Research Article

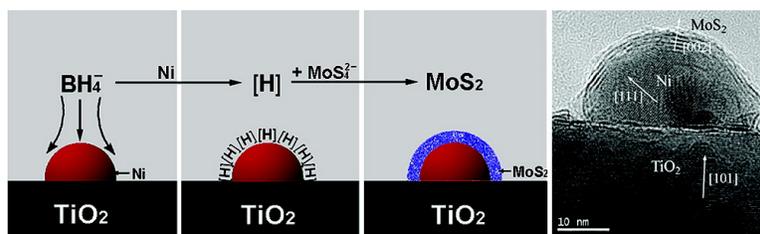# Surface Selective Deposition of Mo(IV) on Ni/TiO Particles in Aqueous Solutions

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Surface Selective Deposition of Mo(IV) on Ni/TiO₂ Particles in Aqueous Solutions

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The selective depositions of MoS₂ and MoO₂ over Ni surfaces are demonstrated on Ni/TiO₂ particles in a mild electroless deposition process. High-resolution transmission electron microscopy (HRTEM) images show the uniform distribution of 10−30 nm spherical and hemispherical Ni particles on TiO₂ surface, and three to six layers of MoS₂ on the surface of Ni particles. The as-prepared MoS₂−Ni/TiO₂ is used as a catalyst for the hydrodesulfurization (HDS) reaction of dibenzothiophene (DBT), and shows a significant increase over commercial catalysts in turnover frequencies as the result of unique distribution of active components in the binary catalyst. The selective material deposition is explained in the context of Ni catalyzed KBH₄ decomposition, which produces strong reducing species responsible for the site selective deposition of Mo. The synthetic method can be potentially used to prepare bimetallic materials with similar nanostructures such as those of Mo−Co, Mo−Pd, and Mo−Rh.

Introduction

Selective material deposition on a nanometer scale is of considerable importance for preparing materials with exceptional properties, and for revealing the structure−function relation.[1−11] Surface selective deposition, i.e., in which deposition takes place only on certain locations, is especially attractive and useful for constructing well-defined nanoarchitectures.[4] At present, surface selective deposition is mainly limited to fabrications of metal-based materials and semiconductor devices by chemical vapor deposition coupled with a surface activation treatment such as sputtering,[9,10] electrochemical or chemical surface modification,[3] and laser or wide-spectrum irradiation[11] prior to deposition. With respect to compounds, selective deposition is generally more difficult than that of metals, and usually requires advanced techniques. For example, the selective deposition of TiO₂ on silicon substrate was obtained by a laser-enhanced technique,[12] and that of crystalline ferromagnetic CrO₂ thin film was obtained on a glass substrate by a vapor transport method.[13]

Molybdenum(IV)-based materials have been widely used in heterogeneous catalysis, ultralow friction, and electrochemical hydrogen storage.[14−17] Recently, nanostructured Mo(IV) materials such as MoS₂ nanotubes, MoS₂ nanorods, MoO₂ nanowire arrays, and fullerene-like MoS₂[18−21] have been synthesized and show many unique properties. We have found a method for the selective deposition of molybdenum compounds such as MoS₂ and MoO₂ on the surface of Ni in Ni/TiO₂ particles by a mild electroless deposition, which is similar to the metal catalyzed electroless deposition in patterning research.[22−25] The catalytic activity of the novel nanomaterial is evaluated using a hydrodesulfurization (HDS) reaction. The novel catalyst shows higher turnover frequencies than commercial catalysts due to the unique arrangement of two active components in the binary catalyst. A mechanism model of the surface selective deposition is also discussed.

Experimental Section

Preparation. Commercially available solvents and reagents were used without further purification. The procedure to make Ni/TiO₂ was similar to that in our previous work.[26] Briefly, 1.0 g of Ag/TiO₂ precursor (0.1 wt % Ag) prepared by a silver mirror reaction was added to 40 mL of an electroless nickel plating solution containing nickelous sulfate (7.1 g/L), ethylenediamine (16.6 g/L), potassium

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Scheme 1. Preparation Process of MoS$_2$−Ni/TiO$_2$
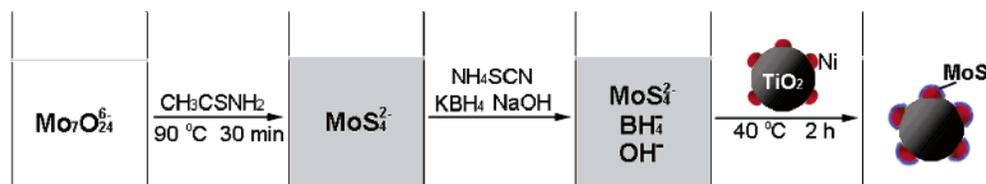
borohydride (3.5 g/L), and sodium hydroxide (30.0 g/L). The reaction lasted for 15 min at 40 °C until the complete decomposition of potassium borohydride (no bubbles in the solution). The resulting solid was washed with deionized water until pH 7 was reached.

Surface selective deposition of MoS$_2$ on Ni/TiO$_2$ particles was conducted as described in Scheme 1. A 0.3 g sample of (NH$_4$)$_6$-Mo$_7$O$_{24}$·4H$_2$O was dissolved in 10 mL of H$_2$O; then 0.51 g of CH$_3$-CSNH$_2$ was added to the solution. The resultant solution reacted in a 90 °C water bath for 30 min to obtain a MoS$_4{}^{2-}$ solution. The MoS$_4{}^{2-}$ solution was diluted with 140 mL of H$_2$O, and then 10 mL of NH$_4$SCN aqueous solution (66.0 g/L) and 10 mL of KBH$_4$ and NaOH solution (KBH$_4$ 14.0 g/L, NaOH 21.0 g/L) were added in turn to get a mixed solution. The above-obtained fresh Ni/TiO$_2$ sample was added to the mixed solution, and the mixture was slowly stirred at 40 °C for 2 h. After filtration, the solid was washed with 500 mL of deionized water and then with anhydrous ethanol three times. The resulting solid was dried at 80 °C for 3 h in a vacuum oven (10^{-1} Pa), and then treated at 350 °C for 1 h in an argon atmosphere to obtain a final sample of MoS$_2$−Ni/TiO$_2$. The sample was stored under nitrogen gas to prevent oxidation. Selective MoO$_2$ deposition was carried out using a similar route except that Na$_2$MoO$_4$·2H$_2$O solution with a suitable concentration substituted for the MoS$_4{}^{2-}$ solution in the above process.

Characterization. X-ray diffraction (XRD) patterns were collected on the Rigaku D/max-2500 diffractometer by using Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The chemical composition of the sample was determined by inductively coupled plasma (ICP) analysis using an IRIS Advantage spectrometer. X-ray photoelectron spectroscopy (XPS) analysis of MoS$_2$−Ni/TiO$_2$ was performed in a Perkin-Elmer PHI (4) 5300ESCA analyzer. Photoelectrons were excited using the unmonochromatized Mg Kα line at 1253.6 eV. A pass energy of 89.45 eV was used to obtain the survey spectra, and 35.75 eV was used for the high-resolution, multiregion scans. The binding energy values were referenced to the C 1s line at 284.8 eV from inadvertent carbon contamination. The transmission electron micrographs were imaged on a JEOL JEM 2010FEF transmission electron microscope (TEM) using an acceleration voltage of 200 kV equipped with an energy-dispersive X-ray analysis (EDX) system. Samples for TEM were prepared by ultrasonically dispersing the powders in ethanol, and part of the suspension was collected on a porous carbon film covered specimen grid. The specimens were dried for several minutes in ambient conditions in a nitrogen atmosphere, and then rapidly transferred to the TEM analysis chamber.

Catalytic Activity Test. The prepared powder samples were pressed, crushed, and sieved to a final size of 20−40 mesh, and then 1.0 g of the sample was pretreated and evaluated using the same procedure shown in our previous work.[27] The hydrodesulfurization (HDS) reaction of dibenzothiophene (DBT) was carried out at 280, 300, and 320 °C with a H$_2$ pressure of 3.0 MPa. The H$_2$ flow rate and liquid feed rate were kept at 200 mL/min and 15.0 mL/h. The liquid products were collected at a 1 h interval and analyzed by gas chromatography. As control samples, Ni/TiO$_2$ catalyst was prepared by treating the Ni/TiO$_2$ sample at 350 °C in an argon atmosphere, and MoS$_2$/TiO$_2$ catalyst was obtained by impregnating TiO$_2$ with a high concentration MoS$_4{}^{2-}$ solution (0.5 mol/L) and then drying. In addition, the catalytic activity of a commercial NiMo/TiO$_2$−Al$_2$O$_3$ catalyst was also evaluated.
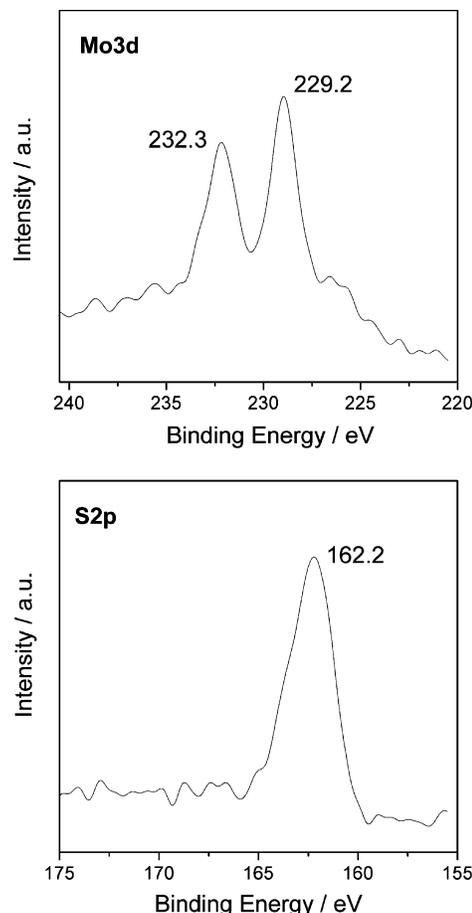

Figure 1. XPS spectra of Mo 3d and S 2p of MoS$_2$−Ni/TiO$_2$.

Results and Discussion

The Ni and B contents were determined to be 6.1% and 0.1% in the as-prepared amorphous Ni/TiO$_2$ by XRD and ICP analysis. Since the small amount of B does not contribute to the selective deposition, the sample was denoted as Ni/TiO$_2$. TEM images show that the supported amorphous Ni exists as 10−30 nm hemispherical and spherical particles. The MoS$_2$−Ni/TiO$_2$ sample contains 6.0 wt % Ni, 1.1 wt % Mo, 0.1 wt % B, and a trace amount of Ag. Figure 1 is the XPS spectra of Mo 3d and S 2s of the sample. Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ peaks center at 229.0 and 232.3 eV, respectively, and S 2p$_{3/2}$ peak centers at 162.2 eV, which is in good agreement with the values reported for MoS$_2$.[28] No peak of Mo(VI) species appears in the XPS spectra. A typical TEM image (Figure 2A) demonstrates that MoS$_2$−Ni/TiO$_2$ maintains the micromorphology of the parent Ni/TiO$_2$ particles in which the hemispherical or spherical particles with a size of 10−30 nm are distributed on the TiO$_2$ surface. The black lines clinging to the edge of Ni particles in TEM images have been confirmed having as the characteristics of supported MoS$_2$,[27,29,30] indicating the deposition of MoS$_2$ on Ni particles. MoS$_2$ black

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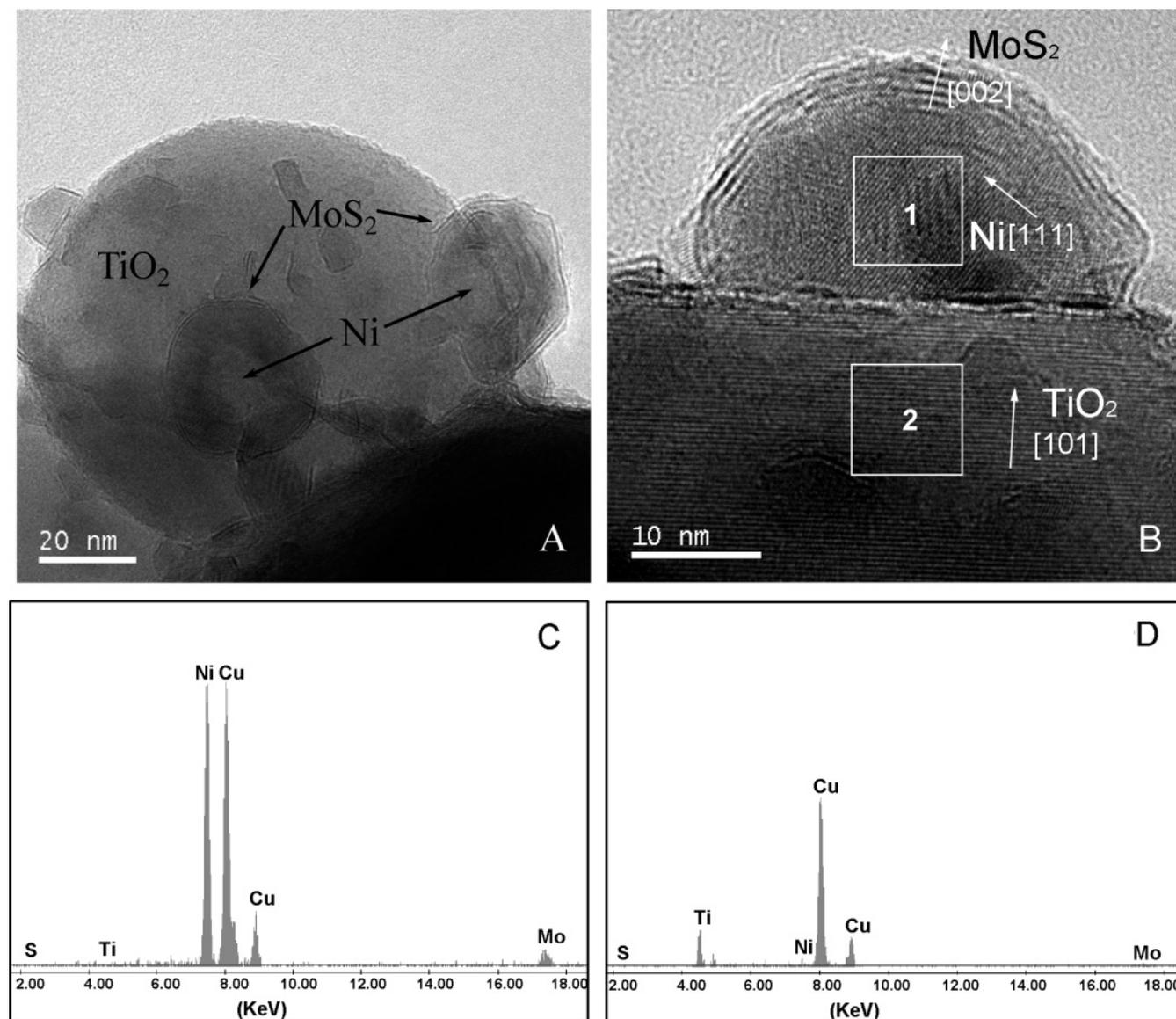(29) Araki, Y.; Honna, K.; Shimada, H. *J. Catal.* **2002**, *207*, 361.

Figure 2. TEM images of MoS₂−Ni/TiO₂ (A, B) and EDX spectra of square area 1 (C) and square area 2 (D).

lines can be easily identified due to a sharp contrast between MoS₂ and TiO₂ in TEM images.[31,32] We found few black lines on the TiO₂ surface, and the estimated amount of MoS₂ supported on TiO₂ is less than 5%. Energy-dispersive X-ray analysis (EDX) shows Mo element exists where Ni element appears, and very few Mo atoms are directly deposited on the TiO₂ surface. This means the deposition of MoS₂ in our process is surface selective. Figure 2B is a high-resolution TEM image of a supported hemispherical particle on TiO₂, showing a unique MoS₂−Ni/TiO₂ nanostructure based on the selective deposition of MoS₂. EDX analysis (Figure 2C) shows that the supported particle (the square area marked as "1" in Figure 2B) consists of nickel, molybdenum, and sulfur (the copper signal comes from the TEM grid). However, no nickel and molybdenum element exists on the TiO₂ area (the square area marked as "2" in Figure 2B), as shown in Figure 2D. In addition, crystal lattice spacing measurements indicate that the core of the supported particle is metallic Ni, the surface layer consists of MoS₂ with a lattice

spacing of 0.63 nm ((002) plane), and the stack number of MoS₂ layer is in the range of three to six.

We have done a series of experiments to study the effects of KBH₄ concentration or reaction temperature on surface selective deposition of MoS₂. When the concentration of KBH₄ decreases from 14.0 to 7.0 g/L, the sample shows a nanostructure similar to that in Figure 2, except that fewer MoS₂ black lines are observed, indicating a selective MoS₂ deposition. When the concentration of KBH₄ is increased from 14.0 to 21.0 g/L, there is no selectivity of MoS₂ deposition, and about half of MoS₂ appears on the surface of TiO₂ in addition to the surface of Ni particles (Figure 3). Meanwhile the deposition will not occur at 25 °C in 20 h, and the MoS₂ deposition is nonselective at 60 °C (figure not shown).

We have achieved similar surface selective deposition of MoO₂ on Ni by using Na₂MoO₄·2H₂O solution. Since the typical morphology (black lines) of MoS₂ can be observed more conveniently in HRTEM than that of MoO₂, MoO₂−Ni/TiO₂ samples were converted to MoS₂ by heat treatment in a 10 vol % H₂S/H₂ atmosphere for 1 h at 350 °C, which is different from the argon atmosphere in the case of MoS₂. A 28.0 g/L concentration of Na₂MoO₄·2H₂O solution is found to be suitable

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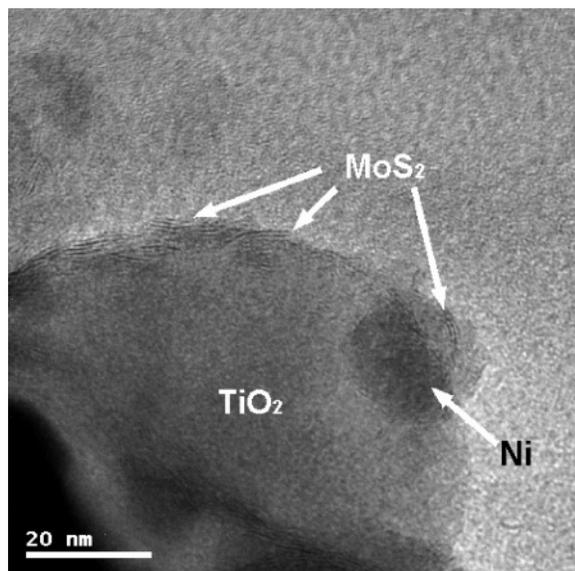(32) Shimada, H. *Catal. Today* **2003**, *86*, 17.

Figure 3. TEM image of the sample prepared with a high concentration of KBH_4 solution.
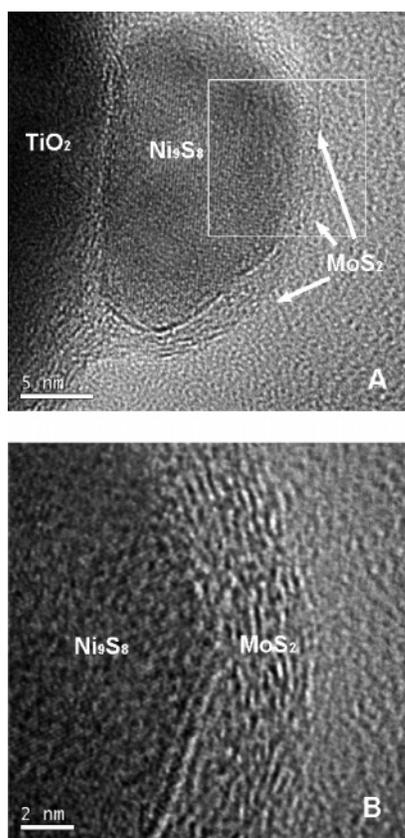

Figure 4. HRTEM images of MoO_2−Ni/TiO_2 pretreated in H_2S/ H_2. (B) Details of the square area in (A).

for selective deposition of MoO_2, on Ni surface as shown in HRTEM images (Figure 4). In the MoS_2−Ni/TiO_2 sample, Ni species exists as nickel sulfide rather than metallic nickel due to the effect of H_2S in the treating process.

The spatial arrangement of each component in binary catalysts is critically important for the efficiency of the catalyst. NiMo sulfides have been used frequently as important binary catalysts for producing clean oils via the hydrodesulfurization (HDS) reaction of dibenzothiophene (DBT), where Ni is the promoter.[14] A key issue in catalyst design is to control the distribution of Ni and Mo at an atomic or nanometer level to create efficient sites

Scheme 2. Mechanism of the Surface Selective Deposition of MoS_2
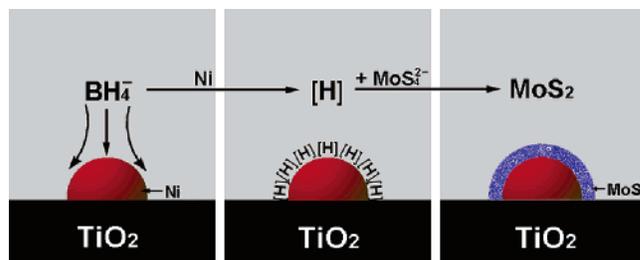
for the reaction. The selective deposition of MoS_2 on Ni produces a unique NiMo nanostructure, which brings two active components together. We have tested the catalytic properties of MoS_2−Ni/TiO_2 and MoO_2−Ni/TiO_2 samples for the HDS reaction of DBT. As a comparison, the catalytic properties of Ni/TiO_2, MoS_2/TiO_2, and a commercial catalyst NiMo/TiO_2− Al_2O_3 (30 wt % TiO_2) were also tested. All these catalysts were pretreated at 350 °C in a 10 vol % H_2S/H_2 flow for 2 h to transform Ni and Mo species into Ni_9S_8 and MoS_2, respectively. Ni and Mo amounts of the catalysts, the corresponding DBT conversion, and the turnover frequency (TOF) of Mo (converted DBT moles per mole of Mo atom per hour) are summarized in Table 1. MoS_2−Ni/TiO_2 and MoO_2−Ni/TiO_2 show similar catalytic activities and TOFs; this is because both samples have the same amounts of Ni and Mo with identical nanostructures. The catalytic activities and TOFs are higher than those of Ni/TiO_2 and MoS_2/ TiO_2, indicating a synergy between Ni and Mo, which has been reported previously.[14] MoS_2−Ni/TiO_2 and MoO_2−Ni/TiO_2 catalysts show higher efficiency in utilizing Mo component: compared with the commercial catalyst (NiMo/TiO_2−Al_2O_3), which has much more Mo and a relatively high activity, MoS_2− Ni/TiO_2 and MoO_2−Ni/TiO_2 show much higher TOFs at each temperature. Because the pretreatment temperature (350 °C) is higher than the highest reaction temperature (320 °C), we assume the unique nanostructure is maintained in the HDS reaction. Thus the surface selective deposition will produce an high-efficiency binary catalyst for the HDS reaction of DBT. The trace amounts of B and Ag contained in MoS_2−Ni/TiO_2 and MoO_2−Ni/TiO_2 catalysts make no contribution to the reaction.

KBH_4 as a reducing agent plays an important role in the process, which can decompose and release active atomic hydrogen or H_2 in solutions to reduce soluble Mo(VI) species to insoluble Mo-(IV) deposit.[33] Increasing the concentration and temperature, or introducing a catalyst, will accelerate the decomposition of BH_4^- to release more reducing agent. Although BH_4^- in a free solution containing MoS_4^{2-} and BH_4^- is relatively stable at room temperature due to the effect of a stabilizer SCN^- and a suitable pH value,[33] it is catalytically decomposed by the Ni species supported on TiO_2 in a process similar to the well-known Ni-based electroless plating. Thus when Ni/TiO_2 is added, the Ni supported on the surface of TiO_2 begins to induce the decomposition of the neighboring BH_4^- ions and generate an active atomic hydrogen layer on the Ni surface (Scheme 2). Subsequently, MoS_4^{2-} around Ni particles is reduced to MoS_2 phase, which is locally deposited on the surface of Ni. When MoS_2 deposition is thick enough to cover the entire catalytic active sites, the local reduction reaction stops and the surface selective deposition of MoS_2 is complete. When KBH_4 concentration or the reaction temperature is increased, the decomposition of KBH_4 in the solution is accelerated to produce active atomic hydrogen

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Table 1. Catalytic Activity of the As-Prepared Sample and a Commercial Catalyst

catalyst	Ni/wt %	Mo/wt %	DBT conversion/%			TOF^a/h^{-1}		
			280 °C	300 °C	320 °C	280 °C	300 °C	320 °C
MoS₂−Ni/TiO₂	6.0	1.1	30.1	40.2	52.9	0.93	1.25	1.64
MoO₂−Ni/TiO₂	6.1	1.0	28.6	43.5	53.8	1.04	1.49	1.83
Ni/TiO₂	6.3	0		8.0	12.5			
MoS₂/TiO₂	0	3.6		4.0	10.8		0.03	0.08
NiMo/TiO₂−Al₂O₃^b	5.1	17.1	79.4	87.6	92.5	0.16	0.17	0.18

^{a} Converted DBT moles per mole of Mo atom per hour. ^{b} A commercial HDS catalyst containing 30 wt % TiO₂.

on the surface of not only Ni but also TiO₂, resulting in the disappearance of the surface selectivity. For an ideal selective deposition, the reaction should be carried out with a KBH₄ concentration lower than 14.0 g/L and at about 40 °C. The success of selective deposition also requires a low MoS₄$^{2-}$ concentration (∼0.0014 mol/L); thus the direct deposition of MoS₄$^{2-}$ on TiO₂ is kept to a minimum. The trace amount of B (0.1 wt %) in Ni/TiO₂ does not contribute to the catalytic behavior of the Ni. Furthermore, since the catalytic Ni species is responsible for the surface selective deposition, other catalytically active species such as Co, Pd, and Rh that have been used in electroless planting will also show similar selectivity to prepare some bimetallic materials such as Mo−Co, Mo−Pd, and Mo−Rh.[34] It is possible to selectively deposit other metal compounds with suitable solutions based on the above mechanism. As the second step toward this direction, we have recently succeeded in the selective deposition of Mo(IV) on Co.

Conclusions

We have shown that surface selective deposition of MoS₂ or MoO₂ on Ni/TiO₂ particles can be realized by an electroless deposition in a mild aqueous condition. HRTEM images clearly show a novel nanostructure based on the surface selective deposition, in which hemispherical or spherical Ni particles are well distributed on the surface of TiO₂, and MoS₂ layers are deposited on the surface of Ni. The catalytic effect of Ni for the decomposition of BH₄$^-$ is proposed to be responsible for the selective deposition. This synthetic methodology provides a potential method for preparing some bimetallic materials with similar nanostructures such as Mo−Co, Mo−Pd, and Mo−Rh. The as-prepared MoS₂−Ni/TiO₂ samples show higher efficiency for the HDS reaction of DBT compared to the commercial catalyst (NiMo/TiO₂−Al₂O₃), providing opportunities of enhancing the catalytic activity of HDS catalysts.

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