



# Temperature programmed reduction of $\text{SiO}_2\text{-Al}_2\text{O}_3$ supported Ni, Mo and NiMo catalysts prepared with EDTA

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## ABSTRACT

In this study, the influence EDTA on the reducibility and metal–support interactions of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  supported Ni, Mo and NiMo catalysts in the dried (uncalcined) and calcined states were investigated using temperature programmed reduction (TPR) technique. EDTA addition delayed the reduction of Ni and caused a remarkable increase (186 °C) in the reduction temperature in the uncalcined state, whereas after calcination both types of Ni/ $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts (with and without EDTA) showed similar reduction behavior. For the Mo/ $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalyst, the presence of EDTA reduced strong interaction between the Mo species and the support in both the uncalcined and calcined states and caused easy reduction of all Mo species at a low temperature region (450–550 °C) whereas, the catalyst prepared without EDTA contained a significant amount of Mo species strongly bound to the support that required higher temperatures (>800 °C) for reduction. In the uncalcined NiMo/ $\text{SiO}_2\text{-Al}_2\text{O}_3$  prepared without EDTA, Ni reduction occurred first at a substantially lower temperature before Mo reduction, while with EDTA, Mo reduction was closely followed by Ni reduction in the temperature region of 400–500 °C. Mo and Ni species strongly bound to the support were substantially low and both the promoter (Ni) and Mo were present in close association in the support surface in both the uncalcined and calcined forms of the catalyst prepared with EDTA, compared to that prepared without EDTA. The catalyst prepared with the addition of EDTA to the impregnation solution was remarkably more active than the catalyst prepared without EDTA both in the calcined and uncalcined forms. Weaker interaction between the support and the active phase precursors (oxidic phases of Mo and Ni) played a prominent role in the HDS activity enhancement of catalysts prepared with chelating agents, particularly, when sulfidation was carried out after calcination.

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## 1. Introduction

Catalysts play a key role in the hydrotreating processes used for production of clean fuels from petroleum distillates and residues. Hydrotreating catalysts usually consist of molybdenum (Mo) supported on an alumina carrier with promoters such as cobalt (Co) or nickel (Ni) [1]. The catalysts enhance the removal of sulfur, nitrogen and other undesirable contaminants present in the refinery streams by promoting hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD) reactions. Conventional hydrotreating catalysts face some new challenges in recent years. A major challenge to the catalysts used in the hydrotreating of petroleum distillate streams comes from environmental legislation, which places increasingly severe restriction on the sulfur content of transportation fuels [2–4]. For example, the latest regulations on diesel fuel specifications require the reduction of sulfur content to ultra-low levels (15 ppm or less). Conventional CoMo and NiMo based catalysts, however, do not have sufficient activ-

ity to desulfurize diesel feed streams to ultra low sulfur levels under normal operating conditions. They require severe operating conditions such as high temperature, low space velocity and high hydrogen partial pressure. Such severe process conditions generally lead to rapid catalyst deactivation, shorter cycle lengths and reduced throughput. The development and application of more active and stable catalysts are among the most desired options for reducing the sulfur content of diesel to ultra-low levels by deep desulfurization [2,5–8]. As a result, intensive efforts have been devoted by catalyst scientists worldwide to develop highly active hydrotreating catalysts for ultra-deep desulfurization of diesel.

Three approaches are mainly used for improving the HDS activity of CoMo- and NiMo-type hydrotreating catalysts. One approach is based on the use of some additives in the catalyst formulations. Phosphorus, fluorine, and boron are the three important additives that have been investigated extensively and found to have beneficial effects on HDS activity of CoMo- and NiMo-type hydrotreating catalysts [1,9]. The second approach is to use new supports. A large number of new materials with high surface area and other properties suitable for support applications have been developed and tested [2,10,11]. These include  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , MgO, carbon,  $\text{SiO}_2$ , zeolites, etc. Attempts have also been made to modify the alumina

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support by mixing with zeolites and other metal oxides such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ , etc. to take advantage of the favorable characteristics of both of the systems.

The third approach involves the modification of the impregnation procedure. Because the active components (e.g., Mo and Co or Ni) of a hydrotreating catalyst are deposited on the support surface by impregnation of molybdate and cobalt or nickel ions from aqueous solutions, the impregnation, step plays an important role in influencing the structure of the active phase and its dispersion. Several studies have shown that remarkable improvements in HDS activity of CoMo and NiMo catalysts can be achieved by the addition of some chelating compounds such as nitrilo-acetic acid (NTA), citric acid, thioglycolic acid, and ethylenediaminetetraacetic acid (EDTA), to the impregnation solution [9,12–34]. These complexing agents have been found to be very effective in the formation of highly active CoMoS (type-II) or NiMoS (type-II) sites with extremely high selectivity.

In many studies, improvements in HDS activity of the catalysts prepared using chelating agents are observed when the catalyst is dried and sulfided without calcination [12,13,16,17,20,23,25,26,31]. However, some other studies report higher activity for the catalysts prepared with chelating agents when the preparation procedure included not only drying but also calcination before sulfidation [30–33]. In most of the studies reported earlier on the effect of chelating agents in influencing the activity of hydrotreating catalysts, silica and  $\gamma\text{-Al}_2\text{O}_3$  have been used as support material [12]. Recently, Rana et al. [35] compared the HDS activity of CoMo catalysts supported on  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3\text{-MgO}$  prepared using EDTA as chelating agent, and found the following order of catalytic activity:  $\text{Al}_2\text{O}_3 < \text{SiO}_2 < \text{Al}_2\text{O}_3\text{-MgO}$ . It was suggested that the changes in HDS activity with the type of support are related to different levels of promotion of Mo by Co and to changes in the sulfidation patterns influenced by different interactions of the active phase precursors with each support. Studies on the effect of complexing ligands on metal-support interactions of NiMo-type catalysts supported on mixed oxide carriers such as  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and  $\text{TiO}_2\text{-Al}_2\text{O}_3$  are scarce. In the catalysts prepared with chelating ligands, the strength of metal support interactions could be different in the calcined and uncalcined states. However, no information is available in this regard.

The primary objective of the present study is to examine the influence of chelating agents on the reducibility of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ -supported NiMo catalysts both in the calcined and uncalcined states. Since metal ions on oxides in weak interaction with the support surface will be reduced more easily than those strongly bound, metal-support interactions could be assessed by examining their reduction behavior. A series of catalysts containing Ni, Mo and NiMo on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support were prepared with and without EDTA. Temperature programmed reduction (TPR) with hydrogen was used to test their reducibility and metal-support interactions in both calcined and uncalcined states. The HDS activities of both uncalcined and calcined NiMo catalysts prepared with and without EDTA were tested and compared. It is worth mentioning here that TPR studies on Ni, Mo and NiMo catalysts prepared with EDTA using silica-alumina or other mixed oxide supports have never been reported before.

## 2. Experimental

### 2.1. Catalysts

$\text{SiO}_2\text{-Al}_2\text{O}_3$  support ( $\text{SiO}_2=30\%$ ;  $\text{Al}_2\text{O}_3=70\%$ ) used in the present study was obtained in the form of extrudates (1.6 mm dia) from Sasol, Germany. The catalysts containing Ni alone, Mo

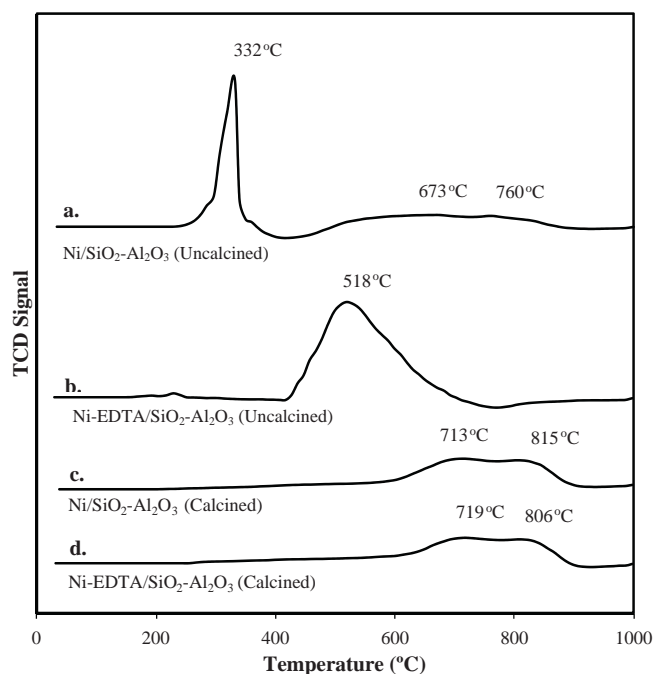
alone and Ni+Mo were prepared by incipient wetness impregnation of the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support. Nickel nitrate and ammonium heptamolybdate (AHM) solutions were used in appropriate concentrations, respectively, to obtain catalysts containing 2.5 wt% Ni and 9.3 wt% Mo. The EDTA containing catalysts, namely, Ni-EDTA, Mo-EDTA and Ni-Mo-EDTA were prepared by impregnation of the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support with ammoniac solutions (pH=9) of EDTA + nickel nitrate, EDTA + AHM, and EDTA + nickel nitrate + AHM, respectively. The concentrations of Ni, Mo and Ni + Mo in the catalysts prepared with and without EDTA were the same. (Ni concentration in Ni/ $\text{SiO}_2\text{-Al}_2\text{O}_3=2.5$  wt%; Mo concentration in Mo/ $\text{SiO}_2\text{-Al}_2\text{O}_3=9.3$  wt%; NiMo/ $\text{SiO}_2\text{-Al}_2\text{O}_3$  contained 2.5 wt% Ni, and 9.3 wt% Mo) The mole ratio between EDTA and the metals in the three catalysts were respectively, Ni:EDTA=1, Mo:EDTA=1 and Ni:Mo:EDTA=0.44:1:1. After impregnation all catalysts were dried at 110 °C for 12 h. A portion of each catalyst was kept in the dried (uncalcined) state, and another portion was calcined at 500 °C for 4 h for TPR experiments.

### 2.2. Temperature-programmed reduction (TPR)

The reducibility of Ni and Mo in the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  supported Ni, Mo and NiMo catalyst, prepared with and without EDTA was examined by TPR. The catalysts were tested in the uncalcined and calcined states. TPR experiments were conducted with a TPR system manufactured by Altamira, Inc. About 0.1 g of catalyst sample was placed in a quartz sample cell (U shaped), and the reducing gas containing 10%  $\text{H}_2$  in argon was introduced into the sample tube at a flow rate of 30 mL/min. The sample was heated at a rate of 15 °C/min from room temperature to 1000 °C. The hydrogen consumption during the TPR of the sample was measured with a thermal conductivity detector.

### 2.3. HDS activity testing

A high-pressure fixed bed microreactor unit manufactured by Vinci Technology, France, was used for testing HDS activities of the calcined and uncalcined NiMo/ $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts prepared with and without EDTA. Straight run gas oil (S = 1.37 wt %; N = 90 ppm; density = 0.84 g/cm<sup>3</sup>; distillation range: IBP = 187 °C; 20% = 248 °C; 50% = 268 °C; 70% = 300 °C; and 90% = 345 °C) was used as feed for HDS activity tests. The catalysts were tested in the form of small grains. For each test 4 ml of the catalyst (crushed & sieved, particle size 12–18 mesh) diluted with an equal volume (4 ml) of carborundum (12–18 mesh) was used. The catalyst was presulfided using a presulfiding feed containing 2%  $\text{CS}_2$  in straight run gas oil. In the case of uncalcined catalysts, presulfiding was carried out without any calcination. The presulfiding feed was introduced into the reactor with hydrogen ( $\text{H}_2$ /oil ratio = 200 mL/mL) at 150 °C, and the catalyst bed temperature was maintained at this temperature for 2 h. The bed temperature was then raised to 230 °C in 4 h at a rate of 20 °C/h and stabilized for 4 h at the same temperature. The catalyst bed temperature was further increased to 300 °C at a ramping rate of 18 °C/h and stabilized for 4 h at the same temperature. Other conditions for sulfiding were as follows: pressure = 50 bar;  $\text{H}_2$ /oil = 200 mL/mL; liquid hourly space velocity (LHSV) = 1.5 h<sup>-1</sup>. The following operating conditions were used for the HDS activity test: temperature (°C) = 350; pressure (bars) = 50; LHSV (h<sup>-1</sup>) = 1.5;  $\text{H}_2$ /oil (mL/mL) = 200.  $\text{H}_2\text{S}$  dissolved in the hydrotreated product oil was removed by online stripping with nitrogen gas before sample collection. The sulfur content of hydrotreated product samples were determined using an Antek 7000 sulfur analyzer equipped with a SCD detector. HDS rate constants were calculated from the



**Fig. 1.** TPR patterns of uncalcined and calcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts prepared with and without EDTA.

sulfur content of feed and products using the rate equation

$$k_{\text{HDS}} = \frac{\text{LHSV}}{n-1} \left[ \frac{1}{S_p^{n-1}} - \frac{1}{S_f^{n-1}} \right]$$

where  $S_f$  = sulfur content of feed,  $S_p$  = sulfur content of product, and  $n$  is reaction order. The reaction order  $n = 1.5$  was chosen based on the kinetic experiments conducted in our laboratory.

### 3. Results and discussion

#### 3.1. Temperature programmed reduction

##### 3.1.1. Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

TPR patterns of the uncalcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with and without EDTA addition are shown in Fig. 1. The TPR profiles for the corresponding catalysts after calcinations are also presented in the same figure for the purpose of comparison. The following trends in the reducibility of nickel can be observed from the TPR data presented in these figures.

- Uncalcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared without EDTA (Fig. 1a) exhibits a strong sharp peak at 332 °C and low intensity broad bands in the 520–800 °C region. With EDTA the low temperature peak at 332 °C is absent (Fig. 1b), and the maximum reduction temperature of Ni is increased substantially to 518 °C. Actually the reduction process starts at 420 °C and continues up to 700 °C forming a broad band centered at 518 °C.
- After calcinations, both types of Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts (i.e. with and without EDTA) show similar TPR profiles (Fig. 1c and d). The high intensity low temperature reduction peaks are totally absent in the calcined samples. Instead two broad overlapping high temperature peaks in the 700–820 °C region are formed in both cases.

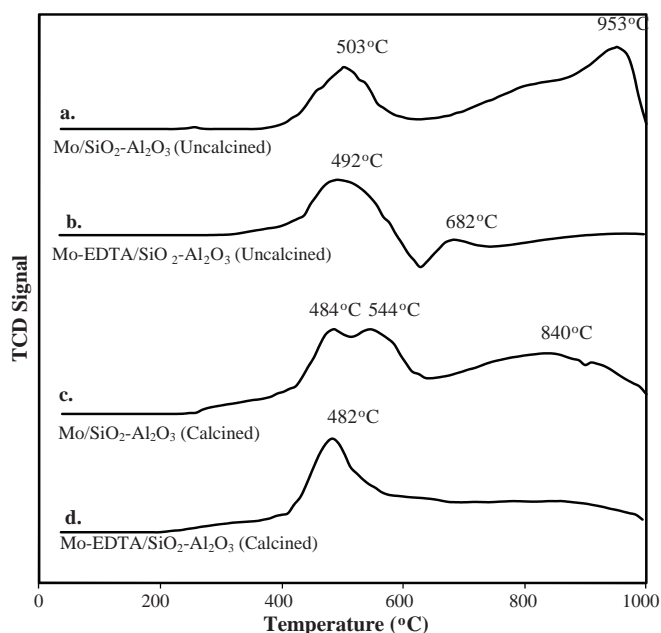
In the dried (uncalcined) Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the impregnation of an aqueous solution of nickel nitrate without EDTA, both Ni and nitrate ions will be present. Ho et al. [36]

reported that decomposition of the nitrates to NO and NO<sub>2</sub> and their reduction to NH<sub>3</sub> together with reduction of Ni<sup>2+</sup> can occur in the temperature region 250–350 °C during the TPR of nickel nitrate impregnated on γ-Al<sub>2</sub>O<sub>3</sub>. Recently, de Haan et al. [37] investigated the TPR of nickel nitrate (4.5% Ni) impregnated on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio 1:1) and calcined at a low temperature of 300 °C. The TPR profiles of the sample showed one sharp peak appearing in the 350–400 °C temperature region and another broad peak in the region of 500–800 °C similar to the results of our studies. The first sharp peak with maxima at 332 °C observed for the uncalcined Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in our experiments could be assigned to the simultaneous decomposition and reduction of nickel nitrate. The broad low intensity peaks appearing in the temperature region 600–800 °C could be ascribed to the reduction of Ni<sup>2+</sup> species dispersed on the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support and stabilized by interaction with the support. The broad nature of the second peak is an indication of the slow reduction of the nickel oxide to metallic nickel because of different levels of interaction with the support.

The remarkable increase in the reduction temperature of uncalcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst caused by EDTA addition could be explained as follows. Studies have shown that chelating agents such as EDTA and NTA form stable complexes with Ni. The reductive decomposition of [Ni(EDTA)]<sup>2-</sup> complex may require higher temperatures. The large reduction band that appears between 420 °C and 650 °C with center around 518 °C could be assigned to the decomposition and combined reduction of Ni and EDTA ligands. The shifting of the reduction temperature by 186 °C to the higher temperature region in the case of the Ni/EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system indicates that Ni[EDTA]<sup>2-</sup> complex structure is more stable and difficult to reduce than the Ni(NO<sub>3</sub>)<sub>2</sub>.

Negrier et al. [38,39] studied the decomposition and reduction of nickel ions complexed with ethanediamine, [Ni(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>. The results showed that after treatment at 230 °C in nitrogen atmosphere Ni(II) ions were grafted to alumina via two O-Al bonds and that the diamine ligands still remained coordinated to the nickel ions but in a monodentate way, bridging the cation with the alumina surface. At 500 °C complete decomposition of the complex occurred with the formation of surface phase containing Ni(II) ions. Temperature-programmed reduction showed that these ions could be quantitatively reduced to the metallic state at 500 °C. The delayed reduction of nickel complex with EDTA observed in the present study is consistent with this. Several other studies have shown that complexing Ni with EDTA or NTA increases the sulfidation temperature significantly because of complex formation between Ni and the chelating agents (EDTA or NTA) [13,14,16]. Interestingly, uncomplexed Ni species in strong interaction with alumina support, that are reduced at higher temperature (670–800 °C) are absent in the Ni/EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample.

In the calcined state, both Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst sample prepared with and without EDTA show two broad overlapping reduction peaks in the 700–820 °C region but the low temperature reduction peaks are absent. Similar peak profiles for Ni reduction have been observed by several researchers during TPR of calcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalyst systems with slight variation in the peak temperatures, and these peaks are normally ascribed to the reduction of highly dispersed octahedral, Ni<sup>2+</sup> present on the support surface at different levels of dispersion and interaction with the support [40–45]. Ni present as nickel hydrosilicate species on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> will be also reduced at this temperature range [43,45]. It is worthwhile to note that the reduction of the NiO species in calcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system occurs at substantially higher temperatures than bulk NiO which is normally reduced in the 230–300 °C region [40,41,46]. The presence of Ni<sup>2+</sup> in a NiAl<sub>2</sub>O<sub>4</sub> spinel structure could be



**Fig. 2.** TPR patterns of uncalcined and calcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts prepared with and without EDTA.

excluded since NiAl<sub>2</sub>O<sub>4</sub> spinel species reduce at 930 °C or higher temperature [45–47].

### 3.1.2. Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts

The TPR patterns of Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Mo-EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts in the uncalcined and calcined states are presented in Fig. 2. The uncalcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared without EDTA (Fig. 2a), shows two main reduction peaks, one at 503 °C and the other at 953 together with an unresolved broad shoulder around 800 °C, whereas the catalyst prepared with EDTA (Fig. 2b) shows a single broad reduction peak at 492 °C without any high temperature peaks. After Calcination, the Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> prepared without EDTA (Fig. 2c) exhibits two overlapping peaks, one at 484 °C and the other at 544 °C and a broad high temperature reduction peak centered at 840 °C. Both low temperature peaks (480 °C and 544 °C) have almost equal intensities and areas. In the catalyst prepared with EDTA, the relative ratio of these two overlapping peaks is changed significantly (Fig. 2d). The low temperature peak at 484 °C is more intense than the other which occurs only as a small unresolved hump. Additionally, the high temperature reduction peak at 840 °C, that was present in the calcined catalyst sample prepared without EDTA is totally absent in the sample prepared with EDTA.

When ammonium heptamolybdate (AHM) is dissolved in water, it forms several molybdate species, like heptamolybdate [Mo<sub>7</sub>O<sub>24</sub>]<sup>6-</sup>, octamolybdate [Mo<sub>8</sub>O<sub>26</sub>]<sup>6-</sup> and monomolybdate [MoO<sub>4</sub>]<sup>2-</sup>. The relative proportion of these species depends on pH and concentration. At higher pH, the monomolybdate ((MoO<sub>4</sub>)<sup>2-</sup>) is dominant, whereas solutions with pH < 5.4 contain mainly polymolybdates [48]. At higher pH levels, both mono and polymolybdates could be adsorbed on the support surface [49].

Thus, in the dried, but uncalcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst samples prepared without EDTA, Mo will be present as a mixture of polymolybdate clusters and isolated monomolybdate [MoO<sub>4</sub>]<sup>2-</sup> ions. Recent studies [22] have shown that Anderson type heteropolymolybdates [Al(OH)<sub>6</sub>Mo<sub>6</sub>O<sub>18</sub>] are also formed on the alumina surface. The polymolybdate clusters are multilayered with octahedral Mo-species whereas the monomolybdates are tetrahedrally coordinated and are strongly

bound to the support surface through Al-O-Mo and Si-O-Mo bonds.

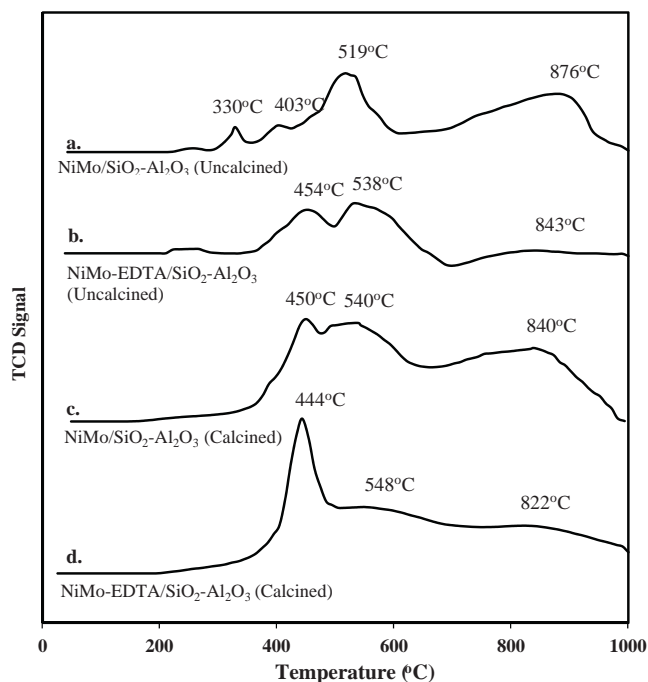
The first reduction peak observed at 503 °C in the TPR profile of uncalcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample prepared without EDTA could be assigned to the reduction of Mo<sup>6+</sup> species in polymolybdate structures to Mo<sup>4+</sup> species. The high temperature peaks appearing in the temperature region 800–950 °C are generally associated with the deep reduction of all Mo species strongly bound to the support including the highly dispersed tetrahedral Mo species [42,50,51].

The TPR profile of the uncalcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with EDTA shows a low temperature reduction peak with center at 492 °C. The high temperature reduction peaks (appearing above 800 °C) are completely absent, which indicates Mo species that are strongly bound to the support by strong Mo-support interaction are completely absent in this sample. The presence of EDTA, thus eliminates strong interaction between Mo and the support in the Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

Another important observation that can be made when we compare the TPR profiles of uncalcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst samples prepared with and without EDTA is that the first reduction peak appears almost in the same temperature region for the both samples. This clearly indicates that EDTA does not have any significant effect on the reduction of Mo<sup>6+</sup> species in polymolybdate structures to Mo<sup>4+</sup> species. Complex formation between chelating reagents such as NTA, EDTA, etc. and molybdate ions in aqueous solutions has been reported [9,12,13,52,53]. However, the stability of Mo-EDTA complex depends on the pH of the impregnation solution used [13] for catalyst preparation. The Mo-EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst used in the present work was prepared with a Mo:EDTA mole ratio of 1:1 in ammoniacal solution at pH 9. Only a fraction of the Mo will be present as Mo-EDTA complex at this pH. Uncomplexed Mo and EDTA adsorbed on the support surface will also be present in the uncalcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst [53,54]. The first reduction peak in the TPR profile of uncalcined Mo-EDTA (Fig. 2b) covers the temperature region 400–580 °C starting from 400 °C and reaching a maximum at 492 °C. It also has a long tail which decreases below the baseline and then rises showing a negative peak at 630 °C. It is likely that the reduction of both the Mo<sup>6+</sup> in the Mo-EDTA complex and uncomplexed molybdenum oxide species occur in the temperature region 400–580 °C with the overlapping of the hydrogen consumption curves. This means that the reduction behavior of Mo on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support is not significantly modified by the presence of EDTA. This is in agreement with a recent study by Lelias et al. [52] who showed that the sulfidation behavior of Mo is not changed by the presence of chelating agents like EDTA.

Ammonia formed during the reductive decomposition of the Mo-EDTA complex and its subsequent reaction with Mo to form molybdenum nitride is probably responsible for the negative peak formed at temperatures around 630 °C. This is supported by the fact that the negative peak is absent in the TPR profiles of the calcined Mo-EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample. There are no high temperature reduction peaks appearing above 800 °C in the calcined Mo-EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample. This could be attributed to the effect of EDTA in suppressing strong interaction of molybdates with the support. This clearly indicates that the calcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with EDTA contains well dispersed octahedral molybdenum oxide species that are all reducible (Mo<sup>6+</sup> → Mo<sup>4+</sup>) easily in the temperature region of 400–500 °C.

Calcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> prepared without EDTA shows significantly different TPR profile compared to that of the calcined Mo-EDTA/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. A broad reduction band with two overlapping peaks at 482 °C and 544 °C and another broad band with center around 840 °C are seen in the TPR spectrum of calcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. This indicates that, calcined Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample prepared without EDTA contains Mo oxide species that are difficult to reduce and require higher temperatures. Poorly dis-



**Fig. 3.** TPR patterns of uncalcined and calcined Ni–Mo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts prepared with and without EDTA.

persed crystalline phases of MoO<sub>3</sub> and highly dispersed tetrahedral Mo species in strong interaction with the support may be present in this catalyst. These species are usually reduced at relatively higher temperatures in various steps [42,51,55]. Interestingly no significant differences in the reduction behavior are noticed between uncalcined and calcined Mo (EDTA)/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts. In both cases, reduction of the Mo species occurs predominantly at the same lower temperature region. The presence of EDTA, thus reduces strong interaction between the support and the Mo species not only in the fresh uncalcined sample but also in the calcined sample.

### 3.1.3. Ni–Mo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts

Fig. 3 shows the TPR patterns of uncalcined NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst prepared with and without EDTA. The TPR results for the corresponding calcined samples are also presented in the same figure for the purpose of comparison. The uncalcined catalyst sample without EDTA (Fig. 3a) exhibits a low temperature peak at 330 °C and three overlapping peaks at 403 °C, 454 °C, and 519 °C. The TPR peak at 519 °C has the highest intensity. Additionally a broad high temperature reduction peak canted at 876 °C is also formed. The low temperature peak at 330 °C coincides with the combined reduction peak of Ni and NO<sub>3</sub> ions observed earlier in the dried (uncalcined) Ni only catalyst prepared by nickel nitrate impregnation (Fig. 1a). The three overlapping peaks in the temperature region 400–520 °C could be reasonably assigned to the reduction of different polymolybdates in weak interaction with the support surface. The high temperature peak at 876 °C represents the reduction of tetrahedral Mo<sup>4+</sup> species strongly bound to the support. The broad low intensity peak that appears in the temperature region 650–750 °C as a tail before the high temperature peak at 876 °C is probably caused by the reduction of surface Ni<sup>2+</sup> ions in interaction with the SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support.

For the NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> prepared with EDTA, the TPR profiles of the sample (Fig. 3b) before calcination is characterized by two major reduction, peaks with poor resolution centered at 454 °C and 538 °C. The second peak at 538 °C is very broad with a long tail

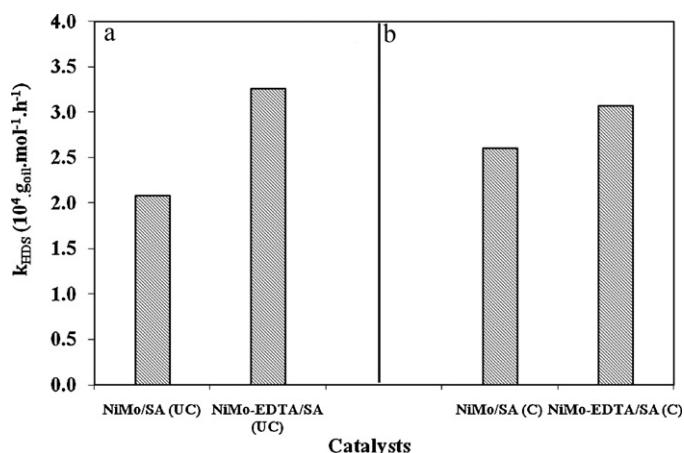
starting at about 500 °C and ending at about 700 °C and indicates complex reduction involving different species. In the NiMo catalysts prepared with EDTA using (Ni + Mo):EDTA = 1.44, nickel ions will be completely complexed by EDTA since EDTA preferentially complexes with Ni. A portion of the Mo may be complexed, but most of the molybdenum will be present as uncomplexed mono and polymolybdates on the support surface. Comparing the TPR patterns of the uncalcined Ni only and Mo only catalysts prepared with EDTA with that of the Ni + Mo containing catalyst prepared with EDTA addition, the first peak could be reasonably assigned to the reductive decomposition of Mo–EDTA together with reduction of the easily reducible polymolybdates in weak interaction with the support.

The broad second peak covering the temperature region 500–630 °C with maximum at 538 °C probably involves overlapping of multiple reduction processes including the reduction of Ni–EDTA complex. As observed in the TPR spectrum of uncalcined Mo–EDTA sample, the concentration of tetrahedrally coordinated Mo species strongly bound to the support are substantially low in NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts prepared with EDTA compared to that prepared without EDTA. It is likely that the chelating ligands of EDTA are preferentially adsorbed and interact with the acidic OH sites and coordinatively unsaturated Al<sup>3+</sup> sites [53,54] and, thereby prevent strong interactions between the molybdate ions and support.

TPR patterns of the calcined NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst prepared without EDTA (Fig. 3c) shows two overlapping reduction peaks in the low temperature region (400–600 °C) with centers at 450 °C and 540 °C. Additionally a high temperature reduction peak is formed at 840 °C. On the other hand, for the calcined Ni Mo–EDTA/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> sample (Fig. 3d) reduction occurs predominantly in the low temperature region as indicated by a major (highly intense) reduction peak at 444 °C and a broad low intensity band in the temperature region 500–600 °C with center at 548 °C. The high temperature reduction peak in the 800–840 °C region with center at 822 °C is very minor for this sample compared to that prepared without EDTA. Interestingly, a close similarity of calcined Mo–EDTA/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (Fig. 2d) and NiMo–EDTA/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (Fig. 3d) catalysts prepared with EDTA addition is observed except that the reduction peak of Mo species is shifted to a lower temperature (i.e. from 482 to 444 °C) after Ni addition indicating the promotional effect of Ni on Mo reduction [41]. Ni appears to be closely associated with Mo and its reduction in the calcined NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst prepared with and without EDTA overlaps with the reduction of Mo species and appears as a broad band in the 500–600 °C. In essence, the TPR data of NiMo catalysts indicate that tetrahedrally coordinated Mo species strongly bound to the support are substantially low in both calcined and uncalcined states of the NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts prepared with EDTA. Ni reduction overlaps with that of Mo reduction. Both metals are reduced easily in the same low temperature region (400–550 °C).

### 3.2. Effect of EDTA on the HDS activity of SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> supported Ni–Mo catalyst

The HDS activities of NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst prepared with and without EDTA were tested in a microreactor using straight-run gas oil feed. The catalysts were sulfided both in the calcined and uncalcined forms before testing. The HDS rate constants for the uncalcined NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts prepared with and without EDTA are compared in Fig. 4a. The activity data obtained for the two catalysts after calcination are presented in Fig. 4b. It is evident from the results presented in these figures that the catalysts prepared with EDTA are remarkably more active than the catalyst prepared without EDTA both in the calcined and uncalcined forms. Interestingly, the HDS activity difference between the uncalcined and



**Fig. 4.** Comparison between the HDS activities of NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts prepared with and without EDTA. (a) Both uncalcined (UC); (b) both calcined (C).

calcined NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts prepared with EDTA addition is relatively small.

Many previous studies have reported higher HDS activity for the catalysts prepared using chelating ligands when they are sulfided without prior calcination. Delayed sulfidation of the promoter (e.g. Ni or Co) due to the formation of a complex between the promoter and the chelating ligand was proposed to be responsible for the enhanced activity. Sulfidation of the promoters (Co or Ni) have been reported to occur either simultaneously with Mo sulfiding [29,33] or after the formation of MoS<sub>2</sub> [13–16,21,34] in the presence of chelating ligands. Such sulfidation order will lead to the formation of highly active CoMoS or NiMoS phase by the deposition of the promoters on the edges of the MoS<sub>2</sub> crystallites without separation into individual sulfide phases.

In some recent studies [30–32] significant enhancement in HDS activity has been observed for the catalysts prepared using chelating agents when the catalysts were sulfided after drying and calcination. Since the complex formed between the promoter and the chelating ligand is decomposed in the calcination step, the mechanism involving delayed sulfidation may not play a major role in the activity enhancement observed for the catalysts sulfided after calcination. It is likely that reduced interaction between the support and the active phase precursors (oxidic phases of Mo and Ni) plays an important role in the activity enhancement of catalysts prepared with chelating agents, particularly, when sulfidation is carried out after calcination.

The TPR results obtained in the present study provide valuable information on the reducibility and metal-support interaction in the calcined and uncalcined forms of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported Mo, Ni and NiMo catalysts prepared with and without a chelating agent such as EDTA. The TPR results showed a large increase (from 332 to 518 °C) in the Ni reduction temperature for the uncalcined Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample prepared with EDTA. Furthermore, uncomplexed Ni species in strong interaction with the support that require high reduction temperatures (600–800 °C) were absent in this catalyst.

Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with EDTA was more easily reducible compared to that prepared without EDTA both in the uncalcined and calcined forms indicating the absence of strong interaction between the support and Mo species not only in the fresh uncalcined sample but also after the decomposition of the Mo-EDTA complex by calcination. In the case of the NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with EDTA the TPR data indicate that both metals (Mo and Ni) are reduced easily in the low temperature region (400–500 °C) with Mo reduction first followed by Ni reduction. During sulfidation both metals will be reduced

and sulfided in the order Mo followed by Ni or together in a narrow temperature region forming a highly active mixed sulfide phase (i.e. NiMoS).

Catalyst activity has been correlated with reducibility in many studies for the Mo-containing catalysts [56,57]. Easily reducible Mo and Ni species will be easily sulfided. Tetrahedrally coordinated Mo species strongly bound to the support are substantially low in both uncalcined and calcined forms of NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> prepared with EDTA compared to that prepared without EDTA. Weaker interactions between the support and active metals (Mo and Ni) will lead to the formation of type II NiMoS phase predominately in the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported NiMo catalyst. Thus, both delayed reduction and sulfidation of Ni-EDTA complex and weaker metal-support interactions appear to play important role in enhancing the HDS activity of NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with EDTA when sulfided without calcination. In the case of the calcined sample, the delayed sulfidation effect will be completely absent because of the decomposition of the Ni-EDTA complex in the calcination step. The improved activity observed in the present study for the calcined NiMo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with could be attributed to the influence of the complexing agent in reducing the interactions between the support and active metals (Mo and Ni).

Weaker interaction between Mo and support will enable complete sulfidation of all Mo species leading to the formation of a higher number of MoS<sub>2</sub> slabs on the support surface. Additionally, EDTA can play a role in reducing the formation of undesirable NiMoO<sub>4</sub> crystalline phases and redispersion of the promoter ions (e.g. Ni<sup>2+</sup>) on the catalyst surface [32]. This will enhance the promoting effect of Ni through increased coverage of Ni on the edges of MoS<sub>2</sub> during sulfidation, forming highly active NiMoS sites and thereby improve catalyst activity as explained below.

CoMo and NiMo type hydrotreating catalysts are usually prepared in the oxide form (i.e. oxides of Mo and Ni dispersed on the surface of a support such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) and sulfided before use in the reactor to produce active CoMoS and NiMoS phases on the support surface. The building blocks of Co-Mo-S (or Ni-Mo-S) structures are small MoS<sub>2</sub> nano-crystals with the Co (or Ni) promoter atoms located at the edges of the MoS<sub>2</sub> layers in the same plane of Mo atoms [1]. Studies on the structure-activity correlation of these catalyst systems led to the identification of two types of Co-Mo-S structures, one type exhibiting substantially higher activity than the other. The low and high activity forms of Co-Mo-S were termed type I and type II Co-Mo-S, respectively [1]. The type I Co-Mo-S structures were proposed to be incompletely sulfided and have some remaining Mo-O-Al linkages to the support. The presence of such linkages was related to the interaction which occurs in the calcined state between Mo and surface alumina OH groups leading to oxygen bridged monolayer type structures that are difficult to sulfide completely.

Several subsequent studies have provided evidence for the existence of Mo-O-Al linkages in type I structures. In type II Co-Mo-S or (Ni-Mo-S) phases, the support interactions are weaker and they are fully sulfided (i.e. have higher sulfur coordination of Mo and Co or Ni). The underlying MoS<sub>2</sub> in Type II Co-Mo-S phases are less disperse, consisting of multiple slabs not linked with the support. Further studies have shown that the degree of staking in MoS<sub>2</sub> and Co-Mo-S structures can be controlled by carefully controlling support properties and preparation parameters and the formation of small stable single slabs of MoS<sub>2</sub> on alumina supports have been achieved [58,59]. These will have a high MoS<sub>2</sub> edge dispersion which can accommodate more Co or Ni atoms to form higher active single slab type II Co-Mo-S or Ni-Mo-S structures.

The single slab MoS<sub>2</sub> structures will also have the advantage of more Mo edge sites (brim sites). Recently, Topsoe and his coworkers [58,60,61] showed that the brim sites (i.e. Mo edge sites in MoS<sub>2</sub>, CoMoS and NiMoS nanoclusters) exhibited metallic character, and

proposed that brim sites due to their metallic character may bind the sulfur containing molecules, and when hydrogen is available at the neighboring edge sites in the form of SH groups hydrogen transfer and hydrogenation reactions can take place. The brim sites are, thus, catalytically active for hydrogenation reactions. The use of EDTA in catalyst preparation can increase the formation of well dispersed highly active type II NiMoS nanoclusters having more brim sites by weakening the interaction of Mo and the promoter ions with the support as well as by reducing the formation of undesirable NiMoO<sub>4</sub> phases.

#### 4. Conclusions

In the present work, a series of catalysts containing Ni, Mo and NiMo on SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> support were prepared with and without EDTA, and their reducibility and metal–support interactions in both calcined and uncalcined states were examined by TPR. The HDS activities of the both calcined and uncalcined NiMo catalysts prepared with and without EDTA were also tested and compared. The following are the important conclusions of the studies. EDTA addition delayed the reduction of Ni and caused a remarkable increase (186 °C) in the reduction temperature in the uncalcined state, whereas after calcination both types of Ni/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts (with and without EDTA) showed similar reduction behavior. For the Mo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst, the presence of EDTA reduced strong interaction between the Mo species and the support in both the uncalcined and calcined states and caused easy reduction of all Mo species at a low temperature region (450–550 °C), whereas the catalyst prepared without EDTA contained a significant amount of Mo species strongly bound to the support that required higher temperatures (>800 °C) for reduction. In the NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> prepared without EDTA, Ni reduction occurred first at a substantially lower temperature (330 °C) before Mo reduction, while in the presence of EDTA, Mo reduction was closely followed by Ni reduction in the temperature region of 400–500 °C. Mo and Ni species strongly bound to the support were substantially low in both the uncalcined and calcined forms of the NiMo catalyst prepared with EDTA compared to that prepared without EDTA. NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst prepared with EDTA was more active than that prepared without EDTA both in the calcined and uncalcined forms. The HDS activity difference between the uncalcined and calcined NiMo/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts prepared with EDTA addition was relatively small. Based on the TPR results, it can be suggested that weaker interaction between the support and the active phase precursors (oxidic phases of Mo and Ni) plays prominent role in the HDS activity enhancement of SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> supported NiMo catalysts prepared with chelating agents.

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