Experimental Study on Combustion Inhibition Effects of Inorganic Salts

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ABSTRACT

Some types of inorganic salts are used as flame retardant and/or fire suppressant. Their combustion inhibition ability can be referred qualitatively, but quantitative analyses on their combustion inhibition mechanisms are insufficient. In this study, they are classified by their combustion inhibition ability measured experimentally. Inhibition ability in gas-phase was measured as extinction concentration for burner flame when they were added to the flame, and that in solid-phase was measured as extinction concentration for burning filter paper when the paper held them.

According to combustion extinction concentration in gas- and solid-phases, combustion extinction phenomena of the inorganic salts were classified in four categories.

INTRODUCTION

Although fire-extinguishing ability of present fire extinguishers is evaluated practically, fire-extinguishing mechanisms of them are revealed only qualitatively. To develop more powerful or low-cost fire extinguisher, basic research on fire-extinguishing mechanism is in need [1-3].

Therefore, basic experiments were conducted in this study to evaluate quantitative fire-extinguishing ability of inorganic salts. Two fire-extinguishing properties were measured. The first is fire-extinguishing ability against pre-mixed flame. Flame extinction concentration for burner flame was measured to evaluate this property. The second is fire-extinguishing ability against solid fuel burning. Flame extinction concentration for filter paper burning was measured to evaluate this property.

Comparing these two properties, it is expected to be revealed in which phase, gas or solid phases each inorganic salt shows fire-extinguishing effect. In addition, quantitative measurement will reveal how each metal or base show fire-extinguishing effect.

EXPERIMENTAL METHOD

Measurement of Gas-phase Flame Extinction Concentration

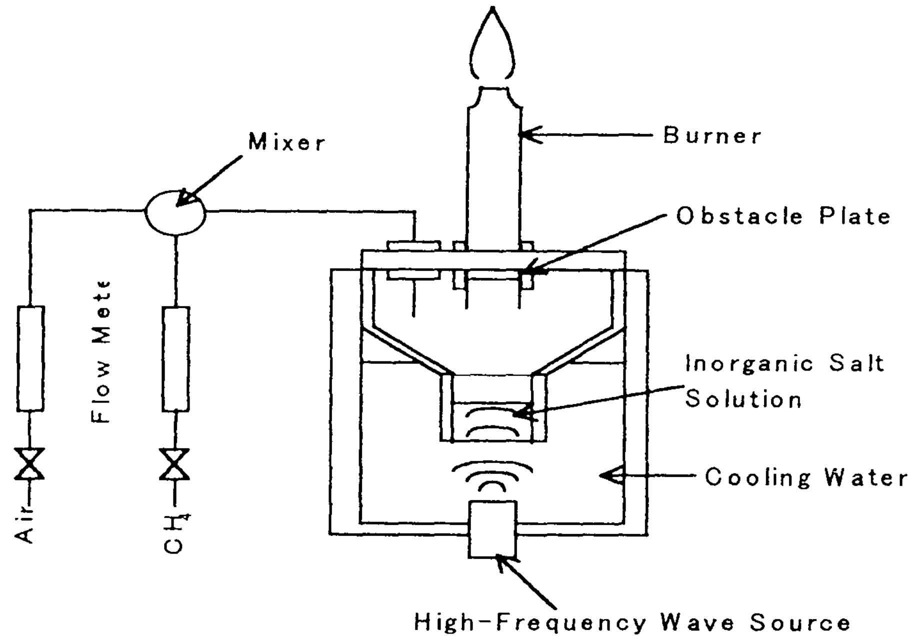

Fig. 1 Experimental Apparatus for Measuring Flame Extinction Concentration against Pre-Mixed Flame

Figure 1 shows experimental apparatus for measuring extinction concentration in gas phase Methane and air are mixed at a mixer, and the mixture passes through a mist generator to a nozzle burner. While passing through the mist generator, mist of inorganic salt solution is added to the mixture. Size of mist is adjusted by an obstacle plate (stainless wire netting of 30 mesh). Measured mist size was under 10 μ m.

The mixture with mist is burned at the burner, and burning rate of the mixture is measured The burner is a stainless circular tube nozzle-burner. Its inner diameter is 30 mm and burner rim diameter is 10 mm, that is, diameter shrinkage is 1/9.

Burning rate is calculated from picture of flame shape. Flame surface area is estimated from the picture. Then, it is divided by flow rate of the mixture to yield the burning rate.

Concentration of inorganic salt solution is increased by 0.01 mol/l each. Extinction concentration is determined by the minimum concentration, on which the burner flame goes out. Amount of generated mist varies with concentration of the solution, so extinction concentration is made correction about amount of the mist. Some inorganic salt reaches saturation concentration before the burner flame goes out, so extinction concentration can not be determined for the salt.

Measurement of Solid-phase Extinction Concentration

In this study, extinction concentration is measured as added mass of inorganic salt on unit area of filter paper, which is made of pure cellulose.

At first, the filter paper is dried in a vacuum desiccator for 24 hours, and weighed. Then, the filter paper is soaked in inorganic salt solution with certain concentration. Well-soaked filter paper is dried in room condition for a while and in a vacuum desiccator for 48 hours in order to remove moisture thoroughly. After removing moisture, the filter paper is weighed again. Difference of weight between before and after the filter paper is soaked in, is regarded as mass of inorganic salt on the filter paper. The filter paper is cut into strips of 100 mm long and 5 mm wide.

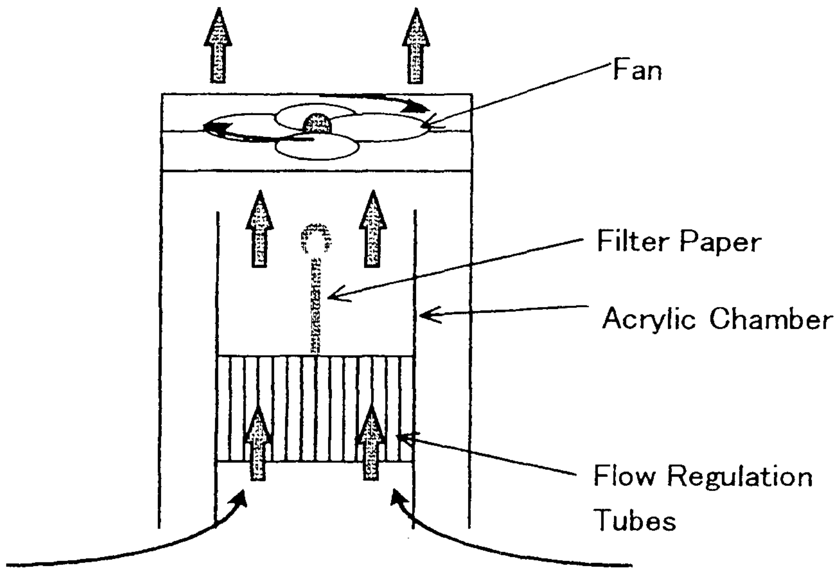

Fig.2 Experimental Apparatus for Measuring Solid-phase Extinction Concentration

Figure 2 shows experimental apparatus for observing burning behavior of the filter paper. The filter paper was burned in an acrylic chamber. The chamber has flow regulation tubes at the bottom and has four iron legs to keep space between the tubes and floor. An electric fan is placed above the acrylic chamber to suck environmental air into the acrylic chamber through the flow regulation tubes. Rotation speed of the fan is arranged for airflow rate at 6 mm above the flow regulation tubes to be 10 cm/s. Cross-section of the acrylic chamber is a 15-cm wide square, and each flow regulation tube was aluminum tube with 1-cm diameter and 15 cm long.

A filter paper with inorganic salt is placed in the acrylic chamber as shown in the figure. It is ignited by a lighter at the top rim, and burning behavior of it is observed. Concentration of the inorganic salt on the filter paper is increased gradually. The minimum concentration, at which burning of the filter paper is not observed even if the lighter flame touched at the paper for sufficiently long time, is determined as combustion extinction concentration in solid phase. The combustion extinction concentration is referred as mass of inorganic salt on unit mass of cellulose.

Inorganic Salts Used in This Study

Inorganic salts used in this study are summarized in table 1. The studied salts are marked with ●. Measurement of gas-phase extinction concentration was done for the salt marked in gas column, and measurement of solid-phase extinction concentration was done for that

Table 1 Inorganic Salts Used in This Study

Base	K^+		Na^+		Li^+		Zn^{2+}		NH_4^+	
	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas
PO_4^{3-}	●	●	●	●	/	/	/	/	/	/
HPO_4^{2-}	●	●	●	●	/	/	/	/	/	/
$H_2PO_4^-$	●	●	●	●	/	/	/	/	●	●
CO_3^{2-}	●	●	●	●	●	●	/	/	/	/
HCO_3^-	●	●	●	●	/	/	/	/	/	/
Cl^-	●	●	●	●	●	●	●	●	●	●
Br^-	●	●	●	●	●	●	●	●	●	●
I^-	●	●	●	●	/	●	/	/	/	●
SO_4^{2-}	●	●	●	●	●	●	/	/	●	●
OH^-	●	●	●	●	●	●	/	/	/	/
CH_3COO^-	●	●	●	●	/	/	/	/	/	/
$B_4O_7^{2-}$	●	●	●	●	/	/	/	/	/	/
$C_2O_4^{2-}$	●	●	●	●	/	●	/	/	/	/

marked in solid. Although they were not listed in the table, measurement was conducted on magnesium and aluminum sulfates.

EXPERIMENTAL RESULTS

Figure 3 shows relation between gas- and solid-phase extinction concentrations for inorganic salts examined.

As shown in the figure, extinction ability of inorganic salts can be classified in the following four categories.

I. A salt in this category shows powerful flame inhibition effect in gas-phase. Consequently, it acts as powerful flame retardant in both gas- and solid-phase.

II. A salt in this category acts as flame retardant in solid-phase, but it shows little flame inhibition effect in gas-phase.

III. A salt in this category acts as flame inhibitor in gas-phase, but it cannot extinguish smoldering combustion in solid-phase. Combustion extinguishing phenomena of cellulose with this salt are described as follows.

1) It burns as usual, i.e. with flame, to some concentration of the salt on cellulose.

2) At some concentration, flame extinguishes, but smoldering combustion remains.
3) At some concentration shown in Fig. 3, smoldering combustion extinguishes.

IV. A salt in this category shows little flame extinguishing effect in both gas- and solid-phase.

ADDITIONAL EXPERIMENTS AND DISCUSSION

Combustion inhibition effects of inorganic salts are categorized as mentioned above. To clarify inhibition mechanisms in each category, additional experiments and numerical discussion were conducted.

Flame Inhibition Effects of Halogenated Alkali Metals

As shown in Fig. 3, halogenated sodium and potassium are categorized in category Ⅰ. They show very powerful flame inhibition effects in gas-phase. Their flame inhibition effects are considered to come from their decomposition products, i.e. halogen atoms and alkali metals. Both of the halogen atoms and alkali metals can terminate combustion chain reactions. Namely, they must decompose first to show combustion inhibition effect. Halogenated alkali metal releases halogen atom and alkali metal easier if bond between them is easy to dissociate. Therefore, bond dissociation energy of the salt is considered to have some relation between extinction concentration of it.

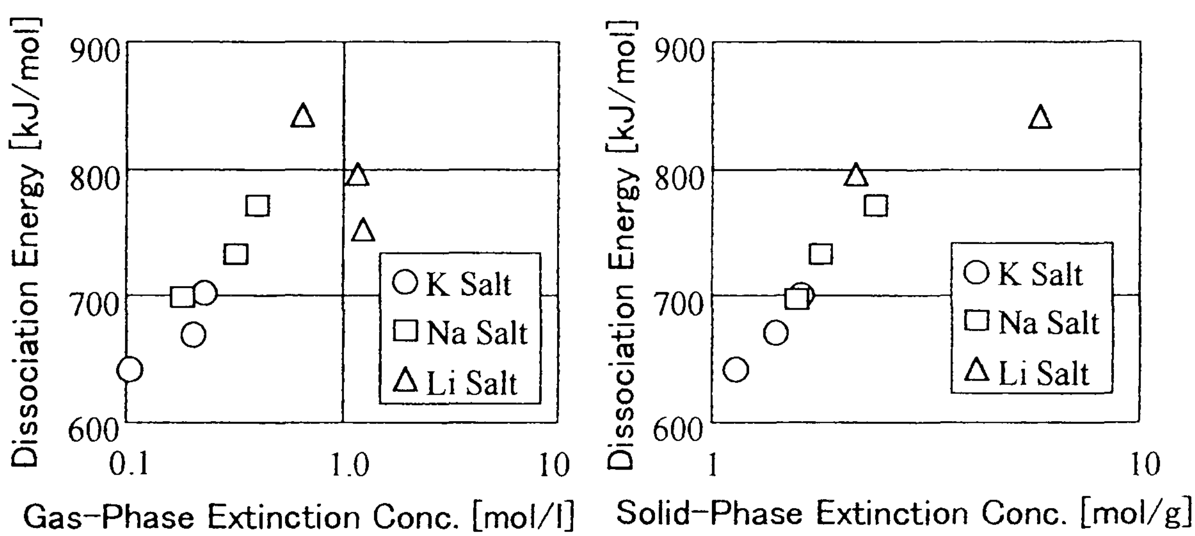

Fig. 4 Relation between Extinction Concentration and Bond Dissociation Energy for Halogenated Alkali Metals

Figure 4 shows relation between bond dissociation energy and extinction concentration for gas-phase (a) and solid-phase (b). Halogenated lithium salts are also shown in this figure, because lithium is also alkali metal like sodium and potassium. Although lithium salts show different tendency, other salts show that extinction concentration depends linearly on bond dissociation energy. As shown in Fig. 3, lithium salts are categorized in category Ⅱ unlike other alkali metals, sodium and potassium. Lithium salts may have different extinction mechanisms from sodium and potassium salts.

Thermal Analysis of Cellulose with Inorganic Salt

To investigate role of the inorganic salts in thermal degradation of cellulose, thermogravimetric analysis (TG) was conducted. Some fire retardant is said to affect thermal degradation.

Same filter paper was used as mentioned above. It was soaked in 0.012 mol/l inorganic salt solution for 5 min, and dried thoroughly. It was cut into 3 mm wide square, which has ca. 0.9 mg weight. The square sheet was used for thermal analysis.

Thermal analysis was conducted on paper with the following eight inorganic salts and virgin paper.

Used inorganic salts

① Phosphates

$NH_4H_2PO_3$, KH_2PO_3, K_2HPO_3, K_3PO_3

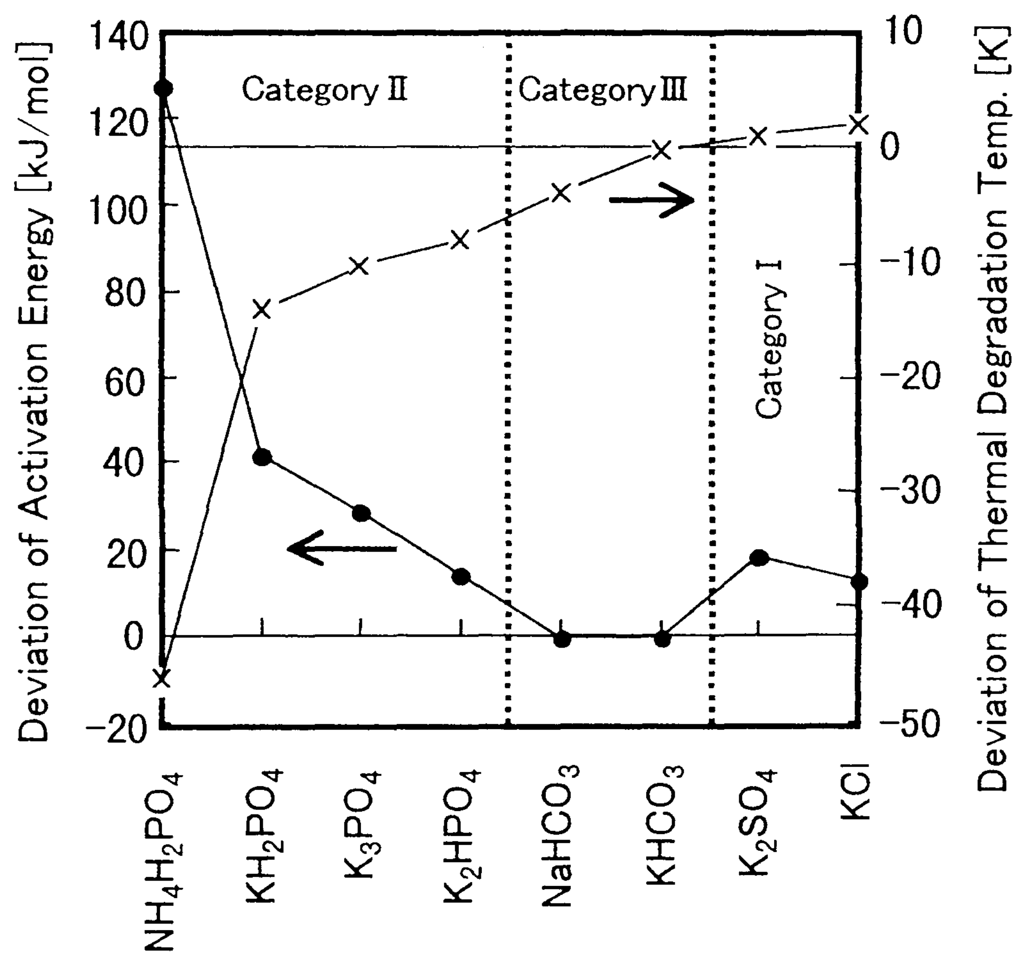

Fig. 5 Deviation of Activation Energy and Initiation Temperature of Thermal Decomposition of Cellulose

② Hydrogen Carbonates
   $NaHCO_3$, $KHCO_3$

③ Others
   KCl, K_2SO_4

From TG curves obtained for each sample, activation energy and initiation temperature for thermal degradation of paper were derived.

Figure 5 shows activation energy and initiation temperature for thermal degradation of each sample. The activation energy and the initiation temperature are both shown as deviation from those of the virgin paper.

As shown in Fig. 5, eight samples tested are classified in three categories identical with those shown in Fig. 3. Variation of the activation energy and the initiation temperature for thermal degradation of paper is described as follows for each category.

I Initiation temperature of the thermal degradation increases a little from virgin paper. Activation energy increases slightly. This means a salt in this category may affect the thermal degradation process, but does not interfere so much.

II Initiation temperature decreases and activation energy increases. This means that a salt in this category affects thermal degradation. Phosphates are usually considered to promote carbonizing of cellulose. Namely, scission of branch occurs at lower temperature and carbonized residue requires higher activation energy to decompose.

III Initiation temperature decreases slightly. Activation energy is identical with virgin paper. This means a salt in this category affects thermal degradation little. Slight change in the initiation temperature may be attributed to thermal degradation of the salt itself.

Base Effects in Solid-Phase Extinction Concentration

In this study, potassium and sodium salts were examined for all bases. Therefore, contribution of bases to combustion extinction can be evaluated from results for potassium and sodium salts.

Figure 6 shows variation of solid-phase extinction concentration with bases for potassium or sodium salt. Order of potassium salts coincides strictly with that of sodium salts. It is as follows from the salt having the smallest extinction concentration.

$$PO_4^{3-} \rightarrow B_4O_7^{2-} \rightarrow HPO_4^{2-} \rightarrow I^- \rightarrow Br^- \rightarrow Cl^- \rightarrow H_2PO_4^- \rightarrow C_2O_4^{2-} \rightarrow SO_4^{2-} \rightarrow CO_3^{2-} \rightarrow HCO_3^- \rightarrow CH_3COO^- \rightarrow OH^-$$

Comparing potassium salts with sodium salts, potassium salt has smaller extinction concentration than sodium salt for all bases. Therefore, it is considered that these salts first dissociate and then decomposition products, i.e. alkali metal and base, intercept combustion reaction, separately.

CONCLUSION

From measured extinction concentrations, inorganic salts were classified in four categories by their quantitative combustion extinguishing ability. The categories are as follows.

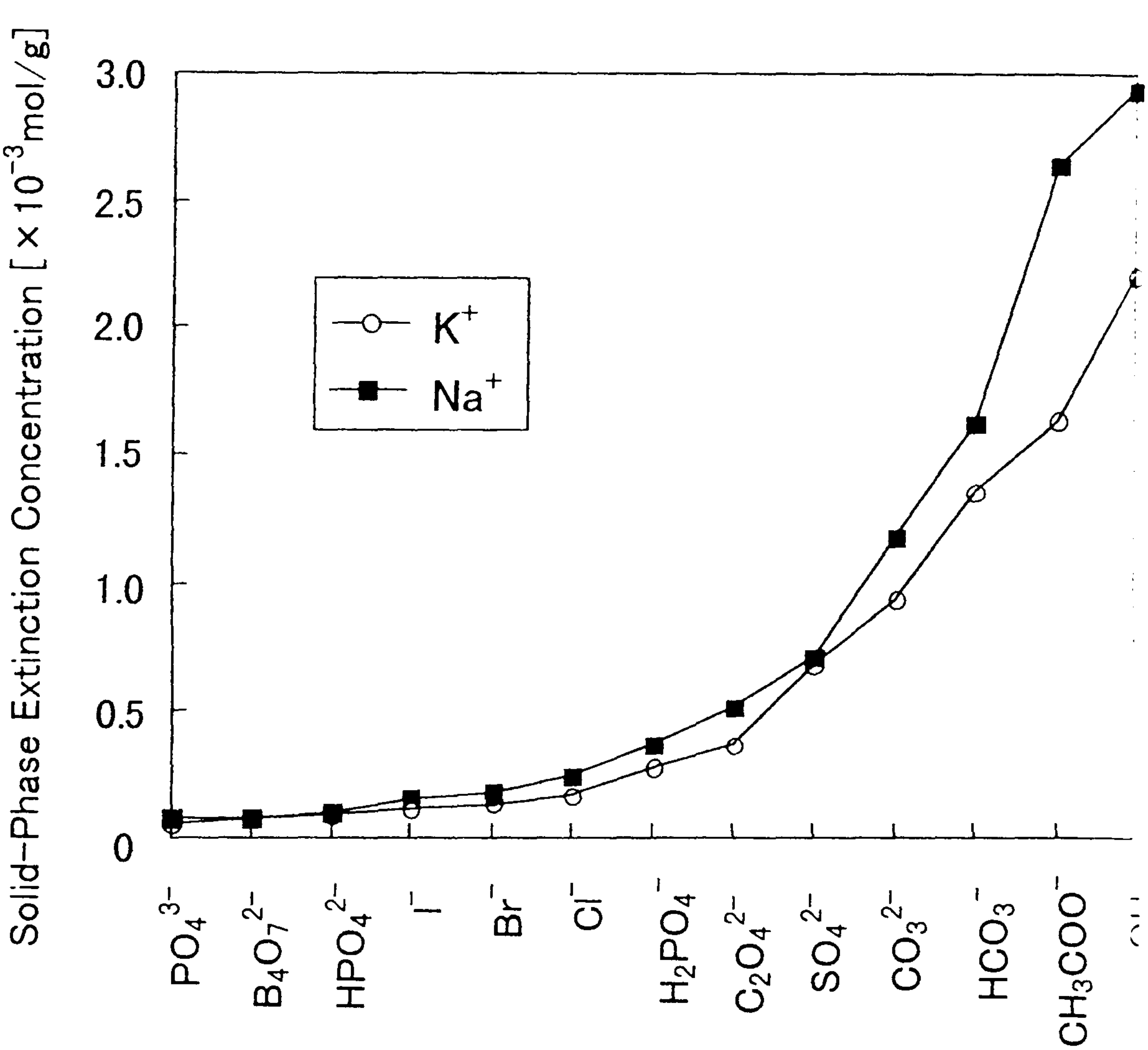

Fig. 6 Order of Extinction Ability by Changing Bases

Category I : A salt in this category acts mainly as flame inhibitor in gas-phase. It affects a little on solid-phase phenomena, but the solid-phase effect is insignificant.

Category II : A salt in this category extinguishing fire by its solid-phase effect. (Solid-phase effect > Gas-phase effect)

Category III : A salt in this category acts as flame inhibitor in gas-phase. Smoldering combustion is promoted in solid-phase. (Gas-phase effect > Solid-phase effect)

Category IV : A salt in this category has little effect as flame inhibitor both in gas- and solid-phases.

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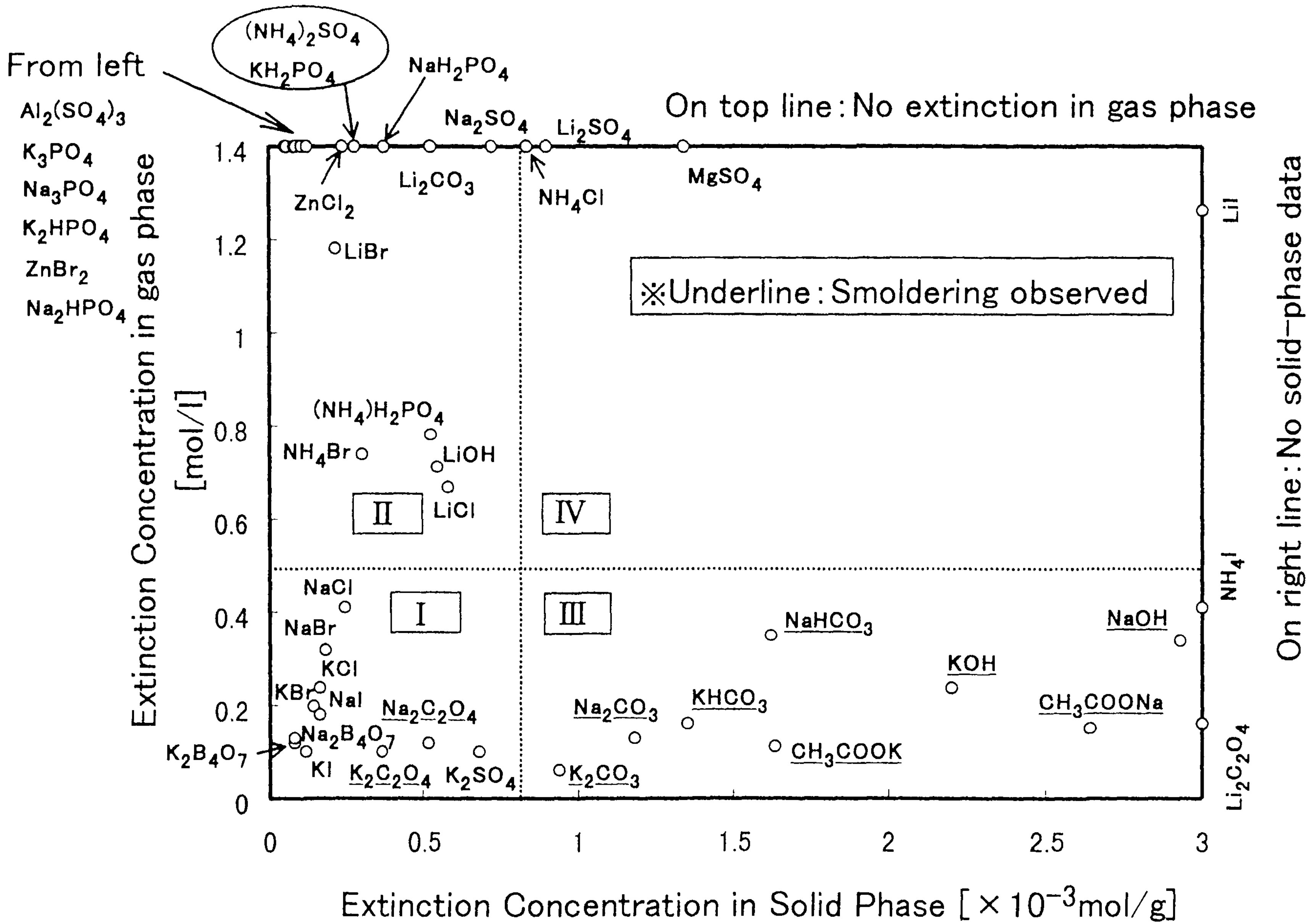

Fig. 3 Extinction Concentrations in Gas and Solid Phases