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Effect of CyDTA on the coordination structure around Ni atom during the preparation steps for NiMo and NiW hydrodesulfurization catalysts

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Introduction

$NiMo/Al_2O_3$ and NiW/Al_2O_3 catalysts are widely used for the hydradesulfurization (HDS) and hydrogenation (HYD) reactions of petroleum feedstock. It is an urgent issue to improve their catalytic activity to meet severe regulations for the sulfur content of the transportation fuels. These catalysts are usually prepared by impregnating Al_2O_3 support with an aqueous solution containing Ni and Mo (or W). The impregnated materials are further underwent a drying process and finally sulfided before the reaction. Recently, the authors found that the addition of some chelating agents such as CyDTA to the impregnation solution greatly improves their HDS and HYD activities [1, 2]. Thermodynamic calculations imply that CyDTA forms a stable complex with Ni ion in the impregnating solution, which survives during the impregnation and drying process and eventually affects the sulfide structures [2]. However, no direct evidence for the role of CyDTA during the preparation steps has been reported yet. Therefore, the present study has investigated the coordination structure around Ni atoms during the preparation of NiMo and NiW catalysts by Ni K-edge EXAFS. The local structures around Mo and/or W atoms in these catalysts are also reported in the separate report.

Experimental

Ni K-edge EXAFS spectra for $NiMo/Al_2O_3$ and $Ni/W/Al_2O_3$ catalysts after drying and impregnating steps were measured at room temperature in a transmission mode at BL10B and BL12C. After the background subtraction, k^3-weightened EXAFS functions were Fourier transformed into a R space and then curve-fitting analyses were carried out in the R space. Backscattering amplitude and phase shift for Ni-O bond in polycrystalline NiO were used for the curve-fitting analyses of the supported catalysts. Detailed procedures for the catalyst preparation were given in ref. [2].

Results and Discussion

Fourier transformed EXAFS spectrum for NiW/Al_2O_3 catalyst prepared without CyDTA after drying process showed only one Ni-O shell. Because the interatomic distance of this shell (0.205 nm, *see* **Table**) is comparable with that of Ni-O bond in $NiCl_2 \cdot H_2O$ [3], it is suggested that Ni species in this catalyst predominantly exists as Ni(II) coordinated by H_2O in an octahedral environment. On the other hand, another Ni-O shell having the interatomic distance of 0.282 nm was observed in Fourier transformed spectrum for NiW/Al_2O_3 catalyst prepared with CyDTA after drying process. It is noted that a similar (but not the same) Fourier transformed spectrum was also obtained with NiW/Al_2O_3 catalyst prepared with CyDTA after the impregnation step (not shown here). In the case of $NiMo/Al_2O_3$ catalyst prepared with CyDTA after the drying process, two Ni-O shells were also observed in Fourier transformed EXAFS spectrum. Their structural parameters are consistent well with those observed for NiW/Al_2O_3 catalyst prepared with CyDTA as shown in **Table**. On the contrary, only one Ni-O shell was observed in the spectrum for $NiMo/Al_2O_3$ catalyst prepared without CyDTA after the drying process. Although the origin of the second Ni-O shell is not clear yet at present, the present study shows that CyDTA affects the coordination structure around Ni atom during both the impregnation and drying process for the preparation of $NiMo/Al_2O_3$ and NiW/Al_2O_3 catalysts.

References

[1] N. Koizumi et al., *Prep. Pap. –Am. Chem. Soc. Dev. Pet. Chem.,* **49** (3), 291, (2004).
[2] H. Itoh et al., *J. Jpn. Petrol. Inst.*, Vol 47, No.4, 2004.
[3] Kagaku Binrann 5th edition, Kiso-henn II, p.813.

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Table Structural parameters[a] of Ni-O shell derived from Ni K-edge EXAFS for NiW/Al_2O_3 and $NiMo/Al_2O_3$ catalysts prepared with or without CyDTA after drying process

	1st Ni-O shell			2nd Ni-O shell			R_f/%
	CN	R /nm	σ /nm	CN	R /nm	σ /nm	
NiW	6.4	0.205	0.0078				1.3
CyDTA-NiW	6.0	0.205	0.0087	6.7	0.282	0.0074	1.3
NiMo	6.0	0.206	0.0089				1.3
CyDTA-NiMo	5.9	0.206	0.0084	6.8	0.279	0.0083	0.9

[a] CN, coordination number; R, interatomic distance; Debye-Waller like factor; R_f, R factor defined as $R_f = [\Sigma\{\chi_{obs}(k) - \chi_{cal}(k)\}^2/\Sigma\,\chi_{obs}(k)^2]^{1/2}$