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Coordination structure around Mo and W atoms of NiMo and NiW hydrodesulfurization catalysts during their preparation steps

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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 activities to meet severe regulations for the sulfur content of the transportation fuels.

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]. In the separate report, we showed 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 by Ni K-edge EXAFS. Here, we have also reported Mo K-edge and W L_{III}-edge EXAFS spectra of these catalysts during the preparation steps.

Experimental

Mo K-edge and W L_{III}-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 W-O bond in polycrystalline WO_3 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 W L_{III}-edge EXAFS spectrum for NiW/Al_2O_3 catalyst prepared without CyDTA after impregnation process shows only one W-O shell as shown in **Fig. 1**. Because the interatomic distance of this shell (0.177 nm, *see* **Table**) matched well with that for W-O bond in WO_3 (0.177 nm), it is suggested that WO_6 species with an octahedral coordination is a predominate species formed on Al_2O_3 after the impregnation. The subsequent drying process hardly affects its coordination structure as shown in **Table**.

When NiW/Al_2O_3 catalyst was prepared with CyDTA, we also observed one W-O shell in Fourier transformed spectra after the impregnation and drying process. Both the interatomic distance and the coordination number of this shell are consistent with those observed in the spectra for the catalyst without CyDTA (**Table**). In the case of $NiMo/Al_2O_3$, we could not find a significant difference in Fourier transformed spectra for the catalyst prepared with and without CyDTA. Therefore, it can be concluded that CyDTA has little influence on the coordination structure around Mo and W atoms of $NiMo/Al_2O_3$ and NiW/Al_2O_3 catalysts during the preparation procedures.

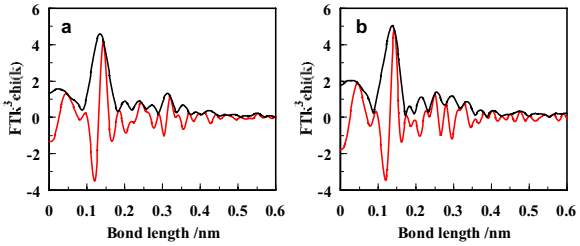

Fig.1 Fourier transformed EXAFS spectra for NiW/Al_2O_3 catalyst prepared without CyDTA after impregnation (a) and drying (b) process.

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.

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Table Structural parameters[a] of W-O shell derived from W L_{III}-edge EXAFS for NiW/Al_2O_3 catalysts prepared with or without CyDTA

	Prepared with CyDTA			Prepared without CyDTA		
	CN	R /nm	/nm	CN	R /nm	/nm
After impregnation	4.7	0.177	0.0085	5.2	0.177	0.0086
After drying	4.4	0.178	0.0081	5.0	0.177	0.0075

[a] CN, coordination number; R, interatomic distance; Debye-Waller like factor