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STRUCTURAL AND TEXTURAL CHANGES OF HYDRODESULFURIZATION CATALYSTS IN CONDITIONS OF ACCELERATING AGING

UDC:

J. Kiurski¹, D. Ž. Obadović¹, A. Kapor¹ E. Kiš², R. Marinković-Nedučin²

¹ Faculty of Sciences, Institute of Physics, 21000 Novi Sad, Trg Dositeja Obradovića 4 ² Faculty of Technology, 21000 Novi Sad, Bulevar Cara Lazara 1, Yugoslavia

Abstract. The examination of stability of two types hydrodesulfurization catalysts $NiO(CoO)-MoO_3/\gamma-Al_2O_3$ shows different structural and textural changes originated in deactivation processes. The catalysts were expose to accelerated aging in the laboratory conditions in different atmosphere. The structural changes were follow by X-ray diffraction, diffuse reflectance spectroscopy and scanning electron microscopy. Cobalt based catalyst showed higher thermal stability in comparison to nickel promoted samples. The critical role of oxidizing atmosphere in catalyst aging caused by phase changes and chemical interactions accompanied by sintering is confirmed, with emphasis on steam atmosphere. Transitional appearance of MoO_3 phase is attribute to deactivation processes accompanied by partial loosing of active phase and forming a spinel-like structure of Ni(Co) ion.

Key words: Hydrodesulfurization, catalyst, aging, structure, texture

1. INTRODUCTION

The aging of the catalyst includes various physical and chemical changes of the initial structure of the catalyst. The physical and chemical processes of deactivation can occur independently, but most often they were relate and mutually conditioned, which makes the deactivation mechanism specially complicated. Thermal deactivation is caused by long-term work at relatively high temperature of hydrodesulfurization (HDS) process as well as by temperature gradient in catalyst bed. Thermal deactivation of the catalyst can be hardly separate from the chemical one, since the processes of sintering, phase segregation, phase transformations, alloy formation and the interaction of the active

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component and the support which take place at high temperatures, are as a rule accompanied by certain chemical reactions, like solid state reactions occurring at the surface and in the bulk of the catalyst grain.

Our previous studies of the process of aging of the HDS catalysts have shown that oxidizing atmosphere is the critical factor in kinetics of structural and textural changes [1] and that sintering is one of the main processes which cause the decay of the activity in unsuitable regeneration conditions [2].

In this paper we have performed the comparative studies of the stability of two types of the commercial HDS catalyst, NiO-MoO₃/ γ -Al₂O₃ and CoO-MoO₃/ γ -Al₂O₃, as the function of laboratory simulated of catalyst aging. The aim of the paper was to determine the possible deactivation mechanism based on structural and textural changes.

2. EXPERIMENT

Two types of standard commercial industrial catalysts were chosen:

NiO-MoO₃/ γ -Al₂O₃ = NiMo CoO-MoO₃/ γ -Al₂O₃ = CoMo

Three different atmospheres: air, steam and nitrogen were applied in the experiments of accelerated aging. The choice of atmosphere is based on the real conditions of the regeneration processes of HDS catalysts. Comparatively high treatment temperature $(500 - 800 \ ^{0}C)$ was applied taking into account the exothermal character of the regeneration reaction, possible appearance of the hot spots in catalysts bed.

The thermal treatment were performed in a flow system, with sample (cca. 3 g) located in the quartz U-tube ($\phi = 15$ mm) in the vertical muffle furnace with controlled temperature (± 10 ⁰C).

The structure of the catalyst was characterized by X-ray diffraction (XRD) (Philips, PW 1050 CuK α), diffuse reflectance spectroscopy (DRS) (SPM-2 monochromator Veb Zeiss, Jena) with reflection cell of the R-45/0 type and scanning electron microscopy (SEM) (JEOL, ISM 35). Low-temperature nitrogen adsorption (LTNA) (Micromeritics, ASAP 2000) was applied for textural examination.

3. RESULTS AND DISCUSSION

The results of XRD analyses point out that in the temperature interval up to 600 0 C (Fig. 1) there are no remarkable changes of catalyst phase compositions independently of promoter type, atmosphere and time of treatment. Minor textural changes (Table 1) registered in this temperature interval can be connected with increasing of crystallinity γ -Al₂O₃ as support.

First significant structural changes were observed at treatment of 700 ^oC in oxidizing atmosphere (air, steam). Segregation of active phase, initial chemical interactions between molybdenum phase and support forming aluminium-molybdate were observed besides partial transformation of support to more stable transitional alumina form (Fig. 1). In inert nitrogen atmosphere no qualitative changes of structure at this temperature were

registered. The results indicate the influence of promoter type on kinetics of structural changes in oxidizing atmosphere, with relatively higher thermal stability of catalysts based on cobalt promoter (Fig. 1, Table 1). Using the Scherer equation [3] crystallite size of γ -Al₂O₃ for crystallographic plane [400] (Table 2) were determined. The changes of crystallite size in function of temperature and time of treatment properly illustrate previously semiquantitative observations concerning the trends of support crystallization.



Fig. 1. XRD patterns of catalysts thermally treated in air atmosphere.

Treatment	Surface area (m^2/g)				
duration (h)	500 ⁰ C	600^{0} C	700^{0} C	800^{0} C	
Fresh	255.3				
1	260.3	248.3	179.4	76.8	
9	228.3	180.9	115.1	47.4	
Fresh	239.6				
1	249.9	240.6	167.5	65.5	
9	245.0	202.7	107.5	49.4	
	Treatment duration (h) Fresh 1 9 Fresh 1 9	Treatment duration (h) 500°C Fresh	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Treatment duration (h)Surface area (m^2/g) fresh 500^{0} C 600^{0} C 700^{0} CFresh 255.3 1 260.3 248.3 179.4 9 228.3 180.9 115.1 Fresh 239.6 1 249.9 240.6 167.5 9 245.0 202.7 107.5	

Table 1. Surface area of catalysts thermally treated in air atmosphere

Table 2. Crystallite size of γ-Al₂O₃ for crystallographic plane [400] in HDS catalysts thermally treated in air atmosphere

Catalyst	Treatment	Treatment Crystallite size (nm		
sample	duration (h)	700^{0} C	$800^{0}C$	
NiMo	1	8.1	12.7	
	9	12.3	16.8	
СоМо	1	7.1	10.7	
	9	9.5	16.1	

Formation of spinel-like structure on temperatures up to 700 ^oC confirmed the changes in coordination of promoter ion of both catalyst types in all treatment atmospheres (Table 3, Fig. 2), pointing out the delicate microstructure changes of system [4].

In both catalyst types besides bands on $\sim 11 \times 10^3$, $\sim 13 \times 10^3$ and $\sim 26 \times 10^3$ cm⁻¹, which can be ascribed to electronic transitions of d-d type of Ni(II) ion in octahedral coordination, a band on $\sim 17 \times 10^3$ cm⁻¹ at temperatures higher than 700 °C was observed. On the basis of distribution of the positions and intensities of the maxima of this band it can be supposed that it results probably from the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transitions, indicating a tetrahedral environment of Ni(II) ion. With temperature increase relative intensity of this band increases too (R decrease, Fig.3), while intensities of d-d transitions bands of octahedral centers Ni(II) ions decrease, which point out the increase of inversion and in that way the incorporation of nickel ion into the support structure. The same types of structural changes were registered in Co-based catalyst (Table 3).

Table 3. Electronic spectral data of Ni(II) and Co(II) in HDS catalysts thermally treated in air atmosphere

NiMo			СоМо				
Transition -	$v \cdot 10^3 (\text{cm}^{-1})$		Transition	$v \cdot 10^3 (\text{cm}^{-1})$			
	Fresh	$700^{0}C$	800^{0} C	Transition	Fresh	$700^{0}C$	$800^{0}C$
$^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)$	11.2	10.8	10.8	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$	10.8	10.4	10.4
$^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)$	15.2	13.0	13.8	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$	13.2	13.2	13.2
${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$	-	17.0	17.0	${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$	-	16.2	15.2
							16.2
$^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)$	25.8	26.4	26.6	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$	17.2	17.2	17.2
		27.2	27.4				
				CT	26.2	26.3	26.4
IL_1	33.5	33.0	33.0	IL_1	32.4	32.4	34.0
IL ₂	42.0	40.0	40.0	IL ₂	40.8	40.8	40.8
Simetry	O _h	O_h+T_d	O _h +T _d	Simetry	O _h	O _h +T _d	O _h +T _d



Fig. 2. DRS spectra of NiMo catalyst thermally treated (800 ⁰C) in various atmospheres.



Fig. 3. DRS spectra of NiMo catalyst thermally treated in air atmosphere.

Both catalysts showed similar structural changes registered by XRD method (Fig.1 and 4) treated in various atmospheres on 800 0 C.

In all atmospheres the phase of aluminium-molybdate $(2\theta \sim 23.3, 26.2, 28.8^{0})$ is present in both catalyst samples with significant increase of content and crystallite size as a function of treatment duration (Fig.5). Besides γ -Al₂O₃ (Table 2) of higher crystallinity, small quantity of κ - ($2\theta \sim 34.6, 42.3, 67.0^{0}$) and θ -modifications ($2\theta \sim 19.0, 30.8, 36.6,$ 54.3⁰) are present depending on promoter type, with additional indication of the presence of cobalt-molybdate and cobalt(II) oxide in CoMo samples (Fig.1). However, lower intensity of all diffraction maxima of CoMo in comparison to NiMo catalyst samples confirms the lower crystallinity of cobalt-base catalyst treated in the same conditions.



 $1 - \gamma - Al_2O_3; 2 - \kappa - Al_2O_3; 3 - Al_2(MoO_4)_3; 4 - Mo_4O_{11}; 5 - MoO_3;$ $6 - θ - Al_2O_3; 10 - NiAl_2O_4; 11 - NiMoO_4$ Fig. 4. XRD patterns of NiMo catalyst thermally treated (800 ⁰C) in various atmospheres.



Fig. 5. Characteristic diffraction maximum $(2\theta \sim 23.4^{\circ})$ of aluminium-molybdate in catalysts thermally treated in air atmosphere as a function of treatment duration.

Intensity of structural changes is remarkably higher in oxidizing than in inert atmosphere, specially regarding the segregation of active phase, with somewhat higher thermal stability of Co-based catalyst. Presence of free MoO_3 phase in oxidizing atmosphere (Fig. 4) creates possibility of liquid phase formation on catalyst surface and essential influenced on sintering and recrystallisation kinetics. The formation of this phase is specially remarkably in steam atmosphere (Fig. 6), with pronounced evaporation from the system, confirmed by condensation of fine orthorhombic crystals of MoO_3 in outlet of flow laboratory system for thermal treatment.



Fig. 6. SEM micrographs of catalysts thermally treated in steam at 800 ^oC (magn. 300×).

Structural changes on temperature higher than $700 \, {}^{0}\text{C}$ are followed by significant textural changes, which confirm previous observation about critical role of temperature and oxidizing atmosphere [4]. Summary review of surface area changes (Fig. 7), as basic

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textural characteristic, properly illustrate a critical influence of oxidizing atmosphere on the sintering kinetics of NiMo and CoMo systems. Higher textural stability of CoMo catalyst is also confirmed.



Fig. 7. Surface area of catalysts as a function of temperature and atmosphere of treatment (CoMo-S and CoMo-N are the catalyst samples from two lots of the same origin).

4. CONCLUSION

The results of laboratory simulated hydrodesulfurization catalyst aging confirmed that the oxidizing atmosphere, especially steam atmosphere, have a critical role in rapid structural and textural changes. Since therefore oxidative regeneration is the most sensitive phase in exploitation cycle of hydrodesulfurization process. Comparative analyses of structural and textural changes of the catalysts point out the dominant influence of temperature regime on nature and intensity of initial structural and textural changes with 800 ^oC as break temperature for rapid sintering based on liquid phase mechanism.

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STRUKTURNE I TEKSTURALNE PROMENE KATALIZATORA ZA HIDRODESULFURIZACIJU U USLOVIMA UBRZANOG STARENJA

J. Kiurski, D. Ž. Obadović, A. Kapor, E. Kiš, R. Marinković-Nedučin

Izvršena su ispitivanja stabilnosti dva tipa katalizatora za hidrodesulfurizaciju, NiO(CoO) – MoO₃/ γ – Al₂O₃, pri ubrzanom starenju u laboratorijskim uslovima. Strukturne promene, nastale deaktivacijom, registrovane su metodama difrakcije x-zraka, difuzne refleksione spektroskopije i skenirajuće elektronske mikroskopije. Na osnovu struktirnih i teksturalnih promena ustanovljena je relativno veća termička stabilnost katalizatora na bazi kobalta u odnosu na katalizator na bazi nikla. Rezultati ispitivanja su pokazali da je oksidaciona atmosfera kritičan faktor u kinetici strukturnih i teksturalnih promena; posebno je kritična atmosfera vodene pare. Intermedijarno izdvojena faza MoO₃ ukazuje na pad aktivnosti katalizatora, praćenim gubitkom aktivne komponente iz sistema i formiranjem spinelne strukture Ni odn. Co–jona.

Ključne reči: hidrodesulfurizacija, katalizator, starenje, struktura, tekstura