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Thermodynamic equilibrium calculations of sulfur poisoning in Ce–O–S and La–O–S systems

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Abstract

Sulfur poisoning is still a problem in many application areas of exhaust gas catalysts despite the fact that the sulfur levels, e.g. in gasoline are being continuously reduced. The aim of this study was to calculate thermodynamic equilibrium compositions of sulfur in Ce–O–S and La–O–S systems in the presence of precious metals (Pt, Pd, and Rh), which all were considered as bulk materials, in order to understand the experimentally observed sulfur poisoning under the real applications of exhaust gas catalysts. Depending on temperature and oxygen partial pressure, sulfur can be present in the form of sulfates, sulfides and oxysulfides. It is thermodynamically favorable that cerium oxide reacts with SO_2 to form cerium sulfate at low temperatures and cerium oxysulfides at high temperatures. Lanthanum oxide reacts with SO_2 to form sulfate under oxidizing conditions and sulfides under reducing conditions.

Keywords: Sulfur; Cerium oxide; Lanthanum oxide; Thermodynamic equilibrium

1. Introduction

Sulfur and sulfur containing compounds are widely known for their interaction with precious metals and other catalyst components. The poisoning effect caused by sulfur results in considerable problems in many application areas of catalysis. In exhaust gas catalysis, sulfur originating from gasoline, diesel or lubricant oils reacts with active metals and washcoat oxides, and poisons the catalyst irreversibly or reversibly.

In order to avoid thermal stability problems and to improve catalyst properties such as durability, textural properties, and catalytic activity, various oxide components are added to catalysts. In particular, cerium and lanthanum oxides are commonly utilized as exhaust gas catalyst components along with aluminium oxide. Cerium oxide is added to a catalyst primarily due to its oxygen storage capacity and lanthanum oxide has a capability to stabilize the specific surface area of the main catalyst components. However, when exposed to even small amounts of sulfur containing compounds, the performance of both cerium oxide and lanthanum oxide is substantially diminished [2,3]. The interaction of cerium oxide with sulfur has been studied to some extent, and according to these studies the poisoning comprises a formation of a complex set of sulfur compounds [2]. For instance under oxidizing conditions, SO_2 forms sulfates and sulfites with cerium oxide, but in contrast, under reducing conditions, the reaction produces oxysulfides [2]. Nevertheless, the interaction of lanthanum oxide with sulfur as well as thermodynamic equilibrium compositions of sulfur in Ce–O–S and La–O–S systems in the presence of precious metals are not very well known, and therefore they are considered in this study.

This study was performed in order to explore the reactions between sulfur compounds and cerium oxide and lanthanum oxide catalyst components in the presence and absence of precious metals. In addition, the aim was to find out new information about the stability of the sulfur compounds and the influence of the reaction conditions on the poisoning phenomena.

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2. Experimental

Thermodynamic equilibrium calculations with cerium and lanthanum oxides in the presence of precious metals (Pt, Pd, Rh), which all were considered as bulk materials, were carried out by using a commercial HSC Chemistry® 5.1 program [4]. Equilibrium compositions and phase stability diagrams were determined by changing the oxygen and sulfur content in the feed gas as a function of temperature and as a function of sulfur and oxygen partial pressures. The oxidizing and reducing conditions were chosen to simulate the conditions of exhaust gas mixtures of diesel engines. In oxidizing conditions oxygen concentration was 5 mol% and in reducing conditions 0.05 mol%. In thermodynamic calculations the following gas mixture was used to simulate the exhaust gas of diesel engines: 0.03 mol% C_3H_6, 0.05 mol% CO, 10 mol% CO_2, 7 mol% H_2O, 0.1 mol% NO, 0.01 mol% SO_2, balanced with N_2. The solid mixture included cerium and lanthanum oxides and precious metals, which were considered as bulk materials.

Thermodynamic equilibrium calculations with cerium and lanthanum oxides and exhaust gas mixture included 0.2 kmol gas input (exhaust gas) and 0.1 kmol solid input (Ce_2O_3 or La_2O_3). Calculations with cerium and lanthanum oxides and the exhaust gas mixture in the presence of active metals (Pt, Pd and Rh) also included 0.2 kmol gas input (exhaust gas) and a 0.1 kmol solid input, which were composed of 1 mol% active metal and 99 mol% oxide. The results were given as figures, which present the mole fractions of the compounds as a function of temperature with the range from 0 to 2000 °C. Cerium and lanthanum oxides were also studied with phase stability diagrams by changing the partial pressures of oxygen (O_2) and sulfur (S_2) at different temperatures.

The HSC Chemistry® 5.1 program can be used as a tool for calculating chemical equilibrium between pure components in ideal and, in some cases, in non-ideal solutions. In these calculations, enthalpies, entropies and heat capacities of compounds are needed. The HSC Chemistry® 5.1 program includes a thermochemical database that contains the values of enthalpies, entropies and heat capacities. The program does not process any kinetic phenomena, but physically possible phenomena can usually be shown by thermochemical calculations. Phase stability diagrams present stability areas of condensed phases in ternary systems, either as a function of temperature or in isothermal conditions. These diagrams are useful for a quick estimation of prevailing phases.

3. Results

3.1. Ce–O–S system

The mole fractions of sulfur were determined in oxidizing diesel exhaust conditions in the presence of cerium oxide, as presented in Fig. 1a, by thermodynamic equilibrium calculations. As can be seen in Fig. 1a, at low temperatures $Ce(SO_4)_2$ is a thermodynamically favorable compound and it starts to decompose to cerium oxysulfide (Ce_2O_2S) at around 500 °C. The formation of $Ce(SO_4)_2$ is thermodynamically favorable at low temperatures also in reducing diesel exhaust conditions and it decomposes to Ce_2O_2S at around 600 °C.

Fig. 1a also shows that at high temperatures, the formation of cerium oxysulfide (Ce_2O_2S) is thermodynamically favorable. Cerium oxysulfide starts to decompose under oxidizing conditions at 1600 °C and under reducing conditions at 1900 °C. Also in the presence of active metals (Pt, Pd and Rh) and cerium, cerium oxide reacts with SO_2 both in oxidizing and reducing conditions to form $Ce(SO_4)_2$ and Ce_2O_2S.

Phase stability diagrams for Ce–O–S system at 500 °C as a function of sulfur and oxygen partial pressures are presented in Fig. 1b. As can be seen in Fig. 1b, the chemical reactions of cerium and sulfur in the Ce–O–S system are complicated. In the most simplified case, when only the oxygen concentration is increased, cerium is oxidized in the following order: $Ce_2O_3 \rightarrow CeO_{1.72} \rightarrow CeO_{1.83} \rightarrow CeO_2 \rightarrow Ce_2(SO_4)_3 \rightarrow Ce(SO_4)_2$. Instead, when sulfur concentration is increased, cerium is reduced in the following order: $Ce_2O_3 \rightarrow Ce_2O_2S \rightarrow Ce_3S_4 \rightarrow Ce_2S_3 \rightarrow CeS_2$.

3.2. La–O–S system

Thermodynamic equilibrium calculations were also carried out in the La–O–S system. Under oxidizing conditions lanthanum oxide reacts with SO_2 to form $La_2(SO_4)_3$ that decomposes at around 900 °C [1]. In Fig. 2a, the mole fractions of sulfur containing compounds in reducing diesel exhaust conditions are presented in the presence of lanthanum oxide. As shown in Fig. 2a, it is thermodynamically favorable that La_2O_3 reacts with SO_2 to form lanthanum sulfides (La_2S_3 and LaS_2) at low temperatures. La_2S_3 starts to decompose already at around 100 °C and LaS_2 at 600 °C.

In the presence of precious metals and lanthanum, La_2O_3 reacts to form sulfate ($La_2(SO_4)_3$) under oxidizing conditions. $La_2(SO_4)_3$ starts to decompose to SO_2 at 800 °C. Also $La(OH)_3$ was formed at low temperatures (<400 °C). Under reducing conditions only in the presence of palladium the formation of lanthanum sulfides (La_2S_3 and LaS_2) is thermodynamically favorable. Furthermore, palladium sulfide (PdS) was also a stable compound which decomposes at around 700 °C. Lanthanum sulfides were formed only at temperatures below 400 °C. The thermodynamical behaviour differs in the case of platinum and rhodium compared to palladium. In the presence of platinum and rhodium, the formation of platinum and rhodium sulfides (PtS and $RhS_{0.889}$) is thermodynamically favorable but not the formation of lanthanum sulfides which were formed in the case

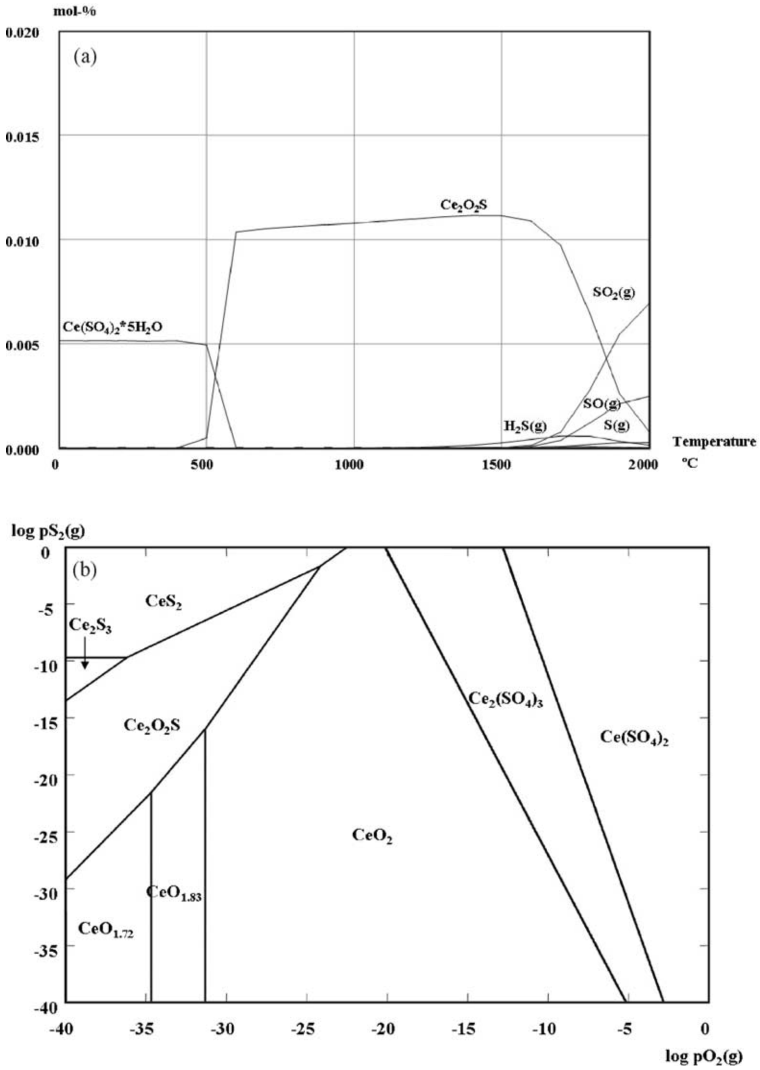

Fig. 1. (a) Mole fractions of sulfur containing compounds in oxidizing diesel exhaust conditions in the presence of cerium oxide (0.03 mol% C_3H_6, 0.05 mol% CO, 10 mol% CO_2, 7 mol% H_2O, 0.1 mol% NO, 5 mol% O_2, 0.01 mol% SO_2, balanced with N_2). (b) Phase stability diagram for Ce–O–S system at 500 °C as a function of log(pO_2) and log(pS_2).

of Pd. Both PtS and $RhS_{0.889}$ decomposed at around 700 °C.

The phase stability diagram for the La–O–S system at 500 °C as a function of sulfur and oxygen partial pressure is presented in Fig. 2b. When oxygen concentration is increased, lanthanum is oxidized in the following order: $La_2O_3 \rightarrow La_2(SO_4)_3$. When sulfur concentration is increased, lanthanum is reduced in the following order: $La_2O_3 \rightarrow La_2S_3 \rightarrow LaS_2$.

4. Discussion

Cerium was known to be thermodynamically unstable in the presence of oxygen, and therefore, different oxides of cerium, Ce_2O_3, and CeO_2 are easily formed [5]. In oxidizing diesel exhaust conditions, several oxides of cerium can be present, and in the presence of sulfur cerium oxide reacts readily with sulfur to form $Ce(SO_4)_2$ at low temperatures. It has been reported [6,7] that cerium oxide reacts with sulfur dioxide to form cerium sulfates at low temperatures, which is consistent with the results of this study. Sulfate formation reduces the ability of cerium oxide to manage the oxygen partial pressure in the catalytic converter and in this way sulfates deactivate cerium oxide severely [2].

The formation of cerium oxysulfide is more probable in reducing conditions than in oxidizing conditions, as has been reported in many publications [2,6,7]. Therefore, the formation of oxysulfide may also be kinetically favorable under reducing conditions. In this case, the sulfur poisoning can be even so strong and irreversible that the catalyst cannot be regenerated e.g. by heating. This phenomenon is not completely understood; on the other hand, it has also been reported that Ce_2O_2S can be reoxidized to sulfates [8], which is inconsistent with the

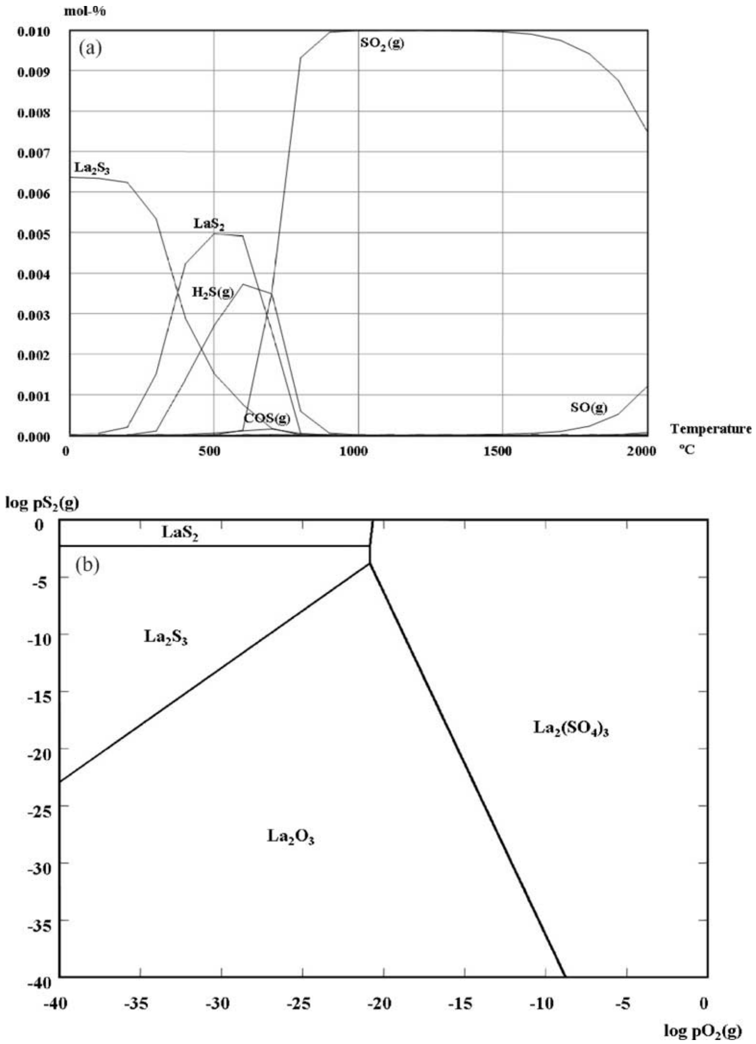

Fig. 2. (a) Mole fractions of sulfur containing compounds in reducing diesel exhaust conditions in the presence of lanthanum oxide (0.03 mol% C_3H_6, 0.05 mol% CO, 10 mol% CO_2, 7 mol% H_2O, 0.1 mol% NO, 0.05 mol% O_2, 0.01 mol% SO_2, balanced with N_2). (b) Phase stability diagram for La–O–S system at 500 °C as a function of $\log(pO_2)$ and $\log(pS_2)$.

results presented in this study and in publications [2,6,7]. However, the formation of oxysulfide may be so slow under oxidizing conditions that sulfates cannot be reduced to oxysulfides in real applications. Once formed, oxysulfide is a very stable compound and it cannot be decomposed.

The formation of lanthanum sulfides under reducing conditions shows that poisoning of lanthanum oxide may be severe. On the other hand, the decomposition temperatures of lanthanum sulfide are relatively low, and therefore, it is possible to decompose lanthanum sulfides by increasing temperature. Under oxidizing conditions and in the presence of precious metals (Pt, Pd and Rh) lanthanum sulfate was a stable compound and decomposed at around 900 °C. Therefore, it seems that the presence of any of these precious metals has a similar effect on the formation and decomposition of lanthanum sulfate. Yet in reducing conditions, lanthanum sulfides were only formed in the presence of palladium. Therefore, lanthanum oxide may be more severely poisoned in the presence of palladium than in the presence of platinum and rhodium.

5. Conclusions

It is thermodynamically favorable that cerium oxide reacts with SO_2 originating from diesel exhaust gas both in oxidizing and reducing conditions to form $Ce(SO_4)_2$ at lower temperatures and Ce_2O_2S at higher temperatures. With lanthanum oxide and diesel exhaust gas it is thermodynamically favorable that La_2O_3 reacts with SO_2 to form in oxidizing conditions $La_2(SO_4)_3$ and in reducing conditions La_2S_3 and LaS_2.

In the systems containing an oxide and a precious metal, sulfur shows in reducing conditions a tendency to form sulfides with precious metals (PtS, PdS and $RhS_{0.889}$) with the exception of cerium oxide that, according to the calculations, forms with sulfur more favorably $Ce(SO_4)_3$ or

Ce_2O_2S than precious metal sulfides. In the Pd–lanthanum oxide system, both PdS and lanthanum sulfides (La_2S_3 and LaS_2) can be formed. In oxidizing conditions, however, the formation of sulfates and in the case of cerium oxide also oxysulfides is thermodynamically more favorable than reactions between sulfur and precious metals.

In this study, it was shown that the reactions between sulfur and oxide (cerium oxide and lanthanum oxide) involve the formation of a complicated set of compounds. In addition, on the basis of calculations, the reaction conditions influence substantially the sulfur poisoning phenomena. Furthermore, by using the calculation program, new information about the stability of the sulfur compounds was found. In further studies, this information could be utilized in finding a mixture of oxides that would stand or prevent sulfur poisoning in the real applications of exhaust gas catalysts.

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