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RESEARCH NOTE

Promoting Synergy in CoW Sulfide Hydrotreating Catalysts by Chelating Agents

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Adding chelating agents such as 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) and triethylenetetraamine-hexa acetic acid (TTHA) to the aqueous solution of cobalt nitrate and ammonium metatungstate used for impregnating the silica support results in enhanced activities for the hydrodesulfurization of thiophene after the catalysts have been sulfided. These chelating agents serve to retard the sulfidation of cobalt with respect to that of tungsten, which facilitates the formation of a phase in which Co atoms decorate the edges of WS_2, analogous to the well-known CoMoS phase. © 2001 Academic Press

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I. INTRODUCTION

It is well known that the addition of Co and Ni to MoS_2, and of Ni to WS_2 hydrotreating catalysts, significantly enhances the activity in the hydrodesulfurization (HDS) of, e.g., thiophene (1, 2). However, such synergy has not been observed in Co-promoted WS_2 catalysts, which is generally regarded as an unsuccessful combination. Reports on supported CoW catalysts are scarce (3) and the reason for the lack of synergy between Co and WS_2 is unclear.

Recently, ways to increase the efficiency of promoter functionality have been reported (4), based on the generally accepted model of the CoMoS phase, in which the promoter atoms are located on the edges of the slab-structured MoS_2 phase. A key element in effective preparation routes toward CoMoS-like phases is that the transition of oxidic Co and Ni to their sulfidic state should occur after MoS_2 and WS_2 phases are formed (5–12). Chelating agents such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), and derivatives of these molecules stabilize Ni and Co with respect to sulfide formation to temperatures where all or most of the Mo or W have converted to sulfides. These procedures enable one to prepare highly active CoMoS, NiMoS, and NiWS catalysts irrespective of the support.

The purpose of this Research Note is to demonstrate that using the appropriate chelating agents to retard the sulfidation of Co with respect to that of W results in notable enhancement of the HDS activity of CoWS catalysts on silica supports.

II. EXPERIMENTAL

Catalysts were prepared on planar silica model supports. Planar silica was prepared by oxidizing a Si(100) wafer at 750°C for 24 h in air, cleaning it in a mixture of H_2O_2 and NH_4OH (3/2 v/v) at 65°C, and rehydroxylating the surface in boiling water for 30 min. The supports were impregnated by spincoating an aqueous solution of ammonium metatungstate (Merck) and cobalt nitrate (Merck). The concentrations of W and Co in the precursor solutions were adjusted to result in a loading of 6 W atoms/nm^2 and 4 Co atoms/nm^2. When desired, the chelating agents 1,2-cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA; Merck) and triethylenetetraaminehexaacetic acid (TTHA; Merck) were added in an ammoniacal solution, which contained the precursors of W, Co, and CyDTA or TTHA in the atomic ratio 6 : 4 : 4, such that the amount of chelating agent was equivalent to that of Co. Catalysts prepared without chelating agents were calcined at 500°C for 30 min; catalysts prepared with chelating agents were used without calcination.

X-Ray photoelectron spectroscopy (XPS) was applied to study the extent of sulfidation of catalysts as a function of temperature. Sulfidation was performed with a mixture of 10% H_2S/H_2 at a heating rate of 5°C/min (2°C/min for catalysts with chelating agents) to the desired temperature, after which samples were kept at that temperature for 30 min. After sulfidation, the reactor was cooled to room temperature under helium and transported to XPS under N_2 atmosphere. For details on the XPS measurements and the

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analysis of spectra we refer to recent publications from our laboratory on NiW/SiO_2 catalysts (10, 11).

Model catalysts were tested in batch mode thiophene HDS carried out in a microflow reactor under standard conditions (1.5 bar, 400°C, 4% thiophene/H_2). About 5 cm^2 of model catalyst was placed inside a glass reactor. First the model catalyst was sulfided at 400°C for 30 min as described above. Then a mixture of 4% thiophene/H_2 was passed through the reactor at a rate of 50 mL/min and at 400°C. After 5 min the reactor was closed and operated as a batch reactor. After the desired reaction time, a sample was taken with a gas syringe for GC analysis of the reaction products. The activity of the model catalysts is expressed as percentage of thiophene converted into products per 5 cm^2 of catalyst and has been corrected for conversion of the empty $SiO_2/Si(100)$ model support.

III. RESULTS AND DISCUSSIONS

The activity of the catalysts in thiophene hydrodesulfurization is shown in Table 1. The yields are based on a surface area of 5 cm^2 of catalyst and have been corrected for conversion obtained with an empty SiO_2 support in a blank experiment. The silica support in the reactor has an order-of-magnitude lower activity than W/SiO_2, and shows mainly cracking products. Both the W/SiO_2 and the Co/SiO_2 catalysts show detectable activity with a product distribution of predominantly the primary product 1-butene. However, CoW/SiO_2 prepared by coimpregnation shows no synergy, as its activity equals that of W/SiO_2 and Co/SiO_2 together, thus confirming the notion that CoW is an unsuccessful combination for HDS reactions.

Table 1 also shows the effect of applying chelating agents in the preparation stage. CyDTA gives a substantial increase in activity with a factor of around 1.8. The highest activity is observed with CoW–TTHA/SiO_2, which is nearly 2.4 times more active than a standard CoW/SiO_2 of the same composition. For this catalyst, the relative amounts of secondary products *cis*- and *trans*-2-butenes are also higher, which is a purely kinetic effect, as we showed before [12].

XPS has been used to monitor the rate at which Co and W convert to the sulfided state during temperature-programmed sulfidation. For convenience, we introduce $T_{1/2}$ as the temperature at which 50% of the cobalt has been converted into the sulfidic state. For W/SiO_2 this $T_{1/2}$ equals 210°C. As the values in Table 1 show, Co–W synergy, as measured by thiophene HDS activity, is observed when the sulfidation of Co is retarded by stabilizing it with a chelating agent, as expressed by $T_{1/2}$. Note, however, that the chelating agents may also affect the dispersion of the resulting CoWS phase, a property that we cannot measure. However, HDS activity measurements on Co–CyDTA/SiO_2 and W–CyDTA/SiO_2 catalysts did not show any increase in activity, indicating that changes in dispersion due to CyDTA in these catalysts do not occur.

Table 1 also gives the Co $2p_{3/2}$ binding energy (BE) of the unsulfided and fully sulfided catalysts. The Co $2p$ binding energy of the unsulfided catalysts containing chelating agents is significantly lower compared with the conventional catalysts. This difference in binding energy is attributed to Co complexed to either CyDTA or TTHA, thereby changing its chemical environment. This phenomenon was also observed for NiMo and NiW catalysts (11, 12). The binding energy of the fully sulfided catalysts can be divided in two groups: catalysts with low HDS activity with a BE of 779.0 eV corresponding to bulk Co_9S_8 and catalysts with enhanced HDS activity with a BE of 779.4 eV. This indicates that in the active catalysts Co is present in a different state than in bulk Co_9S_8. The same difference in BE between low and high HDS active catalysts was found for $NiMo/SiO_2$ (12) and NiW/SiO_2 catalysts (11).

In analogy with $NiWS/SiO_2$ (11) and $NiMoS/SiO_2$ catalysts (12), we attribute the enhanced HDS activity of CoW–CyDTA/SiO_2 and CoW–TTHA/SiO_2 to the retardation of Co sulfidation by the chelating agents to temperatures where WS_2 has already (partially) formed. As a result, the Co–CyDTA (or TTHA) complex decomposes and the Co atoms are released and can directly move to the edges of WS_2 to form CoWS, similar to the phase CoMoS proposed by Topsøe and others (1, 2). In the absence of a chelating

TABLE 1

Percentage of Thiophene Converted into Butenes in a Batch Reactor over 5 cm^2 of $CoWS/SiO_2$ Catalyst at 400°C for 1 h

	W	Co	Co + W	CoW	CoW–CyDTA	CoW–TTHA
1-Butane	0.18	0.09	0.27	0.31	0.55	0.64
trans-2-Butane	0.1	0.04	0.14	0.12	0.22	0.35
cis-2-Butane	0.07	0.02	0.09	0.08	0.13	0.24
Total	0.35	0.15	0.50	0.51	0.9	1.22
$T_{1/2}$ (°C)[a]	210[b]	25	—	75	250	235
Co_{ox} $2p_{3/2}$ (eV)		782.3		782.1	781.6	781.4
Co_{sulf} $2p_{3/2}$ (eV)	—	779.1	—	779.0	779.4	779.5

[a] Temperature at which 50% of the cobalt has converted to the sulfided state.

[b] $T_{1/2}$ of W.

agent, Co is expected to form the relatively stable sulfide Co_9S_8 before tungsten starts to sulfide. This results in a segregated phase for which the HDS activity equals the sum of the constituent phases. The Co $2p_{3/2}$ BE of the fully sulfided catalysts confirms this idea.

IV. CONCLUSIONS

CoWS catalysts supported on silica, prepared by applying chelating agents such as TTHA at the impregnation stage, exhibit notable synergy in the hydrodesulfurization of thiophene. Such synergy is not observed in CoWS catalysts prepared by sulfiding a coimpregnated Co–W catalyst.

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