Reactive Adsorption Desulfurization by Nanocrystalline ZnO/Zeolite A Molecular Sieves

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ABSTRACT

Nanocrystalline ZnO/Zeolite type A composite was prepared by simple method of operation by the precipitation of zinc oxide and loading on zeolite 5A in one step. Characterization was made by X-ray diffraction (XRD), X-ray fluorescence(XRF), N_2 adsorption- desorption for BET surface area, and Atomic force microscopy (AFM). Results showed that zinc oxide was loaded on zeolite as noticed by the characteristic peaks and was of nano scale having an average diameter of 88.57nm. The percentage loading of ZnO on zeolite A was 28.37% and the surface area was 222m^2/g. The activity of the prepared catalyst was examined in the desulfurization of double hydrogenated diesel fuel. The process was investigated in a controlled autoclave with temperature range studied 100-220^{o}C. Results indicated an oxidation of thiophenic compounds on the surface of the catalyst coupled with adsorption. About 35% reduction was obtained and the capacity was 10.56 mg S/g catalyst.

Keywords: reactive adsorption, ZnO, desulfurization

ازالة الكبريت بواسطة الامتزاز التفاعلي باستخدام المناخل الجزيئية الزيولايتAالنانوي/ اوكسيد الخارصين

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الخلاصة

تم تحضير الزيولايت النانوي المركب مع اوكسيد الخارصين بطريقة بسيطة. تم التشخيص بواسطةتقنيات XRD, AFM, XRFوقياس المساحة السطحية. اختبرت فعالية العامل المساعد المحضر في ازالة الكبريت لوقود ديزل مهدرج مرتين. وتمت العملية في مفاعل الاوتوكليف بمدى درجات حرارة^{o}C 100-220. ودلت النتائج على اكسدة المركبات الثايوفينية على سطح العامل المساعد مع الامتزاز. كانت اعلى ازالة 35% وقابلية استيعاب العامل المساعد mg/g10.56.

الكلمات الرئيسة: الامتزاز التفاعلي - اوكسيد الخارصين- ازالة الكبريت

1. INTRODUCTION

The new environmental regulation and stringent specification leads to the demands of lower sulfur content for better transportation of fuel, improved fuel properties, limited SO_x emissions and catalyst poisoning. Reduction of sulfur in fuel is crucial due to its harmful effects such as corrosion problems in refining plants and poisoning (deactivation) of catalyst in downstream refining processes **Zhang, et al., 2013**. Sulfur content in crude oil can vary between 0.05 and 6 wt.%, thus crude oils can be classified as sweet ones for less than 0.5 wt.% sulfur, and sour crudes with more than 1.5 wt.% sulfur **Fahim, et al., 2010 and Gary, 2001.**The sulfur-containing compounds in transport fuel include (a) sulfides R_2S(b) mercaptanes RSH (c) disulfides RSSR (d) thiopenes (e) benzothiopense and (f) dibenzothiopene **Song and Ma, 2006.**

The technological approaches and methodologies for sulfur desulfurization process with non-hydrogen consuming techniques which are (i) oxidative desulfurization (ODS) (ii) biodesulfurization (iii) desulfurization by zeolites, and (iv) adsorption **Song and Ma, 2006, Song, 2003, James, et al. 2008 and Solaimani et al, 2007**. Although, hydrodesulfurization (HDS) is highly efficient in removing sulfides, disulfides, and mercaptanes but it is less effective for aromatic thiopenes **Hernandes-Maldonado, and Yang, 2004**, in addition of remarkable decrease in octane number of the product because of the hydrogenation process which causes the saturation of olefins contained in FCC gasoline.

Several researches on desulfurization by reactive adsorption method have been reported which is considered as a desulfurization process using non-hydrogen consuming technique, such process has been used on industrial scale. A catalyst consisted of silica (20-60 wt.%), alumina (5-15 wt.%), zinc oxide (15-60 wt.%) and nickel and/or cobalt (1-3 wt.%) **Brunet, et al., 2005**. The mechanism of desulfurization in reactive adsorption supposed that zinc oxide (ZnO) behaves as an acceptor for sulfur produced from sulfur compounds on reduced Ni^o **Babich, and Mouijn,2003 , Tawara, et al., 2001, Bezversky, et al., 2008 and Huang, et al., 2010**. Drawbacks exist in the reactive adsorption desulfurization (RADS) process, like the limited sulfur saturation adsorption capacity of zinc oxide leads to frequent regeneration of the adsorbent.

Zhang, et al., 2013 investigated the development of bifunctional NiPb/ZnO-diatomite-ZSM-5 catalyst for FCC gasoline upgrading by (RADS) coupling aromatization, the Pb-modified Ni/ZnO adsorbent has the ability to stop olefin saturation by partly deactivating the hydrogen active sites through small amount of lead deposited on the catalyst. They found that optimal Pb/Ni ratio is about 1:20, and they concluded that improved bifunctional catalyst RADS adsorbent/catalyst showed deep desulfurization coupling olefin aromatization performance. **Al-Bogami, and de lasa, 2013** introduced the catalytic conversion of benzothiophene over H-ZSM5 using temperature range of 350 to 450 ^oC where a reactive mode of adsorption is approved with maximum conversion of about 50% at 450 ^oC.**Song, 2014** investigated desulfurization by metal oxide/graphene composites by using zinc oxide and copper oxide on reduced grapheneoxide (rGO).The author concluded that the addition of copper oxide to zinc oxide increased H_2S adsorption capacity up to 18 times for $Cu_{15}Zn_{85}$/rGO compared to pure ZnO, the H_2S adsorption capacity increased until 15mol% Cu. **Ahmed, et al., 2014** investigated the impregnation of Fe, Cr, Ni, Co,Mn, Pb, Zn and Ag on montmorollonite clay. They found that Zn based adsorbent was the most efficient among other types for desulfurization of diesel oil (1% S), kerosene (0.05 %). Efficiency was 76% for kerosene and 77% for diesel oil. **Boikov, and Vishnetskaya, 2013** had investigated the oxidation of thiophene in a mixture with benzene by chemical analysis to the products of the reaction at temperature ranges of 200-320 ^oC using mixed oxides of MoO and V_2O_5.They concluded that molecular oxygen on the catalyst can oxidize thiophene efficiently where conversion decreased from 77% after 1hr to 49% after 3hrs.

In this research a new composite catalyst containing zinc oxide loaded on zeolite type 5A was prepared and tested for catalytic activity in the reduction of sulfur compounds in double hydrogenated diesel fuel. A precipitation method was adopted to prepare zinc oxide (ZnO) and on the same time was loaded on Zeolite in one step. Investigation of reactive adsorption desulfurization for diesel fuel by ZnO/ Zeolite catalyst was implemented in an autoclave reactor with stirring and heating mode at mild temperatures.

2. MATERIALS AND METHOD

2.1 Chemicals

Diesel fuel was obtained from the Ministry of Oil, which was hydrogenated twice previously in the laboratories of Petroleum Research and Development Center (PRDC). All measurements of sulfur content were carried out by sulfur analyzer (XRF) at the Refining and Gas Researches Department. The feed diesel fuel has sulfur content of 2330ppm. Sodium hydroxide 99% and Zinc nitrate hexahydrate were from local markets. Zeolite 5A (SINOPEC Company, China) was supplied by the Arab company for detergent chemicals (surface area 475m^2/g). The zeolite samples were activated by heating for two hours in at 200 ^oC and kept in desiccator.

2.2 Preparation of ZnO/Zeolite Catalyst

The procedure of ZnO preparation from nitrate salt was adopted by following **Gusatti et al 2009**, but in the present work the idea was explored for zeolite loading in one step. Precipitation of ZnO nanoparticles was implemented through the chemical reaction (Eq.) between zinc nitrate and sodium hydroxide. The final solution (1M) was heated to 70^{o}C with zeolite 5A, dispersed in it (using magnetic heater stirrer Labinco, Holland) in an insulated two neck round bottom flask. Drop wise addition of zinc nitrate solution was proceeded within one hour and further heating of the mixture was continued for another two hours. White precipitate was continuously seen during the reaction time where on completion, was washed several times with deionized water, dried at 65^{o}C overnight, calcined at 350 ^oC for 3 hrs and then sent for characterization.

$$Zn(NO_3)_2.6H_2O+2NaOH \xrightarrow{\qquad} ZnO + 2NaNO_3 + 7H_2O \qquad (1)$$

The crystalline phase analysis was performed by using X-Ray diffraction BRUKER, Germany, diffractometer equipped with a Cukα (K=1.54056 A°). Particle size were tested via Atomic force microscopy (AFM) using an AA3300/Angstrom Advance Inc. Composition was by X-ray fluorescence and N_2 adsorption – desorption for surface area.

The maximum capacity (q_t) of the prepared catalyst was calculated by Eq.2.

$$q_t = (Co-Ct)V/W \qquad (2)$$

q_t is in mg Sulfur/g zeolite, Co= initial concentration (mg/l), Ct= final concentration (mg/l), V= volume of fuel (l), W= weight of catalyst (g).

2.3 Desulfurization Experiments

The prepared catalyst ability for the reduction of sulfur compounds was examined in an electronically temperature controlled stainless steel autoclave (200ml) lined with poly tetraflouroethylene (PTFE)with stirring and heating for temperatures of 100,140,180, and 220^{o}C under autogeneous pressure. Two catalyst loadings were tested using 5 and 10g per 100 ml of diesel fuel. Also, the fuel was oxidized using 5 ml of H_2O_2(20%) and 1ml of acetic acid (CH_3COOH) then was subjected to the same desulfurization reaction in the autoclave. Details of the autoclave can be found elsewhere **Alnaama, 2016.** Analysis of sulfur content was done using XRF sulfur analyzer, in the PRDC, Ministry of Oil.

3. RESULTS AND DISCUSSION

3.1 Characterization of ZnO/Zeolite Composite

3.1.1 XRD

The parent zeolite 5A was characterized by X-ray diffraction and is shown in Fig.1. The crystalline phase analysis was performed by using an XRD BRUKER, Germany, diffractometer equipped with a Cukα (K=1.54056 A°). It can be seen that calcium ion is partly included in the lattice as exchanged with sodium ions. The prepared ZnO/ zeolite A was characterized and its phase confirmation was examined by XRD pattern shown in Fig. 2, where it can be observed that two phases are prepared with no impurities. The first phase is Sodium Aluminum Silicate Hydrate (Zeolite A) and the second is Zinc Oxide. Peaks of ZnO are well observed by the characteristic peaks and compared with the standard peaks. The comparison is the output of the instrument where the standard phases are stored inside. The $d_{spacing}$ values of Zeolite A are 12.3 and 8.7 A^o(12.11 and 8.63 standard) versus their intensities of 65.5% and 35.4% (64.5% and 28.1% standards). Those values for ZnO are 2.8 and 2.469 A^o(2.81 and 2.47 standards) versus intensities of 55.5% and 98% (65.9% and 100% standards). Typical values of zinc oxide are also found in past studies and match the present results as in **Alwan et al, 2015, Sesha, and Rao, 2013 and Rama, et al., 2010**.

3.1.2 AFM

The topography and particle size were tested via Atomic force microscopy (AFM) using an AA3300/Angstrom Advance Inc., where AFM 3D images are shown in Fig. 3. This figure shows the detailed observation of nano-scale events at crystal surface, showing also the layer growth of crystal and height of terraces. Uniform nano pore size distribution and surface roughness can be observed. The particle size is of nano size and the average diameter is 88.57nm, d_{10} is 60nm, d_{50} is 90nm and d_{90} is 110nm as listed in Table 1 and the cumulative particle size distribution is shown in Fig.4.

3.1.3 XRF

The catalyst composition was investigated by X-ray fluorescence. Results revealed that the chemical analysis was as follows; Na_2O: 8.758%, CaO: 5.37%, SiO_2: 11.67, Al_2O_3: 8.107%, and ZnO: 28.37%. It is concluded that the presence of zeolite 5A in the alkali media causes an ion exchange process where zeolite 4A was produced and is the dominant phase containing sodium ions while calcium ions decreased from the prepared composite. Therefore ZnO particles were loaded on the sodium form of zeolite A.

3.1.4 Surface area

Surface area was measured by nitrogen adsorption/desorption. The value for the prepared ZnO/Zeolite composite was found $222 m^2/g$ where a decrease in the surface area is found and could be attributed to the deposition of zinc oxide powder in the pores of zeolite causing the blockage and interferes nitrogen diffusion. However, the value is still acceptable for adsorption compared to the surface area of metal oxides. Pore size was also measured by the same technique and was 4.3nm which is in agreement with AFM results. Pore volume is $0.239 cm^3/g$.

3.2 Desulfurization study

3.2.1 Effect of Temperature and catalyst loading

Fig. 5 shows the effect of temperature increase on the removal of sulfur compounds in diesel fuel. It can be seen that the sulfur content decreases from 2330 to 1802 ppm as the temperature rises from 100 to 220 ^oC using 5 grams of ZnO/ zeolite. Sulfur content decreases to 1515 ppm using 10 grams (Fig. 6). This treatment achieved 22.6 % and 35% removal. This reduction can be explained by that, thiophenic compounds are adsorbed on the surface of the ZnO/Zeolite and acting as adsorbent for thiophenes. Zinc oxide is known as an efficient adsorbent for different sulfur compounds and because of its low surface area (as most of metal oxides) it is sometimes either mixed with sorbents with higher surface area like Al_2O_3or graphite as in the work done by **Shangguan, et al., 2010** or loaded (on zeolite A in the present study) and dispersed on other materials acting as support like ZnO/ SiO_2**Yang, and Tatarchuk, 2010.**

The mechanism for the reduction in the total sulfur compounds can be assumed to occur in many possible ways depending on the past information cited in literature**. Xu, etal., 2014** suggested two ways; the pi-complexation depending on the work of **Takahashi, 2002**, **Hernandez-Maldonado, et al., 2005 and Hernandez-Maldonado, et al., 2005**A. The π-complexation occurs in adsorbents particularly, zeolites especially Y which exhibit high sulfur-adsorption capacity, but show low selectivity for sulfur compounds as the result of competitive adsorption of aromatic compounds but zeolite A in the present study has the selective affinity for sulfur compounds as aromatics cannot be adsorbed due to the narrower pore size in comparison to zeolite Y. The other suggestion is the direct Sulfur–Metal (S–M) interaction based on **Sarda, et al., 2012 and Velu, et al., 2003**. Meanwhile, the desulfurization based on the second mechanism faces difficulties due to the steric hindrance to remove complex sulfur compound such as 2,3-dimethyl benzothiophene (2,3-DMBT),2,3,7-trimethyl benzothiophene (2,3,7-TMBT) and many more. The high affinity of zeolite to sulfur compounds could be attributed to that they are considered as Lewis base, so they are best adsorbed on zeolites having Lewis acid sites **(Xue et al., 2005).**

It was found that the maximum capacity was 10.56mg S/g catalyst. Comparing of this value with the work of **Blanco-Brieva, et al., 2010** for the adsorption on zeolite Y, these values were 7.5, 10 and 16 mgSulfur/ g zeolite for DMDBT(dimethyldibenzothiophene), BT (benzothiophene) and DBT (dibenzothiophene) respectively which is considered of good agreement with zeolite Y of wider pore size and higher surface area (662m^2/g).

3.2.3 Effect of Peroxide addition

In the range of temperature studied in the present work, there is a focus on the oxidation reaction of thiophene and its derivatives to occur on the surface of ZnO as a metal oxide. This explanation is widely encouraged and could be the reason behind desulfurization of diesel fuel in the present study because the oxidation by hydrogen peroxide (Fig. 7) was found to have little impact on the reduction of sulfur compounds and could be attributed to that H_2O_2 is subjected to the double hydrogenated fuel which contains refractory thiophenic compound which are difficult to be oxidized by the peroxide or could be oxidized to a little extent.

Also, it can be seen in Fig.6, the results of treatment of the same diesel fuel by the oxidation using hydrogen peroxide which was done by **Yasameen, 2014** using activated carbon at 80^{o}C. The low extent of desulfurization using peroxide (25%) agrees well with the present results showing the hindered desulfurization of the sulfur compounds in the fuel.

The present results can follow the same trend as those of **Boikov, and Vishnetskaya, 2013** who reported a slight oxidation of sulfur compounds coupled with a reactive adsorption of the produced sulfoxides and/or sulfones on their catalyst**.** The aforementioned findings can be used to deduce a fact that oxidation occurs in the autoclave reactor using the ZnO/Zeolite having catalytic adsorptive property to decompose thiophenic compounds to sulfones and sulfoxides and then reactive adsorption occurs on zeolite surface. Therefore, the oxidation-adsorption process is occurring on the surface of the zinc oxide which attracts the sulfur containing compounds to be oxidized and adsorbed by a coupling technique and can be a promising procedure for future application to produce ultra-fine fuel from different petroleum fractions.

4. CONCLUSIONS

Nano ZnO/Zeolite A composite was efficiently prepared by precipitation of zinc oxide and loading on zeolite molecular sieves type A in situ. The prepared material matches the crystalline structure of standards. Nanomaterial was prepared with average diameter of 88.57nm and d_{50} is 90nm. Surface area of the prepared composite is 222m$^{2/}$g.Pore size is 4.3nm and pore volume is 0.239cm^3/g. The activity of the prepared catalyst was examined in the desulfurization of Iraqi diesel fuel which was double hydrogenated previously. Results indicated the adsorption of thiophenic compounds on the surface of the catalyst also, a slight oxidation coupled with reactive adsorption can be a reason for sulfur reduction. About 35% reduction of sulfur compounds was obtained and the calculated capacity was 10.56 mgS/g catalyst.

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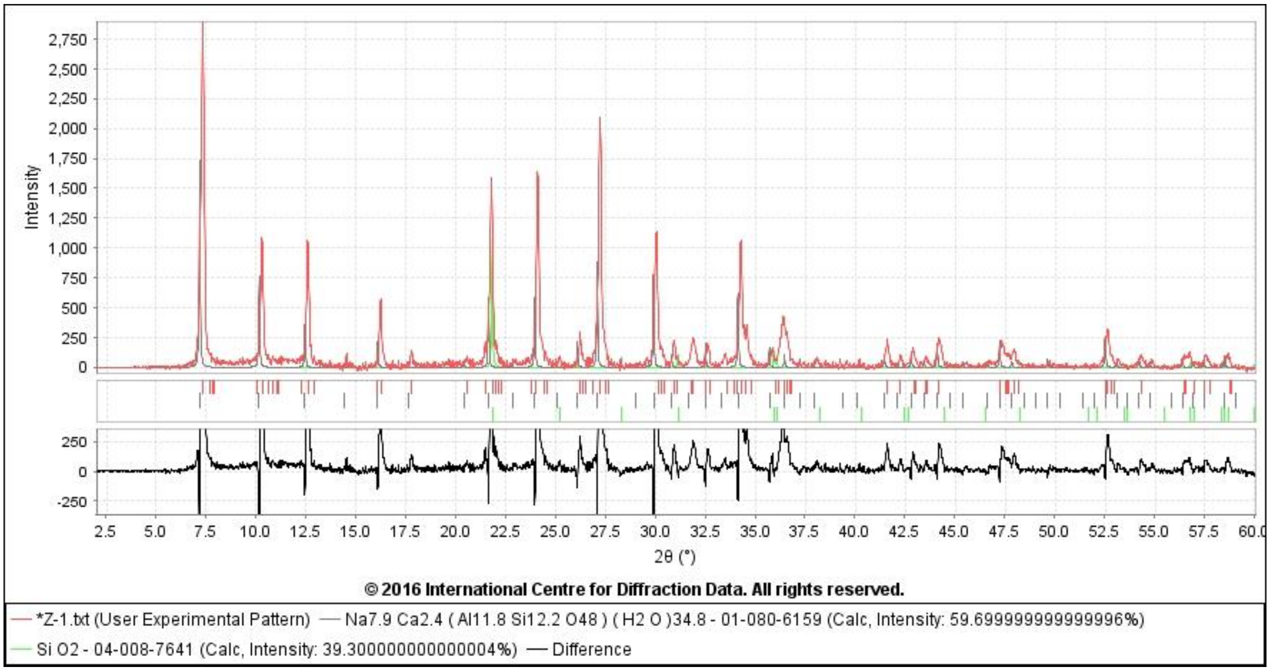

Figure1. XRD pattern of zeolite 5A.

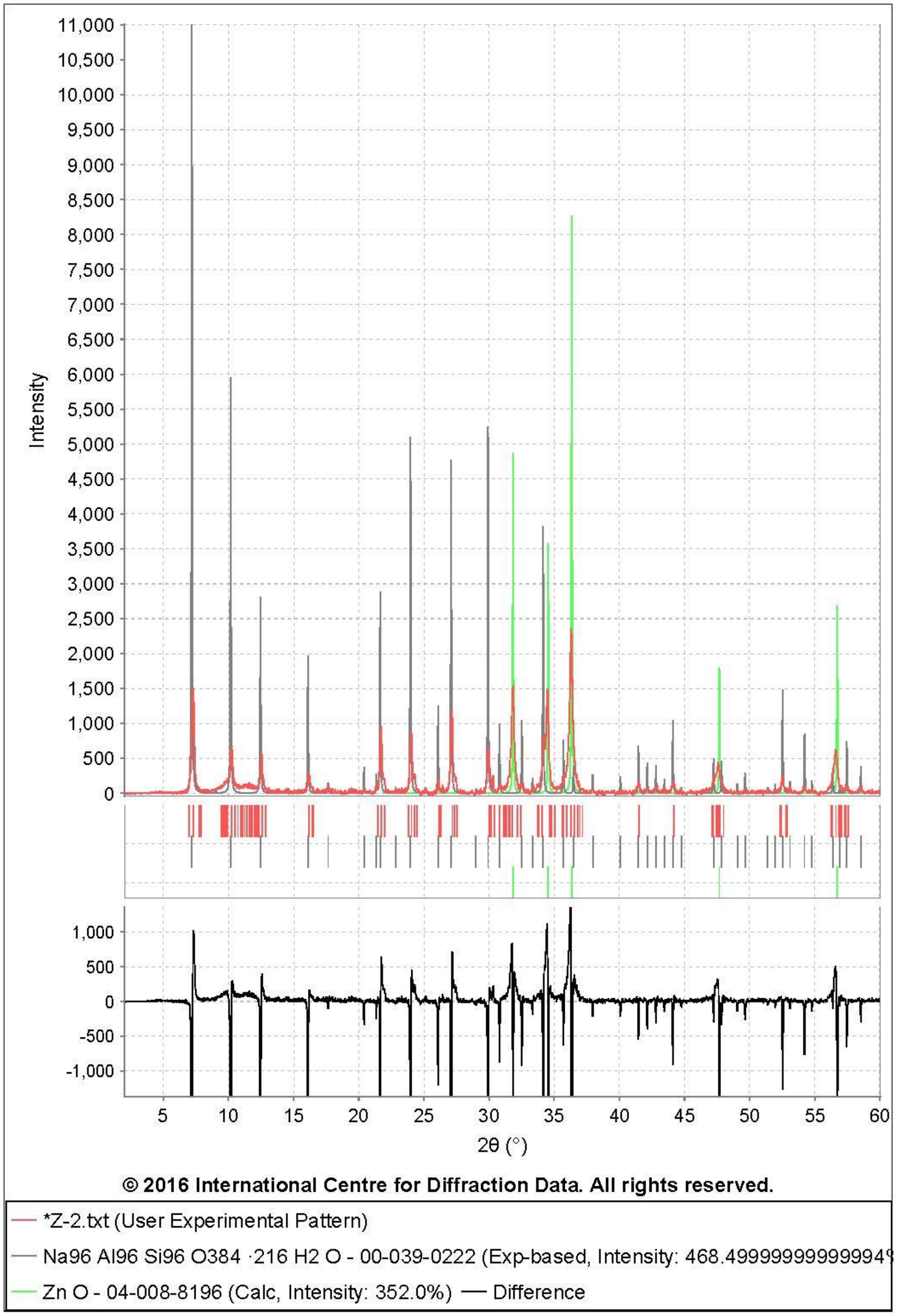

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Figure 2. XRD pattern of the prepared ZnO/Zeolite A.

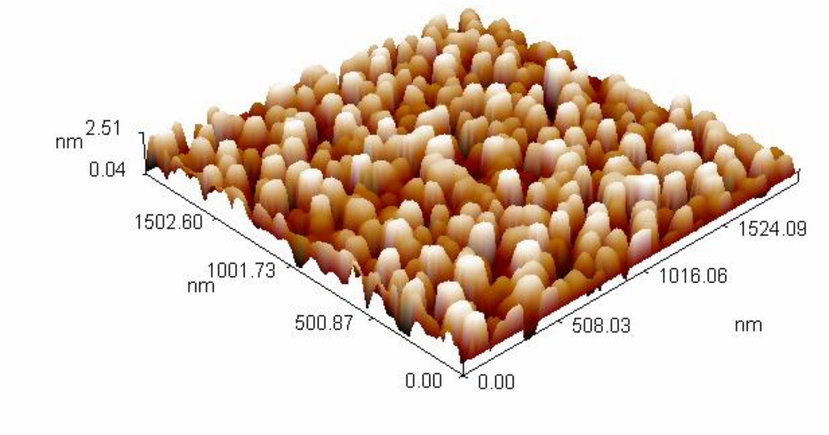

Figure 3. 3D AFM Image.

Table 1.AFM Particle size distribution.

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50	0.5	0.5	90	11.56	49.25
55	3.02	3.52	95	10.05	59.3
60	2.51	6.03	100	12.56	71.8
65	4.02	10.05	105	8.04	79.90
70	6.03	16.08	110	8.54	88.44
75	9.55	25.63	115	7.04	95.48
80	8.04	33.67	120	4.52	100
85	4.02	37.69			

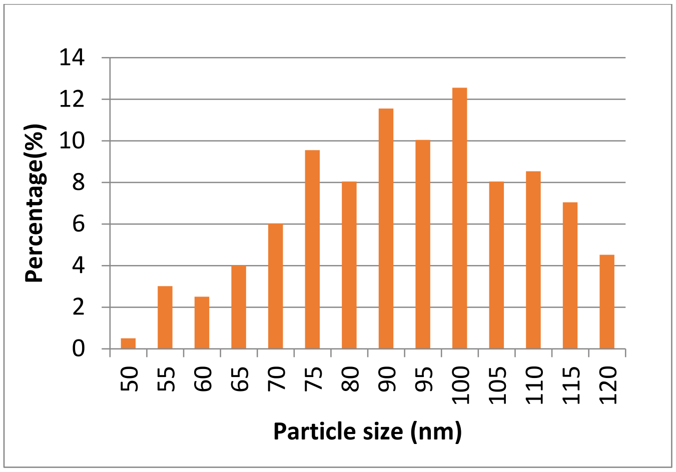

Figure 4. AFM Particle size Distribution Chart.

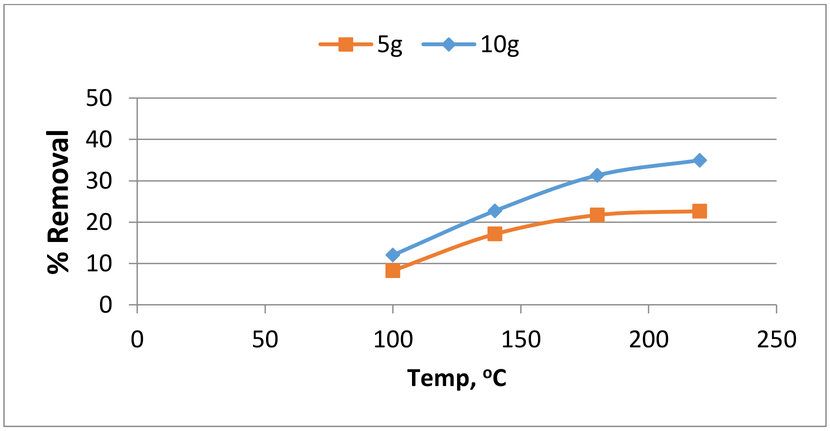

Figure 5. Effect of temperature on sulfur removal.

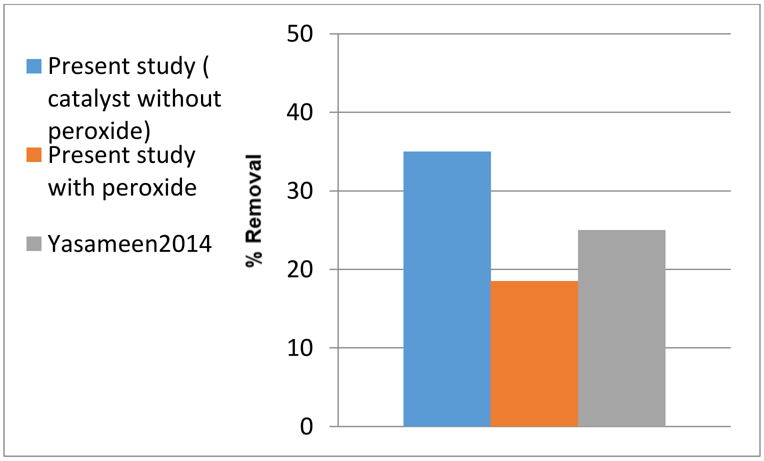

Figure 6. Comparison between desulfurization processes.