

Fraction of the CoMoS phases accessible to NO in Co–Mo hydrodesulfurization catalysts

Yasuaki Okamoto,* Masatoshi Kawano and Takeshi Kubota

Department of Material Science, Shimane University, Matsue 690-8504, Japan.

E-mail: yokamoto@ifse1.riko.shimane-u.ac.jp; Fax: +81-852-32-6466

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It is established by using Co–Mo model sulfide catalysts, XAFS and FTIR that Co atoms constituting CoMoS phases are not oxidized by NO adsorption and that only 55% of the CoMoS phases is susceptible to NO adsorption even at the maximum coordinative unsaturation attainable under usual HDS reaction conditions (623–673 K).

It is of great importance to elucidate the number of active sites on a catalyst surface as well as their structure, in order to understand microscopic mechanisms of catalytic reactions. In conjunction with spectroscopic techniques, chemisorption techniques of probe molecules have been widely employed for this purpose,^{1,2} such as CO and H₂ for metallic catalysts and NH₃ for acidic catalysts. With metal sulfide catalysts,³ among which Co(Ni)–Mo catalysts have received extensive attention for cleaner fuels by hydrodesulfurization (HDS), the chemisorption of NO, O₂ or CO has been frequently and widely used to evaluate the dispersion of active phases. In particular, NO chemisorption is very informative, when combined with IR techniques, to distinguish coordinatively unsaturated (cus) Mo and Co(Ni) sites in the case of supported Co(Ni)–Mo sulfide catalysts.^{4,5} It is well established that NO molecules adsorb selectively on cus Mo and Co(Ni) sites as dinitrosyl forms.^{3,4} The location of Co species constituting active sites, CoMoS phases for Co–Mo sulfide catalysts,^{3,4,6} has been first elucidated on the basis of NO adsorption⁴ and later supported by other techniques including XAFS.^{7,8} Thus NO adsorption is promising for the characterization of Co(Ni)MoS phases. However, in spite of frequent use of NO as a probe molecule and its practical importance, there remain unresolved crucial problems with the NO adsorption on HDS catalysts as to the oxidation and/or reconstruction of cus Mo⁹ and Co or Ni¹⁰ sites and as to the fraction of Co(Ni)MoS phases detected by NO adsorption, the latter issue being closely connected to measuring the number of the active sites from the amount of NO adsorption. No unambiguous answers have been given yet.

In our previous study,^{11,12} we have reported the preparation of Co–Mo model sulfide catalysts, in which the edge sites of MoS₂ particles are preferentially and fully covered by Co atoms forming CoMoS phases, by using Co(CO)₃NO (CVD-technique) as a precursor (CVD–Co/MoS₂ catalysts). Selective formation of CoMoS phases in the CVD–Co/MoS₂ model catalysts has been substantiated by the Co2p XPS, a proportional correlation between Co/Mo and NO/Mo mole ratios and a linear relationship between catalytic activity for thiophene HDS and the amount of Co accommodated.^{11,12} CVD–Co/MoS₂ model catalysts would, therefore, provide a reasonable basis to study the issues in the use of NO as a probe molecule, since the number of active sites, *i.e.* CoMoS phases, is obtained simply from the Co content incorporated. In the present study, we tried by using the model catalysts to determine the fraction of the Co atoms constituting CoMoS phases susceptible to NO adsorption to provide quantitative basis to microscopic understanding of HDS catalysts.

The detailed preparation method of CVD–Co/MoS₂/support model catalysts have been reported previously.^{11,12} Briefly, supported MoS₂ catalysts were exposed to a vapor of Co(CO)₃NO for 5 min at rt, followed by evacuation for 10 min at

rt to remove physisorbed Co(CO)₃NO molecules and subsequent resulfidation at 673 K for 1.5 h in a 10% H₂S/H₂ flow. The supports and Mo contents used in the present study were Al₂O₃ (177 m² g⁻¹, 8.7 and 13 wt.% Mo), SiO₂ (347 m² g⁻¹, 6.7 and 13.3 wt.% Mo), TiO₂ (50 m² g⁻¹, 4.0 wt.% Mo) and ZrO₂ (25 m² g⁻¹, 2.0 wt.% Mo).¹¹ The Co loadings were 2.86 and 2.36 wt.% for CVD–Co/MoS₂/Al₂O₃, 0.98 and 0.96 wt.% for CVD–Co/MoS₂/SiO₂, 1.92 wt.% for CVD–Co/MoS₂/TiO₂ and 1.07 wt.% CVD–Co/MoS₂/ZrO₂, respectively, by XRF.

The amount of NO adsorption on CVD–Co/MoS₂/support was measured at rt using a pulse technique after cooling from 673 K in the H₂S/H₂ stream. The sample was purged with a high purity He stream before periodic introduction of NO pulses. When CVD–Co/MoS₂/Al₂O₃ was treated in a H₂-stream at 623 or 673 K after the sulfidation, the H₂S flow was stopped for a desired period before cooling the sample to rt in the H₂-flow. After replacing the H₂-flow with a He-flow at rt, NO pulses were periodically introduced. The total amount of NO adsorption was determined from the cumulated amount of NO adsorbed in each pulse. It was confirmed by IR spectra that the amount of NO adsorption on the bare surface of the support was negligibly small because of a monolayer loading of Mo. The reproducibility of the amount of NO adsorption was better than ± 5%.

The FTIR spectra of NO adsorption were measured by using an *in situ* cell. A self-supporting disc of the catalyst was presulfided and transferred to the cell in a glove-box, followed by resulfidation at 673 K in the cell. The Co K-edge XANES spectra of catalysts and reference compounds were measured at rt at BL-7C of KEK-IMSS-PF using an *in situ* XAFS cell in a fluorescence mode.

Fig. 1 compares the Co K-edge XANES spectra for CVD–Co/MoS₂/Al₂O₃, Co₃S₈ and a Co–Mo/Al₂O₃ impregnation catalyst. A comparison of these spectra substantiates selective formation of Co species characteristic of CoMoS phases⁸ in the model catalyst and the absence of bulk Co₃S₈ and Co²⁺ oxide species (7725 eV). Fig. 1 also presents the spectrum of CVD–Co/MoS₂/Al₂O₃ after full adsorption of NO. Small but significant changes were caused by NO adsorption: an increase in the edge energy by 0.5 eV and fine structural changes, indicating modification of the electronic state and geometry of Co species. It is worthy of note with the XANES spectra that no white line peak appears around 7725 eV due to oxidized Co species, clearly demonstrating that oxidation of Co species by NO adsorption is negligibly small, if any, on the adsorption of NO at rt by a pulse technique.

The amounts of NO adsorption on supported CVD–Co/MoS₂ catalysts are shown in Fig. 2 as a function of Co content. A single proportional line was obtained for the Co–Mo model sulfide catalysts irrespective of Type I (Al₂O₃, TiO₂ and ZrO₂)¹¹ and Type II (SiO₂)¹¹ of CoMoS phases.³ FTIR spectra of NO adsorption on CVD–Co/MoS₂/Al₂O₃ showed exclusively a set of doublet bands at 1845 and 1785 cm⁻¹ characteristic of NO adsorbed on Co sites.⁴ Hence, the slope of the line corresponds to the NO/Co mole ratio of 0.67 ± 0.03 for the model catalysts. The impregnation catalyst showed an NO adsorption capacity considerably less than the model catalysts. Taking into consideration the formation of dinitrosyl species,³

(NO)₂/Co, it is concluded that NO molecules adsorb on only 34% of the Co atoms constituting CoMoS phases. In order to estimate the maximum amount of Co accessible to NO molecules under usual HDS conditions (reaction temperature: 623–673 K in a H₂ stream), CVD-Co/MoS₂/Al₂O₃ was treated in a stream of H₂ at 623 or 673 K after the sulfidation at 673 K before NO adsorption. The NO/Co ratio increased to 1.1 after

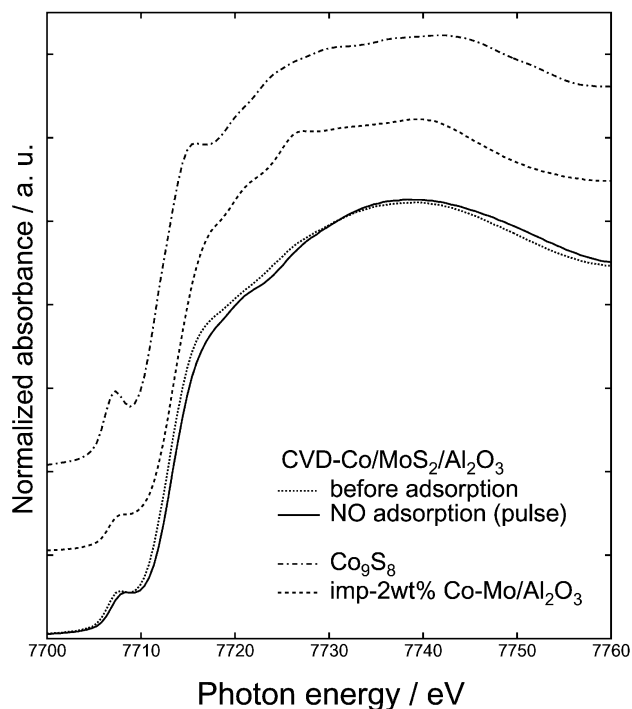


Fig. 1 Co K-edge XANES spectra for CVD-Co/MoS₂/Al₂O₃ (8.7 wt.% Mo) before and after NO adsorption at room temperature by a pulse technique. The XANES spectra are also shown for bulk Co₉S₈ and sulfided Co-Mo/Al₂O₃ (2wt.%Co and 8.7 wt.%Mo) prepared by an impregnation method, for comparison.

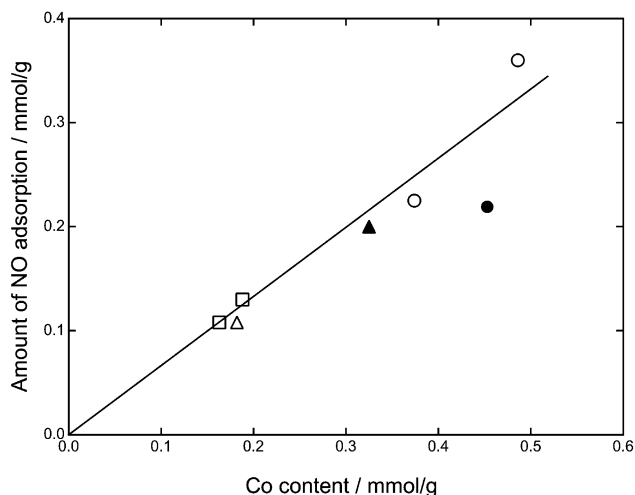
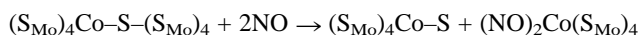


Fig. 2 Amount of NO adsorption against Co content for CVD-Co/MoS₂/support model catalysts. Supports are ○ Al₂O₃, □ SiO₂, ▲ TiO₂ and △ ZrO₂. The amount of NO adsorption on the Co-Mo/Al₂O₃ impregnation catalyst (●) is also shown for comparison.

H₂-treatments at 623 and 673 K for 30 min and remained constant for a prolonged treatment up to 3 h at 673 K. The increase of NO adsorption capacity is apparently ascribed to removal of mobile sulfur as H₂S. No IR bands due to NO adsorbed on Mo sites appeared even after the H₂-treatment at 673 K. It should be noted that the (NO)₂/Co ratio levels off at 0.55. This ratio strongly suggests that only about a half of the Co atoms constituting CoMoS phases is susceptible to NO chemisorption at the highest coordinative unsaturation attainable under usual HDS reaction conditions. As a result, it is concluded that 34% of the Co atoms constituting CoMoS phases is detected by NO adsorption when the catalyst was cooled in a 10% H₂S/H₂ stream and that 55% of the Co atoms on MoS₂ edge sites is accessible to NO molecules after the H₂-treatment at 673 K. This finding can be rationally interpreted by assuming a novel model for CoMoS phases, *i.e.* pair sites of Co atoms on MoS₂ edge sites, (S_{Mo})₄Co-S-(S_{Mo})₄, where S_{Mo} represents a sulfur atom bonding to Mo atoms. When two NO molecules adsorb on the pair site, one of the Co-S bonds is cleaved to form isolated Co species:



Very recently, Raybaud *et al.*¹³ have suggested from DFT calculations the possibility of the formation of energetically stable (S_{Mo})₄Co-S-(S_{Mo})₄ structures on the Mo- and S-edge surfaces of MoS₂ particles promoted by Co, in conformity with the present NO adsorption results.

Summarizing the present results, it is established, for the first time, that NO molecules adsorb only 55% of the Co atoms constituting CoMoS phases at the maximum without oxidation of the sites. The finding provides a concrete base to measure the number of active sites on HDS catalysts of paramount importance. The present surface accessibility of Co was also attained with highly dispersed Co sulfide clusters encaged in zeolite. NO is more attractive as a probe molecule to detect CoMoS phases than CO, which adsorbs on more highly cus and specific sites.

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