



Effect of chelating ligands on Ni–Mo impregnation over wide-pore ZrO₂–TiO₂

J. Escobar^{a,*}, M.C. Barrera^a, J.A. de los Reyes^b, J.A. Toledo^a, V. Santes^c, J.A. Colín^d

^a Instituto Mexicano del Petróleo, Eje Central L. Cárdenas 152, San Bartolo Atepehuacan, Gustavo A. Madero, México, D.F. 07730, Mexico

^b Area de Ing. Química, UAM-Iztapalapa, San Rafael Atlixco 186, Vicentina, Iztapalapa, México, D.F. 09340, Mexico

^c CIEMAD-IPN, Calle 30 de Junio de 1520, Col. Barrio la Laguna Ticomán, Gustavo A. Madero, México, D.F. 07340, Mexico

^d UAM-Azcapotzalco, San Pablo 180, Reynosa, Tamaulipas, Azcapotzalco, D.F. 02200, Mexico

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ABSTRACT

Ethylenediamine tetraacetic acid (EDTA) and citric acid (CA) were used as organic chelating additives during preparation of NiMo catalysts with wide-pore ZrO₂–TiO₂ mixed oxides as carrier. A clear beneficial effect of using either chelator was evident when sulfided catalysts were tested in dibenzothiophene hydrodesulfurization (DBT HDS at 320 °C and 5.72 MPa, batch reactor) although the optimum concentration of EDTA and CA to obtain materials of maximized activity was different to each other (Ni/EDTA = 1 and Ni/CA = 1/2). These molar ratios seemed to correspond to total impregnated nickel chelation. Augmented chelator concentration resulted in catalysts of decreased hydrodesulfurizing properties probably due to delayed sulfidation of complexated molybdenum that could be formed by reaction of Mo⁶⁺ containing species with organic additive excess. In a pseudo-first-order kinetic constant basis, the best catalyst prepared with EDTA had similar HDS activity to that of the optimized formulation with CA (k_{HDS} values of 7.8×10^{-5} and 7.3×10^{-5} m³/kg_{cat} s, respectively), both formulations being clearly superior to a NiMo/ZrO₂–TiO₂ catalyst prepared with no organic additive ($k_{\text{HDS}} \sim 4.7 \times 10^{-5}$ m³/kg_{cat} s). Characterization by thermal analyses (TGA, DTA) and infrared spectroscopy pointed out to delayed Ni²⁺ sulfidation as the main cause of HDS activity improvement in catalysts prepared in presence of either organic chelator.

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1. Introduction

The ever stricter environmental regulations regarding S content in fuels (~10–15 ppm for diesel at the service station) derived from middle distillates hydrotreatment have encouraged the development of more active hydrodesulfurization (HDS) catalyst that could contribute to fulfill those demanding requirements [1]. In this context, the preparation of new supports with physicochemical properties that could make them particularly attractive as carrier for hydrotreating catalysts constitutes a challenging task [2]. Recently, our group has reported the synthesis of wide-pore ZrO₂–TiO₂ mixed oxides through solvo-thermal treatment, these materials showing very promising properties as supports for sulfided molybdenum phases [3,4]. High catalytic activity was observed for MoS₂/ZrO₂–TiO₂ materials, when tested in the liquid-phase dibenzothiophene HDS. However, promotion of Mo by cobalt addition on catalysts prepared by using that binary carrier was limited, in solids prepared by sequential pore filling impregnation (Mo first) [5]. Then, finding a methodology that could enable more efficient incorporation of promoters (Co or Ni) to zirconia–titania-

supported molybdenum remains an issue that deserves attention, as it is well-known that the experimental protocol used for deposition of Mo and the promoter plays a major role on determining their dispersion, sulfidability and promotion degree in final sulfided formulations [6].

Different beneficial effects have been related to the use of chelating agents during Co or Ni impregnation due to their interaction with the metals to deposit [7]. It has been previously reported [7,8] that those organic additives retard sulfidation of promoter (X = Ni²⁺ or Co²⁺) to temperature high enough to allow their proper integration to then already formed MoS₂ (or WS₂), thus optimizing “XMoS” (or “XWS”) phase formation. On the other hand, some studies have shown that nitrilotriacetic acid addition during impregnation of ammonium heptamolybdate on Al₂O₃ resulted in lower edge dispersion of MoS₂ slabs in final sulfided catalysts [6]. It was proposed that this fact was originated in decreased interaction between complexated-Mo and basic hydroxyls present on the alumina surface. It appeared that conversely to promoter complexation, molybdenum chelation could be detrimental on the desulfurizing properties of the corresponding catalysts.

In this work, we prepared NiMo-based HDS catalysts in presence of two different chelating agents (ethylenediamine tetraacetic acid, EDTA or citric acid, CA) at various Ni/organic agent ratios, to try to obtain enhanced hydrodesulfurizing activity in catalysts

* Corresponding author. Tel.: +52 55 9175 8389; fax: +52 55 9175 6380.

E-mail address: jeaguila@imp.mx (J. Escobar).

with wide-pore $\text{ZrO}_2\text{-TiO}_2$ as carrier. Materials characterization included N_2 physisorption, X-ray diffraction, thermal analysis (TGA and DTA) and infrared spectroscopy. Dibenzothiophene was used as model molecule during catalytic tests aimed to evaluate HDS performance of various sulfided formulations prepared.

2. Experimental

2.1. Material synthesis

Solvo-thermally treated $\text{ZrO}_2\text{-TiO}_2$ (30–70 mol-mol, ZT) was synthesized by low-temperature ($\sim 0^\circ\text{C}$) sol-gel method followed by solvo-treatment at 80°C (1 day), according to Barrera et al. [3,4]. The support calcined at 500°C was impregnated by pore-filling to prepare NiMo catalysts (nominal Mo and Ni loadings of 12.5 and 3 wt.%, respectively) with either ethylenediamine tetraacetic acid (EDTA) or citric acid (CA) as organic additives. The former solids (NE-series samples) were obtained by simultaneous impregnation of MoO_3 (Sigma-Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (PQM) and EDTA (Sigma-Aldrich). First, EDTA was dissolved under stirring in concentrated ammonium hydroxide (at $T = 40^\circ\text{C}$, $\text{pH} \sim 10$). After total EDTA dissolution, MoO_3 addition resulted in a whitish solution ($\text{pH} \sim 9.2$). Finally, nickel nitrate was dissolved in the aforementioned alkaline medium. No important variation in pH was observed after this step, the product being a turquoise-blue impregnating solution. The Ni/EDTA mole ratios tried were 0.5, 1 and 2. Impregnated solids were dried at 120°C (4 h). Samples where citric acid (AC, from J.T. Baker) was used as chelating agent (NC-series) were prepared by successive impregnation. MoO_3 dissolved in NH_4OH was deposited first. After drying (120°C), Ni was integrated through an aqueous nickel citrate solution prepared from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid (solution $\text{pH} \sim 1.7$). Various Ni/CA mole ratios were explored, namely: 0.25, 0.33, 0.5, 1 and 2. One reference material (sample N) without citric acid was synthesized by successive impregnation of Mo and Ni at the aforementioned loadings and following a similar methodology (successive impregnation). All the impregnated materials were dried at 120°C (4 h). None of the prepared solids was calcined to avoid organic additive decomposition. The nomenclature used to designate the different materials prepared was based on the $\text{Nx}(y)$ key where $x = \text{E}$ (EDTA) or C (citric acid) and y stands for the Ni/chelator mol/mol ratio.

2.2. Materials characterization

Textural properties (surface area, pore volume and pore size distribution) of the calcined carrier (500°C) were determined by N_2 physisorption (at -196°C , Autosorb-1 from Quantachrome). Materials structural order was studied by X-ray diffraction (Siemens D-500 Kristalloflex, $\text{Cu K}\alpha$ radiation, $\lambda = 0.15406 \text{ nm}$). Thermal analyses of dried samples were carried out with a Netzch Thermische Analize, STA 409 EP apparatus under static air atmosphere. Infrared spectra of selected dried impregnated materials (with organic additive) were measured by using a Spectrum One (Perkin-Helmer Inc.) apparatus (50 scans at 4 cm^{-1} resolution). Previously to the spectra measurement, the samples (impregnated with Ni, Mo and either EDTA or CA) were thermally treated at various temperatures (300 , 350 , 400 , 450°C) during 30 min (heating rate: $10^\circ\text{C}/\text{min}$ from room temperature to the given conditions) at high vacuum (10^{-3} Pa). All spectra were taken at 100°C .

2.3. HDS reaction test

Uncalcined dried (at 120°C , N_2 flow) samples were sulfided under a 15 vol.% $\text{H}_2\text{S}/\text{H}_2$ flow (4 l/h) at 400°C ($10^\circ\text{C}/\text{min}$, heating rate) for 1 h. HDS activity of the obtained catalysts was

studied in a tri-phasic slurry batch reactor (Parr 4842). The reaction mixture was prepared by dissolving $\sim 0.3 \text{ g}$ of DBT in 100 cm^3 of *n*-hexadecane (98 mass% and 99+ mass%, respectively; both from Aldrich) and adding $\sim 0.2 \text{ g}$ of sieved catalyst (80–100 Tyler mesh, $\sim 0.165 \text{ mm}$ average particle diameter). Operating conditions were carefully chosen to avoid diffusional limitations: $P = 5.72 \text{ MPa}$, $T = 320^\circ\text{C}$ and 1000 rpm ($\sim 105 \text{ rad/s}$, mixing speed). Samples were taken periodically and analyzed by gas chromatography (PerkinElmer AutoSystem XL with flame ionization detector and Econo-Cap-5 capillary column from Alltech). HDS kinetic constants were calculated assuming a pseudo-first-order model referred to DBT concentration and zero order with respect to excess H_2 concentration ($x = \text{conversion}$, $t = \text{time}$):

$$k_{\text{HDS}} = \frac{-\ln(1-x)}{t}$$

k_{HDS} values for various catalysts were normalized by considering reaction volume and mass of catalyst used (k_{HDS} in $\text{m}^3/(\text{kg}_{\text{cat}} \text{ s})$). By carrying out repeated HDS activity experiments it was found that the error implied in the determined values of pseudo kinetic constants was less than 10%.

3. Results and discussion

3.1. Support characterization

The amorphous support calcined at 500°C [3] had the following textural properties: surface area of about $\sim 300 \text{ m}^2/\text{g}$, pore volume of $0.61 \text{ cm}^3/\text{g}$ and average pore diameter of $\sim 7 \text{ nm}$. Detailed characterization of solvo-thermally treated wide-pore $\text{ZrO}_2\text{-TiO}_2$ (30–70) mixed oxides can be found elsewhere [3,4].

3.2. EDTA-complexated samples

3.2.1. Thermal analysis

In Fig. 1, thermogravimetric analysis results of EDTA-containing precursors impregnated on solvo-treated zirconia-titania binary carrier are shown. Weight loss at temperatures of about 100°C or lower could be attributed to physisorbed water elimination. A slope change at about $\sim 125^\circ\text{C}$ indicated the onset of the decomposition of the organic additive by combustion. An abrupt slope increase is observed for all materials in the $200\text{--}500^\circ\text{C}$ range. The magnitude of these weight losses augmented with the chelator content in various samples (13.85, 20.25, 23.1 wt.% for

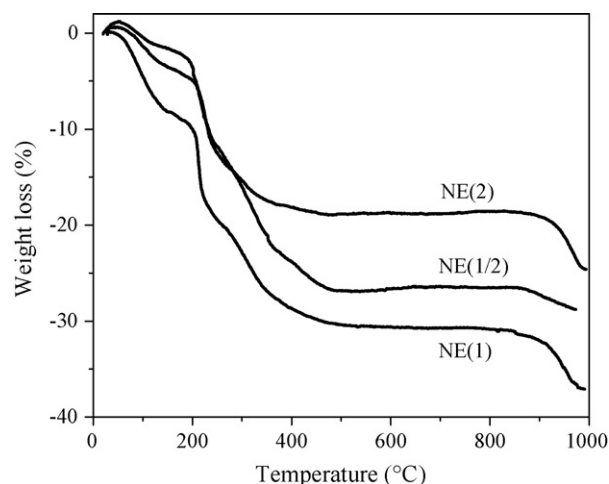


Fig. 1. Thermogravimetric analysis (under static air atmosphere) of NiMo/ $\text{ZrO}_2\text{-TiO}_2$ dried precursors impregnated at various Ni/EDTA ratios.

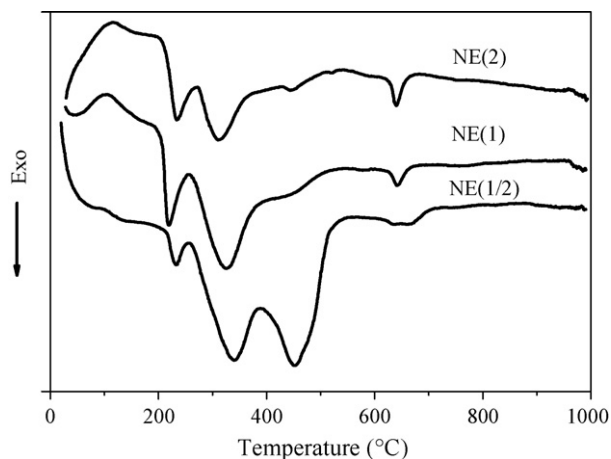


Fig. 2. Differential thermal analysis (under static air atmosphere) of NiMo/ZrO₂-TiO₂ dried precursors impregnated at various Ni/EDTA ratios.

NE(2), NE(1) and NE(1/2), respectively). Interestingly, the temperature at which weight losses essentially ended shifted to higher values as the EDTA content was augmented. An additional inflexion manifested at severe conditions (~ 858 – 897 °C) in thermograms of Fig. 1 was originated by MoO₃ melt and subsequent evaporation [9]. Regarding the differential thermal analysis results shown in Fig. 2, the endothermic signal centered at about ~ 100 °C was related to water evaporation meanwhile the three following exothermic peaks observed at temperature lower than 500 °C seemed to be due to EDTA complexes decomposition. It has been reported that EDTA-chelated Ni is a quinquedentate octahedral complex with one H₂O molecule bonded to Ni²⁺ [10], where one CH₂COOH group could remain unattached to the metallic cation. The first exothermic peak (in the 220–235 °C range) could be originated in initial decomposition of EDTA-complexed Ni in presence of some nitrate groups, the latter coming from the nickel salt used during impregnation. Nitrates decomposition (to NO_x) could promote accelerated combustion of some organic moieties [11,12]. However, due to the stability of EDTA–Ni species [13], most of them could probably stand that process.

The second exothermic signal which clearly shifted to higher temperature as organic additive content was increased (~ 312 , ~ 325 , ~ 339 °C for NE(2), NE(1) and NE(1/2), respectively), also corresponded to EDTA-complexed Ni combustion. In agreement with the observed stepwise decomposition of these species, other authors determined that chelated metallic species were gradually decomposed (by heating), in the case of CoMo/Al₂O₃ formulations prepared in presence of nitrilotriacetic acid (NTA) [14]. They attributed that to the possible formation of different NTA-containing complexes, during either impregnation or drying process.

The third exothermic inflection (in the 446–453 °C range) seemed to be related to thermal decomposition of EDTA–Mo species that could be formed after the totality of Ni²⁺ cations had been chelated (Ni²⁺/chelator ratio < 1) [15]. Their higher decomposition temperature suggested that those complexes were more stable than EDTA–Ni ones. Chelated complex stability could depend on several factors including nature of coordinating agent, size and charge of the central ion [16] and its relative acceptor properties for the electrons of the coordinating group. Taking into account the Ni/Mo ratio used during the preparation of catalysts (~ 0.39), the amount of EDTA needed to complexate all the Mo would correspond to Ni/EDTA = 1/3.6. Thus, in NE(2) and NE(1) probably no organic ligands could be chelating Mo. Even for the highest Ni/EDTA ratio (1/2), just about 40% of the total impregnated molybdenum could

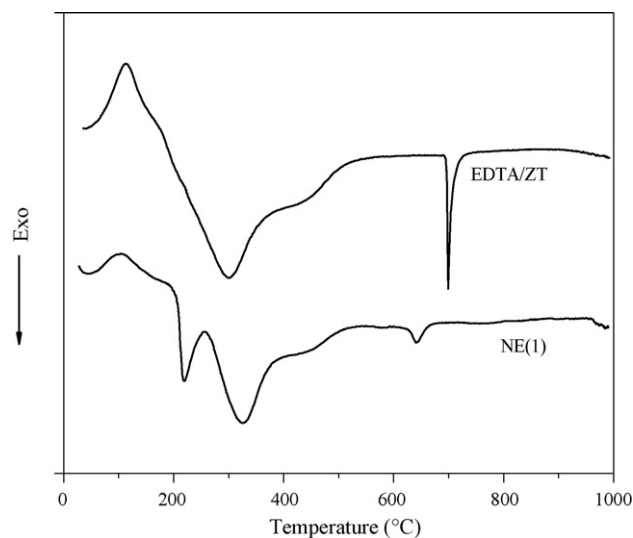


Fig. 3. Differential thermal analysis (under static air atmosphere) of EDTA/ZrO₂-TiO₂ and the corresponding material impregnated with NiMo (NE(1)), at similar organic additive content.

be complexed (supposing one molecule of chelator complexing to one Mo⁶⁺-containing species). However, that could happen just after chelation of the totality of Ni²⁺ cations as it is well known that EDTA preferentially complexate these species [15].

By performing additional thermal analysis experiments, we tried to determine if the signal observed in the 220–235 °C range corresponded to an accelerating effect of the exothermic decomposition of deposited NO₃⁻ counteranions (from nickel impregnation) on the combustion behavior of EDTA–Ni complexes. A sample of ZT support impregnated with EDTA (under basic conditions, pH ~ 10 , provided by ammonium hydroxide addition) at an organic additive concentration similar to that in the NE(1) sample was thus analyzed to this end. In Fig. 3, the corresponding DTA curve is compared to that of the latter solid. Again, the endothermic peak at about ~ 100 °C was related to water evaporation. As expected, the exothermic signal at low temperature was absent in the EDTA-impregnated ZT support pattern suggesting that the inflexions observed in Fig. 2 in the ~ 220 – 235 °C range were indeed related to early organic moieties combustion promoted by NO₃⁻ groups decomposition. A second signal attributed to combustion of EDTA deposited on the binary oxide carrier appeared at ~ 299 °C. It has been reported [17] that alkaline salts of EDTA mainly interact with inorganic supports by adsorption of carboxyl groups on surface hydroxyls. In our case, EDTA could possibly interact with the negatively charged support surface (surface isoelectric point at pH of ~ 6.0 and ~ 6.7 for TiO₂ and ZrO₂, respectively [18]) probably through the partially charged hydrogen atom in $-\text{OH}^{\delta+}$ groups of carboxylate moieties. It is worth mentioning that, according to previous investigations [3] our mixed oxides present ZrO₂-enriched surface. Thus, the properties of this oxide could be preponderant at the surface of our binary materials.

The sharp high-temperature exothermic inflexion related to ZrTiO₄ (which could dissolve titania excess) crystallization [3] was observed at 698 °C (EDTA/ZT profile, Fig. 3). This signal shifted to lower temperature in the impregnated (Ni, Mo and EDTA) samples, Fig. 2 (to 640, 644 and 652 in NE(2), NE(1) and NE(1/2), respectively). This early support crystallization could be originated in the presence of impregnated Mo. In this line, other authors [19] have also found that by increasing molybdenum concentration (in the 2–20 wt.% range) in equimolar SiO₂-TiO₂ mixed oxides prepared by sol-gel route definite anatase domains started to be detectable (by Raman spectroscopy and even by XRD), in the formerly

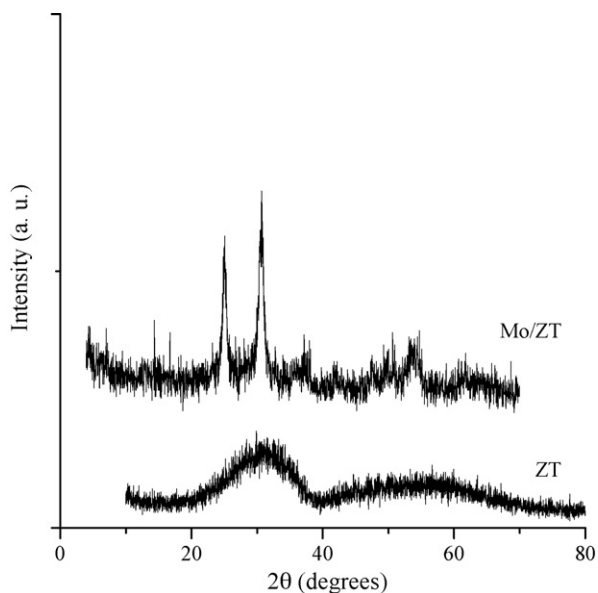


Fig. 4. X-ray diffraction pattern of $\text{ZrO}_2\text{-TiO}_2$ (ZT) support (calcined at 500°C) and the corresponding Mo impregnated material at 2.8 atom/nm^2 (Mo/ZT) calcined at 600°C . Annealing carried out under static air atmosphere.

homogeneous amorphous carriers. Presumably, titania phase segregation was promoted by Mo [19]. To determine if this phenomenon also occurred in our materials, we impregnated Mo (by using ammonium heptamolybdate) at 2.8 atom/nm^2 over our $\text{ZrO}_2\text{-TiO}_2$ carrier. The resulting material was calcined under static air at 600°C (sample Mo/ZT). The XRD patterns of this solid and that of the ZT support are shown in Fig. 4. Segregation of the formerly amorphous carrier matrix (calcined at 500°C) to definite domains of anatase and ZrTiO_4 was evidenced, although amorphous domains were still present (note noise intensity in ZT pattern). Thus, impregnated Mo appeared to induce early phase segregation in the otherwise microcrystalline mixed oxide support. Interestingly, no defined crystallization to MoO_3 was registered.

In samples impregnated in presence of EDTA at the highest concentration used (NE(1/2)), possible Mo complexation could result in species of decreased interaction with the carrier [6,20]. Thus, Mo chelation could be responsible for the presence of larger poly-molybdate domains of lowered influence on the support crystallization temperature.

Finally, endothermal inflections observed at about $\sim 950^\circ\text{C}$ in all thermograms of Fig. 2 were related to MoO_3 melt-evaporation phenomena [9].

3.2.2. Infrared spectroscopy studies

From previous infrared spectroscopy studies it has been determined that the asymmetric stretching frequency of carbonyl groups varies considerably as M species in -CO-O-M moieties is changed. For instance, when $\text{M}=\text{H}^+$ carbonyl absorption occurs at 1700 cm^{-1} but when $\text{M}=\text{K}^+$, the corresponding signal has been observed at 1595 cm^{-1} [21]. Regarding metal complexes, carbonyl absorptions are registered at intermediate values (for example, at 1650 and 1600 cm^{-1} for $\text{M}=\text{Co}^{3+}$ and $\text{M}=\text{Cd}^{2+}$, respectively). In the same line, for EDTA-complexed Cu^{2+} that feature has been observed at 1615 cm^{-1} [22]. Regarding Ni^{2+} chelates the corresponding signal was measured at 1602 cm^{-1} , whereas for Mo^{6+} complexes it was observed at $1630\text{--}1640\text{ cm}^{-1}$ [21]. Based on the aforementioned findings, we decided that in our case the infrared region deserving closest examination was that lying around $1550\text{--}1750\text{ cm}^{-1}$. In Fig. 5 the infrared spectra of NE(1) dried impregnated sample

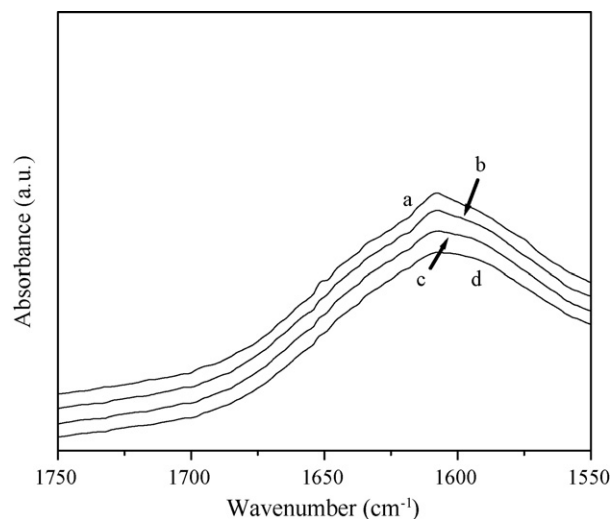


Fig. 5. Infrared spectra of dried $\text{NiMo/ZrO}_2\text{-TiO}_2$ impregnated at Ni/EDTA ratio = 1 (sample NE(1)). Spectra taken at 100°C , after degassing at: (a) 300°C ; (b) 350°C ; (c) 400°C and (d) 450°C .

treated at different temperatures (under vacuum) is shown. The main feature was a broad signal whose maximum was observed at $1608\text{--}1609\text{ cm}^{-1}$, meanwhile a shoulder was registered at $1598\text{--}1597\text{ cm}^{-1}$. The position of these absorptions fairly agreed with that reported for carbonyl groups complexing Ni^{2+} species [21]. No significant differences between the spectra observed for the sample pre-treated (under vacuum) at either 300°C (Fig. 5a) or 450°C (Fig. 5d) were registered. Thus, it was apparent that Ni-EDTA complexes were pretty stable even at the latter severe conditions. The discrepancy between this fact and the behavior observed in the DTA profile of the NE(1) sample in Fig. 2 (Ni-EDTA complexes decomposition at $T\sim 325^\circ\text{C}$) could be originated by the different conditions at which the thermal treatments were carried out (under vacuum vs. under air). No signals related to complexed Mo (absorption at $1630\text{--}1640\text{ cm}^{-1}$) were evident, in agreement with preferential Ni^{2+} chelation at the EDTA concentration used in the NE(1) sample ($\text{Ni/EDTA} = 1$) [15]. Also, no absorption at 1700 cm^{-1} [21] related to non-coordinatively bonded -CO-OH groups was observed in any spectra suggesting that all the C-O-O^- groups in the organic additive molecules were chelating Ni. Probably, quinquedentate species with a water molecule in the nickel coordination sphere [10] were less stable than Ni-EDTA hexa-coordinated ones and were then eliminated at temperature under 300°C (the lowest pre-treatment temperature used during our IR spectroscopy studies), the latter species remaining on the solid surface.

3.2.3. Hydrodesulfurizing activity

In our previous work it was found [5] that in catalysts supported on wide-pore $\text{ZrO}_2\text{-TiO}_2$ mixed oxides Mo promotion by Co was less efficient than in the case of corresponding alumina-supported materials. It could be expected that by using chelating agents integration of promoter (Co or Ni) to the sulfided molybdenum phase could be improved, with the consequential enhancement in hydrodesulfurization activity. It is also important to determine the optimal amount of organic additive to impregnate, as this parameter seemed to be decisive in obtaining materials of increased catalytic activity [23,24].

According to the results shown in Fig. 6, the optimal ratio Ni/EDTA in order to obtain maximized HDS activity corresponded to equimolar stoichiometric concentration. Expectedly, all impregnated nickel could be complexed in this sample due to favored EDTA chelation [15]. In the catalyst of lower

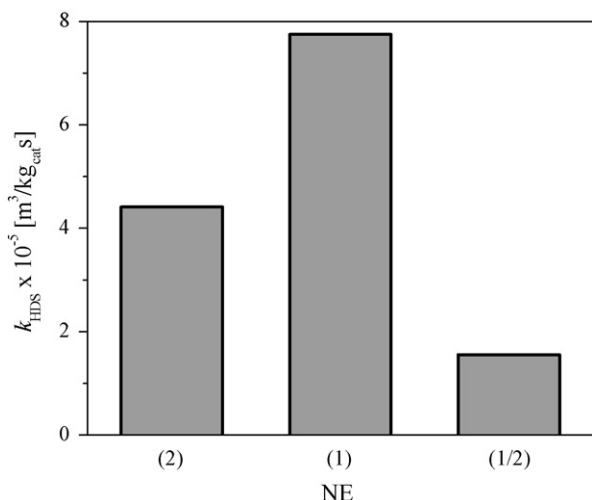


Fig. 6. Dibenzothiophene hydrodesulfurization activity of sulfided NiMo/ZrO₂-TiO₂ catalysts impregnated at various Ni/EDTA ratios. Operating conditions: batch reactor, $T = 320^\circ\text{C}$, $P = 5.72\text{ MPa}$, *n*-hexadecane as solvent, 1000 rpm, mixing speed.

organic additive content NE(2) the amount of chelating agent apparently was not enough to complexate the totality of nickel. Thus, some non-chelated nickel could originate (during activation under H₂S/H₂ flow) segregated NiS_x domains, even at low sulfiding temperature. Conversely, complexated Ni²⁺ (approximately 50% of the total amount deposited) could experiment delayed sulfidation to temperature severe enough where MoS₂ formation had already taken place, that fact resulting in more efficient mutual interaction to produce the so-called “NiMoS phase” [25].

The effect of adding surstoichiometric (regarding loaded Ni²⁺) amount of organic additive was detrimental. As aforementioned, EDTA excess could chelate some Mo⁶⁺ species (see the intense exothermal peak in the 446–453 °C range in the DTA pattern corresponding to NE(1/2), Fig. 2). The high stability of chelated-Mo species [23] could severely limit MoS₂ formation at the conditions used in the present work (see Section 2), decreasing the amount of crystallites in which edges sulfidic nickel could be properly integrated. This fact could be responsible for the strong decrease (~80%) in HDS activity observed for NE(1/2), as to that of NE(1).

3.3. Citric acid-complexed samples

In developing improved CoMo HDS commercial catalysts, citric acid has been preferred over other chelating agents [26] because of its low cost. It is worth mentioning, however, that some detrimental effects related to the addition of that tri-carboxylic acid during HDS catalysts preparation has also been reported [27], but just in cases where the impregnated materials were air-calcined at temperature high enough to provoke organic ligands combustion, previously to the sulfiding step. Thus, no effect of chelation on nickel sulfiding could have been expected in this case. Citric acid has also been added to nickel nitrate aqueous solutions (to form the corresponding citrate) resulting in catalysts of improved active phase dispersion [28,29].

The kind and concentration of formed citrate (Cit) complexes mainly depends on both pH and Ni²⁺/citrate anions ratio [30]. If there is a considerable excess of organic anions in solution at pH lower than neutral (as in our case, see Section 2) the dominating forms are complexes with negative charges (for instance [NiHCit]⁻). Citrate coordination presumably involves the alkoxy group, the central carboxylate group and one terminal carboxylate with the octahedral coordination shell around Ni²⁺ being completed by three water molecules [31].

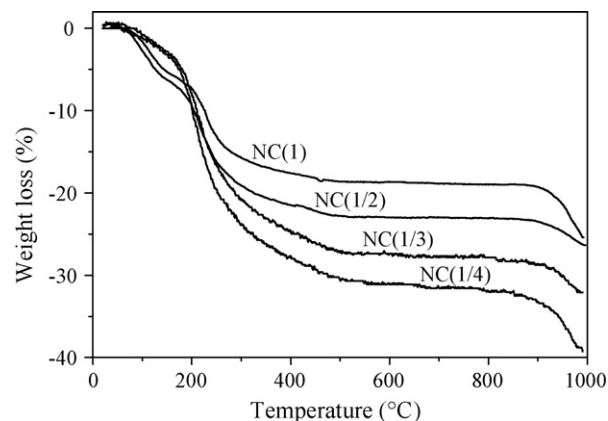


Fig. 7. Thermogravimetric analysis (under static air atmosphere) of NiMo/ZrO₂-TiO₂ dried precursors impregnated at various Ni/citric acid ratios.

3.3.1. Thermal analysis

Thermogravimetric analysis patterns of citric acid (CA)-containing impregnated precursors are shown in Fig. 7. In general, the registered profiles were similar to those of the samples where EDTA was used as chelator. For NC(1) and NC(1/2) the onset of weight losses by CA combustion was registered at about ~150 °C whereas for materials of higher organic additive concentration that feature was less evident. By increasing CA content the initial temperature of the region where the major losses were registered ($T \leq 500^\circ\text{C}$) slightly shifted to lowered values (from ~200 to ~182 °C). The weight losses observed in the aforementioned region increased with organic additive content (11.1, 13.5, 21.8 and 25.1 wt.% for NC(1), NC(1/2), NC(1/3) and NC(1/4), respectively). Similarly to that registered for EDTA-containing samples, the high-temperature weight loss at 885–891 °C was assigned to MoO₃ phase melt-evaporation [9].

Regarding the DTA thermograms shown in Fig. 8, the first exothermal signal attributed to organic moieties combustion promoted by nitrates decomposition was evident just for samples of lower CA content. In the rest of solids analyzed it seemed that the corresponding peak merged with the one related to major combustion of citrate groups complexating Ni²⁺ cations. This exothermal peak shifted to higher temperature by increasing the organic additive concentration (signal centered at 245, 278, 289

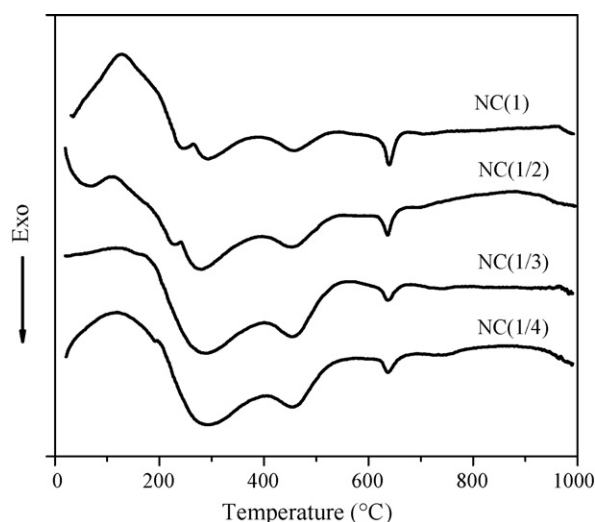


Fig. 8. Differential thermal analysis (under static air atmosphere) of NiMo/ZrO₂-TiO₂ dried precursors impregnated at various Ni/citric acid ratios.

and 295 °C, for NC(1), NC(1/2), NC(1/3) and NC(1/4), respectively). It seemed that also Mo^{6+} -citrate complexes could be formed in all impregnated materials, disregarding citric acid concentration. This fact suggested that differently to the case of EDTA, the tri-carboxylic acid did not preferably complexed nickel. It has been reported [30] that in aqueous solutions with pH between 2 and 8, Mo^{6+} species and citrate anions form relatively stable complexes with mole ratio $\text{Mo}/\text{Cit}=2$ and 1 ($[(\text{MoO}_4)_2\text{Cit}(\text{H}_n)]^{n-8}$ and $[\text{MoO}_4\text{Cit}(\text{H}_n)]^{n-6}$, respectively). In our case, the peak observed at ~ 455 – 459 °C seemed to be related to chelated-Mo decomposition. At the highest Ni/CA ratio tried (1/4), the totality of molybdenum could be complexed (supposing one citric acid molecule bonded to one Mo species). Although in the CA series materials molybdenum was deposited (followed by drying, see Section 2) before contacting with nickel citrate aqueous solutions, during this second impregnation Mo species could be re-dissolved and complexed. In this line, it has been recently reported [32] that the di-ammonium EDTA salt was able to extract Co^{2+} and Mo^{6+} cations (~ 64 and $\sim 5\%$ of those originally present) although these species formerly constituted a well-defined phase (CoMoO_4). In samples with CA as chelator the signal related to support phases segregation (to anatase titania and ZrTiO_4) was observed at ~ 637 – 640 °C. Differently to DTA patterns of EDTA-complexed samples (Fig. 2), for solids of increased citric acid concentration one small shoulder at higher temperature suggested that a fraction of the carrier crystallized to zirconium titanate in the 698–740 °C range. Finally, the endothermic inflexion related to MoO_3 melt and evaporation was registered at about ~ 960 °C [9].

3.3.2. Infrared spectroscopy studies

Regarding the citrate-complexed material NC(1/2), infrared absorptions similar to those registered for the EDTA-chelated solid NE(1) were observed (see Figs. 5 and 9). When the former was annealed at 300 °C (under vacuum, Fig. 9a) a broad maximum at 1611–1595 cm^{-1} was registered. Again, this could be considered as evidence of nickel chelation [21]. After pre-treatment at more severe conditions, the maximum sharpened centering at 1595–1596 cm^{-1} (Fig. 9b–d). This fact suggested that citrate species possibly with some carboxyl groups ($-\text{CO}-\text{OH}$) unattached to the central Ni^{2+} cation (which hexa-coordinated sphere could be completed by H_2O molecules) resisted annealing at 300 °C. However, those species seemed to be removed by heating at more severe conditions. For all spectra in Fig. 9 an additional absorption being

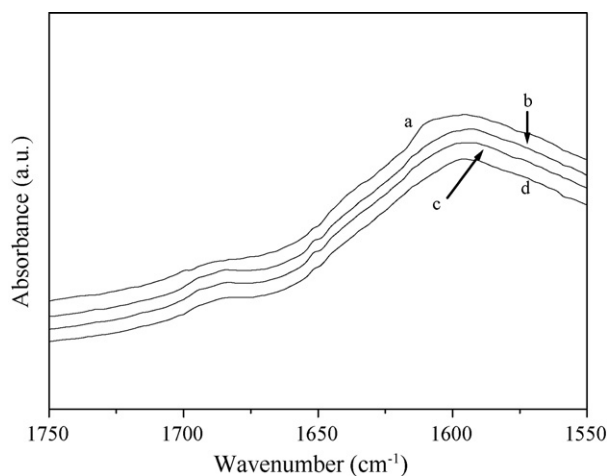


Fig. 9. Infrared spectra of dried NiMo/ZrO₂-TiO₂ impregnated at Ni/citric acid ratio = 1/2. Spectra taken at 100 °C after degassing at: (a) 300 °C; (b) 350 °C; (c) 400 °C and (d) 450 °C.

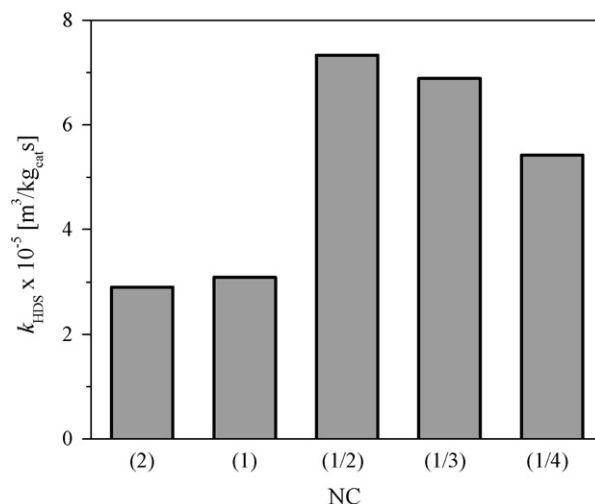


Fig. 10. Dibenzothiophene hydrodesulfurization activity of sulfided NiMo/ZrO₂-TiO₂ catalysts impregnated at various Ni/citric acid ratios. Operating conditions: batch reactor, $T=320$ °C, $P=5.72$ MPa, *n*-hexadecane as solvent, 1000 rpm, mixing speed.

probably related to complexed Mo^{6+} appeared at approximately 1686 cm^{-1} .

3.3.3. Hydrodesulfurizing activity

The DBT HDS activity trend observed over NiMo catalysts prepared in presence of citric acid was rather similar to that found over corresponding materials where nickel was EDTA-complexed (compare Figs. 6 and 10). Noteworthy, the optimal chelator concentration to obtain catalysts of maximized activity was different in each case. For citrate-complexed solids the best hydrodesulfurizing properties were registered when the organic additive was added in a twofold amount, as to that of the nickel promoter (in molar basis). In this line, other authors [33] have found that the optimal amount of citric acid in catalyst (with HY zeolite-modified alumina carrier) to be applied in ultra-low sulfur diesel production was beyond the stoichiometric one, respecting cobalt promoter ($\text{Co}/\text{CA} \sim 0.7$). For samples of Ni/CA ratio higher than 1/2 it seemed that chelator concentration was not enough to complexate the totality of impregnated nickel, this resulting in catalysts where sulfiding of certain proportions of this promoter could start at temperature inferior to that of MoS_2 formation, precluding then its efficient integration to maximize “NiMoS phase” formation.

In materials of high CA content (NC(1/3) and NC(1/4)) it could be that the amount of complexed Mo was too high, considering the organic acid excess added. Thus, MoS_2 formation (during sulfiding, see Section 2) could be hindered at some extent due to the high stability of the formed chelated molybdenum species. Thus, integration of sulfidic nickel (originated after CA-Ni complexes decomposition) could be limited by the decreased MoS_2 edges availability. The final effect could be the trend registered in Fig. 10 where HDS activity progressively diminished by augmenting citric acid concentration in the precursors. It is worth mentioning that Mo-complexation itself is not necessarily detrimental in obtaining efficient promoter integration to the molybdenum phase. Rather, differences in stability of Co and Mo complexes is what really matters. In this line, Frizi et al. [34] have shown that by using thioglycolic acid, a chelating agent able to complexate both Co and Mo, improved HDS catalysts could be prepared. According to those authors, simultaneous complexation of Mo and Co originated species that decomposed in similar temperature ranges. Thus, dur-

Table 1

Promotion degree expressed as DBT HDS pseudo-first-order kinetic constants ratio ($k_{\text{HDSNiMo}}/k_{\text{HDSMo}}$) for NiMo/ZrO₂-TiO₂ catalysts prepared in presence of either EDTA or citric acid

Catalyst	Chelator	$k_{\text{HDSMo}} \times 10^{-5}$ (m ³ /kg _{cat} s)	$k_{\text{HDSNiMo}} \times 10^{-5}$ (m ³ /kg _{cat} s)	Promotion ($k_{\text{HDSNiMo}}/k_{\text{HDSMo}}$)
Mo ^a	–	0.71	–	–
N	–	–	4.7	6.6
NE(1)	EDTA	–	7.8	11.0
NC(1/2)	Citric acid	–	7.3	10.3

The corresponding value over the material synthesized with no organic ligands included as reference. Operating conditions: batch reactor, $T = 320^\circ\text{C}$, $P = 5.72$ MPa, *n*-hexadecane as solvent, 1000 rpm, mixing speed.

^a Mo at ~11.9 wt.% (from Ref. [5]).

ing sulfiding Co atoms could migrate to the MoS₂ edges just formed, avoiding sintering of sulfided Mo by blocking the lateral growth of the corresponding slabs.

The best catalyst prepared with EDTA had DBT HDS activity similar to that of the optimized formulation with CA (Table 1), both formulations being clearly superior to an equivalent NiMo/ZrO₂-TiO₂ catalyst prepared with no organic additive (sample N) confirming the advantage of using organic chelators in obtaining improved hydrodesulfurization catalysts.

To determine promotion improvement by chelators addition we calculated the resulting increase in DBT HDS activity of ZT-supported MoS₂ by incorporating Ni in presence of either complexing agent. In Table 1, we defined promotion degree (in a DBT HDS pseudo kinetic constant basis) as the $k_{\text{HDSNiMo}}/k_{\text{HDSMo}}$ ratio for a given catalyst. Over the material prepared with no organic additive, promotion by Ni incorporation was superior to the maximum enhancement found for CoMo supported on wide-pore zirconia-titania (3.2 vs. 6.6, see Ref. [5]). This agreed with that found by Wang et al. [35] who found increased promotion for NiMo system as compared to CoMo one (3 vs. 4), in catalysts with TiO₂ carrier. Promotion degree of supported Mo phase by nickel incorporation was clearly improved by chelators addition (11.0 and 10.3 for the EDTA- and AC-complexed catalysts, respectively). In line with that we found, Afanasiev [36] reported a thiophene HDS activity increased by a factor of 9.05 in materials where Co could be efficiently integrated to pre-formed MoS₂ phase supported on zirconia-titania (60–40 mol-mol). In spite of very different methodologies used to better promote MoS₂ crystals (Mo pre-sulfiding before Co addition vs. promoter chelation), the aforementioned fact suggested that the main achievement in our work was similar to that gotten by Afanasiev, i.e., improved promoter integration to molybdenum sulfide phase deposited on zirconia-titania.

Regarding yield to various desulfurized compounds in the DBT HDS (at ~30% conversion) over ZT-supported NiMo catalysts prepared with EDTA or citric acid as chelators, biphenyl (BP, from the direct desulfurization route [37]) and cyclohexylbenzene (CHB, from the pre-hydrogenation route) were the only products detected in measurable amount, the former being produced in major concentration (Table 2). Excepting NE(1) and NC(1/2) (the formulations of maximized HDS activity), the rest of materials produced slightly increased BP proportions, as to that found over the material prepared in absence of chelating ligands (sample N). It could be concluded, however, that the use of chelating agents essentially did not exert appreciable influence on the selectivity to various products (in the DBT HDS) over the studied materials.

Finally, both EDTA and citric acid positively contributed to obtain improved NiMo-based HDS catalysts supported on wide-pore zirconia-titania. As previously reported by others [38], we corroborated that addition of complexed promoter could be a highly recommendable strategy to follow in obtaining enhanced hydrodesulfurizing properties in Mo catalysts supported on carriers (as zirconia [38], titania [39] or the corresponding mixed oxides)

Table 2

Yield to different products (dibenzothiophene hydrodesulfurization at ~30% conversion) over catalysts prepared in presence of chelating agents (EDTA, NE-series or citric acid, NC-series) at various concentrations

Catalyst	BP	CHB
NE (2)	0.26	0.035
NE (1)	0.23	0.066
NE (1/2)	0.28	0.016
NC(2)	0.28	0.018
NC (1)	0.27	0.031
NC (1/2)	0.25	0.050
NC (1/3)	0.26	0.035
NC (1/4)	0.27	0.034
N	0.25	0.053

Material prepared with no organic additive (sample N) included as reference (BP: biphenyl, CHB: cyclohexylbenzene). Operating conditions: batch reactor, $T = 320^\circ\text{C}$, $P = 5.72$ MPa, *n*-hexadecane as solvent, 1000 rpm, mixing speed.

where limited promotion of sulfided molybdenum by Co or Ni addition has been commonly found.

4. Conclusions

Ethylenediamine tetraacetic acid (EDTA) and citric acid (CA) were used as organic chelating additives in NiMo catalysts with wide-pore ZrO₂-TiO₂ mixed oxides as carrier. A clear beneficial effect of either chelator was evident when the sulfided catalysts were tested in the dibenzothiophene hydrodesulfurization (DBT HDS at 320 °C and 5.72 MPa, batch reactor), although the optimum concentration of EDTA and CA to obtain materials of enhanced activity was different to each other (Ni/EDTA = 1 and Ni/CA = 1/2). These concentrations seemed to correspond to total impregnated nickel chelation. Augmented chelators concentration resulted in catalysts of decreased hydrodesulfurizing properties probably due to delayed sulfidation of complexed molybdenum that could be formed by reaction of Mo⁶⁺ containing species with organic additive excess. In a pseudo-first-order kinetic constant basis, the best catalyst prepared with EDTA had similar HDS activity to that of the optimized formulation with CA (k_{HDS} values of 7.8×10^{-5} and 7.3×10^{-5} m³/kg_{cat} s, respectively). Both of them were clearly superior to a NiMo/ZrO₂-TiO₂ formulation prepared with no organic additive ($k_{\text{HDS}} \sim 4.7 \times 10^{-5}$ m³/kg_{cat} s). Characterization by thermal analyses (TGA, DTA) and infrared spectroscopy pointed out to delayed Ni²⁺ sulfidation (to temperature high enough to be efficiently integrated to then already formed MoS₂) as the main cause of HDS activity improvement in catalysts prepared in presence of organic chelators.

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