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Hydrodeoxygenation of Phenol Over Hydrotreatment Catalysts in their Reduced and Sulfided States

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Abstract: The influence of the composition of reduced CoMo, NiMo and NiW catalysts on the catalytic performance in hydrodeoxygenation (HDO) of phenol has been investigated. γ-Al_2O_3 and TiO_2 were used as supports. Different activity orders were obtained over γ-Al_2O_3 and TiO_2 supported catalysts reflecting the critical role of the support. NiMo catalyst supported on γ-alumina proved to be the most active followed by the CoMo catalyst supported on titania. CoMo and NiMo lab made catalysts were proved to be more active compared to a reduced industrial CoMo catalyst supported on γ-alumina. An increase of phenol conversion in the range 52-230% was obtained at 350°C.

A series of CoMo, NiMo and NiW catalysts supported on TiO_2 was also prepared using the "Equilibrium - Deposition - Filtration" (EDF) method. The application of this technique, instead of the classical impregnation, increased considerably the activity of the CoMo catalyst supported on titania (48% increase of phenol conversion at 350°C).

The most active lab catalysts (wet impregnated NiMo catalyst supported on alumina, EDF CoMo catalyst supported on titania) and the industrial CoMo catalyst were evaluated after sulfidation for simultaneous HDO of phenol and HDS of dibenzothiophene. These catalysts exhibited comparable HDO activities while the first one proved to be superior in HDS. Overall, taking into account the significantly higher loading of the industrial catalyst in the supported elements compared to the lab made catalysts, the latter seems to be quite promising, even in the frame of a co-processing strategy.

Keywords: γ-Al_2O_3, CoMo, dibenzothiophene, equilibrium-deposition-filtration, hydrodeoxygenation, hydrodesulfurization, NiMo, NiW, phenol, supported catalysts, TiO_2.

1. INTRODUCTION

Bio-oils, derived from biomass by hydrothermal and fast pyrolysis processing, are considered as an ideal petroleum substituting energy source because of the availability of biomass in countries with no fossil fuels, their low sulfur and metal content and their contribution to the neutrality of produced CO_2 [1, 2].

However, in contrast to petroleum-derived feedstocks, bio-oils contain about 50 wt.% of oxygen mainly resulting from carboxylic acids, esters, aliphatic and aromatic alcohols, ethers, ketones, and aldehydes [2]. As a consequence of such composition, the bio-oils possess high viscosity, non-volatility, poor heating value, corrosiveness, immiscibility with fossil fuels, thermal instability, and a tendency to polymerize during storage and transportation [3, 4]. Moreover, there is an undesirable formation of carbon deposits in parts of automotive engines upon combustion in diesel engines [1]. Therefore, upgrading bio-oils by

hydrodeoxygenation (HDO) is necessary to remove oxygen and increase the content of hydrogen if the bio-oil is used directly as liquid fuel for vehicles [2, 5].

The upgrading of bio-oils to improved quality transportation fuels is studied through two different approaches. The first relates to the upgrading of bio-oil during production, following the pyrolysis process, *in situ* (i.e. in the pyrolysis reactor), while the second concerns upgrading processes carried out after the production of bio-oil [6]. In the frame of the second approach, the investigation was initially focused on the HDO of bio-oils by means of industrial $CoMo/Al_2O_3$, $NiMo/Al_2O_3$ and NiW/Al_2O_3 sulfide catalysts, because these catalysts have been used effectively for many years in the hydrotreatment of petroleum fractions for the removal of sulfur (HDS), nitrogen (HDN) and oxygen (HDO).

Unsulfided form of the catalyst showed less activity than the sulfided one [7], which indicates that the addition of a sulfur source or co-processing of bio-oil and petro-oil could be beneficial for these catalysts concerning HDO. However, at the moment the refineries are not willing to adopt co-processing, because of the observed diminution of the HDS activity [8]. Thus, in recent years the research has turned to

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the respective reduced or partially reduced catalysts [9-13], to transition metal catalysts [14] as well as to noble metal carbon [7] or zirconia [15] based catalysts. In a recent review article Mortensen *et al.* [16] concluded that both sulfur containing type catalysts and noble metal type catalysts are quite promising, but these systems still need additional development in order to evaluate their full potential.

Support is another key factor determining the HDO activity of catalysts. The pristine γ-Al_2O_3 was previously used as catalyst support to hydrotreat oxygenated compounds for producing hydrocarbons, but severe carbon deposition was observed [17]. Moreover, alumina is known to be metastable in the presence of water, and will partially transform into boehmite under hydrothermal conditions [18]. To overcome these flaws, catalysts supported on SiO_2 [13, 19], active carbon [20], TiO_2 [17], ZrO_2 [17, 21, 22], zeolites [23], and various mixed oxides [14, 24] have been explored in recent years.

Due to the complex compositions of bio crude oils, most of the HDO studies reported have been focused on model compounds rather than the real bio crude oils. Phenols have been received considerable attentions because of their low reactivity in HDO process and relatively high concentration (~25%) in the bio-oils [25]. Therefore, the HDO of phenols becomes one of the key reactions in pyrolysis oil upgrading. A large portion of the work has been carried out to avoid the rings becoming saturated so as to minimizing the hydrogen consumption in HDO of model compound using phenols.

In the present work we have investigated the influence of the support nature and the preparation method on the catalytic performance of reduced CoMo, NiMo, and NiW catalysts for HDO of phenol in a high pressure fixed bed reactor. γ-Al_2O_3 and TiO_2 were used as supports and the wet impregnation (WI) method was followed for the deposition of active components. A series of aforementioned catalysts supported on TiO_2 was also prepared using the Equilibrium - Deposition - Filtration (EDF) method. This technique usually provides catalysts with better surface characteristics and thus better catalytic behavior than conventional impregnation [26-28]. Finally, the most active catalysts were evaluated after sulfidation for simultaneous HDO of phenol and HDS of dibenzothiophene.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Wet Impregnated Samples: Two CoMo, NiMo and NiW catalysts supported on γ-Al_2O_3 (Houdry Ho 415, specific surface area: 140 m^2/g) and TiO_2 (Alfa Aesar, specific surface area: 150 m^2/g) powders (particle size: 90-150 mesh) were prepared following a two steps wet impregnation method. In the first step (deposition of active component) an impregnating solution containing suitable amount of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck, pro analysi) or $(NH_4)_{12}W_{12}O_{41} \cdot 5H_2O$ (Johnson Mattey, 99.999%) was prepared with bi-distilled water in a volume 20 times larger than the total volume of the carriers' pores. The concentration of impregnating solution was regulated in order an amount corresponding to a monolayer of the active metal (Mo or W) to be deposited on the support surface. 5g

of each support were suspended in this solution. The suspension remained under stirring for 4h at room temperature and pressure in a rotary evaporator (Büchi, Rotavapor R-114) and then the water was removed at 40°C and 30 mbar. The solid obtained was dried overnight at 120°C and was calcined at 400°C for 3h.

In the second step (deposition of promoter) Co or Ni was deposited on the surfaces of the calcined solids following the above described procedure. The impregnating solutions were prepared using bi-distilled water and a suitable amount of $Co(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich, pro analysi) or $Ni(NO_3)_2 \cdot 6H_2O$ (Fluka, pro analysi) in order a synergistic ratio equal to 0.3 to be achieved. The samples of this series have been denominated as $Co(Ni)Mo(W)A(T)_w$.

Equilibrium - Deposition - Filtration samples: 5g of TiO_2 powder was suspended in an impregnating solution containing 2.5×10^{-2} mol Mo (or W) dm^{-3}, totalling 2.0 dm^3. The ionic strength of the solution was adjusted to 0.1 N using NH_4NO_3. The pH of the suspension was regulated using HNO_3 at pH=4.5. The suspension was kept under stirring at constant temperature (25±1°C) for 20h and then it was filtered through membrane filters (Millipore, 0.22 μm). The resulting solid was dried overnight at 120°C and then it was calcined in air at 400°C for 3h. Previous works have shown that under these conditions monolayer coverage of the support surface is achieved [26-28]. Suitable amount of Co or Ni has been deposited on the surfaces of the calcined solids following the incipient wetness impregnation method in order a synergistic ratio equal to 0.3 to be achieved. After the addition of the promoter the final catalyst was dried overnight at 120°C and calcined in air at 400°C for 3h. The samples of this series have been denominated as $Co(Ni)Mo(W)T_e$. An industrial CoMo supported on alumina HDS catalyst ($CoMoA_i$) purchased from AKZO (KETJENFINE 742-1.3Q) was also studied for comparison.

2.2. Catalyst Texture

The determination of the specific surface area (SSA), pore volume (PV), and mean pore diameter (d_p) of the studied samples was based on the nitrogen adsorption-desorption isotherms. A static methodology was applied using a Micromeritics apparatus (Tristar 3000 porosimeter).

2.3. Catalyst Activity Tests

Both the HDO of phenol over reduced catalysts and the simultaneous HDO of phenol and HDS of dibenzothiophene over sulfided catalysts were carried out in a high pressure fixed bed reactor described previously [29].

Reduced Catalysts: The catalysts studied were initially reduced under atmospheric pressure in a fixed bed reactor. The reactor was fed with Ar (50 ml/min) and the temperature increased up to 400°C with a rate 10°C/min. Then the feed was switched to H_2 (30 ml/min) for 2.5h and the catalyst was cooled down to ambient temperature under Ar. Finally, the catalyst was passivated under a stream of a mixture of Ar and synthetic air with gradually increasing portion of the latter. 0.2g of the pre-reduced catalyst was diluted with 4.15g of quartz powder (particle size: 90-150 μm) and was placed in the high pressure reactor where a 3 ml bed was created.

The reactor was fed with Ar (50 ml/min) and the temperature and pressure increased gradually up to 350°C and 15 bar, respectively. Then the feed was switched to H_2 (30 ml/min) for 45 min at the same pressure. After that a mixture constituted by phenol (1%) and hexadecane was pumped to the reactor with a flow rate 0.25 ml/min. The reactor system maintained under these operation conditions for 4h in order a steady state performance to be achieved. Liquid samples were collected at the outlet of the reactor every 0.5h and were quantitatively analyzed in a Gas Chromatograph (Shimadzu, GC-14B) equipped with a FID detector and a capillary column (CHROMPAC WCOTT F 50m x 0.32 mm 1D DF 1.2 μm). The analysis showed that the HDO products of phenol were benzene, cyclohexene, cyclohexane and methyl-cyclopentane. Taking into account the area of the corresponding peaks the conversion of phenol to deoxygenated products was calculated. The reactor temperature decreased to 250°C and the conversion of phenol was determined as before. Then the temperature increased to 300 and again 350°C for confirmation.

No change in the activity was observed between the first and the last catalytic run at 350°C, indicating that no deactivation of the catalysts took place during the whole catalytic test. Experiments performed with various catalyst masses (W) and liquid flow rates (F) (keeping constant the ratio W/F) as well as on various catalyst particle sizes (keeping constant the catalyst mass) proved that the catalytic process was under kinetic control.

Sulfided Catalysts: The most promising catalysts found for the HDO of phenol in their reduced form were tested also in their sulfided form for simultaneous HDO and HDS of a mixture containing 1% w/w phenol and 1% w/w dibezothiophene in hexadecane. The test procedure was similar with that described above. The only difference concerns the activation of the catalysts. The catalyst samples were pre-sulfided at atmospheric pressure in the fixed bed reactor used previously for initial reduction substituting the H_2 stream by a stream of 15% (v/v) hydrogen sulfide in hydrogen. The catalyst was then placed in the high pressure reactor and after being purged with Ar, a gas mixture H_2S/H_2 (3% v/v H_2S) was fed (30 ml/min) at temperature 350°C and pressure 15 bar for 45 min. Then the gas feed was switched

to H_2 and the liquid mixture (phenol-dibenzothiophene-hexadecane) was pumped to the reactor inlet.

3. RESULTS AND DISCUSSION

Table **1** compiles the chemical composition of the prepared catalysts along with their textural characteristics determined by nitrogen physisorption experiments. An inspection of this table shows that, with the exception of the industrial HDS catalyst ($CoMoA_i$), there are not dramatic differences in the active components loading (with the exception of the NiW catalysts) and specific surface area of the examined samples. This facilitates the direct comparison of the influence of the support nature and the preparation method on the catalytic performance of the samples.

Fig. (**1**) illustrates the percentage phenol conversion achieved at 350°C over the catalysts prepared by wet impregnation as well as over the industrial one in their reduced form. Let's first compare the activities of the catalysts supported on alumina. We observe that the NiMo catalyst exhibited the highest activity followed by the CoMo and then the NiW ones. On the other hand the NiMo and CoMo catalysts prepared in the lab proved to be more active than the industrial CoMo one, although the latter posses about double SSA and supported phases loading (see Table **1**). However, at this point we have to stress that the industrial CoMo catalyst is dedicated for HDS processes and exhibits its best behaviour in the sulfided state. The same picture has been obtained also for the other two reaction temperatures studied, namely 250 and 300°C.

The activity order obtained over γ-alumina based catalysts (NiMo>CoMo>NiW) is no longer valid for titania ones, indicating the critical role of the support. In fact, the order obtained for titania (CoMo> NiMo> NiW) shows that this carrier is more suitable for preparing CoMo HDO catalysts. More importantly, an inspection of Fig. (**1**) shows that titania proved to be better support than alumina resulting in more active catalysts in the cases of CoMo and NiW ones. These results are in line with those found previously over sulfided CoMo catalysts used for HDS reactions. For example, Escobar *et al.* [30] prepared CoMo HDS catalyst supported on high surface area (>300 m^2 g^{-1}) nano-structured

Table 1.   Wet impregnated and EDF catalysts supported on alumina and titania, their loading, specific surface area (SSA), Pore volume (PV) and mean pore diameter (d_p).
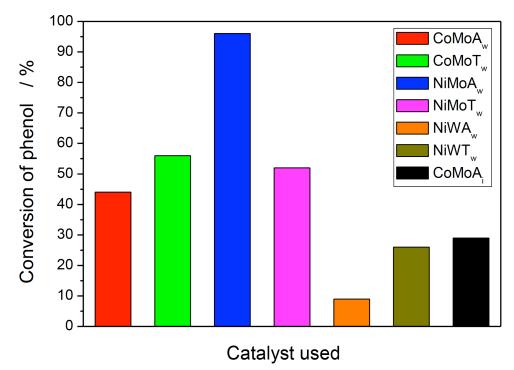
Catalysts	Co (Ni) Loading (%)	Mo (W) Loading (%)	SSA (m^2/g)	PV (cm^3/g)	d_p (Å)
$CoMoA_w$	2.25	6.70	125	0.27	76.0
$CoMoT_w$	1.95	5.82	120	0.41	96.5
$CoMoT_e$	1.95	5.82	122	0.39	91.8
$CoMoA_i$	3.45	9.98	275	0.55	59.0
$NiMoA_w$	2.24	6.70	125	0.26	78.0
$NiMoT_w$	1.94	5.82	118	0.41	98.0
$NiMoT_e$	1.94	5.82	122	0.39	90.5
$NiWA_w$	2.45	14.25	114	0.24	76.5
$NiWT_w$	2.16	12.51	113	0.37	93.3
$NiWT_e$	2.16	12.51	111	0.36	91.3

Fig. (1). Conversion of phenol over reduced wet impregnated catalysts supported on alumina and titania (W= 0.2 g, F=0.25 ml/min, T= 350°C, P= 15 bar).

TiO$_2$ and tested in dibenzothiophene HDS. They found that the activity of CoMo/titania catalyst was two-fold to that of an alumina-supported commercial CoMo catalyst. However, the favourable effect of titania found in the present work is limited to the CoMo and NiW supported phases and does not concern the NiMo supported phase where γ-alumina proved to be more effective. In fact, the HDO activity of NiMoA$_w$ sample was found to be almost double of that of NiMoT$_w$ sample (Fig. **1**). Taking into account similar carrier's comparisons for HDS, this finding is not so surprising. Wang *et al*. [31] have reported greater activity in HDS of dibenzothiophene for sulfided NiMo catalysts supported on alumina than that exhibited by the corresponding catalyst supported on titania.

Combining the performance equation of the integrated fixed bed reactor used in this study with the rate equation of phenol HDO (assuming pseudo-first order kinetics) equation (1) was derived. Using this equation the rate constants ($k_{p,T}$) were calculated at each reaction temperature (T) over the catalysts studied:

$$k_{p,T} = -\frac{F}{W} \times (1 - X_p) \qquad (1)$$

In this equation *F, W* and X_p symbolize the volumetric flow rate of the reaction mixture, the catalyst weight and the phenol conversion, respectively. The $k_{p,T}$ values obtained are involved in Table **2**. Using these values and the Arrhenius equation the apparent activation energies (Ea$_p$) were calculated and are also presented in Table **2**.

An inspection of this table shows that Ea$_p$ values higher than 40 kJ·mol^{-1} have been obtained in all cases verifying that the experimental conditions adopted upon catalytic activity evaluation ensured indeed the kinetic control of the process. Another observation is that the industrial HDS catalyst exhibited the highest activation energy (104 kJ·mol^{-1}) for phenol HDO. This means that it could exhibit better catalytic performance at higher reaction temperatures.

Let's now examine the influence of the preparation method on the activity of the CoMo, NiMo and NiW catalysts for the HDO of phenol. The conversion values obtained over catalysts supported on titania, prepared by EDF and wet impregnation, are presented in Fig. (**2**). It is clear that a significant effect of preparation method on the catalytic activity has been observed in the case of CoMo catalysts. In this case the EDF method resulted to a catalyst exhibiting ca 48% higher activity than that of the catalyst prepared by wet impregnation. This is actually a very useful finding from the practical point of view, illustrating that using EDF we may prepare a very active catalyst supported on titania, a much more stable support than alumina with respect to the deactivation caused by the water molecules released upon HDO.

On the contrary to the above, the Ni promoted catalysts (NiMo and NiW) prepared by EDF exhibited slightly lower catalytic activity than the corresponding catalysts prepared by wet impregnation. A convincing interpretation of this behaviour demands extensive characterization of the samples, which is in order in our lab.

The HDO products of phenol over the catalysts studied were methyl-cyclopentane, cyclohexane cyclohexene and benzene. The selectivity values obtained are involved in Table **3**. These values were determined at a conversion level lower than 10%. One may observe that the fully hydrogenated products (methyl-cyclopentane+cyclohexane) predominate over all the catalysts. It is remarkable that the NiW catalysts supported on titania exhibited lower hydrogenation activity than the other catalysts.

Table 2.   **First order phenol HDO kinetic constant values ($k_{p,T}$) determined at various reaction temperatures and the activation energies calculated over the studied catalysts.**

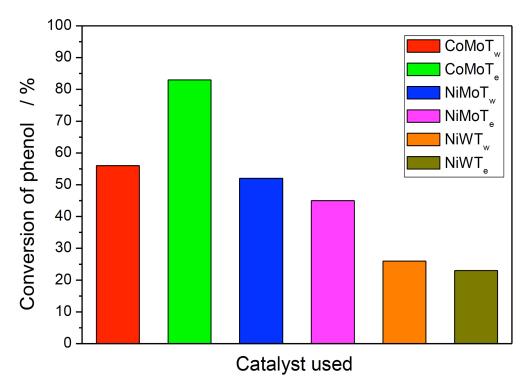| Catalysts	$k_{p,250}$ (L·g^{-1}·s^{-1})	$k_{p,300}$ (L·g^{-1}·s^{-1})	$k_{p,350}$ (L·g^{-1}·s^{-1})	Ea$_p$ (kJ·mol^{-1})
CoMoA$_w$	3.27·10^{-7}	9.05·10^{-7}	1.21·10^{-5}	96
CoMoT$_w$	1.14·10^{-6}	3.66·10^{-6}	1.72·10^{-5}	73
CoMoT$_e$	1.68·10^{-6}	5.22·10^{-6}	3.67·10^{-5}	83
CoMoA$_i$	1.52·10^{-7}	1.08·10^{-6}	7.18·10^{-6}	104
NiMoA$_w$	1.20·10^{-5}	2.16·10^{-5}	6.94·10^{-5}	47
NiMoT$_w$	3.48·10^{-7}	1.90·10^{-6}	1.51·10^{-5}	*102*
NiMoT$_e$	3.45·10^{-7}	1.73·10^{-6}	1.23·10^{-5}	96
NiWA$_w$	-	-	2.01·10^{-6}	-
NiWT$_w$	2.41·10^{-7}	6.80·10^{-7}	6.18·10^{-6}	87
NiWT$_e$	1.98·10^{-7}	7.74·10^{-7}	5.32·10^{-6}	89

Fig. (2). Conversion of phenol over reduced wet impregnated and EDF catalysts supported on titania (W= 0.2 g, F=0.25 ml/min, T= 350°C, P= 15 bar).

Summarizing the findings reported up to this point one can say that investigating the influence of various preparative parameters (composition, preparation method) on the HDO activity of the studied catalysts in their reduced form, the NiMoA$_w$ catalyst proved to be the most active and selective towards hydrogenation products. On the other hand taking into account the well known resistance of titania to water molecules and the very high activity of the CoMoT$_e$ catalyst, it seems that this catalyst is also a quite promising one for a stand-alone HDO process of bio-oil. Moreover, it is remarkable that the industrial catalyst exhibited lower activity than the aforementioned lab made catalysts as well as lower selectivity towards hydrogenation with respect to the NiMoA$_w$ catalyst, under the reactions conditions studied.

In view of the above we proceeded testing the aforementioned two catalysts and the industrial one in their sulfided form for the simultaneous HDO of phenol and HDS of dibenzothiophene, relevant to the co-processing strategy.

The HDO results obtained from these tests are depicted in Fig. (**3**). It can be seen that the CoMoT$_e$ catalyst exhibited higher activity than the NiMoA$_w$ one and comparable or slightly higher activity (depending on the reaction temperature) with respect to that exhibited by the CoMoA$_i$ catalyst. At this point we should mention that the laboratory developed CoMoT$_e$ sample has almost the half supported phases loading and SSA in comparison to the industrial CoMoA$_i$ catalyst (see Table **1**). All the above illustrate the

Table 3.   Products selectivity obtained upon phenol HDO at low conversion level (<10%) over the studied catalysts.

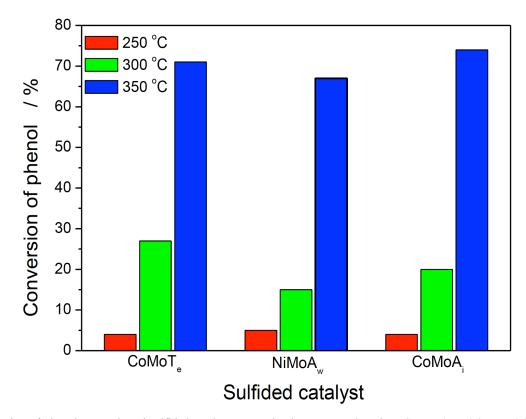| Catalysts	Methylcyclopentane	Cyclohexane	Cyclohexene	Benzene
$CoMoA_w$	53.1	19.7	7.4	19.8
$CoMoT_w$	-	75.8	9.4	14.8
$CoMoT_e$	3.5	66.5	11.1	18.8
$CoMoA_i$	56.3	15.7	14.4	13.9
$NiMoA_w$	-	81.7	9.5	8.7
$NiMoT_w$	-	74.7	14.9	10.5
$NiMoT_e$	-	77.3	12	10.7
$NiWA_w$	20.3	34.6	25.7	19.4
$NiWT_w$	-	64.7	-	35.3
$NiWT_e$	-	56	14.7	29.3

Fig. (3). Conversion of phenol over selected sulfided catalysts upon simultaneous HDO and HDS tests (W= 0.2 g, F=0.25 ml/min, Feed composition: 1% phenol and 1% dibenzothiophene in hexadecane, P= 15 bar).

favorable influence of the EDF method on the catalytic performance of the CoMoS phase in the HDO of phenol.

Comparing the phenol conversion values obtained over the lab made $CoMoT_e$ and $NiMoA_w$ catalysts in their reduced and sulfided forms (compare data from Figs. **1-3**) one can notice that the HDO activity of these samples is higher in a stand-alone process (where they are in reduced form) than that exhibited upon simultaneous HDO and HDS (where they are in sulfided form). However, one must not to forget that in the latter case the active sites are used not only for the phenol conversion but also for the conversion of dibenzothiophene.

On the other hand the HDO activity of the sulfided $CoMoA_i$ catalyst proved to be more than twice of that exhibited by this catalyst in the reduced form (compare data from Figs. **1**, **3**). This behavior should be related to the fact that this catalyst has been developed in order to work in the sulfided form.

Fig. (**4**) presents the dibenzothiophene conversion values obtained over the sulfided $CoMoTi_e$, $NiMoA_w$ and $CoMoA_i$ catalysts at various reaction temperatures upon simultaneous HDS and HDO experiments. An inspection of this figure shows that the lab made $NiMoA_w$ catalyst exhibited comparable if no slightly higher HDS activity than the
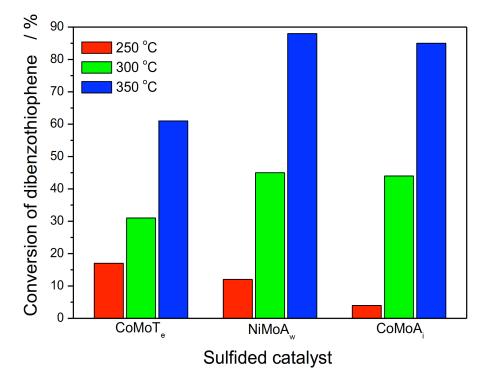
Fig. (4). Conversion of dibenzothiophene over selected sulfided catalysts upon simultaneous HDO and HDS tests (W= 0.2 g, F= 0.25 ml/min, Feed composition: 1% wt. phenol and 1% wt. dibenzothiophene in hexadecane, P= 15 bar).

industrial one. The $CoMoTi_e$ catalyst exhibited remarkable activity especially at lower reaction temperatures. Considering the lower active phases loading and SSA of this sample, it can be concluded that its intrinsic activity is at least comparable to that of the industrial $CoMoA_i$ catalyst.

CONCLUSION

The following conclusions are drawn from the present work.

1. The activity, for the HDO of phenol, over the reduced form of catalysts synthesized on γ-alumina by wet impregnation follows the order NiMo>CoMo>NiW whereas that for the catalysts synthesized on titania follows a different order (CoMo> NiMo>NiW). This points out the critical role of the support. Among the above catalysts the most active and selective towards hydrogenation products is the NiMo catalyst supported on γ-alumina. With the exception of the NiW catalysts, all the catalysts synthesized in the present work are proved to be more active for the stand- alone HDO processes than the industrial CoMo HDS catalyst supported on alumina.

2. The application of the EDF preparation technique, instead of the classical impregnation, increased considerably the activity of the CoMo catalyst supported on titania. Taking into account the much higher water resistance of titania with respect to γ-alumina this corresponds to the development of an extremely promising catalyst for stand-alone HDO processes.

3. The simultaneous HDO of phenol and HDS of dibenzothiophene studied over the wet impregnated

NiMo catalyst supported on alumina, the EDF CoMo catalyst supported on titania and the industrial CoMo catalyst supported on alumina showed that these catalysts exhibit comparable HDO activities while the first one is superior in HDS. Overall, taking into account the significantly higher loading of the industrial catalyst in the supported elements compared to the lab made catalysts, the latter seems to be quite promising, even in the frame of a co-processing strategy.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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