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Kinetic study of NiMo/SBA-15 catalysts prepared with citric acid in hydrodesulfurization of dibenzothiophene

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1. Introduction

Environmental protection requires the reduction of certain heteroatoms present in fuels. Gasoline and diesel, which have large quantities of sulfur, produces SO_x upon combustion. Sulfur elimination from crude oils is one of the major technological challenges imposed by various regulations from countries all around the world [1]. The main industrial process to accomplish this purpose is hydrodesulfurization (HDS). There are two distinct routes in HDS reactions (i) hydrogenation (HYD) and (ii) direct desulfurization (DDS). These are related with the type of active sites of the catalyst and the adsorption mode of aromatic compounds on its surface. The route preference depends on several factors such as support composition, promoter, size of MOS_2 clusters, HDS conditions, S-containing molecules and catalyst preparation [2–9].

The use of chelating agents during the catalyst preparation improves their activity in HDS [10–13]. It is well known that the chelating agents' ability to coordinate metals is dependent of several experimental conditions such as the pH of solution and metal concentrations, collateral equilibria in liquid media and redox reactions under air atmosphere [14–17]. HDS catalysts prepared with chelating agents have shown better promotion of CoMoS phase [18, 19]. CoMoP catalyst prepared with citric acid (CA) and supported on HY-Al₂O₃ has an increasing in S elimination compared with catalyst without CA [20–22]. NiMo catalysts supported on ZrO_2 –TiO₂ were studied with CA addition, chelating agents increase rate constant of DBT HDS, the Ni:CA molar ratio has the

ABSTRACT

We performed a kinetic study of the effect of citric acid (CA) during the synthesis of NiMo catalysts supported on SBA-15 in hydrodesulfurization (HDS) of dibenzothiophene (DBT). The aim of this work is to get a deeper insight with respect to the thermal treatment and the pH of the impregnation solutions on the kinetic behavior of NiMoCA/SBA-15 catalysts. NiMoCA/SBA-15 catalysts were characterized by N₂ physisorption, powder XRD, HRTEM and elemental analysis and tested in HDS of DBT in a Batch reactor at 300 °C for 8 h. The kinetic study of these catalysts showed changes by CA addition on hydrogenation and direct desulfurization reaction routes depending on catalyst preparation conditions.

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largest increment in activity when it has a proportion of 1:2. No selectivity modification was observed for any molar ratio [23].

In this work, we used SBA-15 mesoporous material as support for NiMo sulfided catalysts prepared with CA. Two pH values and two temperatures of treatments were chosen to get insight the effect of the preparation conditions of NiMoCA/SBA-15 catalysts in their activity and selectivity in HDS of DBT.

2. Experimental

2.1. Preparation of catalysts

SBA-15 silica with hexagonal *p6mm* structure was prepared according to reported procedure [24, 25] using the triblock copolymer P123 ($M_{av} = 5800$, EO₂₀PO₇₀EO₂₀, Aldrich) as the structure-directing agent and tetraethyl orthosilicate (TEOS, Aldrich, 99.999%) as the silica source.

NiMoCA catalysts supported on SBA-15 were prepared by a standard incipient wetness co-impregnation technique reported elsewhere [26]. The calcined support was co-impregnated using aqueous solutions of ammonium heptamolybdate, (NH₄)₆Mo₇O₂₄•4H₂O (Merck, 99%), nickel nitrate, Ni(NO₃)₂•6H₂O (Baker), and citric acid, C₆H₈O₇•H₂O (Merck, 99.5%) at pH = 1 and 9. pH = 1 was obtained by compounds dissolved, while pH = 9 was adjusted with ammonia solution. In both cases, the molar ratio was Ni:Mo:CA = 0.5:1:1.3. After co-impregnation, catalysts were thermal treated at 100 °C for 12 h in air atmosphere, and some of these prior at 100 °C for 12 h and then at 500 °C in static airatmosphere during 4 h. The nominal compositions of the catalysts were 12 wt.% of MoO₃ and 3 wt.% of NiO.

The catalysts were characterized by N_2 physisorption, powder XRD, high resolution transmission electron microscopy (HRTEM) and

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elemental analysis (carbon content). N₂ adsorption-desorption isotherms were measured with a Micromeritics ASAP 2000 automatic analyzer at liquid N₂ temperature. Prior to the experiments, the samples were degassed ($p < 10^{-1}$ Pa) at 100 °C and 270 °C (for catalyst prepared at 100 and 500 °C, respectively) for 6 h. Specific surface areas were calculated by the BET method (S_{BET}), the total pore volume (V_{p}) was determined by nitrogen adsorption at a relative pressure of 0.98 and pore size distributions from the desorption isotherms by the BJH method. The mesopore diameter $(D_{\rm P})$ corresponds to the maximum of the pore size distribution. The micropore area (S_{μ}) was estimated using the correlation of t-Harkins & Jura (t-plot method). XRD patterns were recorded in the $3^{\circ} \leq 2\Theta \leq 70^{\circ}$ range on a Siemens D5000 diffractometer, using CuK_{α} radiation ($\lambda = 1.5406$ Å) and a goniometer speed of 1° (2 Θ) min⁻¹. HRTEM studies were performed using a Jeol 2010 microscope (resolving power 1.9 Å). The solids were ultrasonically dispersed in *n*heptane and the suspension was collected on carbon coated grids. Slab length and layer stacking distributions of MoS₂ crystallites in each sample were established from the measurement of at least 300 crystallites detected on several HRTEM micrographs taken from different parts of the same sample dispersed on the microscope grid. Elemental analysis was carried out using an automatic Perkin-Elmer 2400 Series II CHNS/O analyzer with TC detector.

2.2. Catalytic test

The HDS activity tests were performed in a batch reactor at 300 °C and 7.3 MPa total pressure for 8 h with constant stirring. Prior to the catalytic activity evaluation, the catalysts were sulfided *ex situ* in a tubular reactor at 400 °C for 4 h in a stream of 15 vol.% of H₂S in H₂ under atmospheric pressure. The sulfided catalyst (0.15 g) was transferred in an inert atmosphere (Ar) to a batch reactor (Parr) with 40 mL of *n*-hexadecane solution containing DBT (Aldrich) 1300 ppm of S. The course of the reaction was followed by withdrawing aliquots each hour and analyzing them on an HP-6890 chromatograph. To corroborate product identification, the product mixture was analyzed on a Hewlett Packard GC-MS instrument.

3. Results and discussion

The textural properties of SBA-15 and NiMoCA catalysts are given in Table 1. SBA-15 specific surface area (S_{BET}) is 850 m²/g, NiMoCA catalysts decrease S_{BET} for the two pH values. NiMoCA catalyst impregnated with acidic solution, pH = 1, and dried at 100 °C (12 h) (NiMoCA a-d) has a surface area larger than NiMoCA catalyst impregnated with basic solution, pH = 9, and dried at 100 °C (12 h) (NiMoCA b-d). NiMoCA catalyst impregnated with acidic solution, pH = 1, dried at 100 °C (12 h) and calcined at 500 °C (4 h) (NiMoCA a-c) has also larger area than NiMoCA impregnated with basic solution, pH = 9, dried at 100 °C (12 h) and calcined at 500 °C (4 h) (NiMoCA b-c). Calcination at 500 °C under air atmosphere increases the specific surface area on



Fig. 1. Nitrogen adsorption–desorption isotherms of (\blacksquare) SBA-15 support, (\Box) NiMoCA b–d catalyst and (\bigcirc) NiMoCA b–c catalyst.

both catalysts. This effect is present for both catalysts at 500 °C and it is caused by the CA decomposition due to its combustion under air atmosphere. This combustion implies the increase of specific surface area of catalysts supported on SBA-15. Fig. 1 shows the N₂ adsorption-desorption isotherms for NiMoCA catalysts impregnated with basic solution. The form of N₂ adsorption-desorption isotherm and the shape did not suffer an important change after catalyst preparation. All of them exhibit a IV type isotherm and H1 hysteresis loop characteristic for mesoporous materials and well formed SBA-15, indicating that the original type of isotherm for the support was conserved after catalyst preparation. Powder XRD patterns of NiMoCA/SBA-15 catalysts impregnated with basic solution (catalysts impregnated with acidic solutions showed the same behavior) did not show the presence of any crystalline phase (Fig. 2), pointing out a good dispersion of the deposited metal oxide species in all samples.

HRTEM measurements of sulfided NiMoCA catalysts were performed to obtain more information about dispersion of MoS₂ crystallites on SBA-15 by using CA as an organic additive and their behavior with pH and thermal treatment in stacking and length of the particles. The typical fringes due to MoS₂ crystallites with 6.1 Å interplanar distances were observed on micrographs of all sulfided catalysts. Average length and stacking of NiMoCA sulfided catalysts supported on SBA-15 are shown in Table 2. MoS₂ particles of NiMoCA b–d catalyst were the shortest and they have an average stacking of 1.8. The preparation conditions of these NiMoCA catalysts supported on SBA-15 have implications in the morphology of the active phase. CA under different atmospheres could be oxidized or reduced on these materials. Carbon analysis for sulfided catalysts is reported in Table 2. NiMoCA b–d

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Preparation conditions and textural characteristics of NiMoCA catalysts supported on SBA-15.

Sample	pH ^a	Temperature (°C) ^b	$\frac{S_{\text{BET}}^{e}}{(m^2/g)}$	S_{μ}^{f} (m ² /g)	V _p (cm ³ /g)	V _µ (cm ³ /g)	D_{p}^{g} (Å)
SBA-15			850	140	1.09	0.056	65
NiMoCA a-d	1	100 ^c	393	60	0.67	0.024	60
NiMoCA a-c	1	100, 500 ^d	597	73	0.84	0.026	61
NiMoCA b-d	9	100 ^c	340	64	0.62	0.026	61
NiMoCA b-c	9	100, 500 ^d	501	55	0.85	0.020	60

^a pH of impregnation solutions.

^b Thermal treatment of NiMoCA/SBA-15 catalysts before sulfidation.

^c Catalyst dried at 100 °C (12 h) under air atmosphere.

 $^{\rm d}$ Catalyst dried at 100 °C (12 h) and calcined at 500 °C (4 h) under air atmosphere.

e BET specific surface area.

^f Micropore area.

^g Pore diameter corresponding to the maximum of the pore size distribution calculated from the desorption isotherm by the BJH method.



Fig. 2. Powder XRD patterns of (a) SBA-15, (b) NiMoCA b-d catalyst and (c) NiMoCA b-c catalyst.

catalyst has the largest C content (0.741 wt.%). NiMoCA a–d and NiMoCA a–c catalysts have almost the same carbon content no matter if they were calcined before sulfidation stage (0.545 wt.% and 0.527 wt.%, respectively). We also note that CA could act as a carbon source [27].

Catalytic constants of DBT elimination (k_0) for NiMoCA/SBA-15 catalysts are listed in Table 3. The largest values of k_0 are for NiMoCA catalysts impregnating with acidic solution, they are three times higher than NiMo catalyst without CA. The k_0 trends for DBT activity is: NiMoCA a-(d and c) > NiMoCA b-(d and c) > NiMo (d and c). Calcination at 500 °C of NiMoCA catalyst impregnated with basic solution increases drastically the value of k_0 . The increment in catalytic constants of DBT elimination when CA was added is related with its effect in impregnation solutions and physicochemical properties of catalytic materials. In aqueous solution, CA can interact with Ni (II) [23]. Another effect present is the pH values of impregnation solutions; they modify the chemical equilibrium of the Mo (VI) species [28]. Additionally, we note important changes in the properties of sulfided catalysts such as modification in average length and stacking degree and carbon content depending on catalyst preparation conditions.

Selectivity modifications of NiMoCA catalysts supported on SBA-15 in HDS of DBT were studied by their rate constants. The modification of these by preparation conditions revealed important modifications in the type of the catalytic active sites by CA addition. These constants were calculated based on the kinetic model (Scheme 1) proposed by Farag [29, 30]. This kinetic model is based on the assumption of the existence of two different kinds of catalytic active sites of (i) hydrogenation and (ii) direct desulfurization. In this approach, the total rate can be expressed as $R_{\text{Total}} = R_{\text{HYD}} + R_{\text{DDS}}$. The solved differential equations to calculate the catalytic constants are:

$$C_{\rm A} = C_{\rm A^o} \exp(-k_0 t) \tag{1}$$

$$C_{\rm B} = \frac{C_{\rm A^0}k_1^*}{k_3^* - k_0} \left[\exp(-k_0 t) - \exp(-k_3^* t) \right]$$
(2)

Table 2Average length and stacking degree of MoS2 crystallites and carbon content in NiMoCAcatalysts supported on SBA-15.

Catalyst	Average length (Å)	Average stacking	C (wt.%)
NiMoCA a-d	29	2.1	0.545
NiMoCA a-c	30	2.7	0.527
NiMoCA b-d	28	1.8	0.741
NiMoCA b-c	31	2.7	0.576

Table 3

Apparent rate constants of NiMoCA/SBA-15 catalysts for HDS of DBT in the reaction network shown in Scheme 1 [29,30].

Catalyst	Rate constants, $\times 10^4 \text{ s}^{-1} \text{ g}_{\text{cat}}^{-1}$					Ratio	
	k_0	k_1^*	k_2^*	k_3^*	k_4^*	k_1^*/k_2^*	k_4^*/k_3^*
NiMo ^a	2.40	1.05	1.35	3.65	3.50	0.78	0.96
NiMo ^b	2.71	1.03	1.67	3.97	3.83	0.61	0.96
NiMoCA a-d	9.14	0.40	8.44	12.7	1.11	0.04	0.08
NiMoCA a-c	9.20	2.41	7.37	9.20	5.37	0.32	0.58
NiMoCA b-d	3.58	3.02	0.67	0.90	8.67	4.51	9.63
NiMoCA b-c	5.32	2.80	2.29	4.02	4.76	1.22	1.18

^a NiMo/SBA-15 catalyst without CA and dried at 100 °C (12 h).

^b NiMo/SBA-15 catalyst without CA dried at 100 °C (12 h) and calcined at 500 °C (4 h).

$$C_{\rm D} = \frac{C_{\rm A^o} k_3^* k_1^*}{k_3^* - k_0} \left[\frac{1}{k_3^*} \exp(-k_3^* t) - \frac{1}{k_0} \exp(-k_0 t) \right] \\ + \frac{C_{\rm A^o} k_4^* k_2^*}{k_4^* - k_0} \left[\frac{1}{k_4^*} \exp(-k_4^* t) - \frac{1}{k_0} \exp(-k_0 t) \right] + \frac{C_{\rm A^o} (k_1^* + k_2^*)}{k_0}$$
(3)

where $k_0 = k_1K_1 + k_2K_2$, k_1 and k_2 are the intrinsic kinetic rate constants for the DDS and HYD routes, and K_1 and K_2 are the equilibrium adsorption constants of DBT over the catalytic active sites for DDS and HYD, respectively. All of these constants are lumped together as one constant, i.e., k_0 . The apparent rate constants adjusted were $k_n^* = k_nK_n$, where k_n is the intrinsic kinetic rate constant and K_n is the equilibrium adsorption constant of each compound.

Kinetic Eqs. (1, 2 and 3) were compiled and computed with Origin 8.0 software with the Nonlinear Curve Fit option. Fitting was performed with several numbers of iterations until it was converged. The Nonlinear fit for NiMoCA b-c catalyst supported on SBA-15 for biphenyl (BP) production is shown in Fig. 3 and for cyclohexylbenzene (CHB) is shown in Fig. 4. For all of the catalysts tested in this study we obtained good fitting to calculate catalytic constants involved in HDS of DBT network. Rate constants k_1^* and k_4^* are related with hydrogenolysis (HYG) reactions and k_2^* and k_3^* correspond to hydrogenation reactions of DBT and its HDS products. Kinetic analysis of DBT HDS exhibits the effect of preparation conditions for NiMoCA/SBA-15 catalysts in the reaction network. This kinetic model allows us to relate the rate constants with the different type of the active sites of HYD and HYG. We observe k_1^* , k_2^* , k_3^* and k_4^* for NiMoCA/SBA-15 catalysts were modified by the preparation conditions in CA presence (Table 3).

NiMoCA a–d catalyst has the lowest value of k_1^* and k_4^* rate constants: $4 \times 10^{-5} \text{ s}^{-1} \text{g}_{cat}^{-1}$ and $1.11 \times 10^{-4} \text{ s}^{-1} \text{g}_{cat}^{-1}$, respectively. As mentioned above, these are assigned to HYG reactions. This catalyst has the highest values in k_2^* and k_3^* rate constants $8.44 \times 10^{-4} \text{ g}_{cat}^{-1}$ s⁻¹ and $1.27 \times 10^{-3} \text{ s}^{-1} \text{g}_{cat}^{-1}$. In contrast, NiMoCA b–d catalyst has an opposite effect in the DBT reaction network, the k_1^* and k_4^* rate constants have the highest values of all of the NiMoCA/SBA-15 catalysts



Scheme 1. Reaction network used to calculate the catalytic constants based on model proposed by Farag [29, 30].



Fig. 3. Biphenyl (BP) concentration as a function of the reaction time of HDS of DBT over NiMoCA b−c catalyst. ■ Experimental points. — Fitted curve based on Eq. (2).

 $3.02 \times 10^{-4} \text{ s}^{-1} \text{g}_{cat}^{-1}$ and $8.67 \times 10^{-4} \text{ s}^{-1} \text{g}_{cat}^{-1}$, respectively, these constants are assigned to C—S bond cleavage reactions. We observed important changes in catalytic constants by varying pH of impregnation solution, NiMoCA b–d catalyst had the smallest value for stacking degree in HRTEM measurements and the largest C content. It is very important to note that this catalyst was the most selective towards the DDS route, it is well known that HDS catalysts supported on carbon react preferably towards this route [31].

Calcination of NiMoCA/SBA-15 catalysts at 500 °C under air atmosphere before activation stage modified the values of the rate constants, therefore the proportion of DDS and HYD active sites. The modification of the rate constants by CA addition as a function of thermal treatment is different depending on pH of impregnation solution. NiMoCA a-c catalyst increases the apparent rate constant of HYG $(k_1^* \text{ and } k_4^*)$ and decreases the HYD rate constants $(k_2^* \text{ and } k_4^*)$ k_3^*) with respect to NiMoCA a–d catalyst, calcination of this catalyst at 500 °C increases the HYG reaction rates. However, a surprising effect was obtained in the behavior of catalyst impregnated with basic solution when it was calcined at 500 °C. NiMoCA b-c catalyst decreased the k_1^* and k_4^* rate constants with respect to NiMoCA b-d catalyst, see the rate constants related to HYG reactions. Catalytic constant of DBT \rightarrow BP (k_1^*) decreased from $3.02 \times 10^{-4} \text{ s}^{-1} \text{g}_{cat}^{-1}$ at 100 °C to $2.80 \times 10^{-4} \, s^{-1} g_{cat}^{-1}$ at 500 °C and C—S bond cleavage of 4H-DBT \rightarrow CHB (k_4^*) had also a decrement from 8.67 \times 10⁻⁴ s⁻¹g⁻¹_{cat} at 100 °C to $4.76 \times 10^{-4} \text{ s}^{-1} \text{g}_{cat}^{-1}$ at 500 °C, therefore the proportion



Fig. 4. Cyclohexylbenzene (CHB) concentration as a function of the reaction time of HDS of DBT over NiMoCA b-c catalyst. ■ Experimental points._____ Fitted curve based on Eq. (3).

of DDS active sites were decreased and the proportion of HYD active sites were increased. NiMoCA/SBA-15 catalysts impregnated with basic aqueous solutions changed the reaction network ratio drastically with thermal treatment due to the carbon content decrease from 0.741 to 0.576 wt.%. This change in the selectivity also explains the large increment in k_0 for NiMoCA b–c catalyst.

The ratio k_1^*/k_2^* is related with the proportion of DDS/HYD active sites. The largest value for this ratio was 4.51 for NiMoCA b–d catalyst and the lowest value was 0.04 for NiMoCA a–d catalyst. We mentioned above modification of the type of active sites by preparation conditions of NiMoCA/SBA-15 catalysts. This ratio confirmed the changes in DDS/ HYD active sites. The calcination of these catalysts at 500 °C under air atmosphere has the largest effect for NiMoCA/SBA-15 catalyst impregnated with basic solution. The inversion of routes is clearly considerable because the DDS/HYD ratio diminishes drastically.

4. Conclusions

We have shown the outstanding modification in the type of active sites for HYD and DDS of NiMo/SBA-15 catalysts prepared with citric acid. These changes are related to the pH of impregnation solution and temperature of treatment due to the catalyst modifications by CA such as morphology of active phase, as determined by HRTEM. DBT reacts over NiMoCA a–d catalyst towards HYD and over NiMoCA b–d catalyst towards DDS, when this catalyst was calcined at 500 °C it had a surprising selectivity inversion, DBT mainly reacts towards HYD route.

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