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Stability of supported metal and supported metal oxide combustion catalysts

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Abstract

Catalysts used for high-temperature combustion of light hydrocarbons must maintain high activity over long time intervals by avoiding excessive sintering and deactivation in the hot and corrosive combustion environment. The sintering resistance and chemical stability of catalytically active phases is a key technical problem that must be solved for the development of commercially viable combustion catalysts. All noble metals and transition metal oxides that are catalytically active rapidly sinter at temperatures required for high combustion rates. Advanced materials used in the development of stable catalysts include highly sintering-resistant hexaaluminate supports for dispersion of noble metals, chemically and thermally stable supporting oxides for active transition metal oxides, and single-phase, substitutionally activated, sintering-resistant complex metal oxides. This paper will review deactivating phenomena, such as sintering and vapor transport and assess recent progress in the development of durable combustion catalysts.

Keywords: Combustion, catalytic; Catalysts, for combustion of natural gas; Hexaaluminates, as catalyst supports; Vaporization, during catalytic combustion; Fe–Cr–Al alloys, as combustion catalyst substrates

1. Introduction

Catalytic combustion is an environmentally-driven, materials-limited technology that has the potential to lower nitrogen oxide emissions from natural gas fired turbines consistently below 10 ppm. Catalytic combustion also has the potential to lower flammability at the lean limit and achieve stable combustion under conditions where lean premixed homogeneous combustion is not possible. However, materials limitations have impeded the development of commercially successful combustion catalysts. No catalytic materials can long tolerate the (adiabatic) temperatures needed for gas turbines and most industrial heating applications. A combination of new engineering approaches and recent development of durable materials makes commercialization of catalytic combustion technology highly probable within the next several years. Extensive commercialization of this new technology will continually demand the development of more thermally robust materials.

1.1. Historical perspective

Historically, gas turbines with catalytic combustion were offered in the 1970s as an alternative to the internal combustion engine [1]. In the United States,

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gasoline or diesel fueled gas turbine engines were conceived for light- and heavy-duty vehicles. In fact, combustion catalysts were developed successfully and applied to gasoline and diesel fuels despite the failure of the direct drive gas turbine engine concept. Since the 1980s, Japanese electric power and gas utility companies have pursued aggressive research and development programs on catalytic combustion. This work has continued through the 1990s, while interest has been revived in the United States, principally through the commercialization efforts of Catalytica Combustion Systems, for the use of catalytic combustion in gas turbine engines for peak power shaving and for gas pipeline compressor stations. There has also been a recent interest in catalytic combustion for environmental reasons in Europe. At this time, it appears that commercialization of catalytic (gasoline) micro turbo-generators (≈50 kW) and catalytic (natural gas) small (1–5 MW) gas turbine engines is eminent.

Mean while, high-temperature catalysts have been successfully commercialized for combustion of volatile organic compounds (VOC) over the past 10 years [2]. Many incineration processes use catalysts to consume not only VOCs, but in most cases, fuels that are added to increase temperatures so that both complete combustion and VOC destruction are assured. These systems typically operate at 1 atm and 300–800°C temperature. However, VOC combustion catalysts with advanced materials could be extended to higher pressures and operating temperatures up to 1000°C.

The primary new commercially opportunity for catalytic combustion is in low NO_x adiabatic combustion for gas turbine power generators. These systems typically operate at 10–15 atm pressures and adiabatic temperatures from 1200°C to 1300°C. Catalytic combustion is under consideration for use in microturbines for hybrid electric vehicles [3]. The fuel in this case would be vaporized gasoline or diesel fuel with catalytic combustion used in order to achieve the lowest possible NO_x emissions. However, recuperation, which is necessary for high efficiency in micro and small power-generation turbines, also facilitates the use of lean, premixed burners, since the burners are stabilized by the higher inlet temperatures and provide acceptable NO_x emissions. For that reason, natural gas catalytic combustion is perhaps not necessary to meet current emissions standards for small turbines with recuperation.

Catalytic combustion in gas turbine power generators represents perhaps the most severe environment for any catalyst. However, the economic incentives for using small turbines is favorable as power generation is deregulated. Increased commercial use of such small turbines is impeded only by the unacceptable levels of No_x emissions by such engines when implied to environmentally-impacted areas. Recent progress has been made in the adoption of catalytic technology for the retrofit combustors in small gas turbine engines. An example of this involving the application of catalytic combustion to a small engine is the combustor design for the solar mercury gas turbine engine, a 3 MW machine [4]. The requirements of the gas turbine engine for catalytic performance is summarized in Table 1. In general, these requirements are very challenging and perhaps cannot be achieved with current catalytic combustion technology. However, when large post-combustion volumes are allowed by turbine design, the catalytic approach seems to be successful, and Catalytica has begun the commercialization of retrofitted catalytic burners for small engines.

Over the past two decades there have been several key materials innovations in the development of catalytic technology for low NO_x combustion of nat-

Table 1
Typical requirements for gas turbine combustion catalysts

Property	Range
Combustion performance	
NO_x emissions	<10 ppm
CO/NMHC[a] emissions	<20 ppm
Catalytic extinction point[b]	<400°C
F/A[c] for inlet air operating range	$0.1<\phi<0.6$
F/A mixedness	±5%
Alternative fuels	Natural gases, diesel fuels
Catalyst durability	
Lifetime	>8 000 h
Robustness, tolerates	Flashbacks, (briefly) F/A off-specification, exposure to contaminants

[a] NMHC – non-methane hydrocarbons, C mol basis.
[b] Inlet temperature of F/A mixture with >1250°C adiabatic temperature.
[c] F/A – Fuel-to-air ratio as a fraction of the stoichiometric ratio.

ural gas [5–10]. These key materials innovations include:

- Development of oxidation resistance Fe–Cr–Al alloys.
- Development of stabilized alumina and layered aluminate catalyst supports.
- Use of the PdO/Pd transition to control combustion rates [11].
- Passive cooling to allow use of metal monoliths [12,13].
- Substituted hexaaluminates [14].
- Toughened mullite ceramics [15].

These key innovations have extended the durability of combustion catalysts toward commercially acceptable performance.

1.2. Durability of high-temperature combustion catalysts

The durability of catalytic combustion consists of two aspects, structural durability and catalytic durability. Structure durability consists of several key materials properties (see Table 2). The current status of materials development for structural durability is that high-temperature corrosion-resistant Fe–Cr–Al metal alloys are thermal shock resistant and tolerate repeated thermal cycles up to a limit of ~1000°C. There are no ceramic materials that have been proven to perform acceptably through an extended series of high-temperature thermal cycles [16].

A key property of structural materials, in addition to durability, is robustness. A problem with metal substrates is that they are not robust. Brief exposures to very high-temperature conditions would result in melting and combustion of the metal alloy. Ceramic materials, while more robust than the metals, are not as durable. They have poor thermal shock resistances and typically suffer degradation under continuous thermal cycling (if not catastrophic thermal shock under occasional upset conditions) throughout a combustor's lifetime.

1.3. Catalytic durability

Catalytic durability implies a number of special properties. Durable catalysts must be able to resist:

- *Deactivation by sintering*. This excludes all single component oxides. Layered aluminates are promising; stabilized aluminas and perovskites may be marginal under controlled temperature conditions as far as durability, although they may not pass a series of excursions well beyond designed margins.
- *Loss by vaporization*. This property limits the use of noble metals and single-phase transition metal oxides as catalysts, and potentially represents the limiting trade-off between high activity and long, active lifetime independent of the design and structure of the catalyst.
- *Deactivation by corrosion*. The active catalyst must be resistant to chemical reaction with the support and substrate materials including vapor- or diffusion-transported components of the support and substrate materials. In addition, the catalyst must also resist contaminants brought in by airborne dust (containing Si, Al, Cl), or oil particles (containing S, P).
- *Erosion and delamination*. The metal substrates, in particular, can suffer from delamination of the overlying washcoat support. This tends to be a problem for high expansion metals with thick washcoats. Ceramic substrates usually do not suf-

Table 2
Key properties of high-temperature structural catalyst support (substrate) materials

Properties	Status of metals	Materials ceramics
Thermal shock tolerant	Fe–Cr–Al alloy metals are superior	Mosh high-temperature ceramics fail
Resists thermal cycle fatigue	Metals suitable	All ceramics fail
Resists creep/warpage	Metals acceptable depending on fuel mixedness and canning	Ceramics suitable when operating temperatures are well below melting points
Resists oxidation/phase transformation	Limiting property for metals	Some ceramics excluded, e.g., ZrO_2, $TiO_2 \cdot Al_2O_3$

fer a delamination process once the support overlayer has been calcined. Erosion could be a problem if significant amounts of dust are passed through the monolith of a catalytic combustor. In general, the thermal phoretic migration of small particles will be away from the walls as they pass through laminar boundary layers within the channels of a monolith. This would tend to help mitigate erosion by collisions with small micronsized particles. In addition, this migration would reduce deposition of corrosion by dust particles.

This paper discusses in some detail each of the possible modes of catalytic deactivation. The issues of structural durability seem to be met with the use of innovative catalyst designs and will not be discussed further.

2. Technical problems in the development of durable combustion catalysts

2.1. Sintering phenomena

The sintering of supported metal catalysts has been well studied over the years [17,18]. Several important phenomena contribute to the sintering of supported metals. These include surface-and bulk-atomic-self diffusion between contacting metal particles. Typically, a dispersion support is required to separate individual metal particles at such distances that migration cannot result in physical contact between adjacent particles. The migration and coalescence of particles within supported oxides tends to be limited to dimensions comparable to the pore size, because pores restrict the size of a growing particle, and also because the migration of particles is prevented once a particle grows to the size of the smaller pores. The sintering of highly dispersed metals is controlled by a combination of atomic surface diffusion (metal atoms diffusing over the surface of the supporting oxide), and also by vapor transport under high-temperature conditions. Both of these phenomena give rise to the Ostwalt ripening process. An examination of the stability criteria for combustion catalysts suggests that two rough guidelines are important here:

1. bulk atomic diffusion coefficients for self diffusion in metals and limiting cation diffusion in metal oxide particles, must be $<10^{-16}$ cm^2/s, and
2. the mole fraction of volatile metal or metal-oxide components in the combusting gas must be $<10^{-9}$.

Table 3
Limits for sintering of divalent and trivalent metal oxides by cation diffusion[a]

Oxide	Melting temperature (°C)	E_{diff} (kJ/mol)[b]	T_{sinter}(°C)[c]
Al_2O_3	2072	250	870
Y_2O_3	2410	340	790
Cr_2O_3	2266	260	610
Fe_2O_3	1594	490	860
MgO	2852	280	850
CaO	2614	290	816
NiO	1984	180	680

[a] Refs. [19,20].
[b] Effective activation energy for cation diffusion coefficient in air.
[c] Temperature for cation diffusion coefficient$=10^{-16}$ cm^2/s in air.

For catalytically-active metal oxides, surface and bulk diffusion of the limiting metal cation between contacting particles is the primary mode of sintering. Anion diffusion (either as an oxide or hydroxide) is generally not limiting in the presence of gas phase oxygen and water vapor because of high anion mobility and the access of the gas phase to lattice oxygen, or lattice hydroxyl groups. Metal oxide particle migration and coalescence over a supporting oxide is not as likely as with supported metals because of the greater surface tension of metals and perhaps because interfacial adhesion of oxide particles with another oxide is typically greater than metal interactions with an oxide. However, cluster surface diffusion and vapor transport could be important in the sintering of metal oxide particles. The combination of a catalytically-active transition metal oxide with a second non-active metal oxide is necessary, given that most active transition metal oxides rapidly sinter at temperatures below 1000°C (Table 3). When examining the cation migration of transition metal oxide, such as Fe, Cu, or Co relative to the cations of stable oxides, such as alumina and chromia, one can easily show that at appropriate temperature (about 1000°C), the cation migrations of the transition metal oxides are some 100–1000 times faster than those of the more stable but non-catalytically active oxides [19,20].

Aerogel-derived hexaaluminate powders have sintering resistance superior to all other oxide supports investigated [9,10]. Our group has investigated the sintering of a number of high-temperature supporting oxide powders [21]. A series of complex oxide ($MgAl_2O_4$ spinel, $LaAlO_3$, $SrZrO_3$ and $LaTiO_3$ perovskites) all show far less resistance to sintering than $LaAl_{11}O_{18}$ and $BaAl_{12}O_{19}$ hexaaluminates. Our strategy for the synthesis of moderate surface area, sintering-resistant-supporting oxides is to begin with very high porosity powders which grow interlocking oxide crystals with one-, two-, or three-dimensions. Crystallites that have high aspect ratios (e.g., needles or platelets) can possess exceptional sintering resistance. This is caused by the high porosity, which creates minimal zones of contact between crystallites, and relatively low surface tension differences (i.e., very low potential energy differences) between adjacent surfaces. As a consequence of the low potential energy gradient caused by these interlocking high aspect ratio particles or single crystal cubes, there is minimal driving force for additional sintering. By creating high porosity, amorphous aerogels, we except that the different components would react at relatively low temperatures, and crystallize and grow high-aspect-ratio particles. But, one has little control over this process, and in essence, one starts with the highest dispersion of component powders, and simply allows sintering to run its course by calcining to temperatures as high as 1600°C.

Microscopic examination shows that the superior sintering resistance of $LaAl_{11}O_{18}$ is caused by the growth of high aspect ratio platelets some 10 μm in length versus thickness of <1 μm (Fig. 1). The X-ray diffraction investigation of highly calcined and sintered powders of hexaaluminate show almost exclusive growth of hexaaluminate (Tables 4 and 5) and only small residual amounts of the perovskite remain following calcination above 1200°C (see Fig. 2). However, at intermediate temperatures during the growth of these hexaaluminate platelets, considerable loss in surface area may be caused by the growth and sintering of $LaAlO_3$ perovskites.

A series of sintering experiments, both extended time of fixed temperatures and progressively at higher temperature fixed-time intervals, established rate laws for $LaAl_{11}O_{18}$. A rate-sintering expression was developed which showed time exponent of −0.3 for two temperatures (Fig. 3). In addition, the staged sintering experiments established that the apparent activation energy for sintering was approximately 180 kJ/mol (see Fig. 4).

A quantitative description of the sintering process allows one to project the lifetime (Fig. 5) of a hypothetical hexaaluminate support that has been calcined to 1250°C until it possesses a surface area of 50 m^2/g. This analysis, which is considerably extrapolated from the measured time periods, shows that $LaAl_{11}O_{19}$ supports could remain relatively stable (>10m^2/g) for 10 000 h as long as the temperature does not exceed 1450°C. At higher temperatures, the lifetime for sintering (taking 10 m^2/g as the limit of acceptable retained surface area) shows that lifetimes of such catalysts would be abbreviated at higher temperatures (1500°C for 5000 h and 1600°C for 200 h).

Sintering rate expressions that are based on measured surface areas with a specific catalyst are useful for predicting the lifetime of high-temperature-supported oxide catalysts. There is some evidence that dispersed noble metals, such as Pd and Pt, and other additives, enhance the sintering rates of hexaaluminates [9]. Thus, careful sintering rate measurements are essential to predict active catalyst lifetimes.

Table 4
Aerogel synthesis of lanthanum aluminate supporting oxides

Sample	Aerogel 6	Aerogel 8	Aerogel 15
Target phase	$LaAlO_3$	$LaAl_{11}O_{18}$	$LaAl_{11}O_{18}$
Calculated Al/La molar ratio	0.97	10.69	13.52
Measured Al/La molar ratio	1.00	10.05	–
Starting reagents	$Al(OC_3H_7)_3$ (in isobutanol) $La(NO_3)_3 \cdot 6H_2O$ (in isobutanol)	$Al(OC_3H_7)_3$ (in isobutanol and isopropanol) $La(NO_3)_3 \cdot 6H_2O+H_2O$ (in isopropanol)	$Al(OC_3H_7)_3$ (in isobutanol and isopropanol) $La(NO_3)_3 \cdot 6H_2O+H_2O$ (in isopropanol)
Hydrolysis ratio	6.00	2.61	2.50

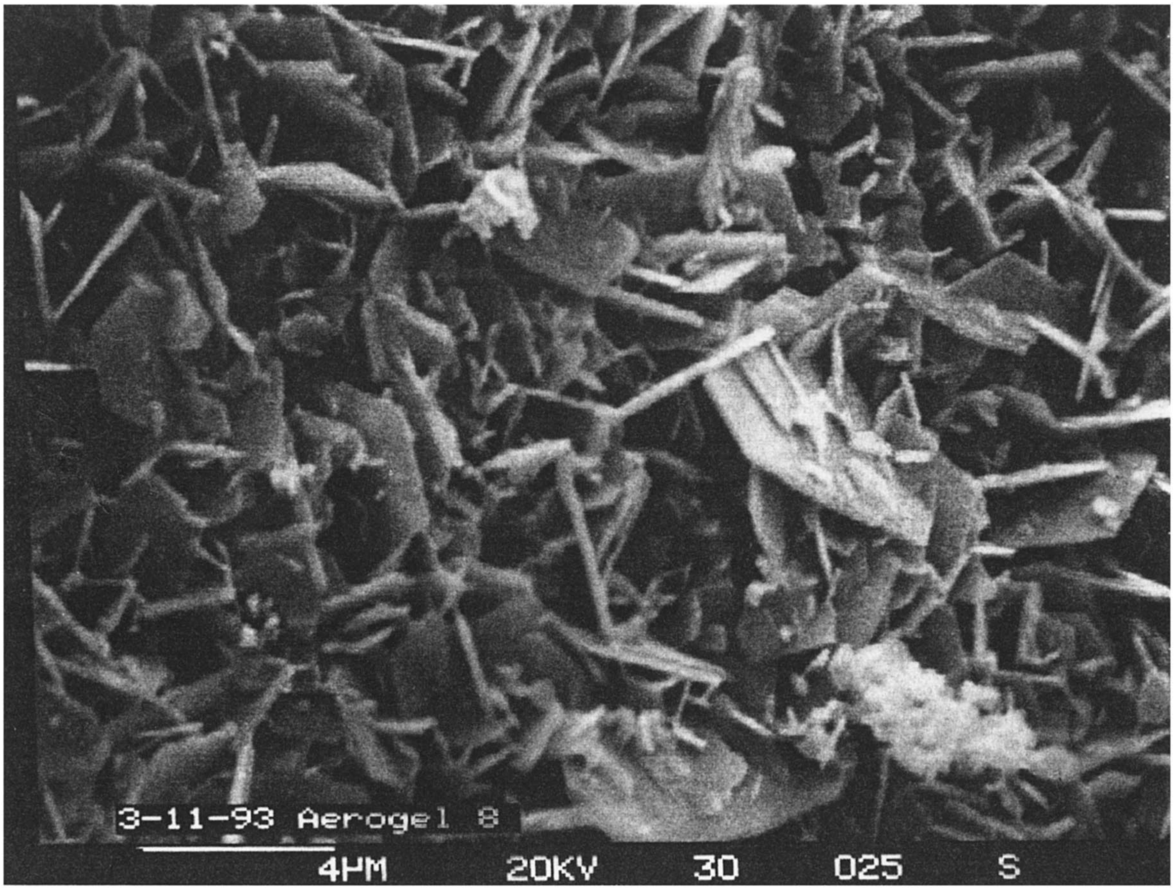

Fig. 1. Agglomerated particle (Aerogel 8) showing hexagonal plates of $LaAl_{11}O_{18}$ and crystallites of $LaAlO_3$.

Table 5
X-ray diffraction phases and specific surface areas for aerogel lanthanum aluminate supports[a]

Calcination temperature (°C)	Sample no.					
	Aerogel 6		Aerogel 8		Aerogel 18	
	XRD phases	BET (m^2/g)	XRD phases	BET (m^2/g)	XRD phases	BET (m^2/g)
300	Amorphous	155	Amorphous	615	Amorphous	566
1000	La_2O_3+$LaAlO_3$	5.1	γ-Al_2O_3+$LaAlO_3$	270	γ-Al_2O_3	160
1100	–	–	$LaAlO_3$+$LaAl_{11}O_{19}$	46	θ-Al_2O_3+γ-Al_2O_3	110
1200	$LaAlO_3$+La_2O_3	2.8	$LaAlO_3$+$LaAl_{11}O_{19}$	40	θ-Al_2O_3	92
1300	–	–	–	–	α-Al_2O_3+$LaAl_{11}O_{19}$	19
1400	$LaAlO_3$+La_2O_3	2.6	$LaAl_{11}O_{19}$+$LaAlO_3$	24	α-Al_2O_3+$LaAl_{11}O_{19}$	6.6
1500	–	–	–	–	α-Al_2O_3+$LaAl_{11}O_{19}$	5.9
1600	$LaAlO_3$+La_2O_3	2.0	$LaAl_{11}O_{19}$+$LaAlO_3$	8.5	α-Al_2O_3+$LaAl_{11}O_{19}$	2.8

[a] Following calcination for 4 h intervals in moist (10 vol% H_2O) air at the listed temperature; the major XRD phase is listed first. All samples calcined at 1200°C and higher temperatures were previously calcined in dry air at 1000°C for 16 h.

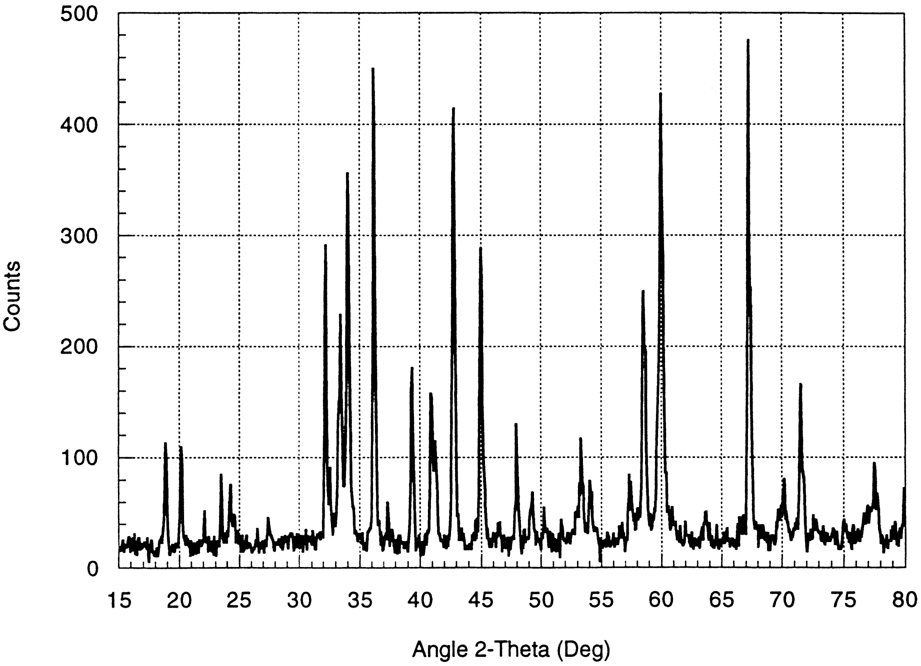

Fig. 2. X-ray diffraction pattern of lanthanum hexaaluminates (Aerogel 6) after calcination at 1000°C and sintering at 1600°C in humid air for 4 h.

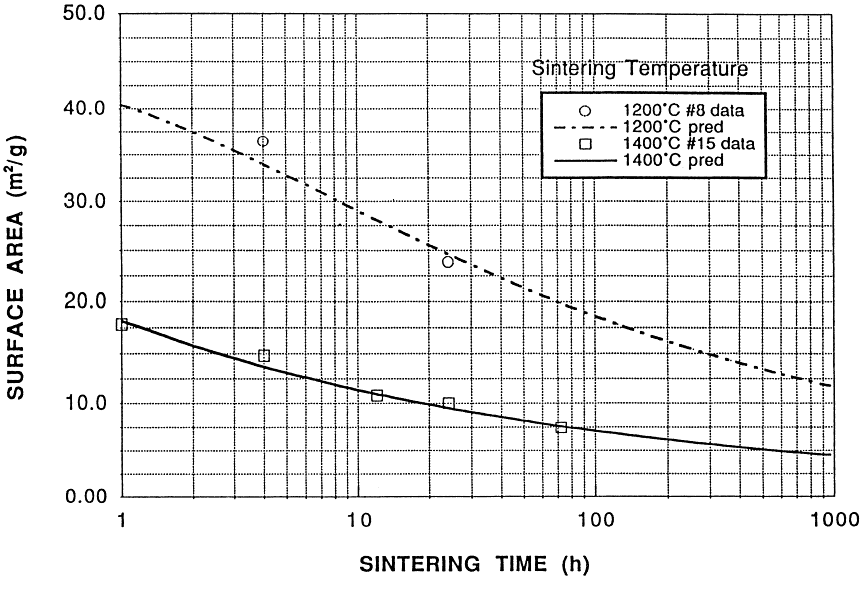

Fig. 3. Sintering rate data for $LaAl_{11}O_{18}$ aerogel powders and fitted rate law curves for specific surface area as a function of sintering time and temperature.

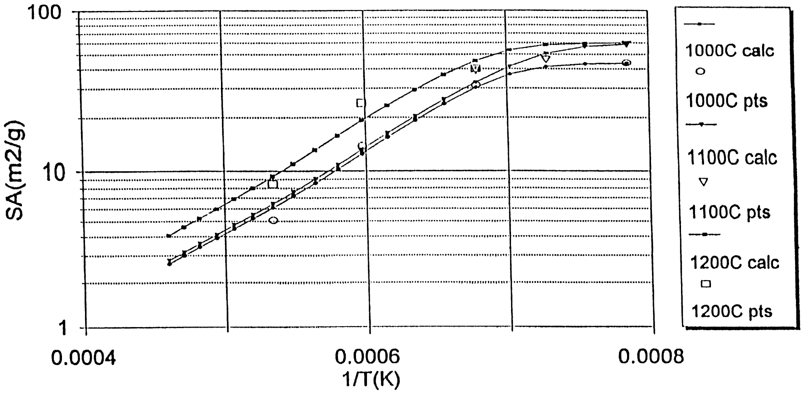

Fig. 4. Sintering rates for three $LaAl_{11}O_{18}$ powders as a function of reciprocal temperature for 4 h calcination in moist air at successively high temperatures with fitted rate curves.

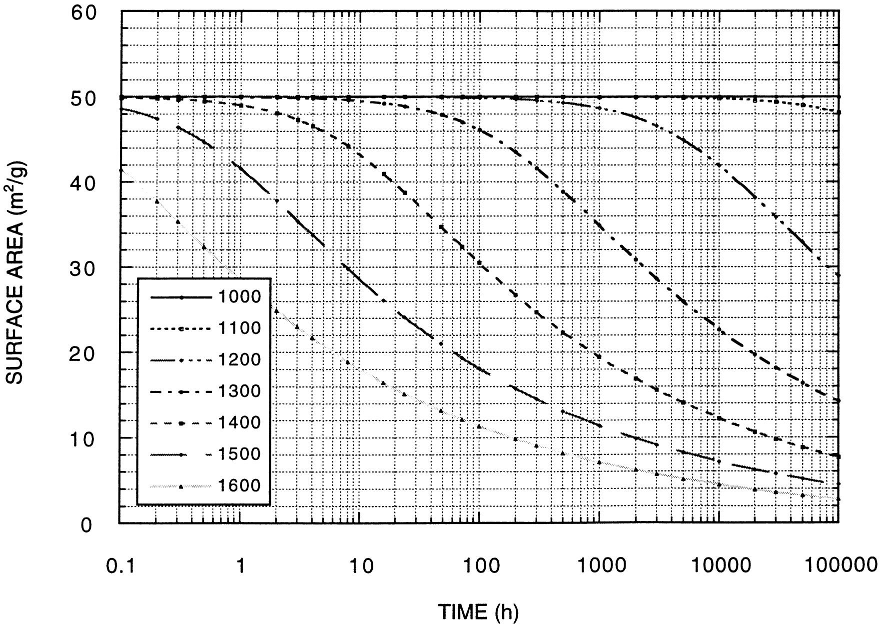

Fig. 5. Predicted specific surface area versus time and temperature (°C) for a $LaAl_{11}O_{18}$ support following initial calcination at 1250°C to 50 m^2/g.

The selection of materials as sintering resistant-supporting oxide requires that we use oxide with inherently low cation diffusivity and low vapor pressures of gaseous hydroxide and oxyhydroxide compounds. Synthesis should start with an amorphous high surface area material, then precalcined to a stabilized powder which could be used for supporting a catalytically active phase. Materials that grow high-aspect-ratio crystallites, such as the hexaaluminates, show the greatest resistance to sintering. It is essential to be able to measure and extrapolate measured sintering rates of single-phase supports in order to estimate the active lifetime of supported metal and supported metal-oxide catalysts. Yet, it appears that high-aspect-ratio La and Ba hexaaluminates, and transition metal substituted hexaaluminates, including Mn and Fe, may meet the demanding catalyst specifications required for gas turbine combustors.

2.2. Vaporization of catalytic materials

Vaporization can contribute to the sintering of supported metal and supported metal-oxide catalysts through the Ostwalt ripening process. If heated excessively beyond a critical temperature, the high concentrations of vapors can also lead to the transport of significant amounts of catalytic materials to either substrates where they can react, or into the gas phase where they are lost in the effluent gas stream. In addition, vaporization can cause the migration of corrosive components from substrates, supports, or from deposited contaminants, and lead to an accumulation of deactivating components on the surfaces of catalytically active phases. Therefore, it is essential to examine the thermodynamics of vaporization in order to assess which materials are potentially stable over very long periods at high temperatures in the combustion environment.

We have estimated the thermodynamic properties of a wide variety of gaseous metal hydroxides and oxyhydroxides by developing a correlation between the bond strengths of metal hydroxides and metal halides [22]. In particular, the bond strengths of metal hydroxides were found to be comparable based on correlations of known measurements to that of the bond strengths of the associated metal chlorides. The bond strengths of metal hydroxides was also proportional to the bond strengths of metal fluorides with an addition of some 130 kJ/mol. After estimating the critical enthalpies for formation for a particular gaseous metal hydroxide and oxyhydroxide using these correlations for metal halide oxy and halide data, and also by extrapolating a series of related compounds (same Periodic Table column), we were able to estimate the full thermodynamic properties of all relevant gaseous metal hydroxides and oxyhydroxides. Thermal functions included enthalpy of formation and heat capacity were calculated using estimated molecular constants, which include moments of inertial for rotational contributions, fundamental modes of vibration, symmetry, and electronic contributions, if any. After compiling these fundamental thermochemistry parameters, we were able to predict the volatility of relevant metals and metal oxides.

In addition to the estimated properties, we measured the thermochemistry of several important vapor species. These measurements were conducted in a Knudsen effusion cell using special line-of-sight vaporization under subambient pressures with flowing O_2 and H_2O vapor mixtures [23]. The gaseous species over silica [24], manganese oxide [25], lanthana, alumina, and palladium metal were detected and relative partial pressure measured as a function of temperature. These vapor pressure measurements were calibrated by using the known metal atom or binary metal oxide volatility as a calibration source. Oxide species concentrations were measured relative to that of a reference compound, e.g., metal atom. The identification of oxide and hydroxide compounds was facilitated by the technique of threshold electron ionization [26]. These data were then evaluated using estimated entropy functions and the third law temperatures (Table 6).

Table 6
Measured third law enthalpy ($\Delta_f H^0_{298}$) of several metal oxides

Gaseous species	($\Delta_f H^0_{298}$) (kJ mol^{-1})	Reference
SiO_2	-280 ± 17	[24]
$SiO(OH)$	-495 ± 17	[24]
$SiO(OH)_2$	-893 ± 17	[24]
MnO_2	-74 ± 13	[25]
$Mn(OH)$	0.4 ± 17	[25]
$MnO(OH)$	-401 ± 17	[25]
$MnO(OH)$	-172 ± 17	[26]
$LaO(OH)$	-531 ± 17	Unpublished data
$Al(OH)_2$	≤-510	Unpublished data
$Al(OH)_3$	≤-933	Unpublished data
PdO	371 ± 17	Unpublished data

Vaporization partial pressures have been predicted by combining the estimated and experimentally-measured thermochemistry. One of the findings is that silica is volatile in the presence of high concentrations of steam, e.g., parts-per-billion concentrations of volatile Si-components are reached at temperatures as low as 850°C. Unacceptably high levels of $SiO(OH)_2$ (100 ppb) occur at temperatures as low as 1100°C. It is well known that platinum dioxide is volatile. Our estimated thermochemistry allowed us to predict that $Pt(OH)_2$ is as volatile as PtO_2 although this was not verified by direct measurements. A series of manganese oxide and oxyhydroxide compounds were also observed in the Knudsen cell experiments with Mn_2O_3 powders. $Mn(OH)_3$ (manganese dihydroxide), which was estimated from halide data, and $Mn(OH)_2$ (manganese dihydroxide), are predicted to be the most

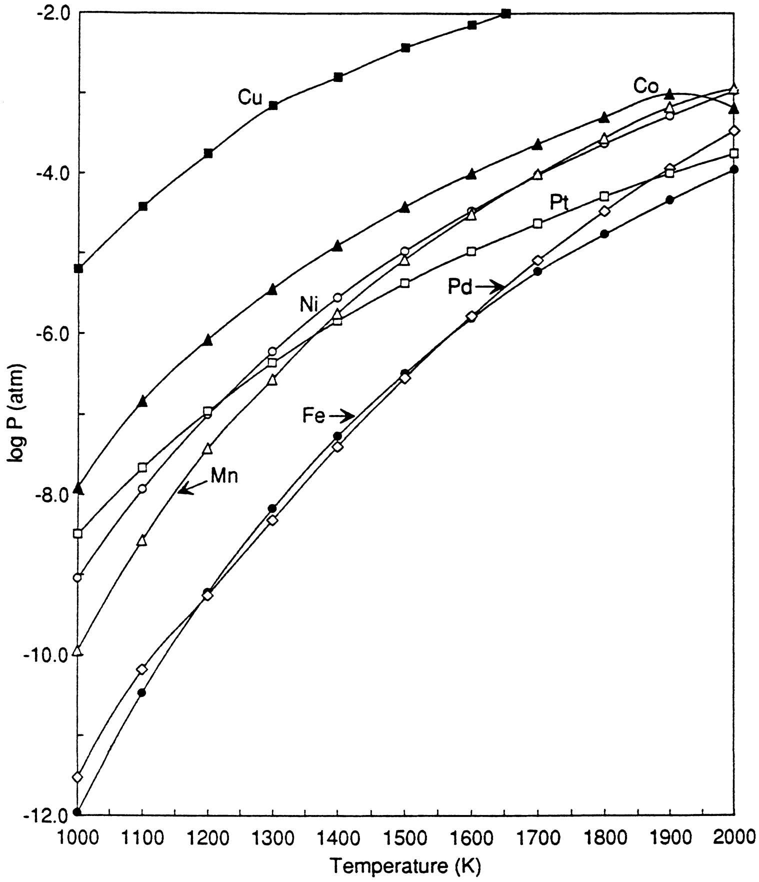

Fig. 6. Total partial pressures of metal-containing species versus temperature for the reaction of Co, Cu, Fe, Mn, and Ni-oxides and metallic Pt and Pd with an equimolar O_2/H_2O mixture at 1 atm.

stable volatile compound over Mn_2O_3 under combustion conditions. Unacceptable levels of vaporization occur for Mn_2O_3 at temperatures as low as 750°C. At temperature approaching 1000°C, these levels could reach as high as 100 ppb in 10 atm combustion environments. This degree of volatility of hydroxides may be typical for the catalytically active transition metal oxides (Fig. 6).

Estimated vapor pressures for a series of metal containing species versus temperature (Figs. 6 and 7) show that of the noble metals, Pd is the most superior with respect to vaporization. For temperatures below 1000°C, Pd is followed by Ir, Pt, and subsequently Ru in order of increasing volatility. Ruthenium is extremely volatile and cannot be recommended as a combustion catalyst. The first row transition metal oxides are also surprisingly volatile. Iron (based on the relatively limited actual data primarily relying on estimates), appears to possess the most stable oxide with acceptable volatility to temperatures as high as 1000°C. The less volatile oxides then are manganese and nickel. Cobalt may have to be considered too volatile to be useful at 1000°C without stabilization in a complex oxide such as $LaCoO_3$. Copper appears to be unsuitable for combustion except at very low temperatures, as its volatility rises well above 100 ppm at 1000°C.

Of the catalytically active materials, iron oxide and Pd appear to show acceptable volatility at temperatures up to 1000°C. Materials which have extremely low volatility and the potential to serve therefore as non-reactive substrates and supports include zirconia,

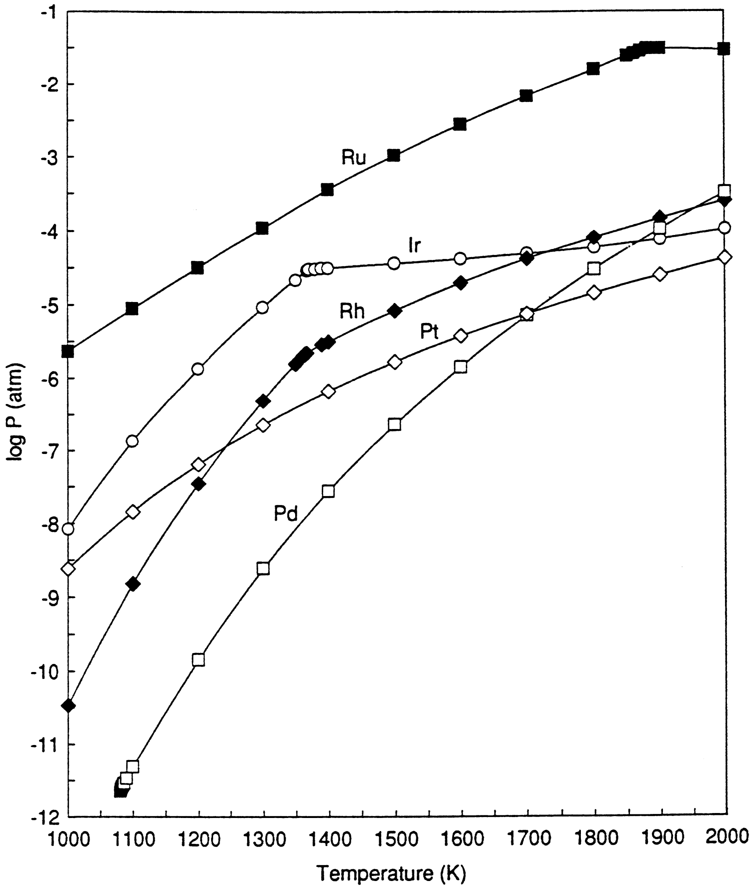

Fig. 7. Total partial pressures of metal-containing species versus temperature for the reaction of metallic Ir, Pd, Pt, Rh, and Ru with O_2 at 0.5 atm.

titania, and alumina. The rare earth oxides represented by lanthana and ceria also show low volatility and would tend to resist vapor-transport-assisted sintering and corrosion. Of the alkaline earth oxides, MgO is superior to all others, although the alkaline earth aluminates can be much more stable (e.g., by a factor of 100 for BaO) than the oxides.

Incorporation of transition metal oxides into complexes with materials such as alumina can lower their volatility by factors from 10 to 1000 depending primarily upon the heat of reaction between the two oxides. However, it is also likely that formation of very stable complex metal oxides such as aluminates, can also greatly lower the chemical activity of the transition metal. As a consequence, there may be a technology-limiting trade-off between the catalytic activity of metals and metal oxides and their chemical stability.

We find that transition metal oxides have high volatility at high temperatures (>1000°C) due to primarily the formation of volatile hydroxides and oxyhydroxides. Silica and chromia have corrosive potential, i.e., their potential vapor pressures are potentially so high that vapor pressures are potentially so high that vapor transport for substrate, support, or dust particles to the catalytically-active phase can lead to deactivation. These materials should be avoided for use in supports and substrates. It would appear that Pt- and Cu-based catalysts are unacceptable for long-term use because of their inherent volatility. The most stable catalytically active materials appear to be Pd and Fe_2O_3, and use of these materials is recommended for long-term use in high temperature combustors.

3. Conclusions

We draw the following conclusions regarding the selection of component materials for catalytic combustors:

- *Thermal shock*. The problem with thermal shock seems to have materials and design solutions. The high-temperature Fe–Cr–Al alloys show acceptable performance up to 1000°C. Ceramic materials, when segmented as monoliths, with limited diameters and limited lengths, seem also to have some potential to avoid thermal shock, particularly those ceramics that are composed of composites that exhibit high degrees of toughness (i.e., the ability to resist propagation of cracks).
- *Sintering resistance*. There are few oxides that show good sintering resistance. Stabilized aluminas, and possibly hexaaluminates (e.g., $LaAl_{11}O_{18}$) or lanthanum aluminate perovskites could be used in temperature-limited first-stage combustors. Long-lived supports for a hot stages in a combustor must be one of the hexaaluminates.
- *Volatility*. High volatility limits the selection of many otherwise useful materials. Use of silica, all alkali, and alkaline earth metals higher than magnesium as components in any substrate or supporting material cannot be recommended. Catalysts with the least amount of volatility include palladium and iron oxide. It may also be possible to form complex oxides with other transition metal oxides, such as Mn, Ni or Co, which could have an acceptable activity and stability. For example, the formation of transition metal aluminates could lower volatility and increase sintering resistance, but at the expense of decreased activity.

Catalytic technologies seem feasible for industrial heat-transfer applications in which the combustion temperature is less than 1200°C. Because the adiabatic temperatures in natural gas turbine combustors are very high (1250–1500°C), some means of controlling surface temperatures must be employed under the transport-limited reaction regimes of catalytic combustion. There are several other engineering problems that also need to be solved to extend this technology to higher temperatures under adiabatic conditions. For example, start up, load response (i.e., fuel turn-down), careful fuel mixing, careful control of the fuel-to-air ratio, the use of by-pass air, and other combustion system engineering problems must be addressed in the development of catalytic combustion for ultra-low emission, gas turbine engines.

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