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# Catalytic properties of metallosilicates

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## Abstract

Metallosilicates with MFI structure containing metal atoms such as Ni, Co, Cu, Zn-Cu and Zn in framework have been synthesized with various metal/silicone (Me/Si) ratios (up to 0.1). The acidities of H-form metallosilicates were evaluated by some acid-catalyzed reactions (decomposition of 2-propanol, cracking of cumene and isomerization of 1-butene). The Zn-Si catalyst showed the highest acidities among various metallosilicates. In the metallosilicates-supported noble metal catalysts, 5%Pt/Zn-Si and 0.1%Pd/Cu-Si catalysts showed the highest activities for hydrodesulfurization of thiophene and hydrodechlorination of chlorobenzene, respectively.

Keywords: Metallosilicates, MFI structure, Catalytic properties,

## 1 INTRODUCTION

The isomorphous substitution of the framework atoms has become very efficient method of modification of molecular sieves and manufacturing of novel materials. The valence, electronegativity, size, nature of the introduced metal atom significantly affects properties and stability of resulting materials. Although the aluminosilicate zeolites remain still the most important group of the molecular sieves, according to the classification they are only one family of metallosilicate. The MFI structure is susceptible for isomorphous substitution and quite a number of metallosilicates (e.g. Ti-Si, Fe-Si, B-Si, Ge-Si, Ga-Si) have been obtained<sup>(1)(2)</sup>. Some of the metallosilicates show the remarkable catalytic activities and high selectivities for the mild oxidation (Ti-Si)<sup>(3)</sup> and

aromatization of hydrocarbons (Ga-Si)<sup>(4)</sup>. We have reported that catalytic activities of Zn-Si modified with cations for various reactions and the effect of cations on the activity of supported platinum catalyst for hydrodesulfurization (HDS) of thiophene<sup>(5)</sup>. The samples that showed the most pronounced acidity appeared high activity for the HDS reaction. Furthermore, synthesis of metallosilicates (Cu-Si, Zn-Si and Zn-Cu-Si) and its catalytic activities for NO reduction were studied<sup>(6)</sup>. However, catalytic examinations of metallosilicates for various reactions are not sufficient to understand catalytic properties of metallosilicates.

In the present paper, we studied the synthesis and characterization of metallosilicates such as Ni-Si, Co-Si, Cu-Si, Zn-Cu-Si and Zn-Si. The samples were examined as catalysts for decomposition of 2-propanol (2-PA), cracking of cumene and isomerization of 1-butene to evaluate the acidity of metallosilicates. Furthermore, hydrodesulfurization (HDS) of thiophene and hydrodechlorination (HDC) of chlorobenzene over noble metal supported on metallosilicates were examined to obtain information of effect of support on the catalytic activities of noble metal catalysts. In the case of the HDS and HDC reactions, the

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metallo-silicates were used as a support for Pt and Pd catalysts.

## 2 EXPERIMENTAL

### 2.1 Preparation of metallosilicates

The conventional hydrothermal preparation procedure was applied for syntheses, described earlier<sup>(5)(6)</sup>. The initial gels were formed from solutions of silica source (water glass, fumed silica, Ludox,  $\text{H}_2\text{SiF}_6$ ), source of metal (Zn(II), Cu(II), Co(II), Ni(II)) and tetra-*n*-propylammonium bromide (TPABr) as a structure directing agent (template). The inorganic acids ( $\text{H}_3\text{PO}_4$  or  $\text{H}_2\text{SO}_4$ ) were always admitted into the initial mixture in order to adjust the pH of the gel to the value of 11. The metal(Me)/Si ratio of the initial mixture varied in the range of 0.0-0.1. The resulted materials were washed with distilled water till pH=7-8, then dried overnight at 75 °C and finally calcined at 450 °C to remove the template. The  $\text{H}^+$  form samples were prepared by ion-exchange with 0.1 mol/l  $\text{NH}_4\text{Cl}$  solution. The products were characterized by means of standard methods such as XRD (Tur M-62 with  $\text{CuK}\alpha$ ), SEM (Philips SEM-515), FT-IR (Bruker, Vector 22, KBr), UV-vis (Varian, Carry 100, diffuse reflectance), DTA, TG (Setsys 12, Setaram, air atmosphere).

### 2.2 Preparation of supported noble metal catalysts

Supported noble metal catalysts were prepared by an impregnation method using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{PdCl}_2$  aqueous solution. However,  $\text{PdCl}_2$  was dissolved in 1.0 mol/l HCl aqueous solution because  $\text{PdCl}_2$  dose not dissolve completely in water. The amount of metal loading was as follows; Pt: 5 wt%, Pd: 0.1 wt%. After impregnation, the samples were dried at 120 °C followed by calcination at 450 °C for 4 h. Supported noble metal catalysts were reduced by hydrogen at 400 °C for 1 h before the reaction.

### 2.3 Catalytic activities of metallosilicates

The catalytic activities of metallosilicates were evaluated by 2-PA decomposition, cumene cracking, 1-butene isomerization, thiophene HDS and chlorobenzene HDC. 2-PA decomposition (250 °C) and cumene cracking (400 °C) were carried out using a pulse reactor. In both reactions, the catalysts (0.03 g) were pretreated at 400 °C for 1 h in helium stream before the reaction. We used  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  (JRC-SAL-2, 13% $\text{Al}_2\text{O}_3$ ) as a reference acidic catalyst. 1-butene isomerization was carried out using a Pyrex glass closed circulation system. 0.05 g of catalyst was evacuated at 400 °C for 2 h. After evacuation, 1-butene isomerization was carried out at 100°C and the initial pressure of 5.3 kPa. Thiophene HDS was carried out at 350 °C using a conventional fixed bed flow reactor under 0.1 MPa. Reaction conditions were as follows: catalyst weight = 0.1 g,  $\text{H}_2/\text{thiophene} = 30$ , W/F = 37.9

g•h/mol. Chlorobenzene HDC was carried out using a pulse reactor at 250 °C. In all reactions, reactants and products were analyzed by gas chromatograph.

## 3 RESULTS AND DISCUSSION

### 3.1 XRD patterns of metallosilicates

Fig. 1 shows the XRD patterns of metallosilicates. The XRD patterns indicate that synthesized products show the MFI structure with good crystallinity of samples at low metal loading ((a), Me/Si = 0.01). The formation of metallosilicate with MFI structure is difficult at higher Me/Si ratio (Me/Si = 0.05, Zn/Si = 0.03) as shown in Fig. 1 (b). The samples with higher metal content required longer crystallization time and always contained some admixture of amorphous material. The crystallinity of the samples depends on the kind of metal. XRD data indicate lower crystallinity of the samples containing Zn and Co as substituted heteroatoms.

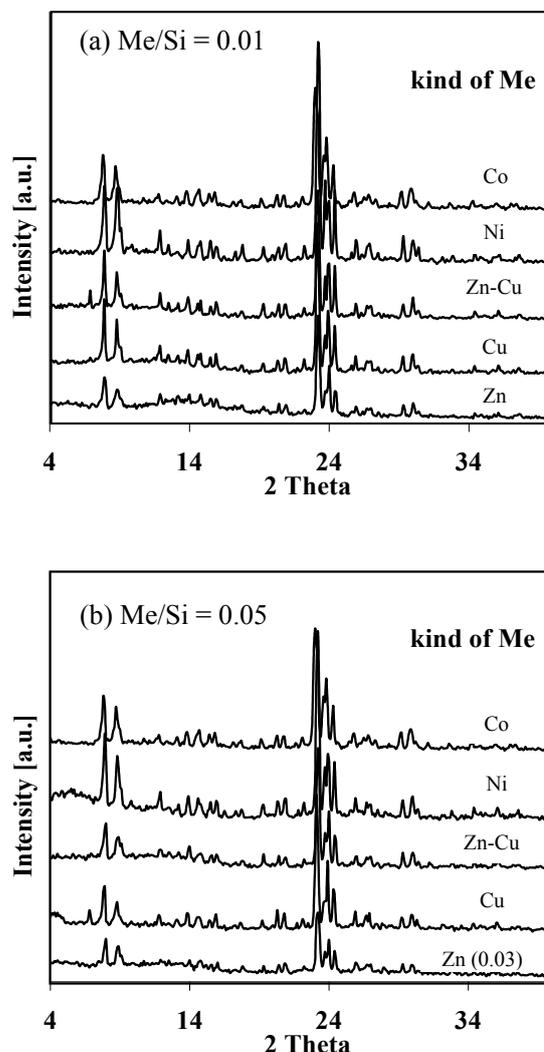


Fig. 1 XRD patterns of metallosilicates.

### 3.2 FT-IR spectra of metallosilicates

Fig. 2 shows the FT-IR spectra of metallosilicates. The IR spectra of the products do not provide any clear evidence on the presence of heteroatoms in the framework positions. The bands at  $\sim 960\text{ cm}^{-1}$  hardly noticeable in spectra can reflect the Me-O bond vibrations<sup>(16)(17)</sup>. The shoulder peaks at  $960\text{ cm}^{-1}$  were observed in the FT-IR spectra of synthesized metallosilicates. Instead, we have noticed an interesting behavior of the asymmetric stretching bands at  $\sim 1100\text{ cm}^{-1}$ . This band is attributed to the framework tetrahedral  $\text{TO}_4$ . In the case of zeolites, silicate,  $\text{AlPO}_4$  and many other zeotypes, the band is sharp and single without any shoulders. Such shape is also seen in spectra of zincosilicate. However, in the spectra of the other series of metallosilicates under study we can notice a splitting of this band. Perhaps, it reflects the lower homogeneity of the framework O–Me–O–Si–O bonds than the analogous bonds (–Al–O–Si–) in zeolites. The split in main stretching bands can be considered as an argument supporting the framework position of the heteroatoms. If the metal atoms were sitting in extra-framework positions, the bands should be similar as that in silicate, i.e. the single ones. These results indicate that heteroatoms incorporated into framework of MFI zeolite.

### 3.3 SEM images of metallosilicates

Fig. 3 shows the SEM images of metallosilicates. The morphology and crystallite size of the products depended on nature of the introduced metal. Usually the samples of the metal rich products formed large

aggregates. The Co-Si catalyst showed very large crystallites which could affect their catalytic efficiency. Furthermore, the Zn-Si showed the larger crystallites than Cu-Si<sup>(6)</sup>. Thus, low crystallinity of Co-Si and Zn-Si (Fig. 1) were explained by high metal content in the  $\text{SiO}_2$  framework.

### 3.4 Thermal analysis of metallosilicates

The thermal analysis in air indicate that the decomposition of organic template takes place in the range of  $350 - 500\text{ }^\circ\text{C}$  as shown in Fig 4. In all samples, it is reflected in very distinctive exothermic effect (DTA,  $\sim 390\text{ }^\circ\text{C}$ ) and significant weight loss (TG). However, weight loss was hardly changed with increasing temperature ( $\sim 500\text{ }^\circ\text{C}$ ). This indicates that metallosilicates show a good thermal stability. The exothermic effect is proceeded with an endothermic effect at  $\sim 420\text{ }^\circ\text{C}$ , which can be attributed to desorption of template oxidation products. The differences in temperatures of these effects are significant for the samples with the same metal loading.

### 3.5 Catalytic properties of metallosilicates

#### 3.5.1 Acidic properties of metallosilicates

The acidic properties of catalysts can be evaluated by dehydration of 2-PA, which proceeds on both Lewis and Brønsted acid sites, and cumene cracking, which proceeds only on Brønsted acid sites. Fig. 5 shows the catalytic activities of metallosilicates for 2-PA decomposition at  $250\text{ }^\circ\text{C}$ . Zn-Si catalyst showed remarkably high dehydration activity. This indicates that Zn-Si have higher acidity than other metallosilicates.

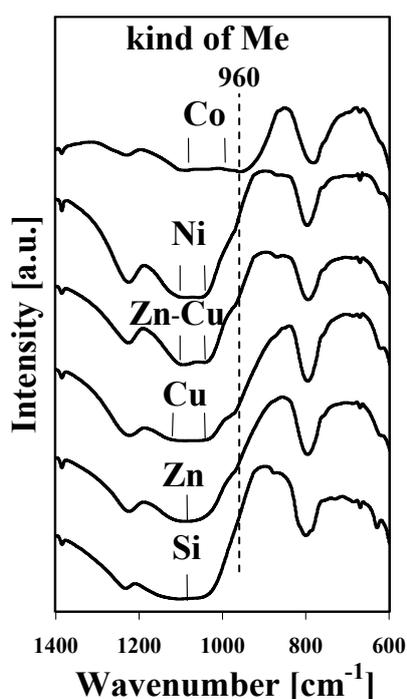


Fig. 2 FT-IR spectra of metallosilicates (Me/Si = 0.01).

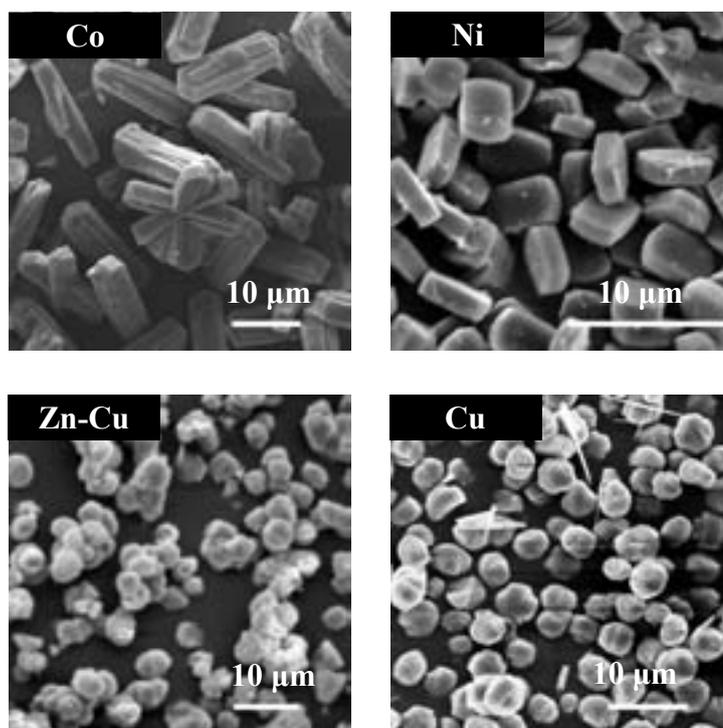


Fig. 3 SEM images of metallosilicates (Me/Si = 0.01).

However, the activities of other catalysts, except Zn-Cu-Si, were very low. Furthermore, the products of 2-PA decomposition over Cu-Si catalyst were propylene and acetone. It is known that 2-PA molecule is dehydrogenated to acetone on metal particle and/or basic site. It was reported that, in the 2-PA dehydrogenation over Cu catalyst, CuO and Cu<sub>2</sub>O act as active sites<sup>(7)</sup>.

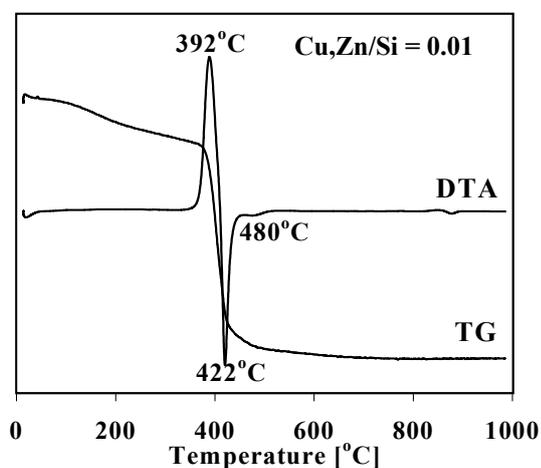
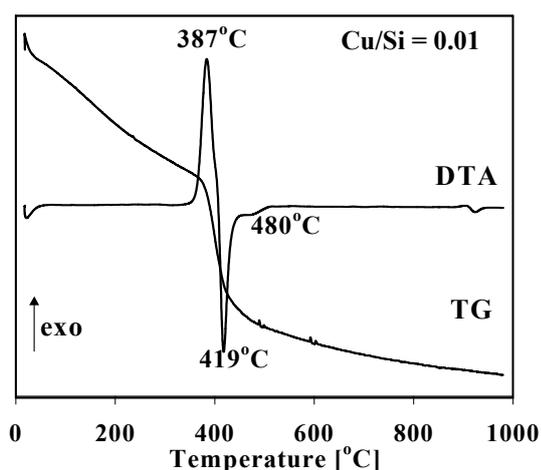
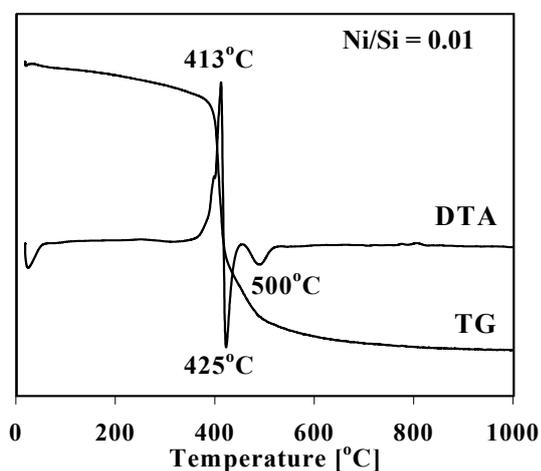


Fig. 4 Thermal analysis of metallosilicates.

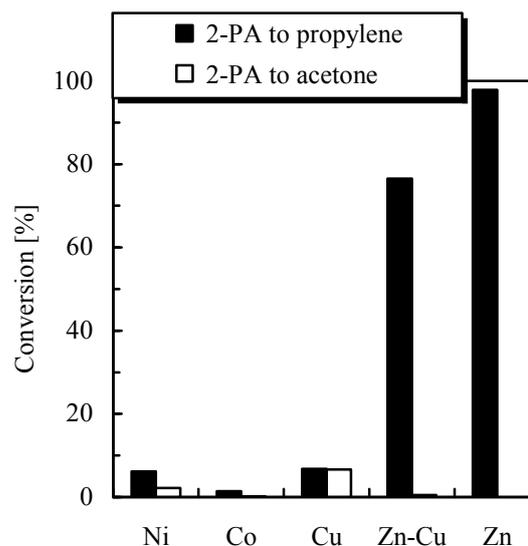


Fig. 5 Catalytic activities of metallosilicates (Me/Si = 0.01) for 2-propanol decomposition at 250 °C.

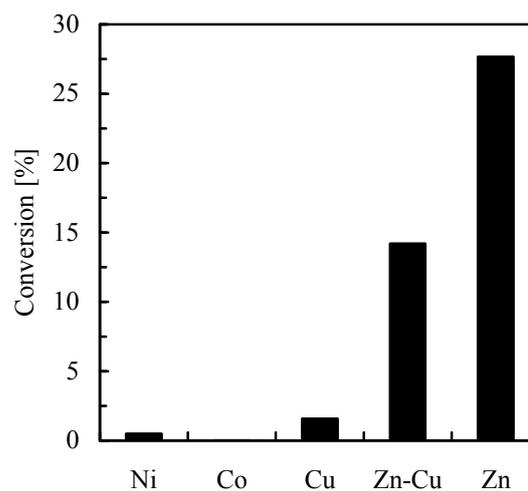


Fig. 6 Catalytic activities of metallosilicates (Me/Si = 0.01) for cumene cracking at 400 °C.

Thus, small amount of extra framework CuO and Cu<sub>2</sub>O species probably exist in Cu-Si catalyst, or Cu atom in framework act as active site as well as Cu oxides. The Co-Si catalyst showed the very low activity for 2-PA decomposition. The order of dehydration activities of metallosilicates was as follows; Zn-Si > Zn-Cu-Si > Cu-Si ≈ Ni-Si >> Co-Si.

Fig. 6 shows the catalytic activities of metallosilicates for cumene cracking. The cracking activity of Zn-Si catalyst was remarkably higher than that of other metallosilicates. The order of catalytic activities of metallosilicates for cumene cracking was almost the same as that for 2-PA dehydration. Thus, Zn-Si catalyst has higher Brønsted acidity than other metallosilicates.

It was reported that the Brønsted acidities of isomorphous substituted ZSM-5 zeolites were theoretically explained by polarization of incorporated metal ion and this result was agreed with experimental data<sup>(15)</sup>. Thus, acidity of metallosilicate would be explained by polarizability of incorporated metal ion. However, since we did not evaluate the metal content in samples, there is a possibility that the metal content in metallosilicates differ from Me/Si ratio. Therefore, the polarization and metal content are necessary to explain the order of acidities of metallosilicates evaluated by model reactions.

We used  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  as reference acidic catalyst to compare with metallosilicates. The catalytic activities of  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  for 2-PA decomposition and cumene cracking were remarkable high as shown in Fig. 7. These activities were higher than those of metallosilicates. These results indicate that the acidities of metallosilicates were weaker than that of  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ .

Furthermore, it is well known that 1-butene isomerization proceeds over both acidic and basic sites. The order of catalytic activities of 1-butene isomerization at 100 °C was  $\text{Zn-Si} > \text{Zn-Cu-Si} \gg \text{Cu-Si} > \text{Ni-Si} > \text{Co-Si}$  as shown in Fig. 8. This result also agreed with the results of former reactions.

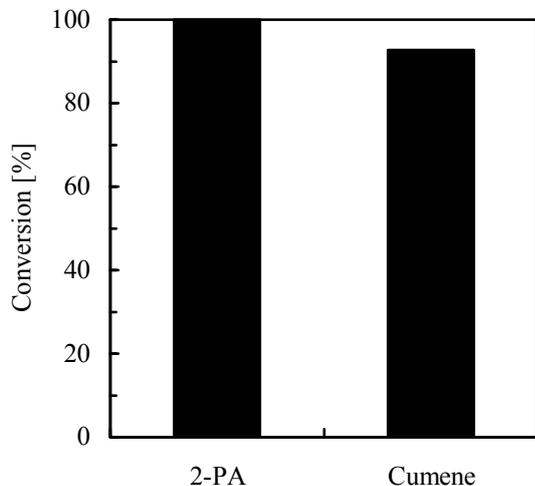


Fig. 7 Catalytic activities of  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  for 2-propanol decomposition at 250 °C and cumene cracking at 400 °C.

### 3.5.2 Catalytic properties of noble metals supported on metallosilicates

Thiophene HDS<sup>(9)(10)(11)</sup> and chlorobenzene HDC<sup>(18)</sup> are proceeded over noble metal catalysts supported on acidic carrier. Thus, we evaluated the catalytic activities of noble metal supported metallosilicates with different acidities.

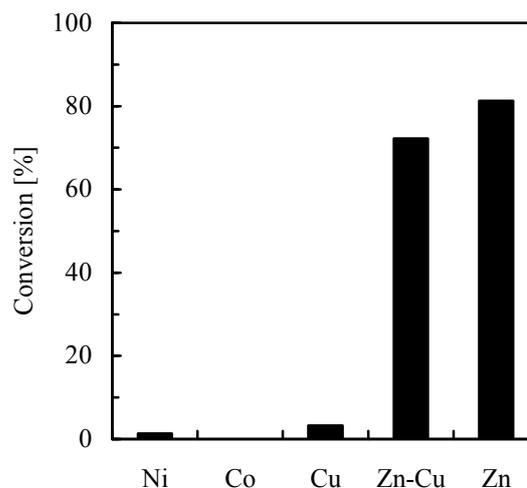


Fig. 8 Catalytic activities of metallosilicates (Me/Si = 0.01) for 1-butene isomerization at 100 °C.

Fig. 9 shows the catalytic activities of platinum supported on metallosilicates for thiophene HDS at 350 °C. The HDS activity of Ni-Si catalyst was remarkably higher than those of other metallosilicates. In the petroleum industry, sulfided  $\text{Co(Ni)Mo/Al}_2\text{O}_3$  catalyst has been widely used in the HDS process<sup>(8)</sup>. In these catalysts, Co and Ni act as promoter to create highly active “Co(Ni)-Mo-S” phase. Thus, high HDS activity of Ni-Si catalyst can be explained by sulfidation of Ni species. However, Co-Si catalyst showed the very low activity for thiophene HDS. The crystallite size of Co-Si was larger than those of other metallosilicates. Thus, since diffusion of reactant into Co-Si catalyst is difficult, Co-Si catalyst showed low activities for some acid-catalyzed reactions (2-PA dehydration, cumene cracking and 1-butene isomerization) and HDS reaction. In the supported Pt catalysts, the order of HDS activities was as follows;  $\text{Zn-Si} > \text{Ni-Si} > \text{Cu-Si} \approx \text{Zn-Cu-Si} > \text{Co-Si}$ . We have reported that Brønsted acid site plays an important role in the highly active supported Pt HDS catalyst<sup>(9)(10)(11)</sup>. However, Pt/Zn-Cu-Si catalyst, which has higher Brønsted acidity than other catalysts, showed lower HDS activity than Pt/Ni-Si catalyst. Some methods of dealumination of zeolites, such as thermal treatment, steaming, acid treatment and  $\text{SiCl}_4$  treatment, were reported<sup>(12)(13)</sup>. We used  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution (pH = 1) as a Pt precursor to prepare supported Pt catalyst. Thus, in the impregnation of Pt, demetalation from metallosilicates would be caused in the catalyst preparation with  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution. Thus, since acidity of metallosilicates would be changed by demetalation, the order of HDS activities of Pt/metallosilicate catalysts was not explained simply by the order of acidity of metallosilicates.

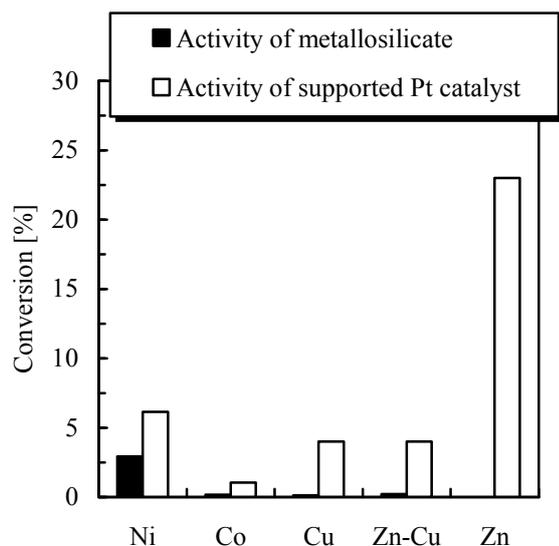


Fig. 9 Catalytic activities of Pt/metallosilicates and metallosilicates (Me/Si = 0.01) for thiophene HDS at 350 °C.

We also examined the catalytic activities of Pd/metallosilicates for chlorobenzene HDC at 250 °C as show in Fig. 10. The HDC activity of Ni-Si catalyst was the highest among those of metallosilicates. However, in the supported Pd catalyst, Pd/Cu-Si catalyst showed the highest HDC activity among supported Pd catalysts. It was reported that Cl atom on Cu surface in Pd-Cu/SiO<sub>2</sub> catalyst was removed by hydrogen which is activated on Pd surface<sup>(14)</sup>. Thus, since Pd and Cu atoms in Pd/Cu-Si catalyst act as active sites for the HDC of chlorobenzene, the HDC activity of Pd/Cu-Si catalyst was the highest among those of Pd/metallosilicate catalysts. However, the Pd/Zn-Si and Pd/Zn-Cu-Si catalysts showed lower HDC activities than other Pd/metallosilicates. This result may be explained by decrease of acidity which was caused by poisoning with Cl atom.

#### 4. CONCLUSIONS

The metallosilicates with transition metals (Co, Ni, Cu, Zn-Cu, Zn) in the framework can be obtained by hydrothermal crystallization and the MFI structure can be attained at as high Me/Si ratio as 0.05. The products show a good thermal stability. They can be modified by cation-exchange which confirms the framework localization of the metal atoms. The order of acidity of metallosilicates was as follows; Zn-Si > Zn-Cu-Si > Cu-Si > Ni-Si > Co-Si. On the other hand, in the metallosilicates-supported noble metal catalysts, 5%Pt/Zn-Si and 0.1%Pd/Cu-Si catalysts showed the highest activities for the HDS of thiophene and HDC of chlorobenzene, respectively.

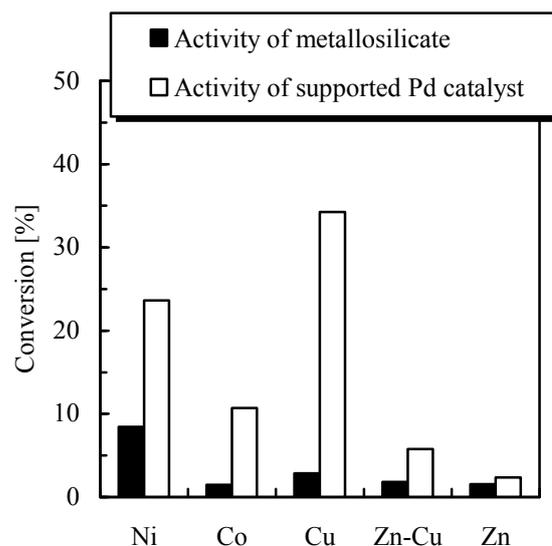


Fig. 10 Catalytic activities of Pd/metallosilicates and metallosilicates (Me/Si = 0.01) for chlorobenzene HDC at 250 °C.

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メタロシリケートの触媒特性

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種々の金属/ケイ素(Me/Si)比(0.01-0.1)におけるNi、Co、Cu、Zn-CuおよびZnを骨格内に含むMFI型メタロシリケートを合成した。H型のメタロシリケートの酸性質はいくつかの酸触媒反応(2-プロパノール分解反応、1-ブテン異性化およびクメン分解反応)により評価した。その結果、Zn-Si触媒は種々のメタロシリケートにおいて最高の酸性質を示した。また、種々のメタロシリケート担持貴金属(Pt, Pd)触媒において、5%Pt/Zn-Siおよび0.1%Pd/Cu-Si触媒はそれぞれ、チオフェンの水素化脱硫反応およびクロロベンゼンの水素化脱塩素反応に対して最高の活性を示した。

キーワード：メタロシリケート， MFI 構造， 触媒特性

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