

## Synthesis MnMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Oxidative Desulfurization Catalyst and Optimized the Operating Conditions of the Catalytic ODS Method of Condensate

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The purpose of this research is to investigate the effect of catalyst and oxidant content, temperature and time of the catalytic oxidative desulfurization method of the condensate. Before assessing these parameters, the mesoporous 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by incipient wetness impregnation method. The prepared catalysts were determined by X-Ray Diffraction, N<sub>2</sub>-adsorption/desorption, Inductively Coupled Plasma Mass Spectrometry, Scanning Electron Microscopy and NH<sub>3</sub>-Temperature Programmed Desorption. The catalytic activity was analyzed with catalytic oxidative desulfurization setup with condensate as feed with 1500 ppm total sulfur. In order to achieve the desired conditions of the catalytic oxidative desulfurization method, different quantities of catalyst, oxidants, temperature and time of the catalytic oxidative desulfurization method were studied. The most favorable case of the catalytic oxidative desulfurization method was 1g 5%Mn10%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 1 ml H<sub>2</sub>O<sub>2</sub> as an oxidant, 30 °C and 120 min. At this optimum condition the total sulfur of condensate reached from 1500 to 123 ppm.

**Keywords:** Catalytic oxidative desulfurization method, MnMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, Oxidative desulfurization of condensate

### INTRODUCTION

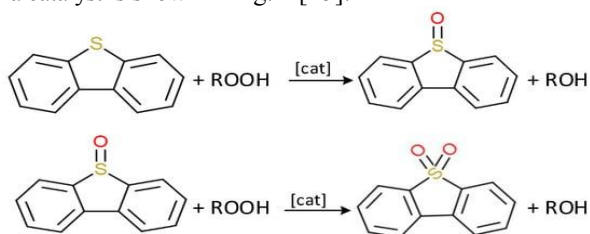
The hydrodesulfurization (HDS) method is the common method of decreasing sulfur components of the condensate. This method is the most useful method for removing some thiophen derivatives and aliphatic sulfur compounds. This method is done under high temperature, high pressure and in the presence of specific catalysts [1,2]. Despite of the advantages, the HDS method is unable to meet extremely low sulfur standard due to the limitations in the treatment on dibenzothiophenes (DBTs) and benzothiophenes (BTs) [3]. In comparison with HDS method, the catalyst oxidative desulfurization (ODS) method is the better option for reducing sulfur compounds in condensate. Hence, the organic refractory of sulfur components are oxidized to their related sulfones. These products can be separated by distillation, adsorption, decomposition or extraction [4]. In the catalytic ODS method, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is

generally used as suitable oxidizing reagent because it is nonpolluting and low price. In addition, it is not an intense corrosive agent and it is commercially available. When there is not catalyst in the reaction, H<sub>2</sub>O<sub>2</sub> is considered as a strong oxidizing reagent. Some researchers have used organic acids, and polyoxometalate acids and their salts in the aqueous solution, as catalysts in the oxidation with H<sub>2</sub>O<sub>2</sub> of organosulfur compounds to the sulfones. It is hard to separate homogeneous catalysts from the reaction products. But, produced the new catalysts is the most favorable progression in the catalytic ODS method [5-7].

Catalytic ODS is performed in two steps. In the first step, sulfur compounds oxidized as a result of a chemical reaction between an oxidizing agent and sulfur. Heavy sulfur compounds are oxidized to sulfone and sulfoxide by taking one and two oxygen atoms (without breaking the C-S bond). The oxidizing agents that are used in this step are inorganic and organic acid, peroxides and, catalyzed hydroperoxies, peroxy salts, nitrogen and ozone dioxide [8-11]. Another oxidant that can be used in the catalytic

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oxidative desulfurization method is hydrogen peroxide with low environmental pollution [4]. In the second step, the oxidized sulfur is extracted from oil due to increase the polarity of the solvent [12-14]. In this method, after converting sulfur compounds to sulfone, they are extracted by methods such as adsorption, distillation and extraction. Oxidation of thiophene derivatives to sulfonates increases their molecular weight and polarity that facilitates separation by distillation, extraction, and adsorption. The oxidation mechanism of 4,6-dimethyl dibenzothiophene (DBT) under mild operating conditions and in the presence of a catalyst is shown in Fig. 1 [15].



**Fig. 1.** The catalytic ODS mechanism of DBT reactions.

In refineries, sulphones are removed with high polarity solvents such as acetonitrile, methanol, dimethyl sulfoxide and dimethylformamide [16]. In the catalytic ODS method, sulfur removal is mostly performed by using solvents that can be recycled and regenerated by distillation method [10]. Another way to remove sulfones is adsorption with suitable adsorbents [17,18]. Some adsorbents like silica gel and silica-alumina are more efficiently sulfonates adsorbents than gamma alumina, zeolites and activated carbon [19].

The Unipure and Sulphu method are two new oxidative desulfurization technology that have been marketed to produce extremely low sulfur oil. The two ODS methods is different in the oxidative process, the sulfone separation process and the type of oxidizing agent [19-22].

In the Sulphu method, ultrasonic energy is applied for ODS and causes to increase the percentage of sulfur removal of condensate. Hydrogen peroxide ( $H_2O_2$ ) is consumed as an oxidant agent. Ultrasonic energy causes to induce cavitation, so that in the present of  $H_2O_2$  as an oxidant agent, it consequences to fast reaction. Simultaneous as cavitation, bubbles get bigger, go unstable, and dissipate, increase in mixing. As well as, ultrasonic

energy increases the rate of the reactions by increasing the level of molecular energy [20]. This method is performed under atmospheric pressure at the temperature 80-70 °C [10].

The Unipure method is developed by Texaco and Unipure. The sulfur compounds are oxidized to sulfone by using a combination of  $H_2O_2$  and formic acid as an oxidant agent. The sulfone is separated, washed and dried. Then, it is crossed through an alumina adsorbent to dispart the sulfonates, and then it is refined by washing with methanol. In this method all of the steps are performed at mild temperature and pressure. The obtained sulfonate is sent to the refinery coking unit [21,22]. The advantages of the Unipure method is low price, low pressure, temperature, and reaction time, and no hydrogen gas consumption. By this method, gasoline fuel and diesel with more than 1500 ppm sulfur can convert to products with sulfur content less than 5 ppm. The costs of this process is less than 50% of HDS method [22].

Chemical properties of the most ODS catalysts are the same. However, differences in the production process affected on their activity, mechanical strength and performance [23]. Gamma alumina is the best catalyst support because of its specific surface area ( $170-270 \text{ m}^2 \text{ g}^{-1}$ ), pore volume ( $0.5-0.8 \text{ cm}^3 \text{ g}^{-1}$ ) and reasonable price [22].

Wagas *et al.* (2021) [24] designed an oxidative desulfurization (ODS) of modeled and real oil samples by using magnetic-reduced graphene oxide nanocomposite ( $MnO_2/MrGO$ ), manganese-dioxide-supported as a catalyst in the presence of an  $H_2O_2/HCOOH$  oxidation agent. The optimum conditions for maximum dibenzothiophene (DBT) removal from modeled oil samples were found to be efficient at 40 °C temperature and 60 min reaction time, 0.08 g catalyst dose/10 ml, and 2 ml of  $H_2O_2$ /formic acid, under which  $MnO_2/MrGO$  exhibited intense desulfurization activity of up to 80%. Under the same conditions, the removal of only 41% DBT was observed in the presence of graphene oxide (GO) as the catalyst, which clearly indicated the advantage of  $MrGO$  in the composite catalyst. Under optimized conditions, sulfur removal in real oil samples, including diesel oil, gasoline, and kerosene, was found to be 67.8%, 59.5%, and 51.9%, respectively. The present approach is credited to cost-effectiveness, environmental benignity, and ease of preparation, envisioning great

prospects for desulfurization of fuel oils on a commercial level. Liu *et al.* (2021) [25] prepared Mn-Based catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and MCM-4. These catalysts were synthesized by an impregnation method were compared to evaluate their NO catalytic oxidation performance with low ratio O<sub>3</sub>/NO at low temperature (80-200 °C). Results of the activity tests showed that the participation of O<sub>3</sub> remarkably increased the NO oxidation. The ODS performance of the catalysts decreased in the following order: Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > Mn/ TiO<sub>2</sub> > Mn/MCM-41. The results indicated that Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> display the best ODS catalytic activity. Wang *et al.* (2018) [26] prepared MnOx-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powdered and analyzed the catalyst activity through self-propagating high-temperature synthesis (SHS) and impregnation methods. The SHS method has a fewer catalyst preparation cycle and simpler preparation method rather than the other impregnation methods. The characterization results showed that mixed crystals of cerium, aluminum, and manganese oxides were formed through the SHS method, the binding energy of Mn<sup>4+</sup> increased, and the active components were distributed uniformly. The BET results of MnOx-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powdered catalyst showed extensive pore volume (0.17 cm<sup>3</sup> g<sup>-1</sup>), and an average pore diameter (5.1 nm). Then, the MnOx- CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> powdered catalyst achieved a NOx conversion higher more than 80% at 100-250 °C. Beshkoofeh *et al.* (2021) [27,28] investigated the effect of pH, molybdenum content and some of the transition metals (such as Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel) on the catalyst properties and performance of oxidative desulfurization. The catalytic activity was measured with catalytic ODS setup. The catalyst with 10wt%Mo (as an active metal) and 5wt%Co content (as a promoter) at pH = 4 represented the optimum performance for oxidative desulfurization.

This work represents the preparation, characterization of the mesoporous 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Moreover, the as-synthesized catalyst was characterized by Scanning Electron Microscopy (SEM), NH<sub>3</sub>-Temperature Programmed Desorption (NH<sub>3</sub>-TPD), N<sub>2</sub>-adsorption/desorption, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and X-Ray Diffraction (XRD). The prepared catalyst is used to the catalytic ODS method of condensate with 1500 ppm sulfur. The operating conditions of catalytic

ODS are investigated in different amount of the oxidant, catalyst, time and temperature. According the results of the catalytic ODS method, optimized operating conditions was selected.

## EXPERIMENTAL

### Materials

The boehmite powder with the Surface Area (SA) > 205 m<sup>2</sup> g<sup>-1</sup>, Pore Volume (PV) = 0.47 cm<sup>3</sup> g<sup>-1</sup>, Average Pore Diameter (APD) = 8.08 nm, 100 mesh was used as the precursor. Table 1 shows all materials with their specifications which are used in this project.

**Table 1.** Specifications of the Raw Materials

No.	Chemical name	Purity	Company
1	Hydroxyethyl cellulose	Industrial grade	Iran
2	Ammonium hepta molybdate tetra hydrate	99%	Merck, germany
3	Manganese(II) nitrate	98%	Merck, germany
4	Distilled water	Industrial grade	Iran
5	Hydrogen peroxide	Industrial grade	Iran
6	Acetonitrile	Industrial grade	Iran
7	Methanol	Industrial grade	Iran
8	Phosphoric acid	Industrial grade	Iran
9	Ammonia	Industrial grade	Iran

### Analysis Equipment

The XRD patterns of the prepared catalysts were described with a P analytical X' Pert Pro model with a CuK $\alpha$  anti cathode ( $\lambda$  = 1.54 Å; 40 kV; 40 mA) between 5°-

85° for 20. It uses a 0.1° step with an integration time of 4 s. The pore volume and specific surface area of prepared catalysts were evaluated by using N<sub>2</sub>-adsorption/desorption porosimetry (Belsorp mini II, BEL JAPAN). All prepared catalysts were clearing at the temperature of 250 °C for 3 h under vacuum before analysis (Belprep vac II, BEL JAPAN). This analysis was made in liquid nitrogen at -196 °C. The N<sub>2</sub>-adsorption/ desorption isotherms are used to specify the Brunauer-Emmett-Teller (BET) specific surface area. Pore volume and pore diameter distribution were determined by using the Barrett-Joyner-Halenda (BJH) method of the isotherm. The total pore volume was assessment from the N<sub>2</sub> uptake value at P/P<sub>0</sub> = 0.98 (ISO 15901-2-2006, ISO 15901-3-2007). The surface morphology of the prepared catalysts was accomplished by using Scanning Electron Microscopy (SEM) by ZEISS (Germany) SIGMA VP. NH<sub>3</sub>-TPD analysis was done with Micromeritics ChemiSorb 2750 apparatus. ICP-MS was done with PerkinElmer, Optima 7300 model (U.S.A.).

Additionally, the catalytic oxidative desulfurization activity test is done under the special feed with 1500 ppm of sulfur. The total sulfur of each case were characterized by Rigaku devices (U.S.A.) with semiconductor Silicone PIN diode detector pursuant to ASTM D: 4294.

### Catalytic Oxidative Desulfurization Activity

Catalytic oxidative desulfurization method was done in a 100 ml jacketed round-bottom flask with recirculation water bath to control temperature and pressure, magnetic stirrer and a condenser. The 50 ml of condensate (1500 ppm total sulfur) was applied as feed in the bottom flask. In a common experiment, the prepared 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and H<sub>2</sub>O<sub>2</sub> were mixed under the strong stirring speed in feed. Then, the mixtures were left at 25°C. After, the oil part of samples was extracted with the suitable agent for three times. The total sulfur was defined by Rigaku devices. Table 2 shows the specification of the condensate.

**Table 2.** Specifications of the Condensate

No.	Analysis	Unit	Result	Method
1	Appearance	-	yellow liquid	Visual
2	Density at 15.6 °C	kg m <sup>-3</sup>	736.1	ASTMD1298
3	Total sulfur	ppm	1500	ASTMD4294
4	Flash point	°C	free	ASTMD93
5	Corrosion at 50 °C	-	1a	ASTMD130
6	Distillation-IBP	°C	75	ASTMD86
7	Distillation-5%	°C	90	ASTMD86
8	Distillation-10%	°C	95	ASTMD86
9	Distillation-20%	°C	101	ASTMD86
10	Distillation-30%	°C	106	ASTMD86
11	Distillation-40%	°C	111	ASTMD86
12	Distillation-50%	°C	115	ASTMD86
13	Distillation-60%	°C	119	ASTMD86
14	Distillation-70%	°C	125	ASTMD86
15	Distillation-80%	°C	134	ASTMD86
16	Distillation-90%	°C	146	ASTMD86
17	Distillation-95%	°C	162	ASTMD86
18	Distillation-FBP	°C	192	ASTMD86
19	Distillation-residue	Vol. %	1	ASTMD86
20	Distillation-loss	Vol. %	0	ASTMD86
21	Distillation at 380 °C	Vol. %	-	ASTMD86

### The Preparation Extrudates 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

Boehmite powder was mixed with 5% hydroxyethyl cellulose (HEC). That time, the powder was mixed with sufficient water (about 5 ml). In order to obtain a homogeneous paste, the mixture was kneaded. Then the paste was crossing through the extruder and dried for 2 h at 25 °C. Afterwards, it was dried in an oven at 120 °C for 24 h. Finally, it was calcined up to 600 °C in the furnace with temperature programming rate of 100 °C h<sup>-1</sup> to get the catalyst support. In this section, the gamma alumina phase is appeared from the boehmite powder. Appropriately, the catalyst support had the subsequent specifications (length = 2-8 mm, outer diameter = 1.70 mm, SA = 155-205 m<sup>2</sup> g<sup>-1</sup>, PV < 0.75 cm<sup>3</sup> g<sup>-1</sup>, APD = 13.58 nm). 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was made by primary wetness impregnation method. According to needed weight percent of Mo and Mn, 0.93 g of ammonium hepta molybdate and 1.53 g Manganese(II) nitrate was dissolved in a particular volume of distilled water, in order to require of 15%Mo and 10%Mn. Then two solution were blended with 0.35 g phosphoric acid. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst support was placed in the rotary evaporator at 50 °C for 2 h with the solution of the mixed of the salts. Afterwards, the wet  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was impregnated in a thermal cabinet with the thermal programming rate of 10 °C/20 min in the temperature range of (50-120) °C. The samples were dried in an oven at 120 °C for 24 h. In order to fix up molybdenum on alumina, it must appear molybdenum oxide. So, the catalyst was calcined up to 600 °C in a furnace with temperature programming rate of 100 °C h<sup>-1</sup>.

### The Effect of Oxidant Agent (H<sub>2</sub>O<sub>2</sub>) Content on the Catalytic ODS

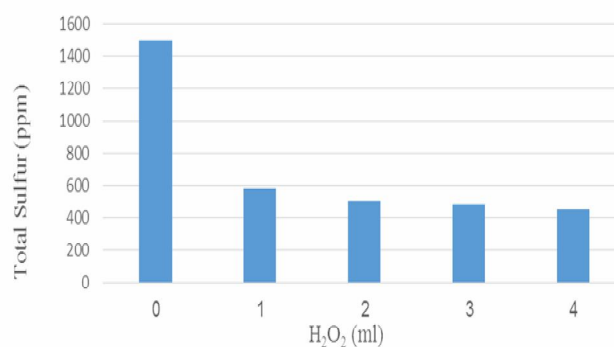
Catalytic ODS experiments were made as the same as the section 2.3. In a typical experiment, H<sub>2</sub>O<sub>2</sub> with various amount (0, 1, 2, 3, 4 ml) were mixed with the condensate under the vigorous stirring speed. After, the mixtures were kept at 30 °C. Then the oil phase of samples was separated with extracted agent for three times. Table 3 and Fig. 2 show the results of the ODS microreactory test with various amount of H<sub>2</sub>O<sub>2</sub>.

**Table 3.** The Results of the Catalytic ODS Microreactory Test with Various amount of H<sub>2</sub>O<sub>2</sub>

H <sub>2</sub> O <sub>2</sub> (ml)	0	1	2	3	4
Total sulfur (ppm)	1500	582	507	487	452

**Table 4.** The Results of the Catalytic ODS Microreactory Test with Various amount of 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

CoMoP/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (g)	0	0.5	1	1.5	2
Total sulfur (ppm)	582	423	257	215	199



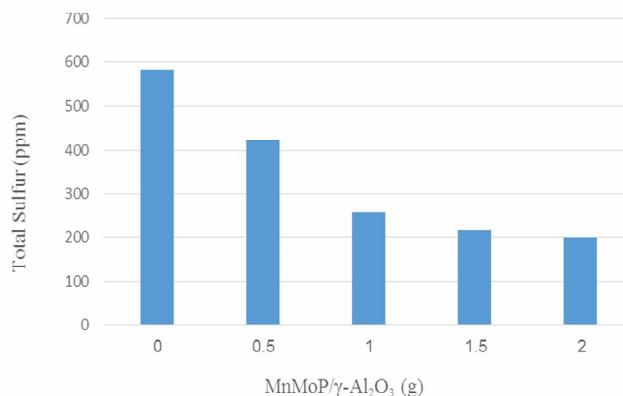
**Fig. 2.** The results of the catalytic ODS microreactory test with various amount of H<sub>2</sub>O<sub>2</sub>.

### The Effect of the MnMoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst Content on the Catalytic ODS

Catalytic ODS experiments were done as the same as section 2.3. In a typical experiment, the 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with various amount (0, 0.5, 1, 1.5, 2 g) were slowly mixed with condensate and 1 ml H<sub>2</sub>O<sub>2</sub> under the vigorous stirring speed. After, the mixtures were kept at 30 °C. Then the oil phase of samples was separated with extracted agent for three times. Table 4 and Fig. 3 show the results of the ODS microreactory test with various amount of 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

### The Temperature Effect on Catalytic ODS

Catalytic ODS experiments were done as the same as



**Fig. 3.** The results of the catalytic ODS microreactory test with various amount of 10%Mn15%Mo0.5%P/γ-Al<sub>2</sub>O<sub>3</sub> catalyst.

previous section at various temperature (30, 40, 50, 60 and 70 °C). The mixtures were kept at 30 °C. Then, the oil phase of samples was separated with extracted agent for three times. Table 5 and Fig. 4 show the results of the catalytic ODS microreactory test with various temperature.

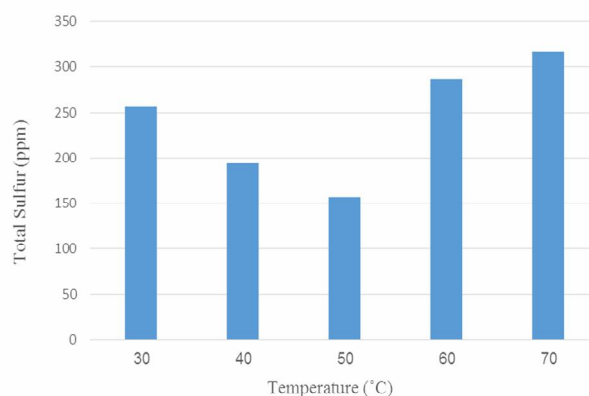
### The Time Effect on Catalytic ODS

Catalytic ODS experiments were done as the same as section 2.6 in various time (30, 60, 90, 120 and 150 min). Then the oil phase of samples was separated with extracted agent for three times. Table 6 and Fig. 5 show the results of the catalytic ODS microreactory test with various time.

## RESULTS AND DISCUSSION

### Catalyst Characterization

Catalyst preparation method can also play an important role in evaluating the performance of the catalytic ODS method. Table 7 shows the physical chemistry specifications, the content of γ-Al<sub>2</sub>O<sub>3</sub> catalyst support and 10%Mn15%Mo0.5%P/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. The N<sub>2</sub>-adsorption/desorption results shows that the amounts of SA, APD and PV of 10%Mn15%Mo0.5%P/γ-Al<sub>2</sub>O<sub>3</sub> reduced with impregnation two metals on the γ-Al<sub>2</sub>O<sub>3</sub> catalyst support [29]. The pore size distribution of the prepared catalysts that were measured by BJH method was shown in Fig. 6. The figure shows that the prepared catalyst has a



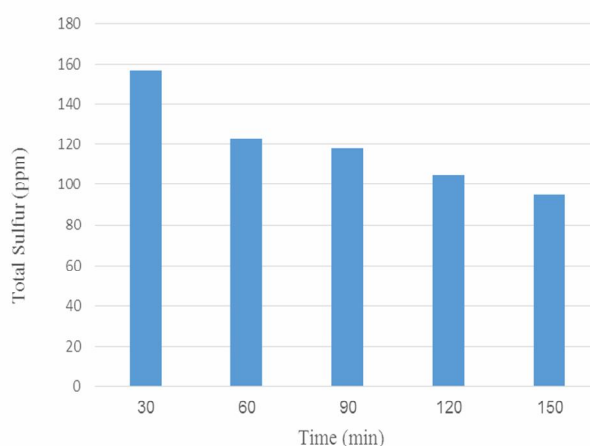
**Fig. 4.** The results of the Catalytic ODS microreactory test with various temperature

**Table 5.** The Results of the Catalytic ODS Microreactory Test with Various Temperature

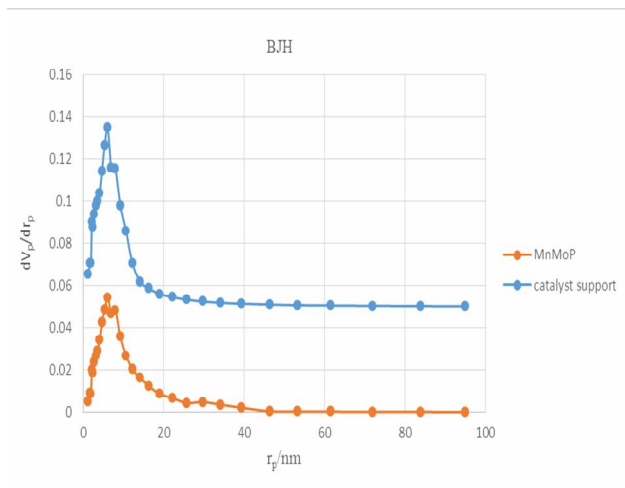
Temperature (°C)	30	40	50	60	70
Total sulfur (ppm)	257	194	157	286	317

**Table 6.** The Results of the Catalytic ODS Microreactory Test with Various Time

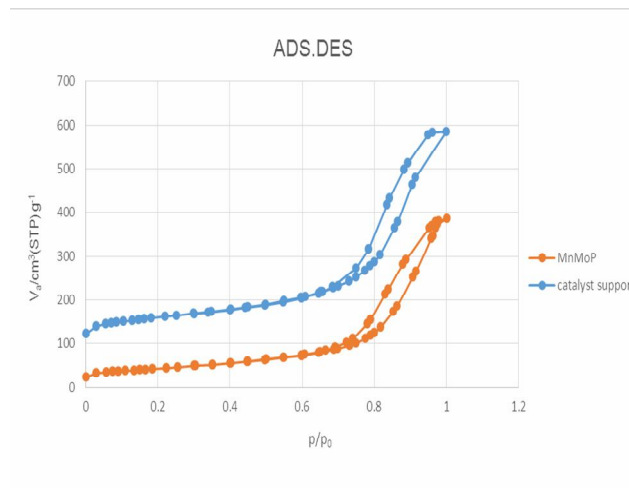
Time (min)	30	60	90	120	150
Total sulfur (ppm)	157	123	118	105	95



**Fig. 5.** The results of the Catalytic ODS microreactory test with various time.



**Fig. 6.** BJH plot of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.



**Fig. 7.** Adsorption/desorption isotherms of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

**Table 7.** The BET, BJH Results of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

Catalyst	BET		BJH (Adsorption branch)			
	Average pore diameter (nm)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore radius (nm)	Surface area (m <sup>2</sup> g <sup>-1</sup> )
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	13.58	215.43	0.75	0.75	6.03	237.97
10%Mn15%Mo0.5%P/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	15.51	151.46	0.58	0.58	6.03	155.98

**Table 8.** ICP-MS Results of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

Catalyst	Al wt. %	Mo wt. %	Mn wt. %	P wt. %
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	54.97	-	-	-
10%Mn15%Mo0.5%P/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	54.93	14.31	9.02	0.48

uniform mesoporous structure. According to the Fig. 7 and IUPAC classification, all of the prepared 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts showed type IV isotherms with H<sub>2</sub> hysteresis loop. Most of mesoporous materials owing to complex pore networks are made up of

pores with wide pore size distribution [29].

Table 8 shows the results of ICP-MS analysis of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst support and prepared 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst [30]. The presence of phosphorus is often used as a secondary promoter. To

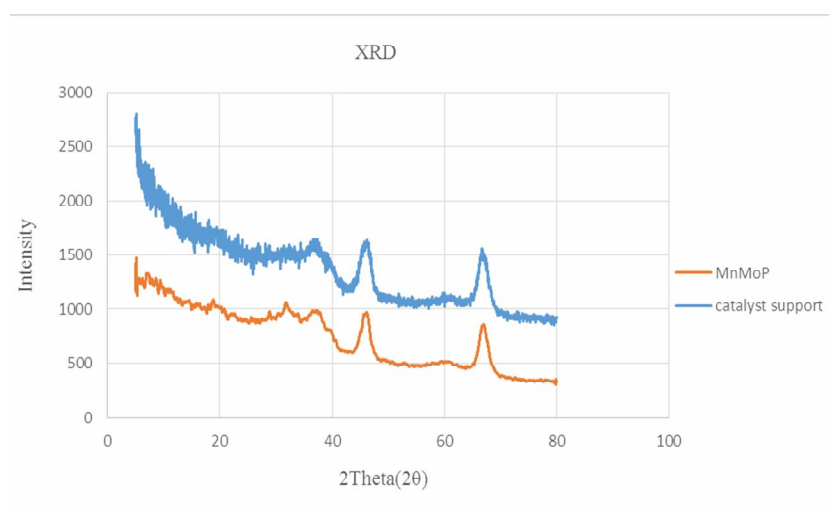


modify the efficiency of the catalyst for catalytic ODS by having a useful influence, addition of phosphoric acid during the catalyst synthesis is needed. The increased influence of phosphorus on the activity of a catalyst is sometimes described as a function of an improvement of dispersion of the precursor on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Due to the great solubility of the metal salts on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the phosphoric acid-containing impregnation solution, the deposition of large crystalline aggregates on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface is minimized [30].

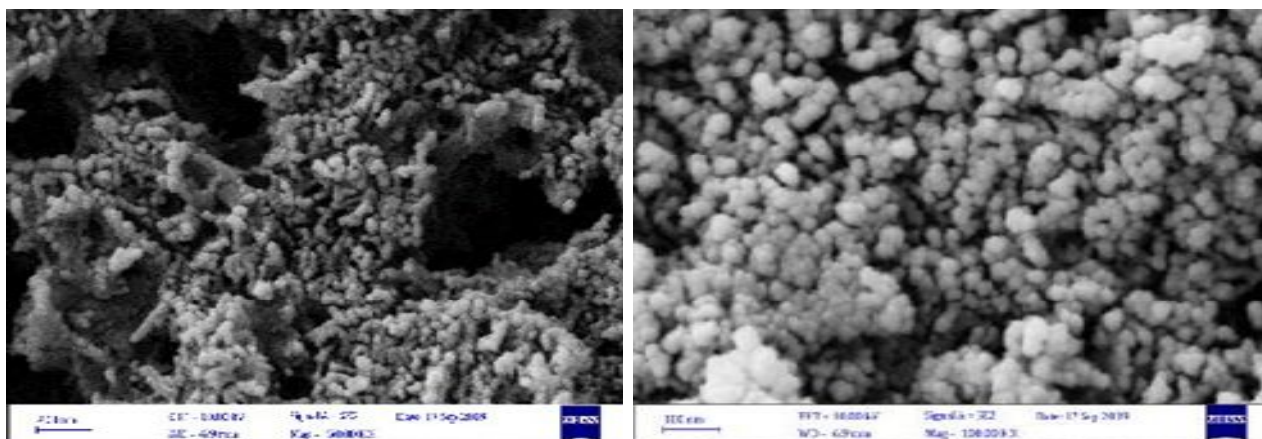
XRD technique was used to gain insight about the crystallinity of catalyst, chemical component and presence Mn and Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts. XRD analyses

were done at  $2\theta$  (5°-80°) and the scans are shown in Fig. 8. Two sharp diffraction peaks that appeared at  $2\theta$  (45° and 67°) for all samples are appointed to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It is concluded that the impregnation of manganese and molybdenum did not effect on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystalline phase of catalyst support [31]. The results of XRD analysis can be confirmed that almost two metals appeared at their previously reported peaks, Manganese oxide (Mn<sub>2</sub>O<sub>3</sub>) at  $2\theta = 17^\circ, 26^\circ, 28^\circ, 32^\circ, 33^\circ, 37^\circ, 40^\circ, 45^\circ$  and  $67^\circ$  [32]. Two peaks exist at  $2\theta = 45^\circ$  and  $67^\circ$  for Mn<sub>2</sub>O<sub>3</sub>. They are near to specific peaks of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and it can be assigned to the overlap of Mn<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [33].

Figure 9 shows the SEM images, and indicates that no



**Fig. 8.** XRD analysis spectrum of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.



**Fig. 9.** SEM Images of the -Al<sub>2</sub>O<sub>3</sub> (left) and optimum sample 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (right).



agglomeration of manganese and molybdenum exist (right figure) on the prepared 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. It was turned out that impregnation and distribution of manganese and molybdenum were take place well. Therefore, a more homogenous impregnation was done. Furthermore, these two metals lead to prepare catalyst with uniform particle size distribution.

Figure 10 shows NH<sub>3</sub>-TPD profile of the 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. For this prepared catalyst, the spectrum showed two well resolved peaks at 420 °C and 880 °C. The results of this section showed that

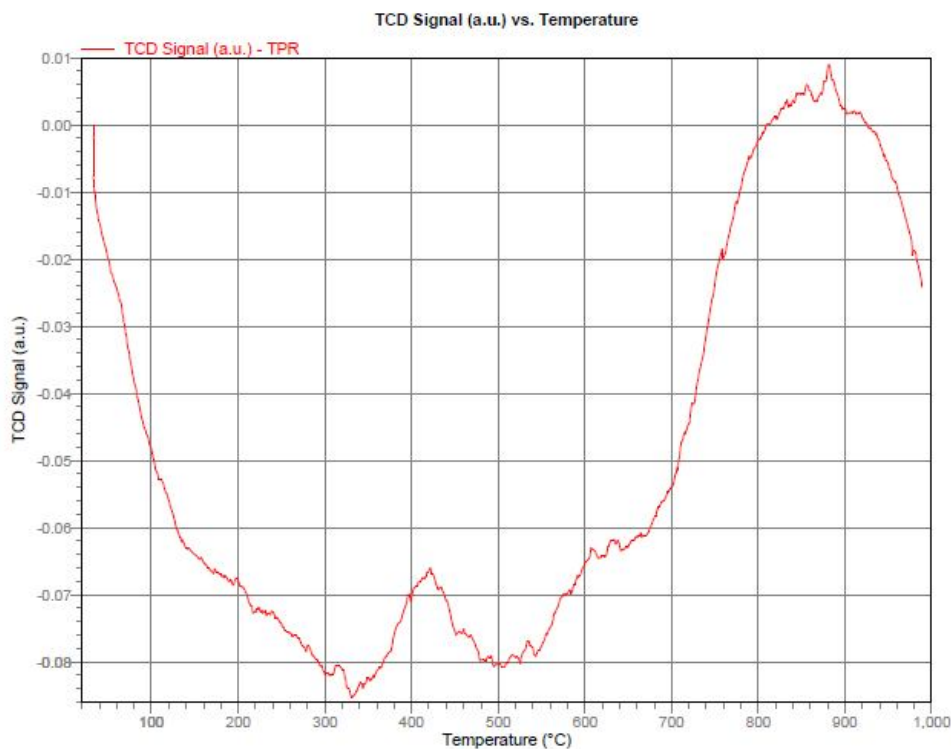
two kinds of adsorption sites for NH<sub>3</sub>-TPD present on the prepared catalyst. The peak at the temperature of 880 °C is explained to N<sub>2</sub> and H<sub>2</sub> gases made from the decomposed of NH<sub>3</sub>. The peak at the temperature of 420 °C is owing to releasing the adsorbed NH<sub>3</sub> from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and presented the intense acidic sites.

### The Oxidant Agent Content Effect on ODS

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was also used as an oxidant

in order to catalytic ODS of condensate. By using of oxidant, two phases as an aqueous polar phase including the oxidant and an oil nonpolar phase was obtained. Consequently, mass transfer challenges can happen making the catalytic ODS method more difficult by the separation of reactants [34].

The amount of H<sub>2</sub>O<sub>2</sub> used could also be one of the main factor that effect on the catalytic ODS method [35-37]. For environmental and economic aspects, minimizing the amount of oxidant is a target in the advancement of catalytic ODS method. When the H<sub>2</sub>O<sub>2</sub> amount was below 1 ml, little significant sulfur conversion was showed. When, the H<sub>2</sub>O<sub>2</sub> amount was between 1-2 ml, sulfur removal is remarkably increased. This high amount of oxidant could be explained, not only by the initial sulfur content, but also by the heavy nature of the condensate used requiring high oxidant amount due to side reactions that can proceed, such as oxidation of aromatic hydrocarbons. Therefore, according to the environmental and economic challenges, the optimum and the best amount of H<sub>2</sub>O<sub>2</sub> (1 ml) was selected.



**Fig. 10.** NH<sub>3</sub>-TPD analysis spectrum of the optimum sample (10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>).

### **The 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst Content Effect on ODS**

The improving conditions are favorable the use of advanced heterogeneous catalytic systems because of the catalyst separation, simple products and excellent performance. The most important parameters must be taken into consideration when it achieves to residue condensate. Firstly, condensate have medium viscosity, accordingly, the conditions of mixing are very important to affirm an overall mixed system.

The reaction was done in the presence of 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a catalyst and H<sub>2</sub>O<sub>2</sub> as an oxidant. In this paper focusing on the catalyst ODS of condensate with 1500 ppm sulfur content, catalysts mostly have one effective phase such as transition metals which impregnated on alumina catalyst support with large specific area [38]. Among transition metals, the molybdenum [39] was used as an active metals and magnesium was used as promoter. Because of environmental and economic aspects, minimizing the amount of catalyst is a purpose in the progression of catalyst ODS method. When the catalyst amount was below 1 g, it was seen no significant conversion of sulfur. Actually, when the catalyst amount was between 1-2 g, it was seen significant conversion of sulfur. Therefore, regarding to the environmental and economic reasons, the best amount of catalyst (1 g) was chosen.

### **The Temperature Effect on Catalytic ODS**

Temperature of the catalytic ODS reaction is an important parameter subsuming in the catalytic oxidative desulfurization method that was studied. The temperature of the catalytic oxidative desulfurization mechanism is commonly between 30 and 70 °C. The reaction with high temperature was also studied because of its expected effect to reduce the viscosity of the condensate. Therefore, it was caused to better diffusion of sulfur molecules and thus direct affected on the catalytic oxidative desulfurization method. In most investigated, when the temperature was increased from 30 °C to 50 °C caused to increased sulfur removal. But above 60 °C, increasing in temperature had an inverse on catalytic oxidative desulfurization method [24].

Table 5 showed the obtained results of catalytic ODS method were done at different temperature of condensate, taking into consideration the complexity and the higher

viscosity of the gas oil mixture. Therefore, 50°C was chosen as the optimum catalytic ODS temperature.

### **The Time Effect on Catalytic ODS**

Reaction time of the catalytic ODS method, is an important parameter. In the catalytic ODS methods, system permit to catalytic oxidative desulfurization in a few minutes. In this research, oxidation time varies between 30 and 150 min [24].

According to the reports in the Table 6, it has indicated desulfurization of condensate in 120 min by using H<sub>2</sub>O<sub>2</sub> and catalyst at 50 °C. This reaction time was frequently related to the multiple steps used for the addition of oxidant and catalyst with condensate. The results showed that increasing up to 150 min of the reaction time has not remarkably reduced the sulfur removal and highest catalytic oxidative desulfurization, Such a way that, the optimum reaction time was chosen at 120 min.

## **CONCLUSIONS**

The catalytic oxidative desulfurization method is studied as supersede method to HDS method to avoid the economic problem related to operating conditions of hydrodesulphurization with high pressure, high temperature and high hydrogen using. Because of this target, we attend to investigate the catalytic ODS method. Firstly, 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared as ODS catalyst. Then, the effect of the quantity of 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, oxidant (H<sub>2</sub>O<sub>2</sub>), temperature and time on the each of catalytic oxidative desulfurization method was specified. Catalytic ODS method was done on the condensate (total sulfur 1500 ppm). The results of this project demonstrated that the optimum value of the 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and oxidant (H<sub>2</sub>O<sub>2</sub>) were rather than 1 g and 1 ml, respectively. Though, according to the environmental and economic aspects, reducing the amount of catalyst and oxidant is a purpose in the progression of catalytic ODS method. Therefore, 1 g of 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and 1mL of oxidant (H<sub>2</sub>O<sub>2</sub>) were chosen as an optimum amount. The catalytic ODS method with 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and oxidant (H<sub>2</sub>O<sub>2</sub>) are investigated at different conditions. According the

outcomes of the experiments, 120 min and 50 °C was chosen as the optimum operating experimental conditions. In this optimized catalytic ODS condition, the total sulfur reached to 123 ppm from 1500 ppm. Therefore, 1 ml H<sub>2</sub>O<sub>2</sub>, 1 g 10%Mn15%Mo0.5%P/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, 50 °C and 120 min was chosen as the optimum condition.

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