Investigation of sulfur behavior on CoMo-based HDS catalysts supported on high surface area TiO$_2$ by ^{35}S radioisotope tracer method

Atsushi Ishihara [a,*], Franck Dumeignil [a], Danhong Wang [a],
Xiangguo Li [a], Hisashi Arakawa [a], Eika W. Qian [a],
Shinichi Inoue [b], Akinori Muto [b], Toshiaki Kabe [a]

[a] *Department of Chemical Engineering, Tokyo University of Agriculture and Technology,*
2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan
[b] *Chiyoda Corporation, 13 Moriya-Cho 3-Chome, Kanagawa-ku, Yokohama, Japan*

Abstract

Three series of CoMo catalysts (MoO$_3$: 6, 11, 16 wt.%) with various Co/Mo molar ratios were prepared by successive incipient wetness impregnations of a titania sample previously prepared by the pH swing method, which provides a TiO$_2$ carrier with a high SSA (134 m^2 g^{-1}) and excellent mechanical properties. DBT HDS activity of the catalysts increased with addition of cobalt up to Co/Mo = 0.4 and then decreased for higher ratios, irrespective of the Mo loading. The results of a [^{35}S]DBT HDS method showed that S_0, the amount of labile sulfur atoms, increased in parallel with the activity when adding Co up to a molar ratio of 0.4. In contrast, unlike on CoMo/Al$_2$O$_3$ catalysts, only a slight increase in k_{RE}, the H$_2$S release rate constant, was observed upon Co addition. This was due to formation of the TiMoS phase: while formation of Ti–S*–Mo bonds favorably induces an increase in sulfur mobility on Mo/TiO$_2$ catalysts, electronic density on Mo atoms increases, which limits the promoting effect of Co on mobility of S_a sulfur atoms bridged between Mo and Co. Further, while the increase in HDS activity upon Co addition on a uniform MoS$_2$ monolayer on TiO$_2$ was in rather good agreement with the quantitative and kinetics data of the ^{35}S tracer method, over MoS$_2$ slabs on TiO$_2$ this increase was larger than that expected from the results of the ^{35}S tracer method. This was attributed to the presence of $\square^*$ and $\square_a$ CUS, i.e. catalytic sites that are not replenished with sulfur, at the steady state. A larger number of $\square^*$ CUS was present at low Mo wt.% or for low Co/Mo. As these particular catalytic sites are in the form of CUS at the steady state, they are not accounted by the [^{35}S] radiotracer method. This explains the differences observed between the experimental DBT HDS promotion and the promotion deduced from the increase in k_{RE} and S_0.
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1. Introduction

Enhancement of the hydrodesulfurization (HDS) catalyst performances is prompted by the urgent need to improve fuel quality. Refineries must face more and more stringent environmental regulations that impose a progressive decrease in the sulfur content of commercial fuels. For example, the current norm of 50 ppm of sulfur in the light gas oils, now in effect in Japan, will be decreased to 10 ppm by 2007. Thus, actual research aims at rapidly proposing more active and selective catalyst formulations [1]. Conventional HDS catalysts consist of MoS$_2$ slabs decorated by Ni or Co atoms supported on a γ-alumina carrier. Several approaches can be envisaged to improve the HDS catalysts. First, the effect of the addition of third elements such as fluorine [2,3], phosphorus [4–12] or boron [11–19] to the Co(Ni)MoS/Al$_2$O$_3$ system can be investi-

* Corresponding author. Tel.: +81 42 388 7228; fax: +81 42 388 7228.
  E-mail address: atsushii@cc.tuat.ac.jp (A. Ishihara).

gated. In addition, use of other active phases such as WS_2 [20–24], CrS_x [25–31], noble metals [32–50], as well as other carriers such as TiO_2 or mixed oxides [51–70] or carbon [71] and zeolites [72,73] can also be investigated. Among these possibilities, use of titania in replacement of the alumina support seems promising. Indeed, Mo catalysts supported on titania were 4.4 times more active than those supported on alumina for thiophene HDS [57]. However, conventional titania supports generally have a low specific surface area (70 $m^2 g^{-1}$) compared with alumina ($\sim$250 $m^2 g^{-1}$). Moreover, the anatase phase exhibits a poor thermal stability at high temperatures [74]. Thus, TiO_2–Al_2O_3 mixed oxides combining the advantages of the good properties of titania (high activity) and alumina (excellent texture, mechanical and thermal properties) were further proposed as HDS catalyst supports. However, use of titania-poor TiO_2–Al_2O_3 mixed oxides did not sufficiently enhance the HDS activity; it appeared that the use of titania-rich TiO_2–Al_2O_3 mixed oxides is essential to sufficiently benefit of the properties of TiO_2. Nevertheless, contrary to the desired morphology, the surface of titania-rich sol–gel titania–alumina mixed oxides is preferentially covered by alumina. Thus, new technologies to directly synthesize high specific surface area (SSA) TiO_2 are actively being developed. Recently, a titania support suitable for catalytic applications, which exhibits a high SSA of ca. 134 $m^2 g^{-1}$ while keeping excellent mechanical properties, was successfully synthesized by Chiyoda Corporation. This new titania support now allows the direct use of titania support in industrial catalytic applications [75,76].

The beneficial effect of titania on HDS performances of MoS_2 catalysts is attributed to a better Mo dispersion [64,65] and a facilitated sulfiding of the MoO_3 oxide precursor into the MoS_2 active phase [66]. In addition, we previously proposed that S atoms with increased mobility are formed through the creation of a TiMoS phase [52,53,67–70]. For a MoS_2 non-promoted phase supported on low SSA titania (70 $m^2 g^{-1}$), DBT HDS activity was higher than on Mo/ Al_2O_3 despite a limitation in the maximal Mo loading (6 wt.%) [53,70]. Optimal Mo loading could be increased to 16 wt.% by using the 134 $m^2 g^{-1}$ titania mentioned above, which provided a further substantial increase in global DBT HDS activity when compared to a conventional Mo/Al_2O_3 catalyst [70]. On the other hand, we found that, over the low SSA titania, the synergetic effect between Co and Mo was not as high as over alumina [52], in good agreement with the results of others [57].

The object of the present work is to evaluate to what extent the addition of Co can enhance the HDS catalytic performances of Mo/TiO_2 catalysts derived from the new high SSA titania (134 $m^2 g^{-1}$). Further, we subsequently investigated the behavior of the sulfur and the promoting effect of cobalt using a ^{35}S-labeled dibenzothiophene (DBT) HDS method [77–80]. The results were compared to those obtained on low SSA TiO_2 and Al_2O_3.

2. Experimental

2.1. Catalysts

The TiO_2 support (anatase) used in this study was a solid with a surface area of 134 $m^2 g^{-1}$ supplied by Chiyoda Corporation. The CoMo/TiO_2 catalysts were prepared by successive incipient wetness impregnations of molybdenum and cobalt. First, a series of Mo/TiO_2 catalysts was prepared: titania was impregnated with an aqueous solution containing the desired amount of ammonium heptamolybdate, followed by drying at 120 °C for 3 h and calcining in air at 500 °C for 15 h. The obtained Mo/TiO_2 catalysts were named MT6, MT11, MT16, in which the numerical values indicate the MoO_3 contents, i.e. 6, 11 and 16 wt.% MoO_3, respectively. Then, the CoMo/TiO_2 catalysts were prepared by a step-by-step incipient wetness impregnation on this series of catalysts. The Mo/TiO_2 solids underwent successive impregnations with an aqueous solution containing a given amount of cobalt nitrate hexahydrate. For each step, an amount of Co equivalent to a Co/Mo molar ratio of 0.1 was impregnated and the procedure was repeated until the desired Co/Mo ratio was reached. After each impregnation step, the obtained solids were dried at 120 °C for 3 h and then calcined in air at 500 °C for 15 h. The CoMo/TiO_2 catalysts were named CMTX(0.2), CMTX(0.4) and CMTX(0.6), where X is the Mo loading, and the values in parentheses indicate the Co/Mo molar ratio, corresponding for instance to a loading of 1.7, 3.2 or 4.8 wt.% in CoO for the CMT16 catalysts.

Amounts of deposited molybdenum and cobalt were checked by X-ray fluorescence measurements with an EDX-800 spectrometer (Shimadzu).

2.2. Apparatus and procedure

The catalysts were packed in a reactor and presulfided under a flow of 5% H_2S/95% H_2 (5 l h^{-1}, 0.1 MPa). After presulfiding, the reactor was cooled to room temperature and then pressurized with hydrogen. The reactant solution (DBT dissolved in decalin) was fed into the reactor pre-heated at the desired reaction temperature using a high-pressure liquid pump (Kyowa Seimitsu KHD-16). Typical HDS reaction conditions were as follows: H_2 flow rate 25 l h^{-1}, WHSV 28 h^{-1}, reaction pressure 5 MPa, and concentration of DBT in decalin 1.0 wt.%. The liquid products were collected every 15 min and analyzed using a gas chromatograph equipped with a FID detector (Shimadzu-17A, Shimadzu Co. Ltd.) and a commercial capillary column (DB-1). The same reaction conditions were used to characterize the solid catalyst properties with the [^{35}S]DBT radioisotope tracer method described elsewhere [77–80]; Fig. 1 presents the result obtained on CMT11(0.4) at 300 °C. Details of the methodology used for the interpretation of the results can be found elsewhere [79,80].