Review on SCR catalysts by focusing impacts of sulfur on SCR performance

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Abstract:

Marine diesel engines are extensively used for transportation and as well as for power generation purpose because of its higher durability, thermal and fuel efficiency than the gasoline engines. But the marine diesel engine produced severe NOx emissions that are currently well discussed issue needed to be solved due to its serious health and environmental problems. At the same time, because of increasing stringent regulations of NOx emissions it is necessary for ships to meet the international maritime organization (IMO) Tier III regulations in NOx emission control areas (ECA). It is enforced for the vessels that are constructed on and after the 1st January 2016. Therefore, a demand for well-functioning NOx reduction technology is required. Currently SCR is the most dominant and mature technology used to reduce the NOx with ammonia over the SCR catalyst. SCR catalyst is the core part of SCR system; hence this review described the different types of catalysts and their behavior under different conditions. Furthermore, the deactivation of SCR catalyst occurs by different mechanisms; however, the most significant mechanism is sulfur poisoning. Reaction temperature and availability of ammonia is also significant parameter for sulfur poisoning. Therefore, it is necessary to investigate how sulfur behaves with SCR catalysts. Even though many studies have been performed on Sulphur poisoning of catalysts but still requires complete understanding. This review covers the sulfur poisoning of vanadium and Cu-zeolites based SCR catalysts with mainly focus on Cu-zeolites because of its sulfur sensitivity.

Keywords: marine diesel engine, selective catalysyt reduction; vanadium;cu zeolite; sulfur

1. Introduction

Because of their high thermal efficiency and durability, marine diesel engines are extensively used for power generation as well as for transport purpose. However, only transportation sectors are producing almost world’s 30% greenhouse gases \cite{1}. Marine diesel engine emissions produced serious

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environmental hazardous gases specially NOx. The carbon monoxide (CO), carbon dioxide (CO2) and hydrocarbon (HC) exhaust emissions is much lower in marine diesel engines, as in comparison to automobile design engines and on the contrary, it produces more detrimental Nitrogen oxides (NOx) emissions [2]. NOx emissions are produced due to the combustion process of diesel engine. There are three main sources of NOx formation named as thermal NOx, fuel NOx and prompt NOx. The involvement of fuel NOx and prompt NOx to the total NOx emissions is negligible [4]. Basically thermal NOx is the major contributor of NOx formation throughout the whole combustion process [3]. NOx is very noxious, hazardous and it creates an irritation. It is responsible for the headache and nausea [5]. NOx can react with existence of sunlight and other organic compounds to form ozone layer. In the troposphere Ozone is named as ground level ozone. When NOx is reacted with water, nitric acid can be formed which is the major source of acid rain [6]. In order to reduce NOx from ships, many national governments and international organizations in the world have promulgated different regulations on shipping emissions, and also enforced strict requirements on NOx emission in the Emission Control Areas (ECA) [7]. In 2016, IMO Tier III standard on NOx emission proposed by International Maritime Organization (IMO) has already been enforced in North America Emission Control Area (ECA), including the East and West coast of the USA and Caribbean [8]. Due to the increasing stringent emission regulations, it is necessary for vessels to meet the IMO Tier III legislations applied for ships constructed on and after the 1st January 2016 in NOx emission control areas. Fig. 1 represents the limits of NOx legislations. It is enforced that, during the operation of ships NOx emissions should not exceed 3.4g/kWh. In the requirement of Tier III NOx emission decreased up to 75% as compared to IMO Tier II [9].

Currently three most mature technologies such as exhaust gas recirculation (EGR), Selective catalyst reduction (SCR) and dual fuel are mostly used worldwide to control the NOx as shown in Fig. 2 [10]. It has been observed that in order to decrease the NOx emission intensely and meet the requirements of IMO Tier III, SCR, EGR and Dual fuel can be the effect methods. SCR and EGR are the most feasible and mature techniques used to decrease the NOx of two stroke marine diesel engines. But the dual fuel is not good option, because the low speed two stroke marine diesel engines are still using HFO (Heavy Fuel Oil). But SCR in comparison to EGR is the front runner technology in marine diesel engine due to its higher DeNOx efficiency [11]. In EGR system NOx can be reduced by diverting the exhaust flow of burned gases into combustion chamber. As the recirculated burned gas entered, it is responsible for lowering the adiabatic flame temperature.

Due to the lowering of in-cylinder temperature NOx formation has been reduced. But as a result of temperature reduction, the efficiency of engine also decreased which tends to increase the fuel consumption. Therefore, SCR is the most
prominent and leading technology because it operates with higher efficiency without compromising on both flame temperature and NOx conversion [12].

SCR is the dominant technology used to meet the most recent emission standards due to its technical maturity, better fuel economy and low cost for the emission reduction. SCR is means of converting NOx into N2 and H2O by using catalyst and oxygen (O2) [13]. However, pressure drop occurs at SCR catalyst therefore more efficient turbocharger is necessary for SCR system.

As the NOx is decreased into N2, between the temperature ranges of 300 - 400 °C, the load of engine must be 40% and above. Ammonia (NH3) will start burning when the exhaust temperature of engine goes beyond the 400 °C which will make the system ineffective. SCR catalyst reaction will become slow and undesirable reactions such as formation of ammonium sulfates will occur when the temperature goes below 270 °C, which ultimately destroy the catalyst. Therefore, SCR reaction is mainly restricted by the catalyst activity, species concentration and reaction temperature [14]. Fig. 3 shows the systematic representation of SCR system.

2. Challenges related to SCR system

The major challenges involved with SCR systems is the reduction of catalytic converter volume at low temperatures and the suitable dosing strategy for NH3 at frequently varying load conditions of the diesel engines. Additionally, the risk associated concerning storing and handling of gaseous NH3 is significant and consequentially it is not commonly used as a reducing agent directly. For reasons of toxic nature of NH3, handling and storing problems, urea is the preferred substitute for NH3 as a reducing agent in automotive applications. The best procedure is injecting Urea Water Solution (UWS) in the form of spray to hot exhaust stream before the entry to the SCR catalyst [15]. Urea is an environmentally benign chemical which makes it more suitable for application of the SCR process. Urea is a fertilizer used in agriculture and available in a number of quality grades at a lower cost. Development of Urea-SCR over NH3-SCR has gained momentum due to various problems involved with the use of NH3. NH3 is corrosive, toxic in nature and also a secondary pollutant. In order to introduce NH3 into the exhaust gas stream, proper dosage control mechanism is required [16].

The main advantage with this SCR system is high De-NOx efficiency (90% or higher). The disadvantages involve the space required for the catalyst, high capital and operating costs, formation of other emissions (NH3 slip) and formation of undesirable species which may lead to catalyst poisoning and deactivation. The NH3 slip can be controlled by installing an oxidation catalyst after the SCR system. Although the SCR system has some drawbacks, the technology has been chosen by the majority of the diesel engine manufactures due to absence of better technology to meet the stringent emission standards [15].
There are two main objectives related to SCR system.
- To minimize the NO\textsubscript{x} emissions
- To minimize the ammonia slip

Following factors should be controlled to get the maximum output in above two objectives.
- Design optimization
- Control system
- Temperature fluctuations
- Low operating temperature
- Poisonous species present in the catalyst
- Mechanical vibrations
- Flow variations

Throughout the low load operating conditions, exhaust temperature is also low; this will put direct effect on the chemical reaction of SCR catalyst, which makes reaction slow at low temperature for characteristic composition of exhaust gas. Variations of engine load influenced the flow rate of exhaust gas, temperature, and composition of exhaust gases. Therefore, it is necessary to control the above factors to improve the NO\textsubscript{x} conversion and to reduce the ammonia slip. In general, there is trade off relationship in between NO\textsubscript{x} reduction and ammonia slip [17].

3. Research evolution of SCR catalyst

Catalyst is the core part of SCR system. It has been used for reducing the activation energy, NO\textsubscript{x} decomposition temperature during reaction, to avoid the incidence of unwanted reactions, increase the amount of N\textsubscript{2} in production side and by this means reaction efficiency has been improved. Catalysts selection is the most important. Particularly, the competent SCR catalysts possessed the characteristics as listed below:
- DeNO\textsubscript{x} ability should be high
- Anti-poisoning capacity should be high
- Strong mechanical strength
- Operating temperature should be proper

3.1. Vanadium based SCR catalysts (VSCR)

A VSCR catalyst is the established technology, mostly used in mobile applications [18]. It is the cheapest of all SCR catalysts [19] and also well known for sulfur tolerance [20]. VCRs operates approximately in the temperature range of 280-500 °C [19, 21, 22]. It is also used at low temperatures, but as a result low NO\textsubscript{x} removal efficiency occurs. A VSCR catalyst is mainly composed with the mixture of WO\textsubscript{3} / V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}, where, WO\textsubscript{3} is the thermal promoter and used to increase the catalyst acidity. V\textsubscript{2}O\textsubscript{5} is worked as an active component and TiO\textsubscript{2} is added as a carrier material [20].

The main disadvantage of VSCR is the sudden decline in the performance of acidity and selectivity at the higher temperatures. Deterioration of catalyst or alkali poisoning starts when the temperature window in between of 550-600 °C [18]. Toxicity of vanadium species is also an important issue [19].

3.2. Cu-zeolites based SCR

During the last few years, Cu-zeolites based SCR catalysts becomes the most preferred catalyst because of its high performance [19]. It is commonly used in movable applications [23]. The key benefits related to Cu-zeolites based SCR catalysts are the hydrothermal stability and higher NO\textsubscript{x} activity within the temperature window of 150 to 600 °C [24]. Cu-zeolites based SCR catalysts have good performance even at low temperatures and it is also less sensitive on activity because of the NO\textsubscript{2} Concentration variations [19]. However, Cu zeolites are recognized for their higher sensitivity towards sulfur than the vanadium-based catalysts [25]. A MFI framework of Cu/ZSM-5 was first discovered in 1986, as an effective catalyst used for SCR system [26]. Currently, keen interest is showed towards catalyst structure based on the small pores; with special focus on the Cu/SAPO-34 and on Cu/SSZ-13. Both catalysts have chabazite type structure but the composition of elements is different. While Cu/SAPO-34...
is silicoaluminophosphates and Cu/SSZ-13 are zeolites [27]. While comparing the small pore structure of zeolites catalyst with the structure of larger pore, the structure with small pores has been observed more hydrothermally stable. Besides a very high NO\textsubscript{x} activity and selectivity can be achieved. Furthermore, less amount of by products such as N\textsubscript{2}O can be formed during operating temperature range [27] and also it is less vulnerable for hydrocarbon poisoning [19].

A number of catalysts proved to be suitable in favor of SCR reactions. The most important proper components are transit oxides of metal, although Al\textsubscript{2}O\textsubscript{3}, zeolite, TiO\textsubscript{2}, SiO\textsubscript{2} and carbon are frequently used

| Type of catalysts | Proper components | Carrier | Advantages | Disadvantages | Ref: |
|-------------------|-------------------|---------|------------|---------------|------|
| Commercial catalyst based on vanadium titanium | V\textsubscript{2}O\textsubscript{5} | TiO\textsubscript{2} | SO\textsubscript{2} resistance is high, SCR activity at high and low temperature | Oxidation of SO\textsubscript{2} | [28-30] |
| Noble metals | Sn, Ag, etc. | TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} etc. | H\textsubscript{2}O and SO\textsubscript{2} resistance is high; high low temperature SCR activity | Narrow temperature window; high cost; generation of NO\textsubscript{2}; ammonia oxidation | [31, 32] |
| Oxides of metal | V\textsubscript{2}O\textsubscript{5}, CuO, CeO\textsubscript{2}, MNO\textsubscript{x}, CoO\textsubscript{x}, FeO\textsubscript{x}, and other composite oxide. | TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} etc. | SCR activity is high at 300-400 C; thermal stability is good; poisoning resistance is high | Poor activity at low temperatures | [33, 34] |
| Zeolite | Mn, Ce, Fe, Co, Cu, Cr, etc. | Zeolite | Wide temperature window | Hydrothermal stability is poor | [35, 36] |
| Carbon catalyst | V\textsubscript{2}O\textsubscript{5}, CeO\textsubscript{2}, MNO\textsubscript{x}, etc. | Active carbon, Active carbon filter, carbon nanotubes | Easy regeneration, Specific surface area is large, chemical stability is high, high low temperature activity | Poor SO\textsubscript{2} resistance; energy consumption is high; frequent regeneration. | [37, 38] |

DeNO\textsubscript{x} properties, which have been described in table. 2.

### 3.3. Catalayst Deactivation

The selectivity and activity loss of catalyst over time is known as catalyst deactivation. Mostly there are three mechanisms for the deactivation of SCR catalysts named as thermal, chemical and mechanical. These mechanisms of catalyst decay can be further elaborated into six sub-mechanisms where thermal decay by thermal deprivation such as fouling, sintering and poisoning. Chemical decay can happen due to...
vapor formation, solid-solid reactions and poisoning. Mechanical decay can occur through crushing or fouling. The most important mechanisms for catalyst deactivation are poisoning and fouling [39].

When poisoning is strong, gas-surface chemisorptions happen on catalyst surface; hence, as a result, it blocks the sites for catalyst reaction. Poisoning of species depends upon the adsorption strength of species. The poisoning of species is either produced due to the change in the electronic or geometrical structure of surface or it just blocks the adsorption sites physically. The poisoning of species can be slow or fast, it mostly depending upon the concentration of poison. It can be irreversible or reversible depends upon the adsorption strength of poison [39]. Fouling is due to deposition of species physically produced from fluid phase over the catalyst pores and in the catalytic surface. This is responsible for the blockage of pores and sites, which ultimately result in the loss of activity of catalyst [39].

4. Sulfur poisoning of SCR catalysts

Deactivation of SCR catalyst occurs by different mechanisms; however, the most significant mechanism is sulfur poisoning. The important factor that influences the sulfur poisoning is the type of catalyst material. Some are more and some are less sulphur tolerant depending on the catalyst materials. Reaction temperature and availability of ammonia is also significant parameter for sulfur poisoning. Therefore, it is necessary to investigate how sulfur behaves with SCR catalysts. Although many studies have been done on sulfur poisoning of catalysts, still it requires complete understanding. This review covers the sulfur poisoning of vanadium-based catalyst and Cu-zeolites SCR catalysts with mainly focus on Cu-zeolites because of its sulfur sensitivity.

Many studies present in this review are to investigate the impact of sulfur on SCR activity by accelerating the lab aging in flow reactors. The accelerated aging in lab has been carried out by using the different catalysts for sulfur under different conditions. There are different sulfation methods named as SO2 exposure in the presence of ammonia, SO2 exposure under different SCR conditions or SO3 exposure at different temperature ranges. Few studies also related to the investigation of sulfur poisoning through experimental setup by using fuel with high sulfur contents. The experimental setup which is mostly used to investigate the sulfur

4.1. Sulfur in exhaust gases
The main source of sulfur at the diesel exhaust is originated from the engine lubricating oil and the presence of sulfur contents in the fuel [40]. Throughout the last few years, contents of sulfur present in diesel fuel decreased extensively. Hence, as a result, SO2 level reduced in the atmosphere and also to avoid the use of highly efficient aftertreatment system at the diesel exhaust which is more sulfur sensitive. Today, In North America and Europe Ultra-low sulfur diesel (ULSD) fuel is used which contains sulfur contents less than 10-15 ppm [41]. At diesel exhaust, sulfur oxides (SOx) concentration depends upon the air fuel ratio and contents of sulfur present in the diesel fuel, this relation is represented in Fig 4 [42]. Sulfur is mostly in the form of SO2 at the exhaust of diesel engine. It can be further oxidized into SO3 when the SCR system is located beyond the diesel oxidation catalyst (DOC) [40].

4.2. SCR operated on Heavy Fuel Oil (HFO)
Heavy fuel oil (HFO) is well known for its challenges and disadvantages related to SCR system because it contains high sulfur contents in the diesel fuel. Therefore, it allows the oxidation of SO2 to SO3 during the SCR reaction. It is responsible for the formation of white plumes and Ammonium Bi sulfate (ABS). Furthermore, with the use of HFO the natural contents of vanadium-based catalysts result in the prominent oxidation of SO2. Therefore, at present it is
necessary to design the SCR system in a way that resists the unwanted side reactions.

In two-stroke diesel engines, because of the high energy efficiency, the temperature of gases at the diesel exhaust is low after the turbocharger. It is in between of the 230-260 °C depending upon the load of the diesel engine. Low temperature at diesel exhaust creates problem for the SCR system when the HFO is used in the diesel engine. Hence, in order to get the high fuel flexibility, the main precedence of diesel engine is to produce the exhaust gases with suitable temperature window, which ultimately results in improving the SCR system. The exhaust gas temperature around 330 to 350°C should be ideal during the working of engine on HFO.

4.3. Formation of ammonium sulfates

Ammonium sulfates are produced when the exhaust temperature is low during the SCR catalyst reaction in the presence of NH₃ and SO₃ as shown in reactions below:

\[
\begin{align*}
NH_3 + SO_3 + H_2O & \rightarrow NH_4HSO_4 \quad (1) \\
2NH_3 + SO_3 + H_2O & \rightarrow (NH_4)_2SO_4 \quad (2) \\
H_2SO_3 + NH_3 & \rightarrow NH_4HSO_4 \quad (3) \\
SO_3 + H_2O & \rightarrow H_2SO_4 \quad (4)
\end{align*}
\]

Ammonium bisulfate (ABS), NH₄HSO₄ and Ammonium sulfate (NH₄)₂SO₄ are responsible for the physical blockage of pores and channels of catalyst. Therefore, the result in the deactivation of catalyst. ABS is the most hazardous of all the species [44]. ABS is generally formed, when the temperature is in between 190-240 °C and it starts to decompose when temperature goes around 350 °C [45]. The (NH₄)₂SO₄ decomposition occurs in two stages, first it decomposed into NH₃ and NH₄HSO₄ at about temperature of 300 °C as represented in reaction 5. Second, NH₄HSO₄ will start decomposing when the temperature reaches at higher level as shown in reaction 6 [46].

\[
\begin{align*}
(NH_4)_2SO_4(s) & \leftrightarrow NH_4HSO_4(s) + NH_3(g) \quad (5) \\
NH_4HSO_4(s) & \leftrightarrow NH_3(g) + SO_2(g) + 1/2O_2(g) + H_2O(g) \quad (6)
\end{align*}
\]

4.4. Impacts of Sulfur on vanadium based SCR catalyst

Many authors have proved that, vanadium-based catalysts are operated at relatively narrow temperature range (300–400 °C) of SCR system [47, 48]. If the operating temperature goes below to the 320 °C, the sulfur poisoning, specially poisoning of SO₂ becomes more imperative and the selectivity and activity of the SCR catalysts decreases significantly. Furthermore, when the temperature goes above to the 400 °C, undesirable side reactions can occur which are responsible to produce N₂O and NO from the oxidation of NH₃ [49]. NOₓ removal efficiency is decreased progressively by means of catalyst aging. Presence of SO₂ can cause the deactivation of SCR catalysts during the SCR operation. Inhibition of SO₂ is the most common problem during the activity of catalyst [47, 50, 51]. Following poisoning mechanism of SO₂ is imagined when NH₃-SCR process is used. On the catalyst surface, SO₂ can be oxidized into SO₃. The produced SO₃ reacts with NH₃ to generate the unwanted reactions such as (NH₄)₂SO₄ and NH₄HSO₄. These two generated undesirable substances deposit in the pores of SCR catalyst, which deactivate.
and block the active sites and cause the rapid decrease in the catalyst surface area [52]. The conversion rate of SO₂ is vary from 1%–2% during the normal operating conditions of SCR system [53]. Many studies have proved that, in vanadium-based catalyst V=O bond shows the important role in the oxidation of SO₂ [54]. Thus, the content of V₂O₅ is generally set to be smaller in the SCR catalyst in order to avoid the generation of SO₃. Water vapors appear in the flue gases and can be condensed on the surface of catalyst. It not only produces the exacerbate poisoning by the alkali metals like Na and K, but also responsible for the vaporization and swelling with the increase of temperature. It damages the structure of catalyst, hence in result SCR catalyst is cracked. It has been reported that for the physical adsorption water vapor is to compete with NH₃ and NO on the surface of catalyst, by this means deNOₓ activity of catalyst decreased [55]. The alkali metals such as (Na, K) available in fly ash also disgrace the performance of catalyst when they deposited in the catalysts. Therefore, lengthy acquisition can block pores, which results the poisoning of catalyst [51].

4.5. Impact of sulfur on Cu-zeolite SCR catalyst

Cu-zeolites are the more sulfur sensitive than vanadium-based catalysts. In this review catalysts with small pores such as Cu/SSZ-13 and Cu/SAPO-34 belong to chabazite family are concerned. The exposure of SO₂, SO₃ and/or SO₂ + NH₃, SO₂ are investigated at different conditions of sulfur poisoning, also by considering the impact of temperature simultaneously.

4.5.1. Impact of sulfur on SCR chemical reactions

The different SCR reactions have different impact on the sulfur poisoning of Cu-zeolites catalysts. Standard SCR reaction is much affected than the fast SCR reaction [56, 57]. Furthermore, at low temperatures catalyst activity is severely impacted than the catalyst activity at high temperatures [58].

4.5.2. SO₂ impact on SCR catalyst activity

Many studies have shown the deactivation of Cu-zeolites catalyst under the SO₂ exposure and absence of NH₃. It was reported that at different temperatures, the poisoning of catalyst is different. The SO₂ exposure of unspecified Cu-zeolite has been reported high deactivation of catalyst at 200 °C as compared with 300 °C. Overall less deactivation has been found at 400 °C after the exposure of SO₂ [58]. Cu/SSZ-13 also showed the same trend as above [22], catalyst was more deactivated at 250 °C as compared to 400 °C after poisoning. But the Cu/SAPO-34 showed the opposite trend than the Cu/SSZ-13, it has been reported that Cu/SAPO-34 was more deactivated at 250 °C than the 150 °C after sulfation [59]. Also it has been shown that the Cu/SAPO-34 was more deactivated at 400 °C as compared to 200 °C after the SO₂ exposure [57].

4.5.3. SO₂ + NH₃ impact on SCR catalyst activity

A comparative study between sulfation and with or without the presence of ammonia reported that, with the presence of NH₃ at the temperature of 300 °C after sulfation, more deactivation of catalyst was found [56]. Also, the same trend has been shown in another study [57], at temperature 400 °C during the presence of NH₃, poisoning of SO₃ produced the more negative affect as compared to the poisoning of SO₂ without the use of NH₃.

4.5.4. SO₂ and/or SO₃ impact on SCR catalyst activity

SO₃ poisoning has produced more significant impact of deactivation as compared with SO₂ poisoning. Unspecified Cu-zeolites was used to investigate the impact of poisoning temperature. With the increase of poisoning temperature (200, 300, 400 °C) more deactivation has been reported [60]. Also, at the same temperature conditions, the impact of SO₂ as compared with SO₃ was investigated. It has been reported that poisoning of SO₂ resulted more significant deactivation than the SO₂ poisoning for all temperature ranges.
During the investigation of Cu/SAPO-34 catalyst it has been observed that for SO$_3$ poisoning temperature was an important parameter [61]. Poisoning of SO$_2$ and SO$_2$ + SO$_3$ at temperature of 200 °C both has same impact on the catalyst activity. However, SO$_2$ + SO$_3$ poisoning at temperature of 400 °C was responsible for the severe deactivation of catalyst than the SO$_2$ poisoning. It has been reported that the mechanism for the poisoning of SO$_2$ and SO$_3$ was different, whereas poisoning of SO$_2$ is due to the adsorption and poisoning of SO$_3$ is because of chemical reactions having activated temperature with catalyst surface.

Cu-zeolite catalyst associated with poisoning of sulfur was studied by putting 35 ppm of SO$_2$ in a “diesel system simulator” (DSS). It consists of diesel oxidation catalyst (DOC) at the upstream of catalyst soot filter (CSF) and followed by SCR system. Since the SCR reactor was located after the DOC, therefore some part of SO$_2$ oxidized into SO$_3$. It has been proved that after the 400 hours the activity of SCR reactor started to lose, which was about 4g of sulfur/litre [62].

4.5.5. Sulfur storage on Cu-zeolites

Many papers have been reported the storage of sulfur on Cu-zeolite and the poisoning of SO$_2$. It has been observed that different temperatures have different impact on sulfur storage. A Cu/SAPO-34 [59] and unspecified Cu-chabazite [57] catalysts with chabazite structure were studied by considering the sulfur storage on catalysts. It has been reported in both investigations that exposure of SO$_2$ at high temperatures first at (350 °C vs 190 °C) and later at (250 °C vs 150 °C) showed sulfur storage in large amount. In another study [58] unspecified Cu-zeolite showed the opposite trend, where exposure of SO$_3$ at low sulfation temperature (Setting temperature for results: 200 °C, 300 °C and 400 °C) reported large amount of sulfur storage. However, it has also been investigated in same study; the catalyst activity showed the larger decline at high temperatures after the sulfation.

It was investigated that sulfur storage impacted with the different forms of sulfur [57, 58] both reported that the sulfur storage as a result of SO$_3$ exposure is more than SO$_2$ exposure. Also, it has been observed that during sulfation period, the sulfur storage at the present of NH$_3$ is more affected than the absence of NH$_3$ [56, 59, 63].

Temperature programmed desorption (TPD) was used to investigate the sulfur storage on the four different sulfur saturated chabazite structure SCR catalysts. Fig. 5 showed the TPD diagram. Sulfur saturation of SO$_2$ and SO$_3$ was shown by solid lines and only SO$_2$ by dotted lines. At the temperature of 190 °C and 350 °C, blue and red lines were sulfur saturated respectively.
4.5.6. Regeneration of sulfated Cu-zeolite

It has been reported that different types of ways showed different results while regenerating the sulfated Cu-zeolites. Sulfation of 200 ppm of SO$_2$ at 130 °C for 3 hours was carried out to regenerate the Cu/SAPO-34 catalyst [46]. Regeneration of a Cu/SAPO-34 catalyst was performed for 12 hours by varying temperatures at 300, 400, 500, 600 and 700 °C. Up to temperature of 600 °C, regenerated catalyst showed the limited recovery in NO removal efficiency. The regeneration of catalyst was fully observed at 600 °C.

Various sulfation methods were used to investigate the regeneration of Cu-chabazite catalyst [57]. It has been observed that the regeneration of SO$_2$ aged catalyst at low temperature (200 °C) was easier than the high temperature (400 °C) aged. Furthermore, during the comparison of SO$_2$ aged catalyst, with and without the presence of NH$_3$, no difference has been observed in the regeneration of catalyst. A repeated activity test has been performed for the regeneration of Cu/SSZ-13 catalyst at temperatures in between of 100 °C to 400 °C [56]. Catalyst with exposure of SO$_2$ poisoning (30 ppm) was investigated at temperature of 300 °C for 1.5 hours. Eight activity tests have been performed to obtain the stable activity. It has been observed from the experiment that by repeating the activity test some activity was recovered but not achieving the fully regeneration of catalyst.

Cu-chabazite catalyst was used to investigate the regeneration also named as chemical deSO$_x$ method [21]. For reducing the environmental problems, low concentration of reductant such as NH$_3$, NO$_2$+NH$_3$, C$_2$H$_6$ and n-C$_{12}$H$_{26}$ was used. By using this technique, it has been observed that at lower regeneration temperatures, recovery of NO$_x$ conversion activity and removal of sulfur was achieved.

4.5.7. Characterizations of sulfated Cu-zeolites

Sulfated catalyst has been characterized in many studies. N$_2$ adsorption is used to determine to surface area and its pore volume. It has been observed that after the sulfation both surface area and pore volume were decreased [20-22, 56]. But after regeneration both could be recovered [22]. X-ray fluorescence (XRF) was used to investigate the framework of SAPO-34 and it has been observed that it was not changed after the poisoning of SO$_2$. This recommends that sulfur only affects the copper sites of catalyst not the framework of zeolite [64].

Analysis of Inductively coupled plasma (ICP) and X-ray photoelectron spectroscopy (XPS) were used to investigate the sulfur distribution, it has been found that, sulfur was uniformly distributed only if the catalyst was saturated [57, 61]. More sulfur has been observed at the catalyst inlet as compared to outlet, if the catalyst was not saturated properly [56, 58].

Numerous methods have been reported to determine the type in which storage of sulfur is taken place over the sulfated Cu-zeolite. It has been observed that there are two primary sulfur species such as ammonium sulfates and copper sulfates depending upon the sulfation conditions [46, 58, 59]. Formation of ammonium and copper sulfates was studied on the Cu/SAPO-34 catalyst [65]. It has been observed that ammonium and copper sulfates are exchangeable depends upon the availability of NH$_3$. Ammonium sulfates can be formed by NH$_3$ exposure of copper sulfates over the catalyst. During the absence of NH$_3$ the usage of ammonium sulfates upon the NO exposure behaves as SCR reactant. However, this reaction is much slow as compared to normal SCR reaction. Also, copper sulfates are formed when the SCR reactants are ammonium sulfates.
4.5.8. Sulfur poisoning mechanism on Cu-zeolite
Cu/SSZ-13 catalyst was used to investigate the active sites. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with NH₃ probing was used to identify the two Cu-sites. In SCR reactions both sites were active but in oxidation reactions only one site was active. Furthermore, also their responses towards sulfur poisoning and hydrothermal aging were investigated. In oxidation reaction the active site was disappeared and in SCR reaction, both active site was reduced extensively [66]. After SO₂ poisoning, the activity loss over the Cu/SAPO-34 catalyst was described by the reduction in the active sites of Cu-zeolite because of the sulfur present in the catalyst. It has been observed that the NO conversion and sulfur exposure showed inverse relationship if sulfur exposure was increased then NO conversion was decreased [64].

4.6. Behavior of sulfur over SCR catalysts with different temperatures (Recent developments)
SO₂ poisoning of NH₃-SCR was evaluated by Yasser [67] over Cu-SAPO-34, mainly to investigate stored S forms/states and the effect of them on reduction activity of low-temperature NOx. There were two types of primary sulfur species found, and it was observed that they both were interchangeable depending upon the availability or the absence of NH₃. Cu sulfate species as well as Ammonium sulfate species could be found in one case, while for the other case only Cu sulfate species would be found. Cu sulfate was available in three different states/forms when ammonia was absent, this was found out by three desorption features while conducting experiments of TPD (temperature programmed desorption). NO adsorption’s DRIFTS (Diffuse reflectance infrared Fourier transform spectroscopy) was utilized for the investigation of accessibility and nature of Cu species prior to and after the sulfate formation, subject to no intrusion by ammonium sulfate; the acquired states showed that the sulfur had completely blocked Cu²⁺ within the six membered rings, and nature of [CuOH]⁺ near the eight-membered ring had changed. On analyzing impacts of dissimilar states of S on reduction activity of NOx, ammonium sulfate having low-temperature was found to have the greatest effect on the loss of performance. Moreover, the data demonstrated that ammonium sulfate have tendency to work as SCR reactant, quite similar to the system incorporating ammonium nitrate. Decomposition of Ammonium sulfate starts at temperatures which can be as small as 300–350 °C, in contrast to that higher temperatures (>480 °C) were required for desorption of other S containing species as illustrated in fig 6.

Fig. 6. SCR changing at 210 °C along with the raw sample, during existence of SO₂ quantity 50 ppm, sample on which CuₓSOᵧ was materialized and later brought to temperatures of 430, 530, 630, 730, and 830 °C in presence of (NH₄)ₓ or N₂

This seems promising, as reaction of NH₃ can occur in the presence of catalyst with reabsorbed sulfur to form ammonium sulfate, having tendency to decompose at smaller temperatures as compared to other forms of sulfate.

Sandra [68] observed the impacts of Sulphur experimentally, upon low-temperature behavior of Cu-SSZ-13 SCR catalyst. The outcomes of exposure
temperature of sulfur, and impacts of NO\textsubscript{2}/NO\textsubscript{x} ratio, are taken into consideration and a comparison of two separate regeneration temperatures is performed. Besides that, samples of catalyst taken from catalyst affected by an engine-aged are analyzed. Exposition temperature of SO\textsubscript{2} possesses important effect on Cu-SSZ-13 catalyst deactivation. The most severe deactivation is caused due to lowest Sulphur exposure temperature (220 °C), whereas during the highest temperature of Sulphur exposure (400 °C) deactivation of the lowest degree is observed as demonstrated in figure 7.

Yulong [69] investigated the hydrothermal aging at prominent temperature. Not the same as the reversible hindrance of SO\textsubscript{2} harming that happens at truncated temperatures, because of the demolition of the zeolite structure the sulfur harming at prominent temperature is long-lasting.

In Figure 8 the benchmark SCR NO\textsubscript{x} and NH\textsubscript{3} transformation exercises of HA-Cu-SSZ-13, FR-Cu-SSZ-13 and SA-Cu-SSZ-13 chemical agents are portrayed by means of a portion of temperature as of 150 to 550 °C. It has been observed the Cu-SSZ-13 showed the finest NH\textsubscript{3}-SCR action on entire temperature ranges. The decrease action of NO weakened somewhat for the Cu-SSZ-13 afterwards it was hydrothermally aged at 750 °C aimed at 32h. For the SA-Cu-SSZ-13 test critical loss of not any decreased movement was watched that was hydrothermally aged within the sight of 100 ppm SO\textsubscript{2}.Throughout hydrothermal aging proposed deactivation of Cu-SSZ-13 was significantly more extreme within the sight of SO\textsubscript{2}. The NH\textsubscript{3} change is a lot advanced than any transformation due to unselective NH\textsubscript{3} oxidation. When the temperatures over 450 °C and 300 °C aimed at the SA-Cu-SSZ-13 and HA-Cu-SSZ-13 tests, the uncritical NH\textsubscript{3} oxidation was fundamentally in charge for the decomposition of not any adaptation at prominent temperatures.

Meiqing [70] investigated the impact of SO\textsubscript{3} poisoning over Cu/SAPO-34.

Fig. 8. NO and NH\textsubscript{3} =500 ppm, 5 vol. %O\textsubscript{2}, 5 vol. % H\textsubscript{2}O, equilibrium N\textsubscript{2}. GHSV =400,000 h\textsuperscript{-1}, NO\textsubscript{x} and NH\textsubscript{3} change of HA-Cu-SSZ-13, FR-Cu-SSZ-13 and SA-Cu-SSZ-13 catalysts below normal SCR circumstances.

Fig. 9. The reaction of NH\textsubscript{3} SCR consisting sulfated and fresh Cu/SAPO-34 catalysts is shown. In comparison to F-Cu, declines in NO\textsubscript{x} conversion are seen of sulfated catalysts when SO\textsubscript{3} to SO\textsubscript{2} ratio increases. Remarkably, throughout the whole temperature region, S-20-Cu was found to be least active catalyst of all kinds of sulfated samples. Unsulfured catalysts having 600 °C (7 ppm) has the highest N\textsubscript{2}O formation on it, and the sulfation action results in reduction of the formation of N\textsubscript{2}O by 1 to 2 ppm. (Fig. 8b).
In this work [71] the deactivation conducts and procedure of a Cu-SAPO-34 catalyst by reactor trial and DFT computations was studied. The dignified steady state of NOx changes for the new catalyst can be determined from the figure 1A, after introduction to SO2, and subsequently regeneration at 550 °C. After introduction of SO2, 1.5 ppm portion was added to the SCR-feed, SO2 concentration is also presumed in automotive diesel exhaust, for 8h we detained the new catalyst at 300 °C, Execution at 550 °C for 1 h in SCR-feed gas in the absence of SO2 for renewal of the catalyst. When SO2 was introduced it resulted in significantly lesser steady state NOx changes in the temperature variety 150–300 °C.

For all intents and practical purposes after probing SO2 deactivation, it is frequently convenient towards quicken the SO2-harming by rising the concentration of SO2 and proportionally abbreviating the exposure period. The outcomes are then construed in appellation of the overall SO2 exposure, considered as the formation of the SO2 fractional pressure and the exposure period, instead of the SO2 concentration. This elucidation needs that a straight proportionality occurs and the exposure period and SO2 concentration, in a way that dual framework can be climbed with respect to SO2-harming. By estimating the outcomes of the non-accelerated SO2 introduction scalability was scrutinized for example introduction to 1.5 ppm SO2, towards the outcomes from a catalyst revealed to an enhanced SO2 introduction. Meant for the enhanced SO2 introduction, the concentration of SO2 was enlarged by a number 10 and the introduction time was harmoniously reduced.

**Fig. 9.** NOx conversion as a relation pertaining to reaction temperature on the raw and sulfated catalysts S-0-Cu = 50 ppm of SO2 for 16h, S-6-Cu = 50 ppm of SO2 (6% SO3) for 16h, S-13-Cu = 50 ppm of SO2 (13% SO3) for 16h and S-20-Cu 50 ppm of SO2 (20% SO3) for 16h (a) and emergence of N2O in course of NH3 SCR reaction over the fresh and sulfated catalysts (b)The execution of reaction was done with a mixture containing NOx 500 ppm, NH3500 ppm, 7% CO2, 5% O2, 3% H2O, and balance N2 owing to GHSV = 72,000 h⁻¹
Fig. 10(A) NOx as purpose of temperature exhibits its conversion for the Cu-SAPO-34 catalyst earlier and later experience to 1.5ppm (B) The temperature for the Cu-SAPO-34 by NOx conversion catalyst earlier and later exposure to 15 ppm (C) After deactivation the sulfated (blue inns) and recovered (red inns) express the Cu-SAPO-34 catalysts assessed at 180 °C, afterwards introduction to 1.5 ppm SO2 aimed at 8h and 15 ppm SO2 aimed at 48 min.

Therefore, in the SO2 in SCR-feed gas was exposed to 15 ppm for 48 min at 300 °C. Figure10B illustrates the stable state of NOx changes earlier and later the accelerated SO2 exposure, and later 1 h renewal at 550 °C inside SCR-feed gas. The outward form of the NOx changes is for the enhanced SO2 introduced catalyst in Fig. 10B, it is very analogous to the revealed inside figure10A, figure10B. Illustrates the NOx vicissitudes of the new catalyst is somewhat underneath those of the new catalyst in figure 10A which is because of slight variances in the catalyst loads. Hence, to check the resemblance of the impact of the enhanced and non-enhanced SO2 exposure circumstances on the SCR presentation of the catalyst, the deactivation (assessed at 180 °C) after SO2 experience and renewal are illustrated in Figure 10C. After both behaviors the degree of deactivation is similar with overall deactivations of 80 and 79% and permanent deactivations of 16% and 18%. For the same total exposure, it signifies that the deactivation is identical, here SO2 concentration and revelation period are scalable.

5. Summary
Vanadium based catalysts can be impacted by sulfur exposure in different ways. If NH3 is absence during poisoning at high temperatures, NOx activity can be increased. If NH3 is present during the sulfur exposure of catalyst, formation of ammonium sulfates can be produced, which ultimately results the physical deactivation of catalyst. The decomposition of ammonium sulfates occurs when the temperature in between 280-350 °C and also by increasing the temperature regeneration of catalyst can be achieved. Consequently, the main problem occurs with vanadium-based catalyst when the high level of sulfur is exposed at low temperatures. Thus, the catalyst temperature never exceeds the decomposition temperature.

NOx activity can be deactivated with sulfur exposure of Cu-zeolites catalysts. SO3 poisoning is capable to produce severe deactivation of catalyst activity, high sulfur storage and very hard to regenerate the catalyst as compared to SO2 poisoning. SO3 and SO2 poisoning are not reliable with impact of temperature. It has been recommended that, at high temperature chemisorption occurs over the catalyst surface and at low temperature formation of ammonium sulfate and physical adsorption...
occurs. Two sulfated species were observed while characterizing the sulfated Cu-zeolite named as ammonium and copper sulfates. It has been recommended that sulfated species is the main cause of deactivation which ultimately blocks the active Cu-sites, either by the formation of ammonium and copper sulfates that blocks the active sites of catalyst physically or by adsorption of sulfur species. Furthermore, sulfur poisoning does not affect the zeolite structure, but it only affects the active sites of copper. Sulfated catalysts have been regenerated in a lean environment by increasing exposure temperature about to 600-700 °C.

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