would allow the direct processing of the exhaust gas from the gas turbine outlet instead of using the NO_x removal system in the middle of the heat recovery steam generator.
4. To apply an on-line predictive control system, able to avoid pollutants emission peaks during transient conditions.

Besides, some open issues of more fundamental character deserve further work. These include a better understanding of the electronic interaction among the components of the ternary catalysts, and the development of a more comprehensive mechanistic and kinetic model incorporating the novel pieces of information provided by the dynamic study.

3. Catalytic combustion for the production of energy

3.1. Catalytic combustion systems

The use of a GT with a catalytic combustion system allows ultra low single digits emissions for NO_x, CO and UHC, by accomplishing the combustion at temperatures much lower than in a conventional flame combustion system (1100–1300°C vs 1800°C). These performances must be obtained under severe operating conditions, including very high gas velocity (10–40 m/s), small overall pressure drop ($<5\%$), very short residence time (10–30 ms), and with a catalyst durability guaranteed for more than 8.000 h. This poses the following major requirements to the system: (i) very high catalytic activity in methane combustion to ensure ignition at temperatures as close as possible to that of compressed air, so that to minimise the temperature rise provided by the pre-burner that is responsible for most of NO_x formation, (ii) high thermal stability of the catalytic materials with respect to deactivation by sintering, phase transformation and volatilisation, and structural integrity upon thermal shocks, (iii) coupling of the heterogeneous and homogeneous reactions to guarantee complete conversion of the hydrocarbon and ultra low emissions of CO.

Fig. 6 shows the most promising system configurations . In the first configuration only a fraction of the fuel is fed to the catalyst, here the inlet fuel to air ratio is carefully adjusted to limit the adiabatic reaction temperature typically below 1000°C, thus reducing the thermal stresses and preventing catalyst deterioration [46,47]. The remaining amount of fuel is premixed with residual air and fed to a downstream section where homogeneous combustion occurs and is assisted and stabilised by the hot gas exiting the catalyst. This configuration has been tested by CRIEPI and Kansai Electric in Japan at a scale equivalent to one combustor of a 10 MW class, multi-can type GT: the design targets on emissions ($NO_x < 5$ ppm, CO and

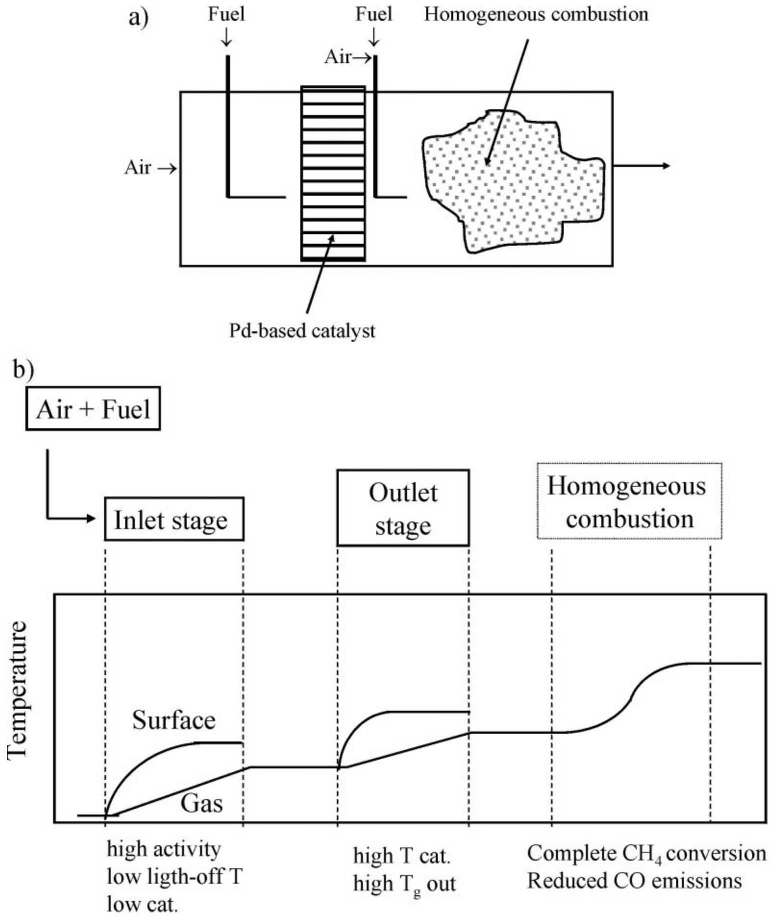

Fig. 6. Catalytic combustion system configurations: (a) hybrid combustor; (b) partial combustor.

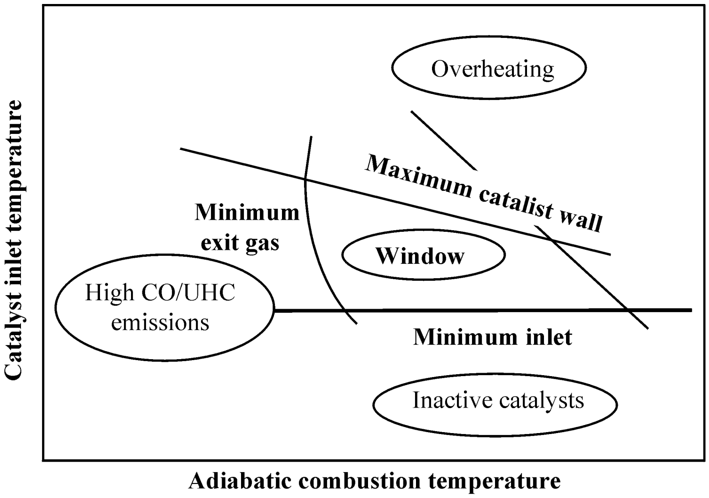

Fig. 7. Operating window in catalytic combustor [48–52].

UHC $<$ 10 ppm) and on pressure drops ($<$5%) have been demonstrated at base load for combustor outlet gas temperature of 1350°C. Still the long term performance of the catalyst and of the combustor has to be estimated and the control method established. In the second configuration [48–52], developed by Catalytica in co-operation with Tanaka Kikinzoku Kogyo KK and GT manufacturers, all the fuel, but that required for the pre-burner, is fed to the catalyst section consisting of an inlet stage capable to provide low light-off temperature and an outer stage designed to operate at higher wall temperature in order to ensure the required high outlet gas temperature while being protected against overheating. In a downstream homogeneous section the combustion of the fuel is completed, CO and hydrocarbons are burned out to the desired levels and the combustor outlet temperature is raised to the levels of modern high efficiency GT. As shown in Fig. 7 stable operation with low emissions are achieved within an operation window that is bounded by the following conditions: (i) the inlet gas temperature must be high enough to ignite the catalyst, (ii) the gas temperature at the catalyst exit must be high enough to stabilise homogeneous combustion and the adiabatic combustion temperature must be high enough to ensure complete burnout of HC and CO within the available residence time, (iii) the maximum catalyst wall temperature of both the catalyst stages must be low enough to ensure long term catalyst durability. Notice that all portion of the catalytic reactor must be within the operating window; accordingly good uniformity of inlet fuel to air ratio (e.g. ±5%) and of inlet catalyst temperature (e.g. $\Delta T = 18$°C) has to be ensured.

During tests at full scale NO_x, CO, and UHC emissions were documented at levels below the emission targets of 5, 10, and 10 ppm respectively, along with low pressure drop, good mechanical stability and negligible pressure dynamics. Besides stable performance with a negligible loss of efficiency and with ultra low emissions of NO_x, CO and UHC during 1000 h operation has been demonstrated in field tests. The commercialisation of this technology has recently been announced by Catalytica.

3.2. Combustion catalysts

The catalysts that have been most extensively investigated for GT applications are Pd supported materials and metal substituted hexaaluminates.

Palladium oxide supported on alumina or zirconia with various additives is the catalyst of choice for the combustion of methane primarily in view of unique capability of temperature self-control associated with the PdO–Pd reversible transformation, superior activity in the combustion reaction, and low volatility of Pd species that may be present under reaction conditions.

Typical TG decomposition–reoxidation patterns detected over a PdO on alumina material are presented

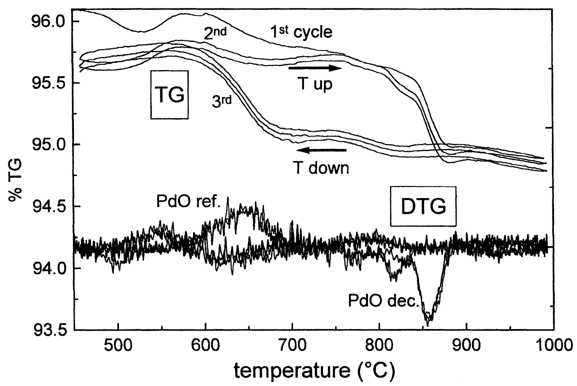

Fig. 8. TG and DTG curves for PdO/alumina.

in Fig. 8 [53]. A large hysteresis between decomposition of PdO to Pd metal during heating and re-oxidation of Pd metal during cooling is apparent. Besides in the second and the following cycles PdO decomposition occurs in two distinct steps. High temperature X-ray Diffraction and TEM proved that palladium sinters upon decomposition to the metal and re-disperses with reformation of the oxide. In similar TG cycles using unsupported Pd oxide powder PdO decomposes to Pd metal with only one sharp weight loss during heating and in the cool down curve only a small weight gain is observed. Table 1, where the data obtained over unsupported PdO and for supported PdO materials are presented [54–57], shows that the extent of hysteresis (T_D-T_R) is strongly influenced by the support primarily because the temperature of re-formation of the oxide from the metal (T_R) is markedly affected by the nature of the support, whereas that of decomposition of the oxide (T_D) is only marginally affected. The onset of the first step of PdO decomposition is apparently governed by the thermodynamics of the decomposition of bulk PdO to Pd (PdO $\rightarrow$ Pd + $\frac{1}{2}O_2$). The kinetics of the decomposition process and the related mechanism have also been studied but under conditions far from those of interest for GT applications [58,59]. Accordingly these points as well as the role of the support in PdO–Pd transformation deserve further investigation.

Table 1
Temperatures of onset of PdO decomposition (T_{D1}: first stage; T_{D2}: second stage) and reformation (T_R) on different supports

Support	T_{D1} (°C)	T_{D2} (°C)	T_R (°C)	$T_{D1}-T_R$ (°C)
Unsup. PdO	810	n.o.	785	25
Al_2O_3	795	840	690	105
La_2O_3/Al_2O_3	800	835	690	110
CeO_2/Al_2O_3	800	845	755	45
$CeO_2/La_2O_3/Al_2O_3$	800	840	750	50
ZrO_2	800	860	730	70

The re-oxidation of Pd metal at low temperatures has been investigated extensively and elucidated to a certain extent but this study has not been extended to the temperatures of interest for GT applications. The hysteresis between PdO decomposition and Pd metal re-oxidation has been tentatively associated to the capability of Pd metal to chemisorb O_2 only below T_R or to the formation of a passive layer of chemisorbed oxygen [60–62]. However, none of these explanations are fully convincing, so that re-oxidation of Pd metal at high temperature is still a complex and poorly understood process.

There is a general consensus in the literature that while PdO is highly active in methane combustion, when only Pd metal is present at high temperature the catalyst is inactive. However, there are also indications that the partial reduction of PdO results in a significant enhancement of the methane combustion activity; this was ascribed to the role of Pd metal in the activation of methane through dissociative adsorption or to the presence of site pairs consisting of oxygen atoms and oxygen vacancies on the surface of palladium oxides crystallites, where the activation of methane is believed to occur [63]. The activity variation associated with the PdO–Pd reversible transformation is responsible for the unique self-regulating capability of Pd catalysts during methane combustion under adiabatic conditions. However, runaway ignition during start-up has been observed [64], which suggests that the dynamics of the combustion reaction could be faster than the dynamics of PdO–Pd transformation. The dynamics of this transformation has not been studied so far at the temperature levels of interest for GT applications and deserves further investigation. In order to control (or to mitigate) runaway combustion in the case of methane to air ratio corresponding to high adiabatic temperatures the following remedies have been proposed: (i) the use of a diffusion barrier on the top of the catalyst layer to reduce the apparent activation energy of the combustion reaction, (ii) the use of a monolith metal support where the catalyst is applied to only one side of the structure, so that the heat generated inside the active channel is transferred to the nearby inactive channel by conduction through the washcoat and the metal, (iii) the choice of zirconia as a support for Pd oxide.

Commercial Pd catalysts for GT application typically have high Pd loading in the range 10–20% (w/w) referred to the washcoat to ensure high activity and low light-off temperatures. It has been observed that the size of PdO particles is not affected to a great extent by the loading of PdO, and that the dimensions of the PdO crystallites compare well with those of the catalyst pores, which indicates that sintering of PdO is primarily controlled by the morphology of the washcoat.

The assessment of a reliable kinetics for the combustion of methane over PdO catalysts is another important issue for the development of catalytic combustor for GT. Kinetic studies reported in the literature have been customarily performed under conditions far from those of real interest. Under these conditions the methane combustion was found to be first order with respect to methane, zero order with respect to oxygen and strongly inhibited by water. However, it has been demonstrated that water inhibition is significantly reduced under real conditions. In order to develop representative kinetics it is important to collect lab scale kinetic data under conditions as close as possible to the industrial ones. A promising device in this respect is the annular reactor proposed by Mc Carty that allows for operation with extremely high space velocities and negligible pressure drops, favours heat dispersion through radiation and can provide data under controlled conditions, e.g. with respect to transport limitations, and in the temperature range of interest for industrial applications [58,59,64].

Metal substituted hexaaluminate catalysts have also been extensively investigated for GT applications in view of excellent thermal stability and catalytic activity. These materials can be prepared by hydrolysis of the alkoxides or by co-precipitation from the nitrates of the constituents by using $(NH_4)_2CO_3$ as a precipitating agent [65–74]. In both cases monophasic samples with a layered alumina structure and surface areas in the range 10–15 m^2/g are obtained upon calcination at 1300°C. The sintering resistance of hexaaluminates is strictly related to their layered structure consisting of alternate stacking of Al^{3+} containing spinel blocks and mirror planes in which large alkaline, alkaline earth and/or rare earth ions are located [65–74]. These materials crystallise as hexagonal planar particles with marked anisotropic shape because the crystal growth along the *c*-axis is suppressed due to inhibition of ions diffusion along the stacking direction. Manganese-substituted hexaaluminates were found to be most active in the combustion of methane. Manganese was demonstrated to enter the structure at low concentration preferentially in tetrahedral sites with dominant oxidation state 2+, and at high concentration in octahedral sites with dominant oxidation state 3+ [75] (see Fig. 9a). Introduction of even higher Mn amount results in the segregation of extra phases ($BaAl_2O_4$) and in a marked drop of surface area. The catalytic activity increases with Mn loading in $BaMn_xAl_{12-x}O_{19}$ up to $x = 2$, keeps constant for $x = 3$ and then decreases (see Fig. 9b). The catalytic activity is also influenced by the composition in the mirror plane: maximum catalytic activity is reported by Arai and co-workers [65–74] for $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$.

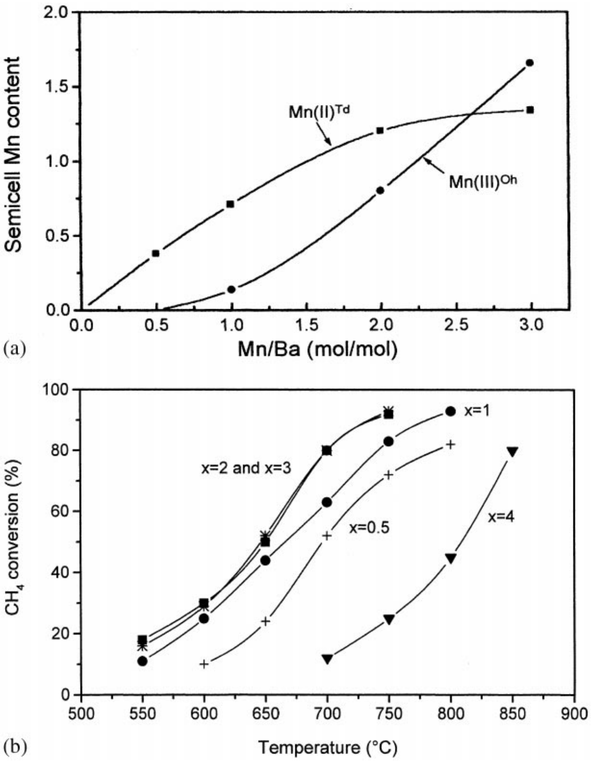

Fig. 9. Valence and location of Mn in the structure and CH_4 combustion activity of $BaMn_xAl_{12-x}O_{19}$ hexaaluminates.

Mathematical models of monolithic combustor were used for extrapolation of the lab-scale data obtained over powder materials to industrial operating conditions in the case of $BaMn_2Al_{10}O_{19}$ [76]. It was concluded that hexaaluminate catalysts can be used as end-stage catalysts in segmented configurations to allow for high gas temperature at the exit of the catalyst section, and that their activity towards the combustion of CO/H_2 mixtures, although much higher than in the case of methane, is still insufficient to fulfil the requirements of gas turbine combustor in most demanding conditions (idle and partial load).

3.3. Catalytic combustion of fuels other than methane

There is a growing interest to use low-heating-value (LHV) fuels obtained by gasification of coal, tars, biomass and wastes or liquid fuels (diesel or distillate No. 2) as alternative fuels or as back-up fuels in catalytic combustion for GT application. Few investigations have been performed along these lines. The following conclusions have been drawn from these studies [77–80]: (i) due to the high content of methane in the bio-gas noble-metals based catalysts are required for ignition at low temperature, (ii) both PdO and metal substituted hexaaluminates are very active in the oxidation of ammonia, that is present in the bio-gas, to NO. A reduction of undesired fuel NO_x has been observed in a narrow temperature and composition window, that possibly occurs through SNCR (selective non-catalytic reduction) mechanism. However, such mechanism is not effective under actual GT conditions. Accordingly ultra-low NO_x emissions can be obtained only if NH_3 is removed from the bio-gas before combustion, (iii) over PdO based catalysts CO and H_2 combustion is not affected by sulphur compounds whereas methane combustion is markedly depressed, (iv) PdO based catalysts are highly active in the combustion of synthetic diesel fuels. Upon catalytic ignition the catalyst temperature could be maintained well below the adiabatic reaction limit, but homogenous ignition within the catalyst section results in marked temperature increase that may cause serious material damage.

Still a number of issues have to be addressed for diesel and other liquid fuels. These include fuel prevaporisation and pre-mixing with air avoiding flashback, catalyst tolerance to small liquid fuel droplets, catalyst deactivation by cocking, relevance of intraparticle and gas–solid diffusion limitations, possibility to avoid homogeneous combustion inside the catalyst section, feasibility of operation in dual fuel combustors.

3.4. Mathematical models of catalytic combustors

Mathematical models represent a powerful tool for the design, analysis and operation of both catalyst and homogeneous sections of catalytic combustor for GTs [81].

In principle many phenomena have to be included in the model of the catalyst section (Fig. 10): (i) heterogeneous reactions at the catalyst wall and homogeneous reaction in the gas phase, (ii) heat, mass and momentum transfer by convection and diffusion in the gas phase and at the gas–solid interface, (iii) mass and heat diffusion in the active catalyst phase, (iv) heat transfer in the solid phase, (v) channel-channel interactions. In view of the number of complex phenomena to be accounted for and of the strong non-linear temperature effects, the computational labour for solution of the governing equations of rigorous models is so severe that any adequate approximation is attractive. Several aspects on the relative importance of the above phenomena have been assessed by comparing simulation results of progressively simplified models with those of a rigorous one under laminar flow conditions [82–84]. Such conditions correspond to the lowest limit of operation of hybrid catalytic combustors and to standard conditions of pilot catalytic combustor operated at atmospheric pressure. Besides some

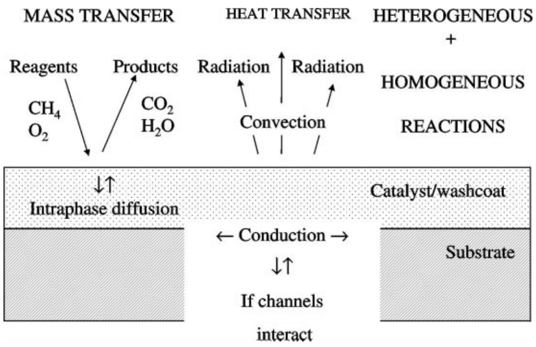

Fig. 10. Relevant physical and chemical phenomena in catalytic combustor modelling.

practical applications of mathematical models of the catalyst section have been documented in the literature, including prediction of activity levels required to achieve ignition temperature at relevant operating conditions, scale up of lab-scale data, and determination of the thickness of an inert diffusion barrier suitable to mitigate runway phenomena by reducing the reaction rate at the inlet [76,85,86].

Mathematical models of the homogeneous section which incorporate detailed kinetics for gas phase combustion have also been used to provide guide-lines for operation in order to match emission targets within reasonable constraints on combustor size. By this way it has been demonstrated by Dalla Betta and Loffler [87] that in order to reduce the CO emissions below the design target of 10 ppm the combustor outlet temperature should be 1100°C or higher (and the catalyst exit temperature sufficiently high) for typical residence times of a GT combustor namely 10–30 ms.

It is worth mentioning that while mathematical models developed for GT applications customarily refer to laminar conditions turbulent or transitional flow conditions prevail under most operation regimes of GT combustors. Modelling of monolithic channels under such conditions represent a challenge for future research work. Besides model validation by comparison of model predictions and experimental results is rather scarce so far and joint efforts from experimental and theoretical research groups are strongly recommended.

3.5. *Open issues and future opportunities*

Although important developments has been reported recently the catalytic combustion for power application has not reached yet a commercialisation stage and additional tests at the pilot and full scale laboratory and field level have to be done to improve the reliability of the most promising system configurations and to better address the issues still open. These include long-term performance of the catalyst and of the different components of the combustor, enlargement of the load range of operation, improvement of coupling between the heterogeneous and the homogeneous sections, establishment and validation of the control method, specifications for natural gas and other fuels.

From what has been reported so far the following major research opportunities can be envisaged:

1. To enhance CH_4 combustion activity of Pd-based catalysts to minimise the impact of diffusive preburner which is responsible for most of NO_x formation in natural gas combustors.
2. To improve the dynamic response of Pd catalyst on fast temperature rise to reduce runaway risks.
3. To develop catalyst with enhanced thermal stability and thermal shock resistance to reduce post-combustion volumes required to achieve the emission constraints.
4. To develop system configurations and catalyst designs able to operate with dual fuel (e.g. natural gas and diesel) combustors.

To achieve these goals several fundamental issues should be addressed including: the dynamics of the PdO–Pd transformation and influence on CH_4 combustion activity depending on the nature of the support and on noble metal load; the assessment of reliable and comprehensive chemical kinetic rate expressions for catalytic and homogeneous reaction; the role of intraphase and interphase diffusion with components with markedly different behaviour such as hydrogen and heavy hydrocarbons; the assessment of mass and heat transfer rates under transitional and turbulent regime in the monolith channels.

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