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N K-edge XANES analysis of coke on CoMo catalyst used in HDS unit using feeds of LGO mixed with components of heavy fuel oil

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Introduction

When a mixture of light gas oil (LGO) and light cycle oil (LCO), a component of heavy fuel oil, is fed into a hydrodesulfurization (HDS) unit to produce diesel fuel, the catalyst in the HDS unit is rapidly deactivated. In contrast, when the feed is LGO mixed with residue desulfurization gas oil (RDS-GO), another component of heavy fuel oil, the catalyst is deactivated slowly. We focused on the coke, or carbon deposits, formed on the catalyst during the HDS reaction, which is thought to be one of the causes of deactivation, in order to understand the catalyst deactivation behavior. In this study, we investigated the effectiveness of nitrogen K-edge XANES measurements for elucidating the chemical states and structures of nitrogen compounds in the coke formed on CoMo catalysts, since nitrogen compounds in the feed have been reported to affect the HDS activity of these catalysts.

Experimental

N K-edge XANES measurements were performed on spent alumina-supported CoMo catalysts which had been used in the HDS unit of a bench scale plant for 2300 hours, using LGO mixed with 15 vol% of either LCO or RDS-GO as feeds. Before the XANES measurements, the catalysts were subjected to Soxhlet extraction using toluene for 12 hours to remove the oil on them. The XANES spectra of various reference compounds were also collected for comparison with those of the catalysts. The XANES measurements were conducted in total electron yield mode on station BL-7A at the Photon Factory (PF).

Results and Discussion

The photon energies of the peaks in the N K-edge XANES spectra of the carbazoles, indoles, quinolines and anilines in the LGO, LCO or RDS-GO and aromatic nitro compounds differed depending on their nitrogenated functional groups (Fig. 1). As Fig. 1 shows, the photon energy of the N K-edge XANES peaks corresponding to the nitrogenated functional groups in the compounds ranged from around 397 eV to around 410 eV.

The shape of the N K-edge XANES spectrum for the spent catalyst used in the HDS unit using LGO mixed with LCO differed from that for the catalyst used in the unit using LGO mixed with RDS-GO (Fig. 2), indicating that the chemical states and structures of the nitrogen compounds in the coke on each catalyst may be different. Furthermore, as Fig. 1 and Fig. 2 show, there was almost no overlap between the two main peaks in the Mo M-edge XANES, which were observed in the N K-edge XANES region, of the active species MoS_2 on the CoMo catalyst and the peaks characteristic of the nitrogen compounds.

These results indicate that the chemical states and structures of the nitrogen compounds in coke on the catalysts can be elucidated by comparing the photon energies of the N K-edge XANES peaks for the catalyst with those for the nitrogen compounds. Thus, N K-edge XANES measurement is an effective method for elucidating the chemical states and structures of nitrogen compounds in the coke formed on CoMo catalysts.

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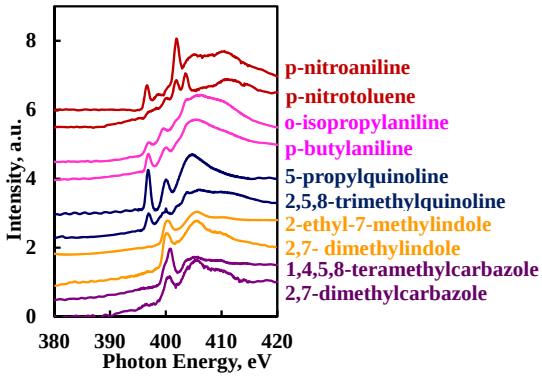

Fig. 1: N K-edge XANES spectra of nitrogen compounds.

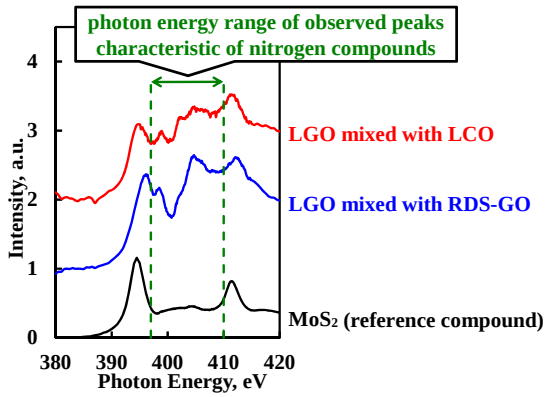

Fig. 2: N K-edge XANES spectra of CoMo spent catalysts and Mo M-edge XANES spectrum of MoS_2.

References

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