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# Direct comparison of the flame inhibition efficiency of transition metals using metallocenes

Yusuke Koshiba [a,*], Saori Agata [b], Tomohide Takahashi [b], Hideo Ohtani [c]

[a] Department of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[b] College of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[c] Department of Safety Management, Faculty of Environmental and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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ABSTRACT

This study aimed to directly and systematically compare the flame inhibition abilities of various transition metals, including vanadium, ruthenium, osmium, chromium, manganese, iron, cobalt, and nickel, by using the corresponding metallocenes: vanadocene, ruthenocene, osmocene, chromocene, manganocene, ferrocene, cobaltocene, and nickelocene. The downward flame spread rates over filter paper samples on which each metallocene was adsorbed were measured. In addition, thermogravimetric measurements were carried out to finally determine the phase in which each metallocene produced its flame inhibition effect. The results indicated that all these metallocenes, with the exception of vanadocene, exhibit a flame inhibition effect solely in the gas phase, whereas vanadocene shows fire suppression ability in the solid phase. This work also found that, in terms of their fire suppression abilities, the transition metals can be ranked in the following order: Cr > Mn > Fe > Co > Ni > (V > )Os > Ru.

## 1. Introduction

Accidental deaths due to fire in Japan average approximately 2000 a year and hence the development of high-performance fire extinguishing agents is required as a means of preventing such loss of life. Transition metals exhibit a wide range of oxidation states, thereby enabling these materials to scavenge radicals present in the chain reactions within flames, and this implies that transition metal compounds should exhibit highly efficient fire-extinguishing capabilities [1–4]. Among the various transition metal compounds, it is well known that iron pentacarbonyl ($Fe(CO)_5$) is a good flame inhibitor [5,6] and thus this chemical has been proposed as an alternative to the halons. $Fe(CO)_5$, however, is highly toxic [7] and this seriously limits its application as a fire extinguishing agent. In contrast, ferrocene ($FeCp_2$, see Fig. 1), which is also an iron coordination compound, has received much attention because of its good fire suppression performance and low toxicity [8]. A number of studies have been reported on the fire suppression abilities of transition metal salts having different counter ions [9]; however, the suppression abilities of the various transition metal compounds cannot be directly compared from the resulting data. This is because the counter ions, including chloride and bromide, also possess some fire suppression ability and the physical and chemical properties of the transition metal compounds may greatly vary depending on their counter ions.

In order to circumvent this problem and directly compare the suppression ability of transition metals, we have examined the suppression effects of transition metals by using metallocenes ($MCp_2$) such as chromocene ($CrCp_2$), manganocene ($MnCp_2$), ferrocene, cobaltocene ($CoCp_2$), and nickelocene ($NiCp_2$) [10]. The major advantages of using these metallocenes are that (1) these compounds form a homologous series, (2) the oxidation states of their central metals are identical (i.e., +2), (3) their counter ions are identical (i.e., cyclopentadienyl anions, $Cp^-$), (4) cyclopentadienyl anions exhibit no fire suppression effect, and (5) these metallocenes easily decompose at elevated temperatures because the bond dissociation energy of metal–Cp ring bonds is low [11]. These factors allow a direct comparison of the inhibition abilities of transition metals and the results of such testing have indicated that the relative suppression effects of these compounds can be ordered as: $CrCp_2 > MnCp_2 > FeCp_2 > CoCp_2 > NiCp_2$ [10]. Interestingly, this progression reflects the order of the atomic number of the central metals of these compounds.

The objective of the present study was to systematically and directly compare the inhibition efficiency of transition metals by employing three metallocenes: ruthenocene ($RuCp_2$), osmocene

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* Corresponding author. Fax: +81 45 339 3985.
*E-mail address:* ykoshiba@ynu.ac.jp (Y. Koshiba).

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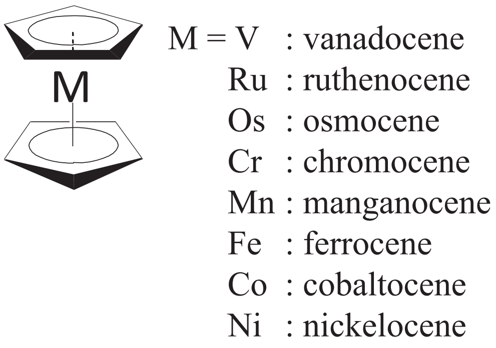

**Fig. 1.** Chemical structures of vanadocene, ruthenocene, osmocene, chromocene, manganocene, ferrocene, cobaltocene, and nickelocene.

($OsCp_2$), and vanadocene ($VCp_2$). Ruthenium and osmium belong to the same group in the periodic table as iron (Group 8), while vanadium is in the same period as chromium, manganese, iron, cobalt, and nickel (Period 4). Thus, the influence on fire suppression ability of both the group and the period in the periodic table was investigated. The fire suppression ability of a flame inhibitor is typically evaluated using a cup burner flame [12]; however, the experiments in this study were carried out by combusting a filter paper on which the metallocene was adsorbed, owing to the very low vapor pressures of these compounds. In the combustion experiments, the downward flame spread rate was measured to determine whether the metallocene produced its flame inhibition effect. Downward flame spreading over the filter-paper samples used in this study resulted from the transfer of sufficient heat from the flame to the thermally thin cellulosic fuel, since this heat transfer was sufficient to produce combustible gases from the cellulose through a pyrolysis process [13]. The flame spread rate could potentially be reduced in cases in which the metallocene produced a flame inhibition effect when in the gas phase. If the metallocene in its solid phase hampered the decomposition of the cellulose, the production of combustible gases was inhibited, resulting in a decrease in the flame spread rate. These mean that the combustion experiments alone was not enough to determine the phase in which the metallocene exerts its flame inhibition effect, since both the gas- and solid-phase flame inhibition effects would be observed in such trials. The determination of the phase is of great importance in terms of understanding the inhibition mechanisms. In this study, in addition to the combustion trials, the metallocenes were evaluated with regard to their flame inhibition efficiency in the solid phase using thermogravimetric analysis (TGA) in order to finally determine the phase, gas and/or solid, in which the metallocene generated its suppression effect. Cheng et al. performed TG measurements in air to determine the kinetic parameters associated with the combustion of cellulose, including the activation energy ($E_a$) and pre-exponential factor ($A$) [14]. The present study evaluated the metallocenes with regard to their solid phase flame inhibition abilities by comparing the kinetics parameters (that is, the activation energy and pre-exponential factor) and char yields of various metallocene/cellulose systems with those for pure cellulose.

## 2. Material and methods

### 2.1. Chemicals and materials

$RuCp_2$ (purity > 99%), $OsCp_2$ (purity > 99%), and $VCp_2$ (purity > 95%) (see Fig. 1 for molecular structures) were purchased from Strem Chemicals, Inc. (Newburyport, MA, USA). All three commercially available metallocenes were employed as-received. Dehydrated solvents (toluene and *n*-hexane, purity > 99.5%) were purchased from the Kanto Chemical Co., Inc. (Tokyo, Japan) and filter paper with a uniform thickness of 0.18 mm and a density of 87 g/m$^2$ was obtained from Tokyo Roshi Kaisha, Ltd. (Tokyo, Japan).

### 2.2. Flame spread rate measurements

Flame spread rates on filter papers were measured to evaluate the fire suppression ability of each of the metallocenes. A filter paper made from natural cellulose was utilized as a typical combustible solid. The paper was cut into rectangular shapes (5.0 mm wide × 120.0 mm long) using Teflon-coated scissors. After drying in a desiccator for 48 h, the paper sections were weighed in a dry glovebox filled with dry nitrogen (> 99.99%). The cut paper was subsequently immersed in a toluene solution of the metallocene for 15 min. The exception was $VCp_2$, which was instead dissolved in *n*-hexane since it is completely insoluble in toluene. The cut paper was then allowed to dry in a desiccator and was again weighed. In this manner, filter paper samples on which the metallocenes were homogeneously adsorbed were prepared. The amount of metallocene adsorbed per unit weight of the cut paper, $C$, can be expressed by the following equation:

$$C = (W_s - W_0)/W_0/M \qquad (1)$$

where $W_s$ is the weight of the sample, $W_0$ is the dry weight of the cut paper and $M$ is the molar mass of the metallocene. That is, $C$ is the concentration of the metallocene on the rectangular paper sample.

The experimental setup was adopted from our previous study [10] and is shown in Fig. 2. Each prepared sample was fixed on a sample holder in an acrylic tube (80 mm in diameter × 300 mm in height), after which dry air was passed upward at a flow rate of 5.0 L/min. The filter paper samples were sufficiently sturdy such

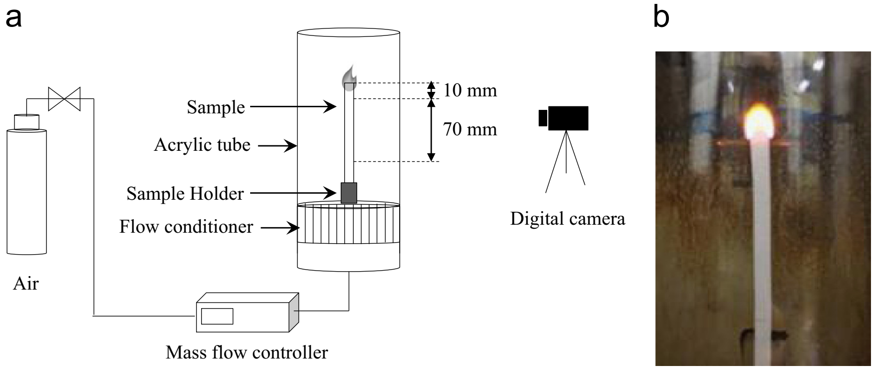

**Fig. 2.** (a) Experimental apparatus for assessment of filter combustion and (b) a photographic image of ruthenocene-treated paper sample during combustion.