

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 NO_x 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 NO_x emissions it is necessary for ships to meet the international maritime organization (IMO) Tier III regulations in NO_x 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 NO_x reduction technology is required. Currently SCR is the most dominant and mature technology used to reduce the NO_x 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 catalyst 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 [1]. Marine diesel engine emissions produced serious

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environmental hazardous gases specially NO_x . The carbon monoxide (CO), carbon dioxide (CO_2) 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 (NO_x) emissions [2]. NO_x emissions are produced due to the combustion process of diesel engine. There are three main sources of NO_x formation named as thermal NO_x , fuel NO_x and prompt NO_x . The involvement of fuel NO_x and prompt NO_x to the total NO_x emissions is negligible [4]. Basically thermal NO_x is the major contributor of NO_x formation throughout the whole combustion process [3]. NO_x is very noxious, hazardous and it creates an irritation. It is responsible for the headache and nausea [5]. NO_x 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 NO_x is reacted with water, nitric acid can be formed which is the major source of acid rain [6]. In order to reduce NO_x from ships, many national governments and international organizations in the world have promulgated different regulations on shipping emissions, and also enforced strict requirements on NO_x emission in the Emission Control Areas (ECA) [7]. In 2016, IMO Tier III standard on NO_x 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 NO_x emission control areas. Fig. 1 represents the limits of NO_x legislations. It is enforced that, during the operation of ships NO_x emissions should not exceed 3.4g/kWh. In the requirement of Tier III NO_x 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 NO_x as shown in Fig. 2 [10]. It has been observed that in order to decrease the NO_x 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 NO_x of two stroke marine diesel engines. But the dual fuel is not good

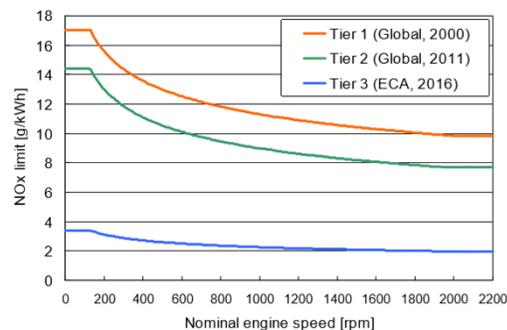


Fig. 1. Represents the limits of NO_x legislations [9]

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 De NO_x efficiency [11]. In EGR system NO_x 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 NO_x 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

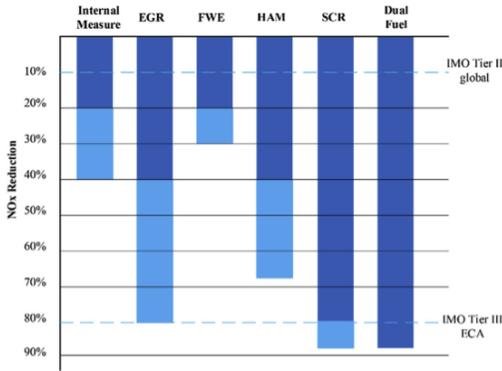


Fig. 2. NO_x Removal Technologies

prominent and leading technology because it operates with higher efficiency without compromising on both flame temperature and NO_x 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 NO_x 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.

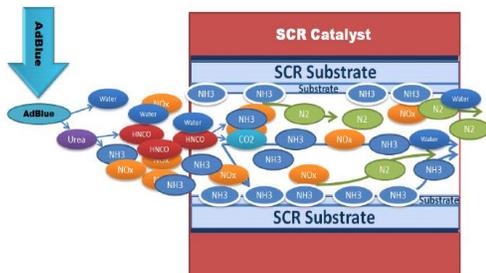


Fig. 3. Systematic representation of SCR System

As the NO_x 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-NO_x 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_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_x conversion and to reduce the ammonia slip. In general, there is trade off relationship in between NO_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_x decomposition temperature during reaction, to avoid the incidence of unwanted reactions, increase the amount of N₂ 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_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]. VSCRs 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_x removal efficiency occurs. A VSCR catalyst is mainly composed with the mixture of WO₃/ V₂O₅/TiO₂, where, WO₃ is the thermal promoter and used to increase the catalyst acidity, V₂O₅ is worked as an active component and TiO₂ 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_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 NO₂ 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 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_x activity and selectivity can be achieved. Furthermore, less amount of by products such as N₂O can be formed during operating temperature range [27] and also it is less vulnerable for hydrocarbon poisoning [19].

While the comparing of Cu/SAPO-34 and Cu/SSZ-13, it was observed that Cu/SAPO-34 has been more hydrothermal stable rather than Cu/SSZ-13 [26].

A number of catalysts proved to be suitable in favor of SCR reactions. The most important proper components are transit oxides of metal, although Al₂O₃, zeolite, TiO₂, SiO₂ and carbon are frequently used

Table I. Summarized description of main SCR catalysts

Type of catalysts	Proper components	Carrier	Advantages	Disadvantages	Ref:
Commercial catalyst based on vanadium titanium	V ₂ O ₅	TiO ₂	SO ₂ resistance is high, SCR activity at high and low temperature	Oxidation of SO ₂	[28-30]
Noble metals	Sn, Ag, etc.	TiO ₂ , Al ₂ O ₃ etc.	H ₂ O and SO ₂ resistance is high; high low temperature SCR activity	Narrow temperature window; high cost; generation of NO ₂ ; ammonia oxidation	[31, 32]
Oxides of metal	V ₂ O ₅ , CuO, CeO ₂ , MnO _x , CoO _x , FeO _x , and other composite oxide.	TiO ₂ , Al ₂ O 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 ₂ O ₅ , CeO ₂ , MnO _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 ₂ resistance; energy consumption is high; frequent regeneration.	[37, 38]

like carriers. All catalysts have possessed different advantages and disadvantages and DeNO_x properties, which have been described in table. 2.

3.3. Catalyst 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

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

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].

4.1. 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 (SO_x) 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.

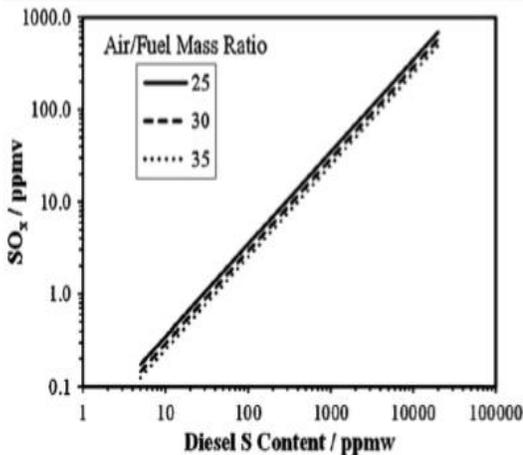
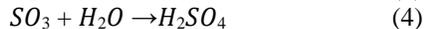
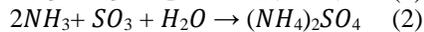


Fig. 4. Relation in between the contents of sulfur in the diesel fuel and SO_x concentration at diesel exhaust for three air to fuel ratio

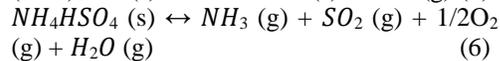
In two-stroke diesel engines, because of the high energy efficiency, the temperature of gases at the diesel exhaust is low after the turbocharger. It is in between of the 230- 260 °C depending upon the load of the diesel engine. Low temperature at diesel exhaust creates problem for the SCR system when 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 [43].

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 SO_x as shown in reactions below:



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].



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]. NO_x 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 deNO_x 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 least 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 SO_x produced the more negative affect as compared to the poisoning of SO_x 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 SO₃ 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 $\text{SO}_2 + \text{SO}_3$ at temperature of 200°C both has same impact on the catalyst activity. However, $\text{SO}_2 + \text{SO}_3$ 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].

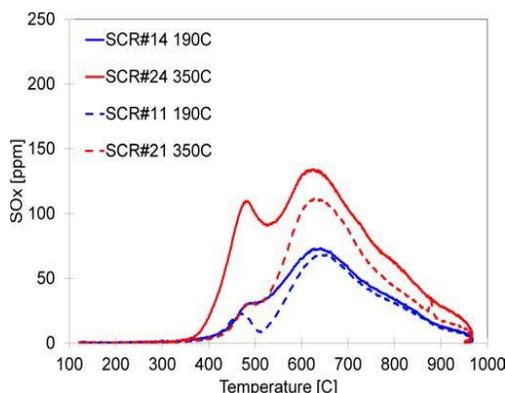


Fig.5. SO_x released during TPD on four different sulfur saturated chabazite structure SCR catalysts. Sulfur saturation of SO_2 and SO_3 was shown by solid lines and only SO_2 by dotted lines. At the temperature of 190°C and 350°C , blue and red lines were sulfur saturated respectively

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. At DOC, SO_2 was oxidized into SO_3 , therefore the ratio of SO_3 and SO_2 largely depends upon the sulfation temperature. At high sulfation temperatures, significant amount of SO_3 can be estimated. Two peaks have been shown in all TPD curves first at ca 480°C and second at ca 650°C . It has been concluded that for both SO_3 and SO_2 , sulfur storage was much more after sulfation as compared to only SO_2 . Furthermore, at high temperature (350°C), more sulfur storage occurs after sulfation than the low temperature (190°C) [57].

4.5.6. Regeneration of sulfated cu-zeolite

It has been reported that different type of ways showed different results while regenerating the sulfated Cu-zeolites. Sulfation of 200 ppm of SO₂ 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 SO₂ aged catalyst at low temperature (200 °C) was easier than the high temperature (400 °C) aged. Furthermore, during the comparison of SO₂ aged catalyst, with and without the presence of NH₃, 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 SO₂ 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 NH₃, NO_x+NH₃, C₂H₆ and n-C₁₂H₂₆ 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. N₂ 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 SO₂. 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 NH₃. Ammonium sulfates can be formed by NH₃ exposure of copper sulfates over the catalyst. During the absence of NH₃ 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 NH_3 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 SO_2 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)

SO_2 poisoning of NH_3 -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 NH_3 . 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 Cu^{2+} within the six membered rings, and nature of $[\text{CuOH}]^+$ near the eight-membered ring had changed. On analyzing impacts of dissimilar states of S on reduction activity of NO_x , 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.

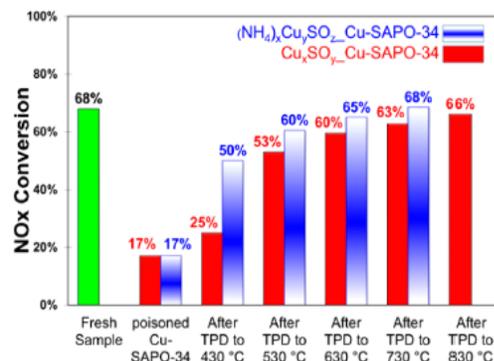


Fig. 6. SCR changing at 210 °C along with the raw sample, during existence of SO_2 quantity 50 ppm, sample on which Cu_xSO_y was materialized and later brought to temperatures of 430, 530, 630, 730, and 830 °C in presence of $(\text{NH}_4)_x$ or N_2

This seems promising, as reaction of NH_3 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_x/NO_2 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_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_2 harming that happens at truncated temperatures, because of the demolition of the zeolite structure the sulfur harming at prominent temperature is long-lasting.

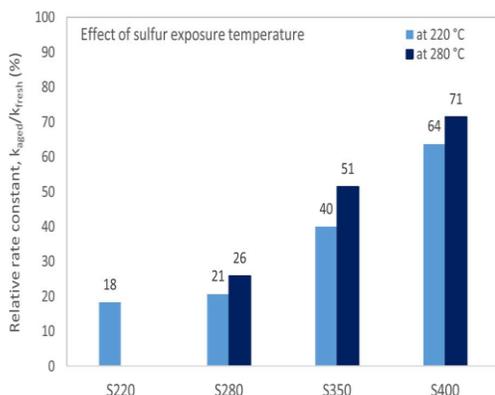


Fig. 7. Relative rate constants for catalyst exposed at different temperature ranges. Note that, the sample which was brought at 220 °C to SO_2 had no test at 280 °C. 5 vol.-% H_2O , 10 vol.-% O_2 1000 vol.-ppm NH_3 , 1000 vol.-ppm NO , 120,000 h^{-1} GHSV during the test of activity.

In Figure 8 the benchmark SCR NO_x and NH_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 new Cu-SSZ-13 showed the finest NH_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_2 . Throughout hydrothermal aging proposed deactivation of Cu-SSZ-13 was significantly more extreme within the sight of SO_2 . The NH_3 change is a lot advanced than any transformation due to unselective NH_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_3 oxidation was fundamentally in charge for the decomposition of not any adaptation at prominent temperatures.

Meiqing [70] investigated the impact of SO_3 poisoning over Cu/SAPO-34.

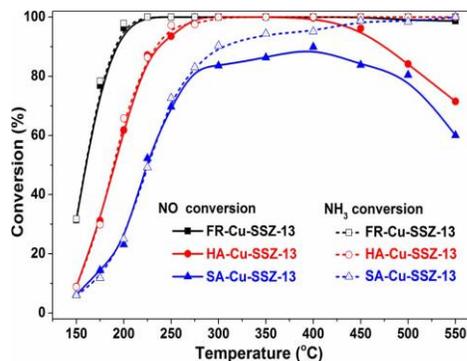


Fig. 8. NO and $\text{NH}_3 = 500$ ppm, 5 vol. % O_2 , 5 vol. % H_2O , equilibrium N_2 . GHSV = 400,000 h^{-1} . NO_x and NH_3 change of HA-Cu-SSZ-13, FR-Cu-SSZ-13 and SA-Cu-SSZ-13 catalysts below normal SCR circumstances.

Fig. 9 The reaction of NH_3 SCR consisting sulfated and fresh Cu/SAPO-34 catalysts is shown. In comparison to F-Cu, declines in NO_x conversion are seen of sulfated catalysts when SO_3 to SO_x ratio increases. Remarkably, throughout the whole temperature region, S-20-Cu was found to be least active catalyst of all kinds of sulfated samples. Unsulfated catalysts having 600 C (7 ppm) has the highest N_2O formation on it, and the sulfation action results in reduction of the formation of N_2O 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 NO_x 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 NO_x changes in the temperature variety 150–300 °C.

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.

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

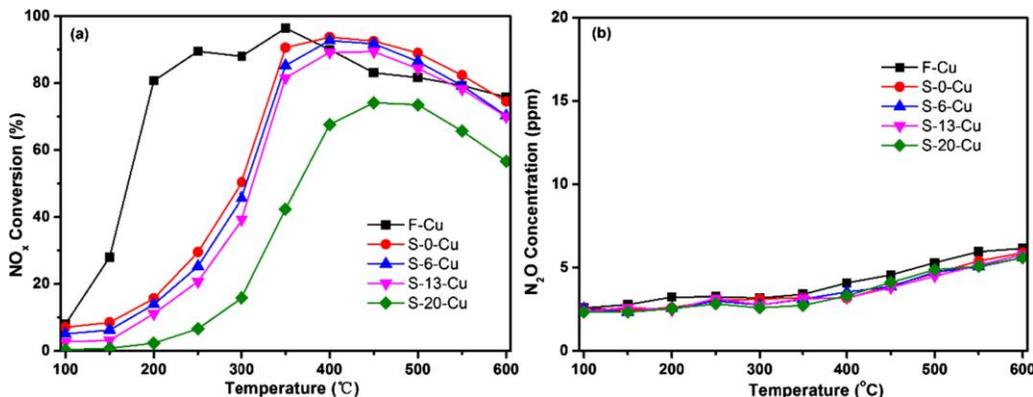


Fig. 9. NO_x conversion as a relation pertaining to reaction temperature on the raw and sulfated catalysts S-0-Cu = 50 ppm of SO₂ for 16h, S-6-Cu = 50 ppm of SO_x (6% SO₃) for 16h, S-13-Cu = 50 ppm of SO_x (13% SO₃) for 16h and S-20-Cu 50 ppm of SO_x (20% SO₃) for 16h (a) and emergence of N₂O in course of NH₃ SCR reaction over the fresh and sulfated catalysts (b) The execution of reaction was done with a mixture containing NO_x 500 ppm, NH₃ 500 ppm, 7% CO₂, 5% O₂, 3% H₂O, and balance N₂ owing to GHSV = 72,000 h⁻¹

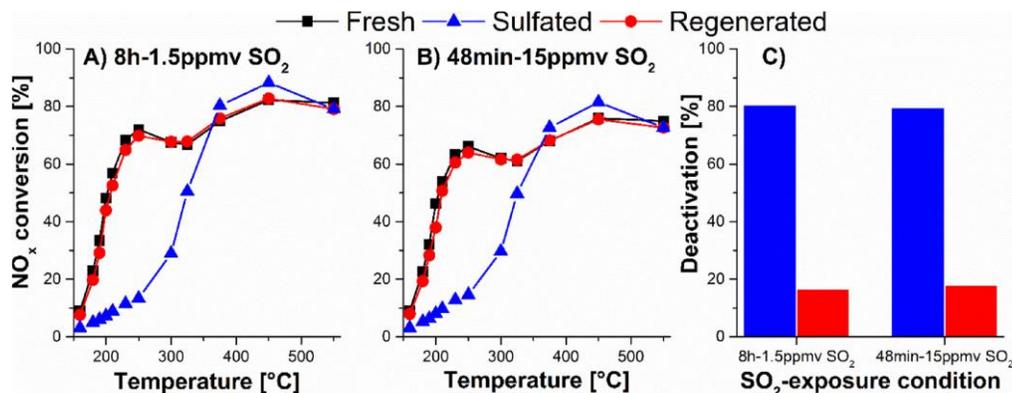


Fig. 10(A) NO_x as purpose of temperature exhibits its conversion for the Cu-SAPO-34 catalyst earlier and later experience to 1.5ppm **(B)** The temperature for the Cu-SAPO-34 by NO_x conversion catalyst earlier and later exposure to 15 ppm **(C)** After deactivation the sulfated (blue inns) and recovered (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. Figure 10B illustrates the stable state of NO_x 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 NO_x changes is for the enhanced SO₂ introduced catalyst in Fig. 10B, it is very analogous to the revealed inside figure 10A, figure 10B.

Illustrates the NO_x 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, NO_x 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.

NO_x 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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