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Oxidative Desulfurization of Kerosene in Batch Reactor using Magnetite Mesoporous Silica Composite Zeolite Catalyst

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Abstract

The petroleum refining sector has increasingly prioritized the creation of clean fuel as a crucial priority. The objective of this project is to generate environmentally friendly fuel through the use of a straightforward and uncomplicated method. Using a novel synthetic nano-catalyst, batch oxidative desulfurization (ODS) eliminates sulfur compounds in Kerosene. The new Catalyst's silica nano-particle support is initially manufactured utilizing the sol-gel technique. Subsequently, the support is employed to fabricate a synthetic composite nano-catalyst composed of ferric oxide, utilizing the techniques devised for extracting a novel synthetic handcrafted (Fe_2O_3/composite support) Nano-catalyst. The composite supports used for the robust studies on the desulfurization process contain different levels of HY-zeolite (100 percent Nano silica). These levels include 10% HY-zeolite + 90% Nano silica, 20% HY-zeolite + 80% Nano silica, and 30% HY-zeolite + 70% Nano silica. The supports and manufactured Catalyst underwent characterization tests, including SEM, XRD, XRF, TGA, FTIR, BET, and particle size distribution. The tests showed an ideal distribution of the active metal (Fe), different surface structures, and a high active metal dispersion were achieved. The prominent locations are identified as limited in number, and the catalysts exhibit metal-support solid interaction. The existing Catalyst's performance was evaluated using a batch reactor. The assessment involved testing the Catalyst at different reaction temperatures (303 to 393 K) and batch times (30 to 120 minutes) while varying HY-zeolite quantities in the composite supports.

Keywords: Oxidative Desulfurization, composite Catalyst, sulfur removal.

إزالة الكبريت من الكيروسين بعملية الاكسدة في مفاعل الدفعات باستخدام حفاز الزيوليت المركب من السيليكا المسامية والحديد الممغنط

الخلاصة:

لقد أعطى قطاع تكرير البترول أولوية متزايدة لإنتاج وقود نظيف كأولوية حاسمة. والهدف من هذا المشروع هو توليد وقود صديق للبيئة من خلال استخدام طريقة مباشرة وغير معقدة. باستخدام محفز نانوي صناعي جديد، تعمل عملية إزالة الكبريت بالاكسدة في مفاعل الدفعات للتخلص من مركبات الكبريت الموجودة في الكيروسين. يتم تصنيع دعامة الجسيمات النانوية من السيليكا في المحفز الجديد باستخدام تقنية

السول-جيل. بعد ذلك، يتم تصنيع محفز نانوي مركب صناعي يتكون من أكسيد الحديديك. تم تحضير عوامل مساعدة تتضمن نسب مختلفة من الزيولايت نوع HY والسيلكا (10% زيولايت 90% + HY نانو سيليكا، و20% زيويولايت 80% + HY نانو سيليكا، و30% زيولايت 70% + HY نانو سيليكا). خضعت نماذج الحفاز المصنّع لاختبارات تشخيصية مثل المجهر الإلكتروني الماسح، وXRD، وXRF، وTGA، وFTIR، وBET، وتوزيع حجم الجسيمات. أظهرت الاختبارات توزيعًا مثاليًا للمعدن النشط (Fe)، وهياكل سطحية مختلفة، وتم تحقيق تشتت معدني نشط عالي مع تحديد المراكز الفعالة ، وتُظهر الحفازات تفاعلًا كفاءة سطحية عالية خلال تقييمها في مفاعل الدفعات . تضمن التقييم اختبار الحفاز عند درجات حرارة تفاعل مختلفة (303 إلى 393 كلفن) وأوقات دفعات (30 إلى 120 دقيقة) مع تغيير كميات العامل المساعد المركب.

1. Introduction:

Sulfur compounds are crucial non-hydrocarbon petroleum chemicals primarily responsible for air pollution. They generate sulfur oxides, which contribute to the formation of acid rain. The corrosion of engines is attributed chiefly to these compounds in gasoline and diesel, particularly during winter when water includes sulfur dioxide emanating from internal combustion engines.

However, the corrosion of brass and copper is attributed chiefly to the presence of sulfur in the presence of air, which adversely affects the color stability of automotive fuel and other liquid fuels. The conventional method employed in oil refineries to eliminate sulfur compounds is catalytic hydrotreating (HDT). This process involves the conversion of sulfur compounds into H2S and hydrocarbons. Producing an environmentally friendly diesel fuel is challenging due to the strong resistance of benzothiophene (BT) and dibenzothiophene (DBT) to the hydrogenation process [4]. This process requires more potent catalysts and a significant amount of H2 under harsh reaction conditions, making it more costly than alternative methods [1-4]. A more contemporary method for removing sulfur is the oxidative desulfurization process (ODS), which has shown promise due to its operation at low pressure (1 bar), cost-effectiveness, and safe operating settings (below 373 K). Unlike other methods, ODS does not require hydrogen gas but utilizes air as an oxidant [5]. Oxidative Desulfurization, is a highly sought-after and favored method for eliminating stubborn sulfuric compounds that are resistant to removal by HDS or Hydrodesulfurization.

Additionally, most sulfur compounds resistant to heat and chemical reactions exhibit a strong tendency to undergo oxidation reactions in the presence of ODS reactions. The ODS process involves the oxidation of sulfur compounds in oil using suitable oxidants to convert the components into their corresponding sulfones and sulfoxides. The extraction of such compounds from the oil is based on their relative polarity, and any remaining oxidant in the oil will be removed or separated by water [6,7]. A non-miscible solvent can extract an oxidized component from the oil. The oxidized constituents and solvent are subsequently eliminated from the oil using either gravity separation or centrifugation, contingent upon the solvent employed during the extraction procedure. The ODS method is considered the primary procedure for sulfur removal, as it relies on selecting an appropriate catalyst. The reactivity of transition metal oxides towards sulfur compounds and the extent of their reaction is influenced by the specific metal oxide, as well as its availability and high activity for such reactions. Air is an oxidant in the ODS process due to its several advantages over alternative oxidizing agents, including safety, low-temperature selectivity (few side reactions), cost-effectiveness, availability, and environmental friendliness with no byproducts. The oxidation rate can be achieved by passing air through a petroleum fraction using sulfuric acid. The presence of an unstable emulsion is responsible for reducing the limitations of phase transfer and improving the interface between oxidants and organosulfuric chemicals [8,9].

2. Experimental Work

2.1 Materials

2.1.1 Oil Feedstock (Kerosene)

Kerosene is used as an oil feedstock in this study. Kerosene (total sulfur content = 0.1966 wt. % has been obtained from Baiji Refinery/ Tikrit—the feedstock specifications are tabulated below in Table (1).

Table (1): Condition of Kerosene

Test	Result
DENSITY @15˚C	0.7904
API	47.5
FLSH PT ˚C	40.5
COLOUR	+20
DR. TEST	+ve RSH
IBP ˚C	147
REC AT 185 ˚C	50%
SULFUR PPM	1966

2.1.2 Air

Air is used as an oxidizing agent, which is applied using a compressor. Oxygen present in the air is used to oxidize the sulfur compound to form hexavalent sulfur (sulfones).

2.1.3 Active Components for Catalyst Preparation

The chemical compound used for catalyst preparation for the active components employed in this study is ferric nitrate with a chemical formula of $Fe(NO_3)3.9H_2O$ purity of 98%.

2.2 Composite Support Fe / (Nano silica + HY-zeolite Nano-Particle)

Initially, nano silica was synthesized using the precipitation process. The bentonite sand and sodium hydroxide have been crushed to a particle size of 45 µm, weighing 50 g. A mixture of sodium hydroxide and 20g of Bentonite sand was combined and heated in a programmed electric boiler at 550 °C for 30 minutes. The combination added water incrementally until a homogeneous and transparent solution was obtained. Subsequently, sulfuric acid (98%) was added progressively until the pH reached 3. The end product is rinsed with deionized water until it reaches a pH level and then let to dry overnight at 110 °C. We successfully acquired nano-silica. Subsequently, magnetite was infused onto Nano silica + HY zeolite using ferric nitrate Fe (NO3)3 .9H2O. The resulting catalyst samples were dried at 110 ^{O}C overnight and calcined at 550^{o} C for 3 hours.

3. Results and Discussions

3.1 Characterization: The characterization of catalysts using various techniques like X-ray fluorescence, XRD, TGA, BET, FTIR, Particle Distribution, and SEM. It also discusses the impact of process variables like temperature, time, and HY-zeolite percentage on sulfur compound conversion using the ODS process.

3.2 X-ray diffraction Study (XRD) is a method used in catalyst portrayal to identify crystalline phases and particle magnitude. XRD measurements were used to record catalyst samples using XRD-6000, Shimadzu, Japan. The technique provides data on section identification and deviates from the complete structure. The crystal structure of particles was recorded, and a broad diffraction peak indicated the existence of an amorphous silicon fraction, as shown in Figure (1).

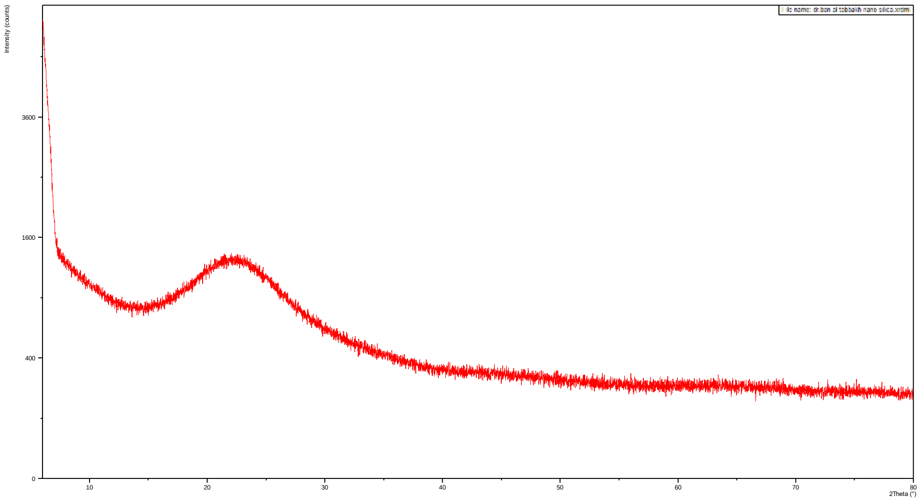


Fig. (1): XRD Patterns of Nana silica

3.3 Study of Surface Area and Porosity of Prepared Catalyst: as shown in Table (2), the surface area, pore volume, and pore diameter of the composite carrier and Catalyst. The carrier loading increases the zeolite's large surface area and pore volume. After impregnation, the bulk density of the active ingredient increases while pore volume and surface area decrease slightly due to the active ingredient's space occupancy in the sample. This indicates that the active ingredient can be applied with high certainty to the ODS reaction.

Table (2) Surface Area of Prepared Catalyst

catalyst	Surface area (m^2/gm)	Pore volume (cm^3/gm)	Pore size (nm)
NanoSilica	341.31	0.853	4.79419
CAT-1*	242.67	0.606	4.92913
CAT-2**	249.35	0.623	4.51586
CAT-3***	250.138	0.625	4.51439
CAT-4****	335.67	0.737	5.03550

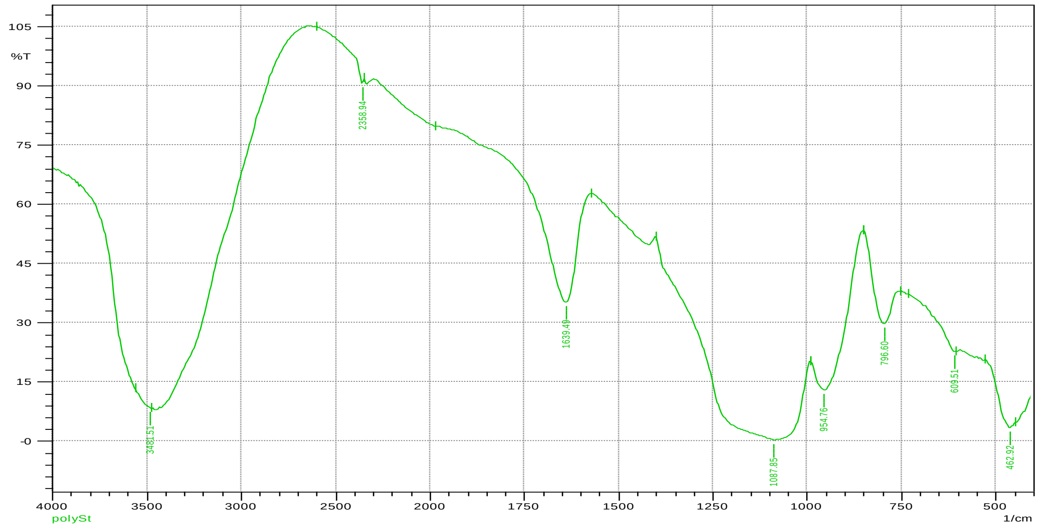
*CAT-1 = 10 wt. % Fe2O3/ Nano-silica nano-particle.
**CAT-2 = 10 wt.% Fe2O3/ (Nano-silica+10% HY-zeolite) nanoparticle.
***CAT-3 = 10 wt. % Fe2O3/ (Nano-silica+20% HY-zeolite) nanoparticle.
****CAT-4 = 10 wt. % Fe2O3/ (Nano-silica +30% HY-zeolite) nanoparticle.

3.4 The FTIR Study:

The FTIR examination of the extracted Nano silica showed both asymmetric and symmetric stretching modes of Si-O-Si. A band with a frequency of 462.92 cm-1 was observed, which corresponds to the bending frequency of Si-O-Si. The significant bandwidth at 3481.51 cm-1 arises from the extension of vibrational frequencies of OH in silanol and water. The spectral band centered at 1639.49 cm-1 corresponds to the oscillations of water molecules attached to the silica matrix and exhibits flexibility. No discernible peak was observed in the 2,800 to 3,000 cm−1 range, suggesting the absence of any natural mixes in the silica post-calcination. High surface area silica is an optimal substrate for catalysts, and the reactivity of silica is directly associated with its surface area.

The mesoporous nanosphere sample, synthesized by Gasan Dong et al., exhibits distinct peaks at 1700 cm-1 and 3430 cm-1, indicating carboxyl and hydroxyl groups. The adsorption peak is attributed to the Si–O stretching vibration of the Si–OH bond at a wavenumber of 960 cm-1. Delicate peaks at 2855 and 2920 cm-1 suggest the absorption of certain naturally occurring organic groups. The prominent peaks observed at 1100, 802, and 467 cm-1 indicate the occurrence of silicon alkoxide condensation. The user's text is "[10]".

All catalysts exhibit four prominent absorption bands of the SiO_2 carrier in their FTIR spectra. Nevertheless, the continuous flow of supported catalysts exhibits a modification compared to unpolluted SiO_2, attributable to the interaction between the dynamic phase and the surface carrier. The cooperative strength of the group attached to Fe and Zeolite rose with the molar ratio of Zeolite and Fe to SiO_2. Two more bands emerge at 993 and 870 cm-1 on catalysts 1, 2, and 3.



No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	449.41	1.325	0.084	457.13	399.26	62.523	2.559
2	607.58	0.581	0.022	752.24	596	70.051	-3.705
3	796.6	0.486	0.171	852.54	752.24	39.221	8.4
4	956.69	0.872	0.303	991.41	852.54	85.32	21.288
5	1085.92	2.404	1.814	1402.25	991.41	481.309	281.027
6	1421.54	0.312	0.025	1568.13	1402.25	44.382	2.296
7	1639.49	0.419	0.222	2341.58	1573.91	119.189	17.293
8	3477.66	0.942	0.015	3790.12	3471.87	195.846	0.618

Fig. (2): FTIR of Nano silica

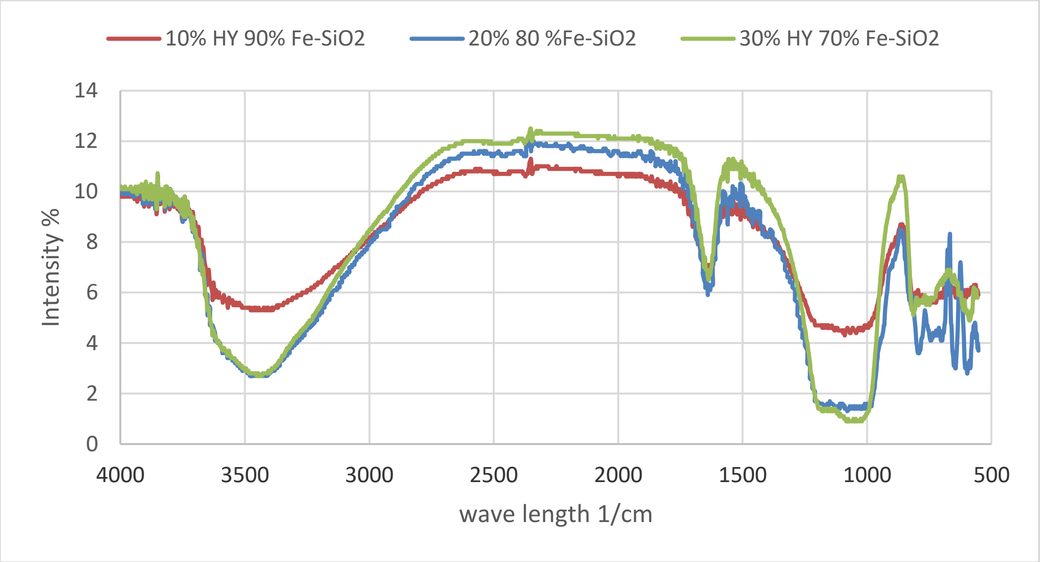


Fig. (3): FTIR of prepared Composite Catalyst at different loading as shown: 10% HY 90% Fe-SiO$_2$, 20% HY 80% Fe-SiO$_2$, 30% HY 70% Fe-SiO$_2$

3.5 Particle Size

The particle size distribution is well-defined as the association amid an assumed particle magnitude and the frequency, or figure of particles, with that convinced diameter or size. For carrier nano-silica: The average nano-particle size is 87.272727 nm, and the diameter range is 50-130 nm. The maximum volume percentage of particles is 23.5%, the size distribution is 85 nm, and the minimum volume percentage is 2, 23% for particles sized at 130 nm [9], [10], As shown in Figure (4).

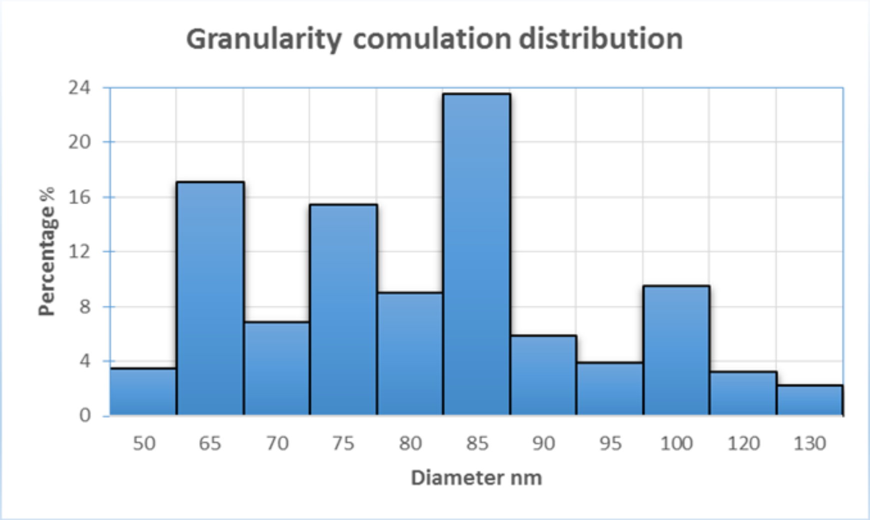


Fig. (4): Particle size distribution of nano-silica

4. Study the Activity:

The efficacy of the catalysts is evaluated in an oxidative desulfurization procedure employing Kerosene and Air. The investigation focuses on variables such as reaction duration, temperature, and HY-zeolite percentage in various composite supports.

4.1 Effect of Reaction Condition (Temperature, Time)

The study found that desulfurization efficiency increases with reaction time, as more prolonged reactions allow reactants to interact and react with each other, leading to an increase in conversion rate and contact duration between reactants with the Catalyst's active site.

The Arrhenius equation states that temperature positively impacts the reaction rate constant, increasing sulfur compound conversion. The reaction rate constant and activation energy are directly proportional to the temperature of the reactants. As temperature rises, the number of molecules with activation energy increases, increasing the conversion rate, as literature describes. [11-16]

The study focuses on the impact of reaction temperature on the surface properties and cross-sectional structure of nano silica powder synthesized by flash calcination. It reveals that higher temperatures increase the likelihood of reactant collisions and release highly adsorbed sulfones from the catalyst surface. The calcination temperature also significantly influences the activity of the Catalyst, with the optimal temperature being 550°C for maximum surface area, pore volume, and average pore size, as in Figures (5) to (8).

Once the oxidization process begins, the rate at which molecular air is absorbed into the liquid, the rate at which sulfur compounds are scattered, and the rate at which air is dissolved within the catalyst pores and reaches the active sites increases with increasing temperature.

Raising the reaction temperature accelerates molecular motion, enhancing the probability of reactant collisions. Moreover, sulfones with the highest adsorption capacity can be readily desorbed from the catalyst surface at high-temperature conditions, as shown in Figures (6), (7), and (8).

The firing temperature of the completed support significantly impacts the development of surface characteristics and cross-sectional structure. The oxidation temperature has a significant impact on the catalyst's activity. The calcination temperature of the catalyst has a significant impact on the density of acidic centers. It has reached its maximal size and enhanced the removal of sulfur compounds from diesel fuel. All of these findings are consistent with those found in earlier studies conducted under these reaction settings. [17]

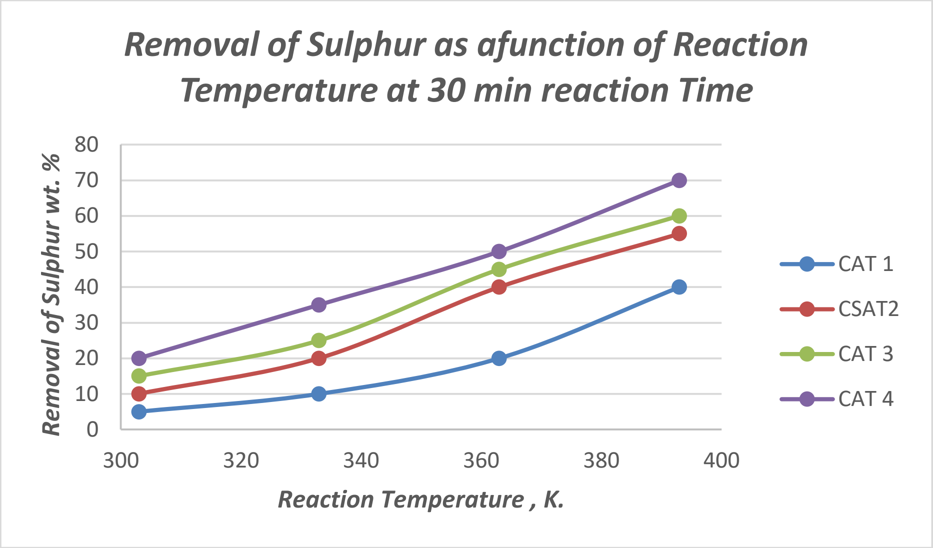


Fig. (5): Effect of Reaction Temperatures on Sulphur Removal wt. % after 30 min of Reaction Time for different Catalysts.

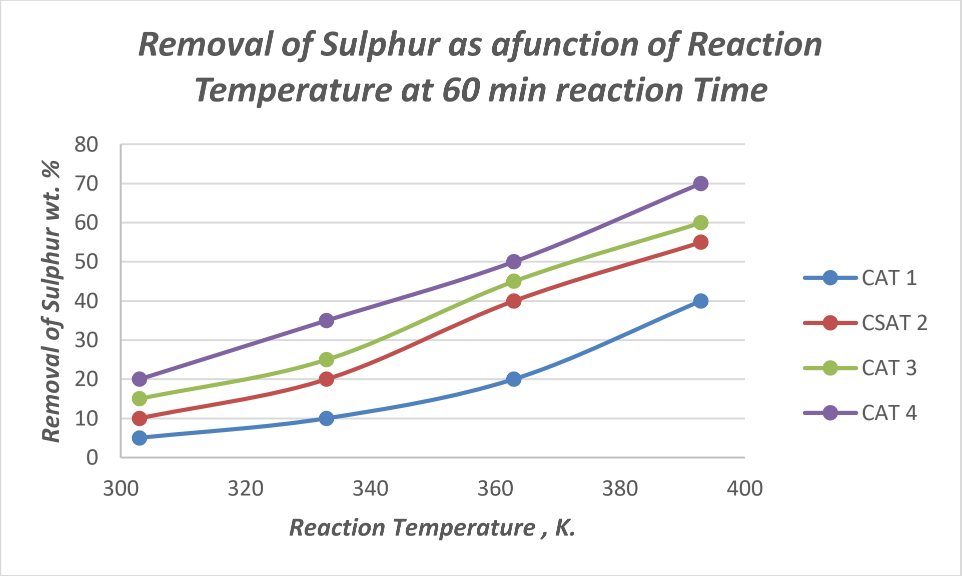


Fig. (6): Effect of Reaction Temperatures on Sulphur Removal wt. % after 60 min of Reaction Time for different Catalysts

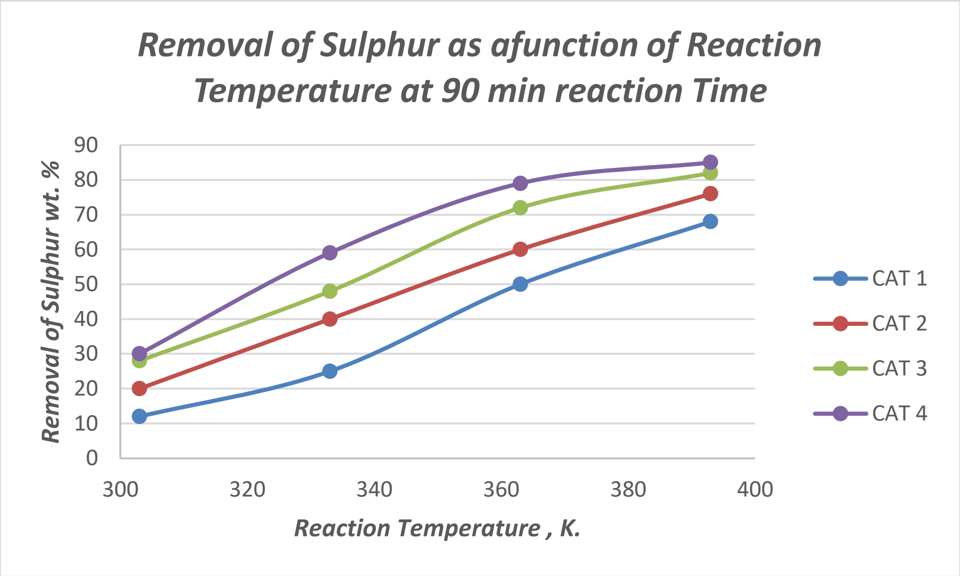


Fig. (7): Effect of Reaction Temperatures on Sulphur Removal wt. % after 90 min of Reaction Time for different Catalysts

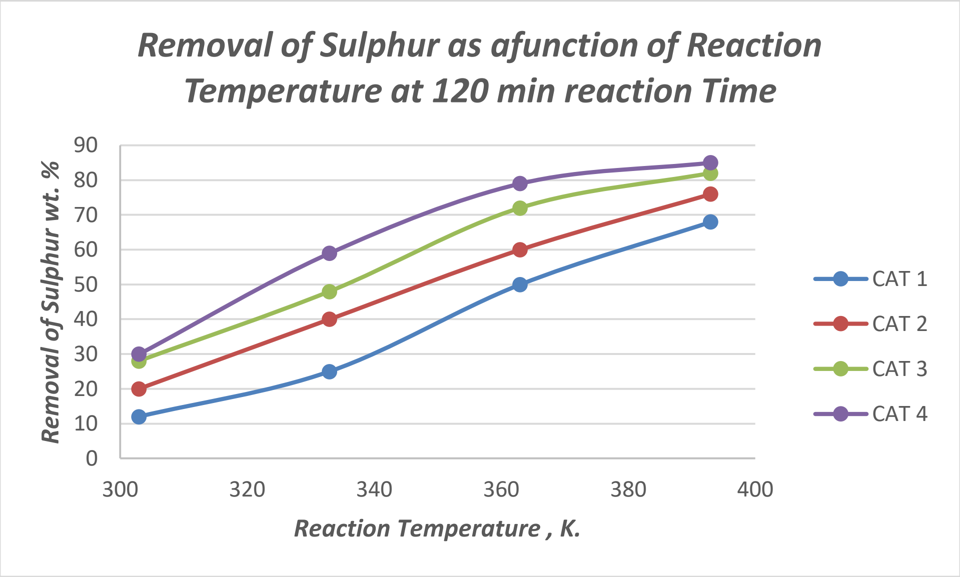


Fig. (8): Effect of Reaction Temperatures on Sulphur Removal wt. % after 120 min of Reaction Time for different Catalysts

4.2 Impact of Hy- zeolite and most active Catalyst

CAT-4 exhibited the highest ODS conversion among all catalysts, attributed to its superior zeolite content, exclusive pore structure, high surface area, and accessible acid locations.

CAT-3 and CAT-4 exhibit significant activity for ODS of sulfur compounds in Kerosene, with maximal conversion rates of 85.35% and 89.83%, respectively, enhancing sulfur removal through adsorptive and oxidative Desulfurization as shown in Figure (9). Zeolite supports have a large surface area, allowing for better sulfur removal due to increased contact area for sulfur compounds. They can accommodate large molecules like alkylated benzothiophene and have higher selectivity for substituted thiophenes and benzothiophenes in Kerosene. Zeolite's high acidity and hydrothermal stability make it a popular choice for sulfur removal. Its unique three-dimensional pore and easily adjustable structures enhance sulfur capacity and selectivity. [13,14,15,16]

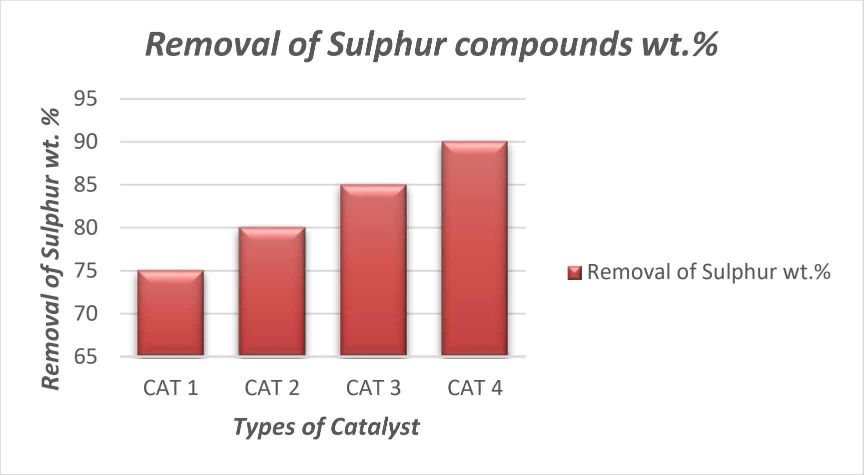


Fig. (9): Total Sulphur Removal as a function of Catalyst Types CAT 1 , CAT2, CAT 3, CAT 4

5. Conclusions:

This research led to the development of a novel method for synthesizing nano silica from Bentonite. Consequently, the nano-silica produced by this method has a large surface area and excellent mechanical properties. The nano-catalyst that is manufactured by hand is considered to be one of the most significant catalysts. It is made up of Fe2O3 and is supported by a composite material that is made up of nano silica and HY zeolite. It is possible to make use of it in ODS procedures. The most extraordinary conversion of sulfur compounds in Kerosene was achieved at a temperature of 393 degrees Celsius and a reaction period of 120 minutes. This resulted in an 89.83 percent conversion over CAT-4. An exceptionally high level of effectiveness was proven by the utilization of nano-particles throughout the catalytic process.

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