

## Local structure analysis of the active sites on Co-Mo sulfide catalysts prepared by the post-treatment with citric acid

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### Introduction

Mo sulfide catalysts promoted by Ni or Co are widely used in the industrial hydrodesulfurization (HDS) process. Therefore, the preparation method of HDS catalysts has been extensively improved in order to achieve higher HDS performance. One of the promising ways is to use chelating agents [1] such as citric acid (CA) in the preparation process.

CA reportedly increases the HDS catalytic activity by improving the dispersion and by increasing the sulfidation temperature of Co or Ni atoms [2]. Recently, we have found that the addition of CA in the catalyst preparation by a post-treatment was more effective than that by a simultaneous impregnation. However, detailed mechanisms of the roles of citric acid are still unclear. In the present work, we investigated the influence of CA on the active site structure of Mo/Al<sub>2</sub>O<sub>3</sub> catalysts, in particular at a higher Mo content.

### Experimental

Mo/Al catalysts (20 wt% Mo) were prepared by a impregnation method and calcined. Then, the calcined catalyst was impregnated with CA (CA/Mo mole ratio: 0-2) and just dried (without calcination). The catalyst thus prepared is designated as CA/Mo/Al hereinafter. Co-Mo catalysts prepared by the simultaneous impregnation was included in this study for comparison (CA-Mo/Al). The prepared catalysts were sulfided in a 10% H<sub>2</sub>S/H<sub>2</sub> flow at 673K for 1.5h.

Mo K-edge XAFS spectra for Mo/Al with and without the CA addition were measured in a transmission mode at room temperature at NW-10A in the PF-AR.

### Results and Discussion

Fig.1 shows Fourier transforms (FTs) of the Mo K-edge EXAFS oscillation for the Mo catalysts before the sulfidation. With Mo/Al, the Mo-Mo atomic distance is 0.33 nm for dried states, suggesting that Mo is present as polymolybdate-like species in these catalysts. The Mo-Mo atomic distance is increased and becomes close to that for the Mo-CA complex [3] when citric acid has been added by the post-treatment or simultaneous impregnation method.

Fig.2 shows FTs of the Mo K-edge EXAFS oscillation for the Mo catalysts after the sulfidation. The intensities of a peak assigned to Mo-S and Mo-Mo shells were increased by the addition of CA. However, this change is not attributed to the increase of particle size of MoS<sub>2</sub> because NO adsorption capacity was not decreased but rather increased by the addition of CA. These results indicate that the increased HDS activity is related to the degree of sulfidation of Mo due to the Mo-CA complex formation.

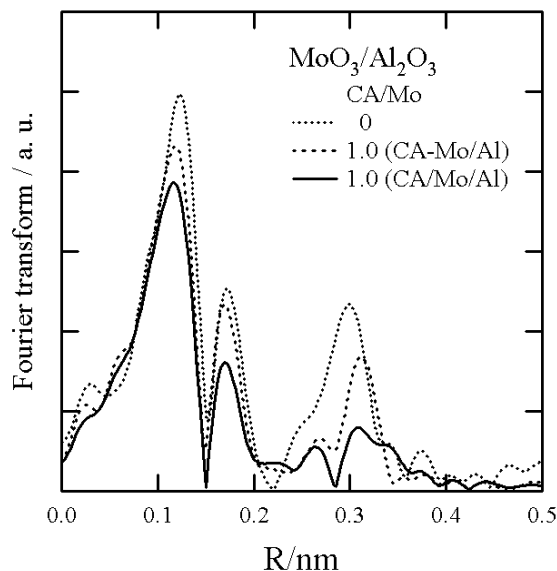


Fig.1 Fourier transforms of the Mo K-edge EXAFS oscillation for the Mo oxide catalysts.

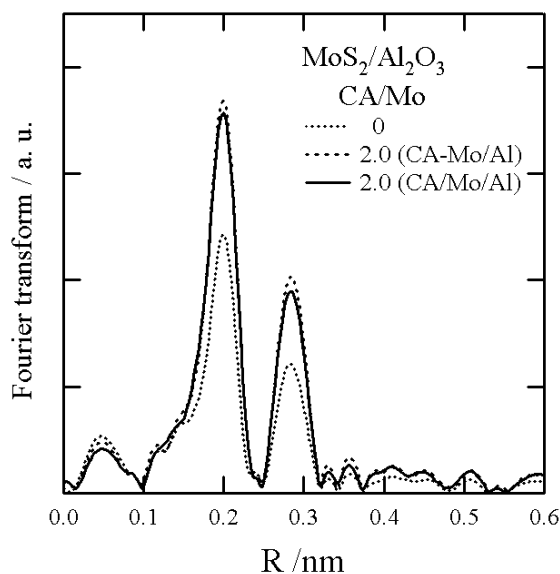


Fig.1 Fourier transforms of the Mo K-edge EXAFS oscillation for the Mo sulfide catalysts.

### References

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