# X-ray Absorption Spectroscopy and X-ray Powder Diffraction Characterizing Transition-metal-exchanged Zeolite Sorbents for Deep Desulfurization

**J.-F. Lee (李志甫)[2], H.-S. Sheu (許火順)[2], C.-Y. Chen (陳昱誠)[1], and J.-R. Chang (張仁瑞)[1]**

[1]**Department of Chemical Engineering, National Chung Cheng University, Chiayi, Taiwan**
[2]**National Synchrotron Radiation Research Center, Hsinchu, Taiwan**

Environmental restrictions regarding the quality of transportation fuels produced and the emissions from the refinery itself are currently the most important issues for refinery. Removal of sulfur-containing compounds from liquid fuels can normally be achieved by using hydrodesulfurization (HDS) with a Co-Mo/Al2O3 or Ni-Mo/$Al_2O_3$ catalyst. However, because of the stereo-hindrance of refractive sulfur compounds, such as 4,6-dimethyl-dibenzothiophene, deep desulfurization is not possible for conventional Co-Mo or Co-Ni catalysts. Adsorptive desulfurization, specifically, transition-metal-exchanged zeolite sorbent has been thought to be the most promising material for the removal of sulfur-containing compounds from gasoline or diesel via π–complexation mechanism.The goal of this study is to understand the effects of the structure of nickle-oxides-entraped Y-zeolite adsorbents (NiO/Y) on the adsorption of sulfur compounds in transportation fuel. The adsorbents are prepared by both impregnation and ion-exchanged methods with Si/Al ratio, cation form, and calcination temperature as operating parameters. The efficacy of the adsorbents was examined by deep desulfurization of 150 ppm sulfur-containing octane and benzothiophene was used as model-sulfur compounds. The desulfurization tests were carried out at an adsorption column under 1 atm and room temperature. The structures of adsorbents were characterized by FT-IR (Fourier transform-Infrared spectroscopy), synchrotron XRD (X-ray diffraction), and XAS (X-ray adsorption spectroscopy). With the complementally characterization techniques, the adsorption performance can be correlated with adsorbent structure and the following conclusions have been drawn:

1. Even Y-zeolite with high Si/Al ratio (Si/Al=55) presents higher thermal stability, whereas lower Ni dispersion was observed for the NiO/Y adsorbents. Hence, the adsorbent exhibits much lower adsorption capacity in comparing with adsorbents prepared from low Si/Al-ratio (Si/Al=5) Y-zeolite (Fig. 1,2).
2. Calcination temperature strongly affects the structure of NiO/Y adsorbents and the adsorption capacity is in the following order: 450℃＞350℃＞250℃.
3. Suggested by EXAFS results, during air calcination, thermal decomposition of the ligand bonded to Ni occurred concomitantly with the aggregation of NiO before the oxidative disruption of NiO clusters. High temperature calcination is necessary for the pre-treatment of transition-metal-exchanged zeolite sorbent. (Fig. 3).

.

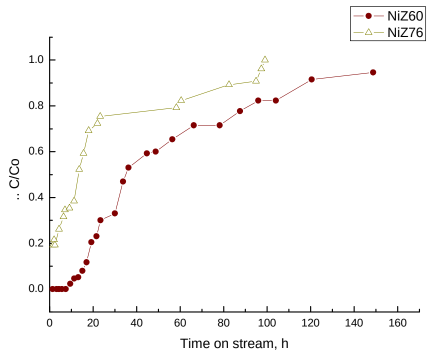


**Fig. 1:** Breakthrough of total sulfur in a fixed bed adsorber with NiZ60 (Si/Al=5) and NiZ76 (Si/Al=55).

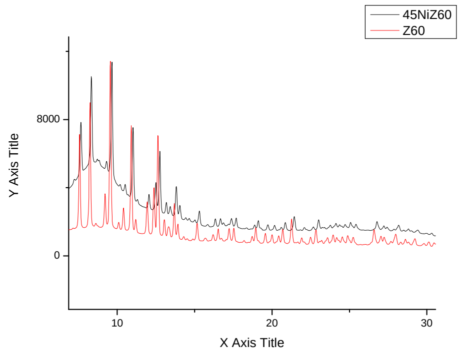


**Fig. 2:** Comparison of XRD characterizing the structure of low Si/Al Y zeolite before (Z60, Si/Al=5) and after (45NiZ60) NiO deposition (energy=13keV，wave length= 0.953732Å).

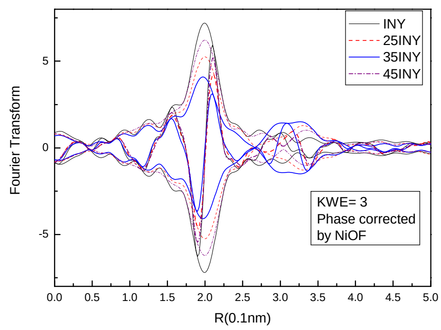


**Fig. 3:** Imaginary and magnitude of Fourier transform (k3 weighted, 3.5<k<14, Ni-O phase corrected) of the EXAFS characterizing the structure of the Ni exchanged NaY(NaY with Si/Al=3); INY: sample after ion exchange, 25INY, ion exchanged sample after 250 ˚C calcination, 35INY, after 350 ˚C calcination, after 450 ˚C calcination.