# NOTE

Characterization of Supported Tungsten Sulfide Catalysts ex Ammonium Tetrathiotungstate

Active sulfide catalysts are conventionally prepared by converting the respective oxides to sulfides. Reductive sulfiding of the oxides is usually difficult and does not proceed in a regular manner. On the other hand, a supported molybdenum sulfide catalyst prepared by the decomposition of ammonium tetrathiomolybdate (ATTM) in hydrogen or helium is unique in two respects, namely, the lower valence state of the supported molybdenum sulfide catalyst and the presence of few oxygen atoms in the catalyst (1). In the case of supported molybdenum sulfide, it was found that the lower valence state resulted in a higher concentration of anion vacancies (or coordinated unsaturation sites) which are believed to act as active sites of the catalyst (2, 3). It was also found that the catalysts prepared by this technique displayed much higher activities in the hydrogenolysis of thiophene and in the hydrogenation of propylene than a conventional catalyst prepared by reductive sulfiding of the oxide (2, 3).

In this article, the activity of a tungsten sulfide catalyst (prepared by the thermal decomposition of ammonium thiotungstate (ATT) in helium or in hydrogen) in the hydrogenation of propylene and in the hydrogenolysis of thiophene are compared with the activity of a conventional tungsten sulfide catalyst.

Ammonium tetrathiotungstate was prepared by bubbling hydrogen sulfide through a solution of ammonium metatungstate in ammonium hydroxide and water according to the procedure outlined by Ramanathan and Weller (4). The impregnation was carried out at room temperature by introducing γ-alumina in a saturated solution of ATT under a nitrogen blanket. The metal content in the supported catalyst was determined by a standard ASTM method using a Jones reductor column (Method D-3943), which was modified to make it applicable to tungsten. Prior to analysis, the catalyst was first oxidized by air calcination at $500°C$ for 3.5 h. The final catalyst had a loading of 2.2% WO_3 by mass.

Thermal decomposition of ATT in helium produces tungsten sulfide containing excess sulfur according to the reaction

$$(NH_4)_2WS_4 \rightarrow 2NH_3 + H_2S + (3 - y)S + WS_y.$$
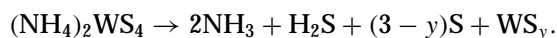
The supported ATT was decomposed *in situ* in the reactor, thereby preventing exposure of the resulting sulfide to air in any of the subsequent procedures. The heating schedule used in this experiment consisted of temperature-programmed heating, where the catalyst was heated at a rate of $10°C/min$ up to $450°C$ and held at that temperature for 15 min.

In some experiments, thermal decomposition of supported ATT was carried out in a stream of H_2 instead of He. The heating rate was $15°C/min$ until the sample reached $650°C$, and the sample was then held at that temperature for 1 h. Thermal decomposition of supported ATT in hydrogen is assumed to produce tungsten sulfide according to the reaction

$$(NH_4)_2WS_4 + yH_2 \rightarrow (NH_4)_2S + yH_2S + WS_{3-y}.$$

The Ni-promoted catalyst was prepared by impregnating vacuum dried ATT/Al_2O_3 with nickel nitrate solution of appropriate concentration under a nitrogen blanket. The final catalyst had an off-white color with a metal content equivalent to 3.0% NiO and 2.2% WO_3 by mass. Thermal decomposition of Ni-promoted catalyst in helium and hydrogen was conducted in a manner similar to the ATT catalyst.

A conventional oxide catalyst, WO_3/Al_2O_3, was used for comparison of catalyst activity. The conventional oxide catalyst was prepared by the calcination of ATT/Al_2O_3 in a muffle furnace at $590°C$ for 12 h and it therefore had the same W loading as the WS_y catalyst.

An integrated apparatus was used to measure the temperature-programmed reduction profile, hydrogen sulfide chemisorption, reaction rates, and activities. The details of the system are described elsewhere (2, 3). In order to pretreat the catalyst, tungsten sulfide catalyst prepared by the decomposition of ATT in helium was cooled to room temperature and heated at a rate of $15°C/min$ in hydrogen (temperature-programmed reduction, TPR) until it reached the desired temperature of either 480 or $650°C$ and then held at that temperature for 1 h. H_2S evolution was monitored by gas chromatography using an empty Teflon column of small diameter (1/4 in.). The conventional

tungsten oxide catalyst was not decomposed in helium. After calcination, the catalyst was heated at 15°C/min in a 15.3% H_2S/H_2 mixture to 650°C and kept at that temperature for 1 h. The sample was cooled to room temperature while being purged with H_2 and then subjected to TPR.

The catalyst activity was measured by a continuous method in which the catalyst was cooled to 600°C after pretreatment, and its activity was measured by flowing high purity hydrogen through a saturator containing thiophene maintained at a constant temperature. For each run, 0.2 g of catalyst was used, and the flow rate of hydrogen through the saturator was kept the same. The products of the reaction, n-butane, butenes (butene-1 and trans- and cis-butene-2) and H_2S, and unconverted thiophene were separated in a Durapak column and analyzed by gas chromatography. Details of the activity measurements are described elsewhere (2, 3). Propylene hydrogenation (HYD) was selected to test the hydrogenation activity of the catalysts. In propylene hydrogenation, the catalyst was cooled to 400°C after subjecting it to various pretreatments, and its activity was also determined by a continuous method. Propylene was mixed with H_2 in a stoichiometric ratio by controlling the flow rate of each. The combined flow passed through the reactor at about 90 mL/min. The reaction product propane and unconverted propylene were analyzed by gas chromatography equipped with a Durapak column at 45°C.

For unsupported ATT, Ramanathan and Weller (4) found that the tungsten sulfide formed by thermal decomposition of ATT in He at 450°C contained excess sulfur (S/W = 2.2). Ramanathan and Weller (4) observed two H_2S peaks during TPR at about 200 and 380°C for the unsupported ATT catalyst. For supported ATT, TPR had to be continued up to a temperature of 650°C in order to obtain two distinct H_2S peaks corresponding to the loss of excess sulfur from the surface and bulk. Consequently, the peak temperatures for supported catalyst at about 430 and 570°C were much higher than the corresponding values of about 360 and 430°C for unsupported ATT obtained by us. A similar shift has been observed for supported Mo catalyst compared to the unsupported catalyst (2).

Supported ATT catalyst was subjected to a variety of pretreatments, and the results of activity measurement in the hydrogenolysis of thiophene are shown in Table 1. The WS_y/Al_2O_3 catalyst prepared by the decomposition of ATT in hydrogen alone showed the highest reaction rate (calculated by normalizing the rate to the BET area of the catalyst). The sample prepared by thermal decomposition in He followed by TPR had the second highest reaction rate. The conventional oxide catalyst with the same W loading as the WS_y/Al_2O_3 catalyst and prepared by reductive sulfiding had the lowest reaction rate. No change in the BET area was found as a result of a change in the method of pretreatment.

TABLE 1

Effect of Pretreatment on Thiophene Conversion

Catalyst	Pretreatment	Rate $\times 10^4$ (mmol/s · m²)	Conversion (%)
WS_y/Al_2O_3	Hydrogen reduction	3.5	85
WS_y/Al_2O_3	10°C/min in He + TPR (650°C)	2.6	63
WO_3/Al_2O_3	Reductive sulfiding + TPR (650°C)	2.1	50

Note. The BET area of the tungsten sulfide catalysts was 176.4 m²/g.

During reductive sulfiding, conventional molybdenum oxide catalysts are not completely converted to sulfides (5, 6). XPS results have also indicated that the sulfiding is incomplete (7). Since the sulfur atom is a greater electron donor than an oxygen atom, this results in an increase in the electron density of the tungsten ions on the surface of the catalyst created during reduction. The higher electron density probably leads to an enhanced electron donation to the reactant molecule, thus increasing the activity per site of the catalyst (3).

The effect of reduction temperature on catalyst activity in the hydrogenation of propylene is shown in Fig. 1, in which the activities of supported ATT catalyst subjected to 10°C/min thermal decomposition in helium followed by
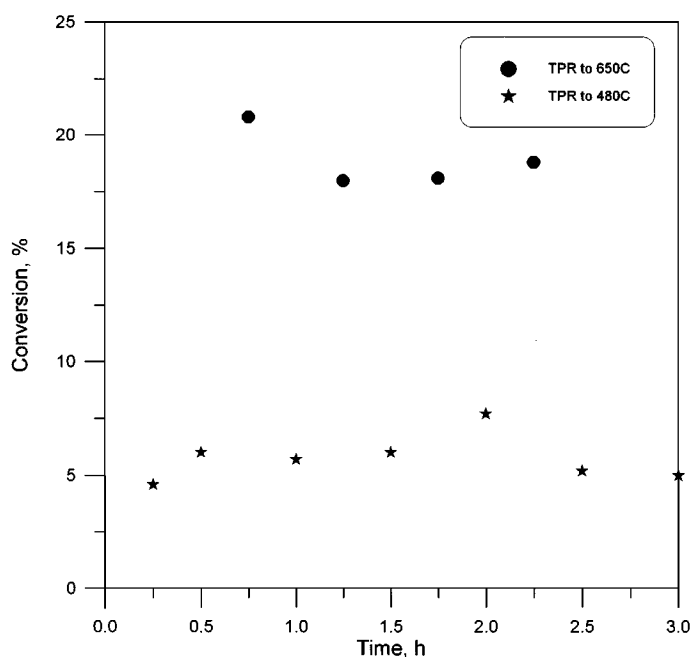

FIG. 1. Effect of reduction temperature on catalyst activity. Catalyst prepared by decomposition of ATT in He followed by temperature-programmed reduction (TPR) in H_2. Catalyst weight 0.2 g.

TABLE 2

Effect of Pretreatment on Propylene Hydrogenation

Catalyst	Pretreatment	Rate $\times 10^5$ (mmol/s · m^2)	Conversion (%)
WS_y/Al_2O_3	Hydrogen reduction	1.72	20
WS_y/Al_2O_3	10°C/min in He + TPR to 650°C	1.2	13
WO_3/Al_2O_3	Reductive sulfiding + TPR to 650°C	0.63	7
WS_y/Al_2O_3	10°C/min in He + TPR to 480°C	0.52	6

temperature-programmed reduction to 480 and 650°C are compared. The catalyst activity after the second TPR peak (650°C) is clearly higher and may be attributed to an increase in the number of coordinated unsaturation sites. It is also clear from Fig. 1 that there is very little deactivation of the catalyst. Similarly, very little deactivation was observed in the hydrogenolysis of thiophene as well. The activity of the catalyst prepared by decomposition of ATT was found to be consistently superior to a catalyst prepared by reductive sulfiding of the oxide, even at long times and at high conversions.

The effect of catalyst preparation technique on propylene hydrogenation was determined, and the reaction rates are compared in Table 2. The WS_y/Al_2O_3 catalyst prepared by hydrogen reduction of ATT/Al_2O_3 showed the highest activity followed by a catalyst prepared by thermal decomposition in He at 10°C/min and subjected to TPR to 650°C. The conventional catalyst prepared by reductive sulfiding of the oxide and the catalyst prepared by thermal decomposition in He at 10°C/min followed by TPR to 480°C had approximately the same low reaction rates.

Previous studies by Vasudevan and Weller (1) have shown that the catalyst prepared by H_2 reduction of ATTM on an alumina support has a valence state lower than 4 (determined by measuring the H_2 consumption in the decomposition of ATTM), which is lower than the valence state of Mo(IV) in MoS_2–MoO_2 catalysts prepared by reductive sulfiding of conventional oxides. Results from activity measurements of molybdenum sulfide catalysts (2, 3) clearly indicate that the activity of the catalyst in the hydrogenolysis of thiophene and in propylene hydrogenation has a direct correlation with the number of anion vacancies (as determined by temperature-programmed desorption studies) or the number of coordination unsaturation sites (CUS). Based on these results, it is likely that the higher catalyst activity observed with tungsten catalyst prepared by decomposition of ATT in H_2 may also be attributed to the presence of more anion vacancies (or more CUS). The higher activity could also result from a better or higher dis-

persion of MoS_2. A lower activity in the case of the catalyst prepared by reductive sulfiding of the oxide can occur because of a strong interaction of the tungsten oxide with the support upon calcination, so that the oxidic precursor of the active phase is less sulfidable. In fact, this is a good reason for starting from a different precursor such as ATT.

Tungsten-based catalysts are usually promoted with cobalt or nickel. It is important to point out that there does not appear to be any study on catalyst activity of Ni-promoted tungsten catalysts prepared by the decomposition of the corresponding thiosalt.

Previous studies with Co-promoted molybdenum sulfide catalyst prepared by the decomposition of ATTM (3) have clearly shown an enhancement in the intrinsic activity of the molybdenum sulfide catalyst. Our aim was to investigate the enhanced performance in HDS and HYD activities, and its correlation with different pretreatments for Ni-promoted tungsten sulfide catalysts. After testing the promoted catalyst prepared, it was found that Ni had no effect on the activity. In other words, there was no enhancement in activity in both HDS and HYD reactions. In the case of the molybdenum sulfide catalysts, the omission of a calcination step following impregnation with cobalt nitrate did not have any adverse effect on the catalyst activity. It is not clear if this may have been a problem with tungsten sulfide catalysts impregnated with nickel nitrate (a calcination step cannot be employed since the aim is to keep O atoms out). We believe that due to the low loading of tungsten on the alumina support, the Ni reacted with alumina to form Ni aluminate. It is well known that Ni interacts with alumina and is present in the form of bulk Ni aluminate (8). TPR studies of Ni supported on amorphous silica alumina (ASA) catalysts have shown that this interaction results in a broad peak and can be associated with the development of a spinel $NiAl_2O_4$ phase (the interaction occurring with the Al_2O_3 component of the ASA carrier) (9).

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