Sulfur-tolerant NO_x storage traps: an infrared and thermodynamic study of the reactions of alkali and alkaline-earth metal sulfates

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The sulfur tolerance of a barium-containing NO_x storage/reduction trap was investigated using infrared analysis. It was confirmed that barium carbonate could be replaced by barium sulfate by reaction with low concentrations of sulfur dioxide (50 ppm) in the presence of large concentrations of carbon dioxide (10%) at temperatures up to 700 °C. These sulfates could at least be partially removed by switching to hydrogen-rich conditions at elevated temperatures. Thermodynamic calculations were used to evaluate the effects of gas composition and temperature on the various reactions of barium sulfate and carbonate under oxidizing and reducing conditions. These calculations clearly showed that if, under a hydrogen-rich atmosphere, carbon dioxide is included as a reactant and barium carbonate as a product then barium sulfate can be removed by reaction with carbon dioxide at a much lower temperature than is possible by decomposition to barium oxide. It was also found that if hydrogen sulfide was included as a product of decomposition of barium sulfate instead of sulfur dioxide then the temperature of reaction could be significantly lowered. Similar calculations were conducted using a selection of other alkaline-earth and alkali metals. In this case calculations were simulated in a gas mixture containing carbon monoxide, hydrogen and carbon dioxide with partial pressures similar to those encountered in real exhausts during switches to rich conditions. The results indicated that there are metals such as lithium and strontium with less stable sulfates than barium, which may also possess sufficient NO_x storage capacity to give sulfur-tolerant NO_x traps.

KEY WORDS: sulfur tolerance; NO_x storage; barium sulfate decomposition; thermodynamics; alkali and alkaline-earth metals, SO_2, H_2S.

1. Introduction

Lean-burn gasoline and diesel engines offer considerable energy efficiency advantages when compared with conventional engines which operate within a narrow air : fuel ratio close to the stoichiometric mix. However, the high concentration of oxygen in lean-burn engine exhausts means that three-way catalyst (TWC) technology used to remove NO_x from conventional engine exhausts cannot be used. Instead another method of NO_x removal is required. One such method is the so-called NO_x storage/reduction (NSR) concept pioneered by Toyota [1]. The storage component, typically barium carbonate, stores NO_x as nitrates during normal lean-burn operation; these nitrates are then decomposed by switching momentarily to fuel-rich conditions, the resultant NO_x being reduced to N_2 using conventional TWC technology [2,3]. This technology works well and can give high NO_x conversions (up to 100%) over a broad temperature range of 250–450 °C. Unfortunately, barium carbonate also has a strong affinity for sulfur in the exhaust gas, forming stable sulfates that are difficult to remove at temperatures that are optimum for NO_x storage [4–8]. These bulk sulfates cause deactivation of the NO_x storage capacity and inhibit the ability to reduce NO_x and the ability to oxidize NO [7].

In practice, periodic switching to fuel-rich conditions at elevated temperatures (>600 °C) for several minutes can regenerate the sulfur poisoned trap [9]. However, there are obvious penalties in using this strategy. First, there is the added complexity of designing a system in which temperature cycles in addition to lean/rich cycles need to be engineered. Second, there are the associated fuel penalties of running rich for several minutes to completely remove sulfates. Third, further after-treatment is required to deal with high concentrations of H_2S and SO_2 being emitted in a short space of time [10]. Finally the effects of thermal aging on the trap system are likely to be significant. Thus, there is a strong incentive for the design of a NO_x storage material that either has little or no affinity for sulfur or that has affinity for sulfur but can be readily regenerated under the same conditions of feed and temperature used to decompose and reduce NO_x. Given the similarities between the sulfate and nitrate storage mechanisms, the latter strategy of investigating NO_x storage materials with lower sulfate stabilities than barium sulfate under reducing conditions holds more

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promise. However, research on sulfur-tolerant non-barium-containing traps has been limited. Matsumoto *et al.* [6] investigated the stability of sulfates on Pt/Rh/Ba/γ-Al_2O_3 traps in which the γ-Al_2O_3 was modified by doping with various alkali and alkaline-earth metals. They found that the addition of lithium in particular significantly reduced the stability of the sulfate.

Recent research has indicated that barium sulfate is too stable to be removed at temperatures as low as 350 °C under hydrogen-rich conditions [4]. This theme is further explored in this paper. Thermodynamic calculations were carried out in order to ascertain the temperatures and gas mixtures under which barium sulfate can be converted to barium carbonate or barium oxide. These calculations were extended to other alkali and alkali-earth metals, the results indicating that some of the other metals have less stable sulfates and may as a result be more suitable than barium in sulfur-tolerant traps.

2. Experimental

A ceria–zirconia supported 1 wt% Pt/8 wt% Ba trap (Pt/Ba-MC) was prepared and characterized using methods described elsewhere [4]. The diffuse reflectance FT-IR measurements were carried out *in situ* in a high-temperature cell (® Spectra-Tech) fitted with ZnSe windows. The sample for study (~30 mg) was finely ground and placed in a ceramic crucible the temperature of which could be varied from 20 °C to 800 °C. The sample was pre-treated *in situ* at 400 °C in a stream of 5% O_2/He prior to analysis. The temperature of the sample was then decreased to 350 °C and held at this temperature for 30 min. The reactants were then passed through the catalyst bed in a 50 ml/min stream. The absorbance measured in the presence of the reaction stream over the catalyst relative to that of the same material at the same temperature under a stream of helium is reported. Samples were collected every minute, each sample consisting of 32 scans recorded at a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Reaction between carbonates and sulfates

The reaction of $SO_2 + O_2$ over the Pt/Ba-MC trap was studied at 350 °C using *in situ* diffuse reflectance infrared Fourier transform (DRIFT) analysis. The results of this experiment (reported elsewhere [4]) were used to identify a peak at 1144 cm^{-1} which could be attributed to the formation of a bulk barium sulfate species. Having identified a region at which bulk sulfates absorb most strongly (1144 cm^{-1}) and noted that bulk carbonates absorb strongly at 1450 cm^{-1} [4], it was possible to track the intensities of absorbances due to sulfates and carbonates over time under different reactant gases at various temperatures (figure 1). Figure 1 clearly shows that, as the intensity due to bulk sulfates increases, bulk carbonates are lost from the trap as evidenced by the increasing intensity of the negative bulk carbonate peak, this occurring even in the presence of a large excess (×2000) of CO_2 to SO_2. Ramping the temperature up to 700 °C accelerated this replacement process.

At 700 °C oxygen was then removed from the feed stream and replaced by hydrogen at 700 °C. This resulted in initial rapid removal of bulk sulfates and carbonates from the trap. Interestingly, over time under these reducing conditions the carbonates slowly reform to almost the same level of intensity attained before reduction but, in contrast, the sulfate peak remains at the same level for the duration of the H_2-rich conditions.

3.2. Thermodynamic studies

The results of the DRIFT analysis clearly showed the occurrence of a replacement reaction under oxidizing conditions that can be summarized by equation (1), where $BaCO_{3(s)}$ and $BaSO_{4(s)}$ refer to bulk species.

$$\Delta G_r = \Delta G^\theta + RT\left[\ln\left(\frac{P_{CO_2}}{P_{O_2}^{0.5}P_{SO_2}}\right)\right] \tag{1}$$

$$BaCO_{3(s)} + SO_{2(g)} + 0.5O_{2(g)} \Leftrightarrow BaSO_{4(s)} + CO_{2(g)}$$

The thermodynamics of this reaction, and indeed other reactions involving carbonates and sulfates under reducing and oxidizing conditions, can be studied and can provide very useful information regarding the conditions under which either the carbonate or sulfate is stable. The reaction Gibbs function (ΔG_r) is used to establish the conditions under which various reactions should occur spontaneously. These calculations are similar to those carried out by Rodrigues *et al.* [11], who used thermodynamics to evaluate the conditions under which bulk barium nitrate could be formed. Equation (1) gives an example of the equation used to evaluate the ΔG_r for the reaction of barium carbonate with sulfur dioxide and oxygen. ΔG^θ was calculated at each temperature by using HSC Chemistry (Outokumpu Research Oy) software.

Table 1 gives the values of partial pressures of gases used to calculate ΔG_r for a range of reactions.

It must be noted that some caution is required when applying thermodynamics to real systems, as thermodynamics does not give any information on the kinetics of reactions. However, the results of the thermodynamic calculations presented here can be used to give a useful indication of reactions that are favored at specific temperatures.

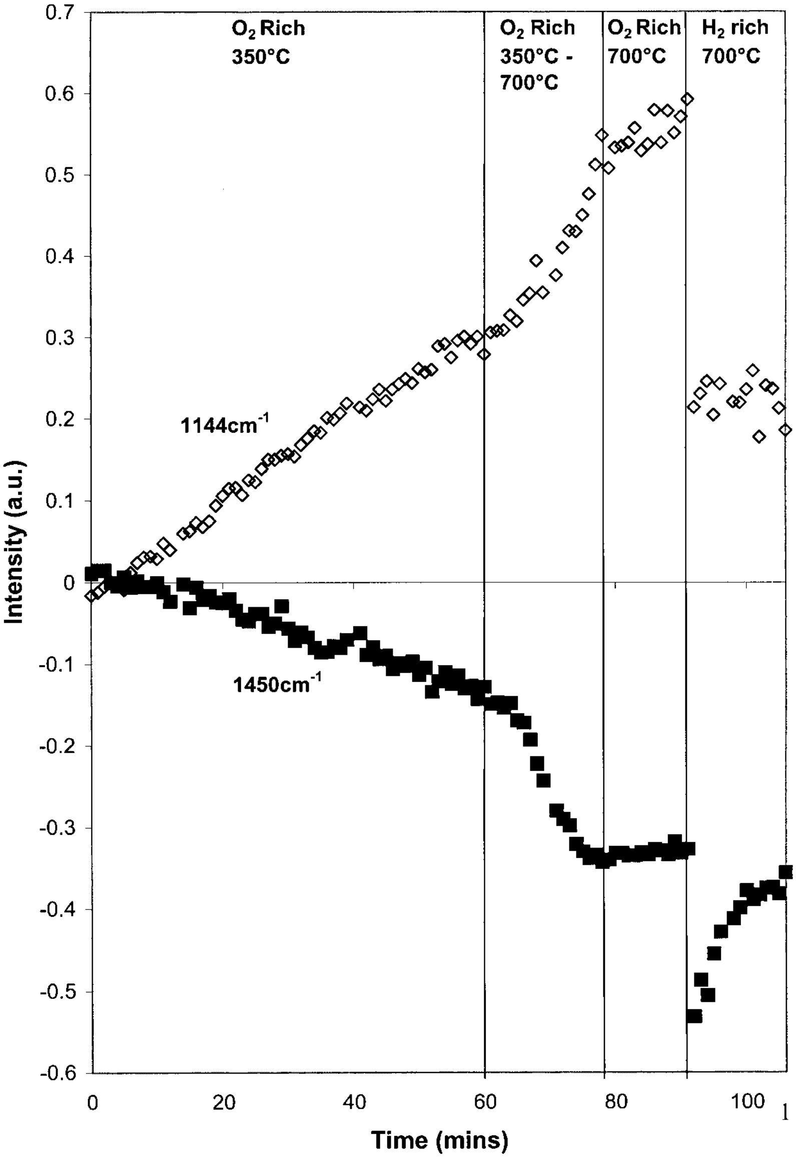

Figure 1. Concentration of bulk carbonate (■) and bulk sulfate (◇) species over time during *in-situ* DRIFT analysis of Pt/Ba-MC at different temperatures under various feed compositions. Feed: 50 ppm SO_2, 5% O_2, 10% CO_2 (90 min); 50 ppm SO_2, 5% H_2, 10% CO_2 (15 min). Total flow: 50 ml/min.

3.2.1. Reactions of $BaCO_3$ and $BaSO_4$

Figure 2 shows a plot of the ΔG_r as a function of temperature for the various reactions given in table 2; the values of temperature at which $\Delta G_r = 0$ ($T_{\Delta G_r=0}$) are also given in table 2. For temperatures $>T_{\Delta G_r=0}$, the products of reaction will spontaneously be formed, and at temperatures $<T_{\Delta G_r=0}$, no reaction will occur.

Table 1
Partial pressures of gases used in thermodynamic calculations

Gas	Partial pressure (bar)
CO_2	1×10^{-1}
H_2O	1×10^{-1}
O_2	5×10^{-2}
CO	5×10^{-2}
H_2	5×10^{-2}
SO_2 or H_2S	5×10^{-5}

Figure 2 (line (a)) shows the inherent stability of $BaSO_4$, and spontaneous decomposition only occurs at temperatures >1393 °C. $BaCO_3$ is also stable but not as stable as $BaSO_4$. Indeed figure 2 indicates that $BaSO_4$ will replace $BaCO_3$ ((a) − (b)) at temperatures up to 1471 °C even under conditions where the partial pressure of CO_2 far exceeds that of SO_2 (table 1). The results of the *in situ* DRIFT analysis confirm that barium sulfate does replace barium carbonate at temperatures at least as high as 700 °C.

The behavior of $BaSO_4$ under reducing conditions is particularly interesting. The reaction of barium sulfate with hydrogen to give barium oxide, SO_2 and H_2O (c) occurs, as expected, at a much lower temperature (963 °C) than the decomposition of barium sulfate to

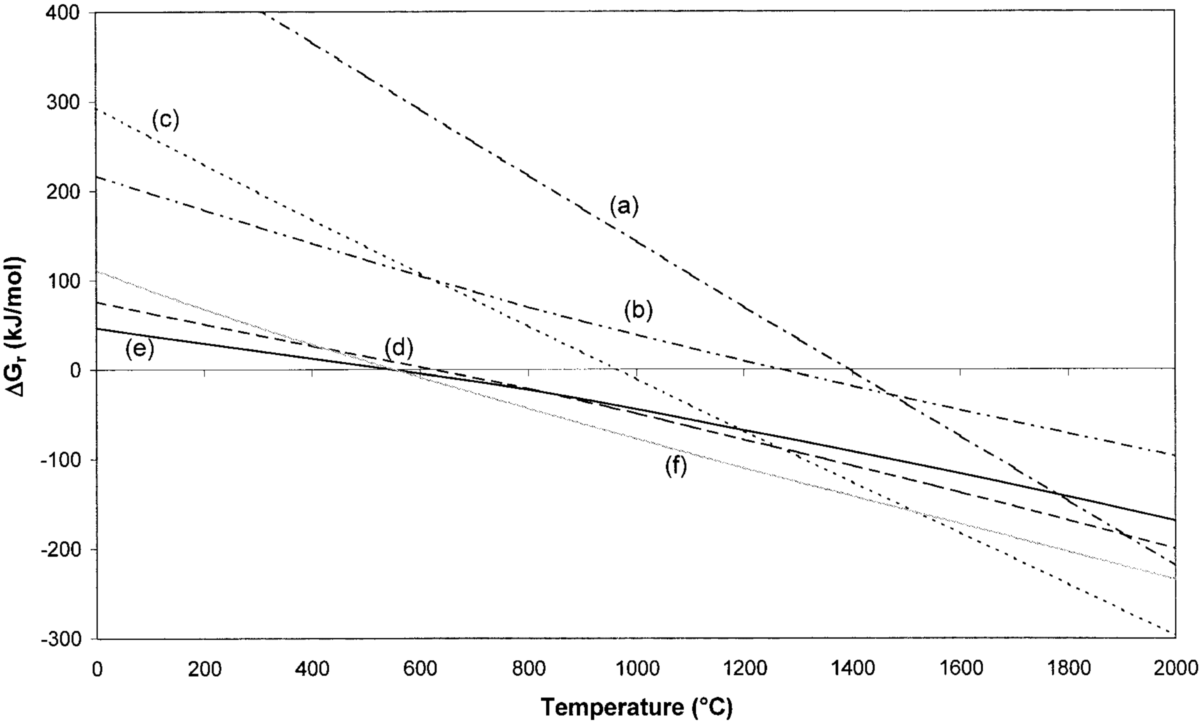

Figure 2. ΔG_r as a function of temperature for various reactions given in table 2.

barium oxide in the absence of hydrogen (1393 °C). However, the temperature for the substitution of barium sulfate can be further reduced to 623 °C by including CO_2 in the gas mixture and allowing for the formation of barium carbonate rather than barium oxide (d). This is important because it shows that the addition of CO_2 to the gas mix can considerably lower the temperature at which the stable sulfate can be removed. By using only carbon monoxide as the reducing agent, the temperature of carbonate substitution of sulfates can be further reduced to 547 °C (e).

If hydrogen sulfide is formed instead of sulfur dioxide under rich conditions then the ΔG_r changes considerably. The decomposition of $BaSO_4$ to BaO (f) can occur at a much lower temperature (553 °C) than the temperature of 963 °C required to decompose the $BaSO_4$ to BaO with SO_2 rather than H_2S as a product (c). This same trend is evident when using barium sulfate, carbon dioxide and hydrogen as reactants and barium carbonate, hydrogen sulfide and water as reactants (g). In this case the forward reaction is thermodynamically favored at temperatures <0 °C. This is important because it shows that by allowing for the formation of H_2S the temperature at which $BaSO_4$ can be decomposed or replaced (by carbonate) can be lowered considerably. In practice, the decomposition of $BaSO_4$ tends to occur at temperatures of 600–700 °C, indicating that any one of reactions (d), (e), (f) or (g) or a combination of these reactions are the most likely routes for $BaSO_4$ removal.

Table 2
Temperatures at which $\Delta G_r = 0$ for various reactions

Reaction	$T_{(\Delta G_r = 0)}$ (°C)
(a) $BaSO_{4(s)} \Leftrightarrow BaO_{(s)} + SO_{2(g)} + 0.5O_{2(g)}$	1393
(b) $BaCO_3 \Leftrightarrow BaO_{(s)} + CO_{2(g)}$	1337
(a) – (b) $BaSO_{4(s)} + CO_{2(g)} \Leftrightarrow BaCO_{3(s)} + SO_{2(g)} + 0.5O_{2(g)}$	1471
(c) $BaSO_{4(s)} + H_{2(g)} \Leftrightarrow BaO_{(s)} + H_2O_{(g)} + SO_{2(g)}$	963
(d) $BaSO_{4(s)} + H_{2(g)} + CO_{2(g)} \Leftrightarrow BaCO_{3(s)} + H_2O_{(g)} + SO_{2(g)}$	623
(e) $BaSO_{4(s)} + CO_{(g)} \Leftrightarrow BaCO_{3(s)} + SO_{2(g)}$	547
(f) $BaSO_{4(s)} + 4H_{2(g)} \Leftrightarrow BaO_{(s)} + H_2S_{(g)} + 3H_2O_{(g)}$	553
(g) $BaSO_{4(s)} + 4H_{2(g)} + CO_{2(g)} \Leftrightarrow BaCO_{3(s)} + H_2S_{(g)} + 3H_2O_{(g)}$	<0

3.2.2. *Reactions between the sulfates and carbonates of various alkali and alkali-earth metals*

Barium tends to be the trap material of choice due to its high NO_x storage capacity and rate of uptake of NO_x. However, the temperature at which sulfates can be removed from barium-containing traps under reducing conditions is considerably higher than the optimum temperature at which nitrates are stored under oxidizing conditions [4,6]. This effectively means that in order to remove sulfates from the trap, it is not sufficient simply to switch to rich conditions; the temperature of the trap also needs to be increased. This results in a reduction in the overall efficiency of the system. Ideally, sulfate removal from the trap should occur under reducing conditions at the same temperature at which optimum NO_x storage occurs under oxidizing conditions.

It is readily apparent that barium carbonate is not an ideal trap with respect to the stability of barium sulfate. Are there other alkaline-earth metals or even alkali metals that have less stable sulfates than barium? To answer this question, thermodynamic calculations were carried out. The ΔG_r were calculated as a function of temperature for equations (h)–(k), where A refers to the alkaline-earth metals Mg, Ca, Sr and Ba or to alkali metals Li, Na, K, Rb and Cs, in which case A represents Li_2, Na_2, K_2, Rb_2 or Cs_2.

$$\text{(h)}\quad 2A\mathrm{SO}_{4(s)} + \mathrm{H}_{2(g)} + \mathrm{CO}_{2(g)} + \mathrm{CO}_{(g)} \Leftrightarrow 2A\mathrm{CO}_{3(s)} + \mathrm{H_2O}_{(g)} + 2\mathrm{SO}_{2(g)}$$

$$\text{(i)}\quad A\mathrm{SO}_{4(s)} + 3\mathrm{H}_{2(g)} + \mathrm{CO}_{(g)} \Leftrightarrow A\mathrm{CO}_{3(s)} + \mathrm{H_2S}_{(g)} + 2\mathrm{H_2O}_{(g)}$$

$$\text{(j)}\quad 2A\mathrm{SO}_{4(s)} + \mathrm{H}_{2(g)} + \mathrm{CO}_{(g)} \Leftrightarrow 2A\mathrm{O}_{(s)} + 2\mathrm{SO}_{2(g)} + \mathrm{CO}_{2(g)} + \mathrm{H_2O}_{(g)}$$

$$\text{(k)}\quad A\mathrm{SO}_{4(s)} + 3\mathrm{H}_{2(g)} + \mathrm{CO}_{(g)} \Leftrightarrow A\mathrm{O}_{(s)} + \mathrm{H_2S}_{(g)} + \mathrm{CO}_{2(g)} + 2\mathrm{H_2O}_{(g)}$$

The results are given in table 3, which shows the temperature at which $\Delta G_r = 0$ for the reaction of each metal sulfate with mixtures of carbon dioxide, carbon monoxide and hydrogen. The partial pressures of the gases used in these calculations were based on those found in real lean-burn exhaust systems during the switch to fuel-rich conditions, *i.e.* 10% CO_2, 10% H_2O, 6% CO, 2% H_2 and 50 ppm SO_2 or H_2S.

Table 3 shows that, of the alkaline-earth metals, barium has the most stable sulfate for each of the reactions. The other alkali-earth metals form less stable sulfates that can be more readily replaced by carbonates or decomposed to the metal oxide under rich conditions. The stability increases with increasing atomic weight, *i.e.* in the order Ba > Sr > Ca > Mg. For the alkali metals, potassium, rubidium and cesium sulfate are the most stable, being much more stable than any of the alkaline-earth sulfates. The order of stability of the alkali metal sulfates is K ≈ Rb ≈ Cs > Na > Li.

Table 3
Ionic potentials of various alkali and alkali-earth metals and temperatures at which $\Delta G_r = 0$ for equations (h)–(k)

Element	$T_{(\Delta G_r = 0)}$ (°C)				Ionic potential (Å^{-1})
	Eqn. (h)	Eqn. (i)	Eqn. (j)	Eqn. (k)	
Cs	882	<0	1891	>2000	0.60
Rb	840	<0	1599	>2000	0.68
K	967	<0	1731	>2000	0.75
Na	611	<0	1367	1580	1.03
Li	281	<0	799	68	1.47
Ba	617	<0	984	622	1.31
Sr	457	<0	792	238	1.79
Ca	278	<0	568	<0	2.02
Mg	<0	<0	151	<0	3.03

Miyoshi and Matsumoto [12] noticed a strong correlation between the amount of NO_x stored on various alkali and alkali-earth metals and the ionic potential (ionic charge/ionic radius) of the metals. The NO_x storage amount was found to increase with decreasing ionic potential. In order to give an indication of the NO_x storage properties of the various metals, the ionic potential of the metals is included in table 3. Using the values for ionic potential and sulfate stability it is possible to identify potential candidates for a sulfur-tolerant NO_x trap. Barium, sodium, potassium, rubidium and cesium are automatically excluded on the basis of high sulfate stability. The remaining metals all have higher ionic potentials than barium and as a result it is expected that they will be less suitable than barium in terms of NO_x storage capability. Magnesium can be excluded on the basis of very poor NO_x storage capability. Of the remaining three metals, lithium seems to be the most promising. It has a slightly higher ionic potential than barium, indicating that it should be slightly less active for NO_x storage than barium. However, the stability of its sulfate is much lower than that of barium, indicating that it should be possible to remove lithium sulfate at low temperatures (>281 °C). Perhaps this explains why Matsumoto *et al.* [6] add lithium to their trap to improve tolerance against sulfur poisoning, the only drawback to the use of lithium in a real exhaust system being the solubility of the nitrate, sulfate and carbonate. This could present a problem when the engine is not in use, allowing condensation formed under certain atmospheric conditions to dissolve the lithium compounds from the trap. Strontium, on the other hand, is similar to barium, in that the carbonate and sulfate are insoluble. Its ionic potential is higher than that of both lithium and barium, indicating that its NO_x storage properties may not be as good. However, strontium sulfate can be removed at a significantly lower temperature than barium sulfate under rich conditions, signalling that strontium oxide or strontium carbonate may be another potential candidate as a replacement for barium in a sulfur-tolerant trap.

4. Conclusions

In situ infrared analysis showed that barium carbonate can be replaced by barium sulfate by reaction with low concentrations of sulfur dioxide (50 ppm) in the presence of large concentrations of carbon dioxide (10%) at temperatures up to 700 °C. These sulfates could at least be partially removed by switching to hydrogen-rich conditions at elevated temperatures.

Thermodynamic calculations were used to evaluate the effects of gas composition and temperature on the various reactions of barium sulfate and carbonate under oxidizing and reducing conditions. These calculations clearly showed that barium sulfate is very stable under oxidizing conditions. It is less stable under a hydrogen-rich atmosphere and can be decomposed to barium oxide at a temperature of 553 °C if H_2S (or 963 °C if SO_2) is taken to be the decomposition product of $BaSO_4$. The calculations showed that if, under a hydrogen-rich atmosphere, carbon dioxide is included as a reactant and barium carbonate as a product then barium sulfate can be removed by reaction with carbon dioxide at a much lower temperature than is possible by decomposition to barium oxide.

Similar calculations were conducted using a selection of other alkaline-earth and alkali metals. In this case calculations were simulated in a gas mixture containing carbon monoxide, hydrogen and carbon dioxide. The results indicated that there are metals such as lithium and strontium with less stable sulfates than barium, which may also possess sufficient NO_x storage capacity to give sulfur-tolerant NO_x traps.

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