

Review

# Poisoning of SCR Catalysts by Alkali and Alkaline Earth Metals

Luciana Lisi \*  and Stefano Cimino \* 

Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili (STEMS),  
Consiglio Nazionale delle Ricerche (CNR), Via Guglielmo Marconi 4/10, 80125 Napoli, Italy

\* Correspondence: luciana.lisi@cnr.it (L.L.); stefano.cimino@cnr.it (S.C.)

Received: 19 November 2020; Accepted: 10 December 2020; Published: 16 December 2020



**Abstract:** SCR still represents the most widely applied technique to remove nitrogen oxides from flue gas from both stationary and mobile sources. The catalyst lifetime is greatly affected by the presence of poisoning compounds in the exhaust gas that deactivate the catalysts over time on stream. The progressive and widespread transition towards bio-derived fuels is pushing research efforts to deeply understand and contrast the deactivating effects of some specific poisons among those commonly found in the emissions from combustion processes. In particular, exhaust gases from the combustion of bio-fuels, as well as from municipal waste incineration plants and marine engines, contain large amounts of alkali and alkaline earth metals that can severely affect the acid, redox, and physical properties of the SCR catalysts. This review analyzes recent studies on the effects of alkali and alkaline earth metals on different types of SCR catalysts divided into three main categories (conventional  $V_2O_5$ - $WO_3/TiO_2$ , supported non-vanadium catalysts and zeolite-based catalysts) specifically focusing on the impact of poisons on the reaction mechanism while highlighting the different type of deactivation affecting each group of catalysts. An overview of the different regeneration techniques aimed at recovering as much as possible the original performance of the catalysts, highlighting the pros and cons, is given. Finally, current research trends aiming to improve the tolerance towards alkali-poisoning of SCR catalysts are reported.

**Keywords:** SCR catalysts;  $V_2O_5$ - $WO_3/TiO_2$ ; Mn-Ce/ $TiO_2$ ; zeolite; alkali; alkaline earths; deactivation; poisoning; reaction mechanism; acid sites; redox properties; regeneration; alkali-tolerance

## 1. Introduction

Nitrogen oxides are among the most widespread polluting species produced by both industry and transportation. New regulations have been introduced in Europe in recent years concerning emissions from both industrial activities and vehicles. Limitations of the emission standards have been also introduced by the EPA (Environmental Protection Agency) in the USA. Furthermore, to limit  $NO_x$  emissions in the marine environment, more recently, strict regulations have been established by the international maritime organization (IMO) also for naval transportation [1].

SCR is the most widely used  $deNO_x$  process to clean exhaust gases involving the reduction of  $NO_x$  to  $N_2$  by a suitable reducing agent, generally ammonia. This is a well-established catalytic technique for the treatment of industrial and power plant emissions. As a consequence, a vast majority of recent studies on the topic is devoted to improving catalytic performance for less conventional applications operating in challenging conditions, such as those working in a low-temperature range or requiring high tolerance to the presence of specific poisoning agents.

Examples of low-temperature applications are special configurations of the de-polluting train of exhaust gases from a power plant, i.e., the location of the  $deNO_x$  unit in a tail-end configuration

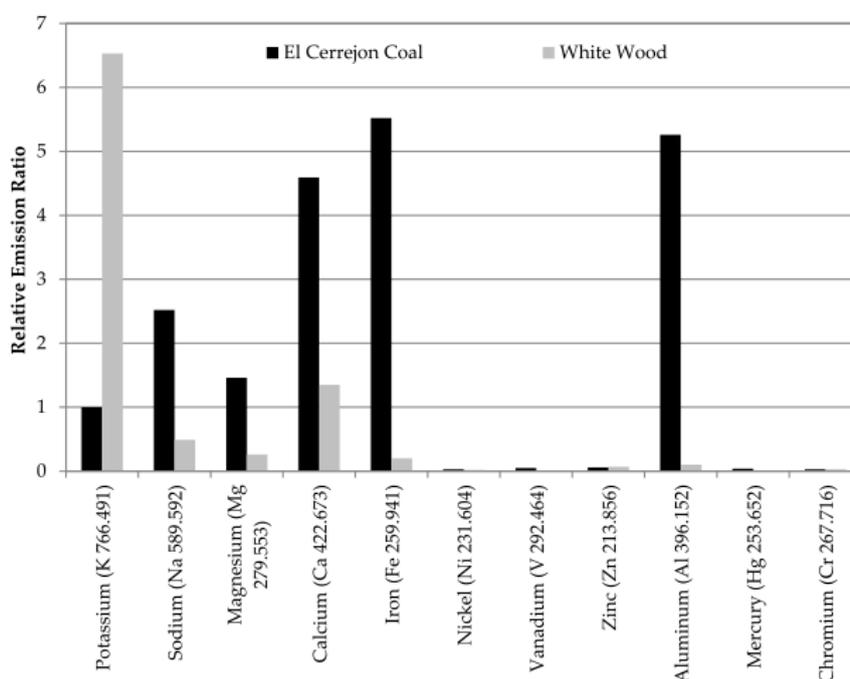
(downstream the electric precipitation and desulfurization unit) [2,3] or the after-treatment of exhausts from diesel engines, typically exiting at a temperature  $<350\text{ }^{\circ}\text{C}$  [4].

The other important issue is the poisoning of catalysts by different compounds present in the flue gas, requiring the development of catalysts with an enhanced tolerance towards specific substances that, otherwise, can significantly shorten the life-time and negatively affect the economics of the  $\text{deNO}_x$  process [5].

Sulfur, largely present in fossil fuels, mainly coal and heavy distillate fractions, is a typical poison for SCR catalysts, especially when the catalytic unity is located just at the exit of flue gas from a coal-fired power plant (high dust configuration). However, when its concentration is strongly reduced in the desulfurization unit, this represents a minor concern. On the other hand, the increasing use of alternative feedstocks differing from traditional fossil fuels, such as bio-fuels, woody biomasses, municipal wastes, etc., has raised new issues related to the presence of significant levels of alkali and alkaline earth metals [6] (see Table 1 [7]). As an example, Figure 1 shows that the average emission of potassium from wood combustion is as much as 6.5 times larger in comparison to the average data from coal combustion [8].

**Table 1.** The elemental composition of fly ashes (wt.%) from the combustion of commercial biomass (miscanthus straw). Adapted from Reference [7].

$\text{Na}_2\text{O}$	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	$\text{K}_2\text{O}$	CaO	$\text{Fe}_2\text{O}_3$	Cl
wt.%									
2.5	1.0	0.2	6.6	3.0	18.3	32.0	16.8	0.1	19.1



**Figure 1.** The average relative emission concentration ratios from coal and biomass combustion, compared to the average data for potassium from coal combustion (standardized to 1). Reproduced from Reference [8].

As a consequence, it is reported that catalyst deactivation rates by these compounds are 2–4 times higher when bio-fuels substitute a fossil fuel such as coal [9,10], although fly ashes from coal-fired power plants already contain large amounts of K, Na, Mg, and Ca as well [11]. Alkali are also present in biodiesel, which is produced through transesterification of oil or fat with methanol catalyzed by sodium or potassium hydroxide [12,13]. Residual amounts of Na and K unavoidably remain in the

fuel, and besides, calcium and magnesium can be added to purify the final product [12]. Calcium and magnesium are also present in lubrication oils that are emitted as carbonates, sulfates, and oxides after the combustion process [14] (see Table 2 [14]).

**Table 2.** Na, K, Ca, and Mg content of different biodiesel samples (mg/kg). Adapted from Reference [14].

	Na	K	Ca	Mg
Palm kernel biodiesel	49.15 ± 0.07	73.2 ± 1.98	0.24 ± 0.01	1.56 ± 0.49
Neem biodiesel	0.26 ± 0.08	111.3 ± 0.1	0.2 ± 0.04	1.49 ± 0.13
Palm biodiesel	19.1 ± 0.14	5.17 ± 0.08	0.00	1.81 ± 0.12

The most common catalysts for the NO<sub>x</sub>-SCR process are V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> [1], often named VWT, and many literature reports have focused on the poisoning effects due to alkali and alkaline earth metals on these materials.

Two main deactivation mechanisms can be activated by alkali and alkaline earth metals on SCR catalysts: chemical deactivation, mainly related to the neutralization of acid sites of the catalyst [9–11], and plugging/masking, due to formation and deposition of ammonia salts or fly ashes [15]. The strongest chemical deactivation potential for V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> is generally attributed to potassium [16], whereas poisoning by alkaline earth metals is considered less harmful than that of alkali [17]. Moreover, the anion of the potassium or sodium salt also affects the poisoning strength, increasing the fly ash formation and deposition [10].

In order to improve the alkali resistance of the catalysts, many strategies have been attempted, such as the increase of the total surface acidity of the catalyst through the use of more acid supports [18] and the substitution of vanadium, having a strong Brønsted acidity easily neutralized by alkali, for metals with a prevailing Lewis acidity, which are less prone to deactivation by basic compounds [19].

The presence of alkali also negatively affects catalysts used for low-temperature applications, such as MnO<sub>x</sub>-based systems, reducing their acidity, as in the case of VWT catalysts, but also affecting their redox properties and the amount of chemisorbed oxygen [3,20]. On the other hand, higher alkali resistance is reported for zeolite-based catalysts due to the strong surface acid properties of materials as ZSM-5 or SAPO-34, ensuring a longer catalyst lifetime [21,22].

Peng et al. [23] summarized and quantified the main poisoning effects of alkali metals on SCR catalysts, giving the following order of impact:

1. The reduction of surface acidity that suppresses the adsorption of NH<sub>3</sub>, very fast for acid catalysts such as vanadia-based systems and representing the rate-determining step. As a consequence, the effect on the reaction rate is strong.
2. The formation of KNO<sub>3</sub>-like species by the reaction of potassium with inactive NO<sub>x</sub><sup>-</sup> species, hindering the activation of NH<sub>3</sub> by surface oxygen.
3. The loss of the catalyst reducibility, inhibiting the transfer of surface oxygen species required to activate adsorbed NH<sub>3</sub> or NO<sub>x</sub>. This is an important factor, but less crucial than surface acidity in determining the SCR activity.
4. Inhibition of the adsorption and activation of NO<sub>x</sub> weakly affecting the reaction rate, especially in the medium/high-temperature range, where the Eley-Rideal mechanism plays a prevailing role with respect to the Langmuir-Hinshelwood mechanism.

This paper reviews the poisoning effect of both alkali and alkaline earth metals, analyzing the poisoning mechanism, the possible regeneration strategies, and the approaches to limit deactivation of SCR catalysts divided into three main categories: (i) conventional V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts; (ii) systems based on metals different from vanadium; (iii) zeolite-type catalysts.

## 2. Impact and Mechanism of Poisoning by Alkali and Alkaline Earth Metals

### 2.1. $V_2O_5$ - $WO_3$ / $TiO_2$ Catalysts

Emissions of  $NO_x$  from the combustion of fossil fuels such as coal, oil, and natural gas have been traditionally reduced using  $TiO_2$  supported  $V_2O_5$  catalysts generally together with  $WO_3$  or  $MoO_3$ , which increase the surface acidity, promote vanadia dispersion, and thermally stabilize the  $TiO_2$  support [1,13,24,25]. The same catalytic systems are widely applied also in SCR units of biomass-fired plants. The fast transition from fossil to bio-fuels occurring in recent years in all industrial countries has stimulated research efforts to investigate the extent and the nature of poisoning by alkali and alkaline earth metals in addition to the impact of sulfur and arsenic, widely studied in the past and mostly found in the exhaust gases from coal-fired power plants.

Many studies in the relevant literature reported experimental data from full-scale installations investigating the effect of poisoning on catalysts exposed to flue gases from power plants rather than simulating poisoning by deposition of alkali and alkaline earth salts [1,6,9,15,16,26].

Zheng et al. [15] investigated the catalytic behavior and life-time of a  $V_2O_5$ - $WO_3$ / $TiO_2$  monolith operated in a high dust de $NO_x$  unit for the treatment of exhaust gases from a straw/wood fired grate boiler. They observed a fast deactivation of about 1% per day that corresponded to residual activity of about 50% after only 1100 h. The hash particles impacting the SCR reactor mostly consisted of potassium chloride and sulfate with minor amounts of phosphorus and sodium. The main difference with respect to fly ashes from a coal-fired plant is represented by the smaller average characteristic dimensions: as a consequence, more particles can be deposited by Brownian and turbulent diffusion, thus penetrating the pores of the catalyst. Furthermore, the compounds in the biomass fly ash (mostly  $KCl$  and  $K_2SO_4$ ) have a lower melting point than typical coal fly ashes, resulting in an enhanced sticking tendency of the particles to the catalyst surface. Although potassium salts are mainly located on the outer surface and in the mouth of macropores, they also penetrate the catalyst wall, resulting in a  $K/V$  ratio (0.3–0.5) that can be reasonably associated with a chemical deactivation in addition to channel plugging. Indeed, the catalytic activity loss was much faster than the loss of specific surface area (due to plugging), and the occurrence of a chemical poisoning mechanism was confirmed by the inactivation of Brønsted acid sites.

Kling et al. [9] also found a linear correlation between the time exposure of a  $V_2O_5$ / $TiO_2$  catalyst in high dust configuration of a biofuel power plant and its deactivation by ultra-fine alkali particles (<100 nm), whereas no correlation was found for larger particles.

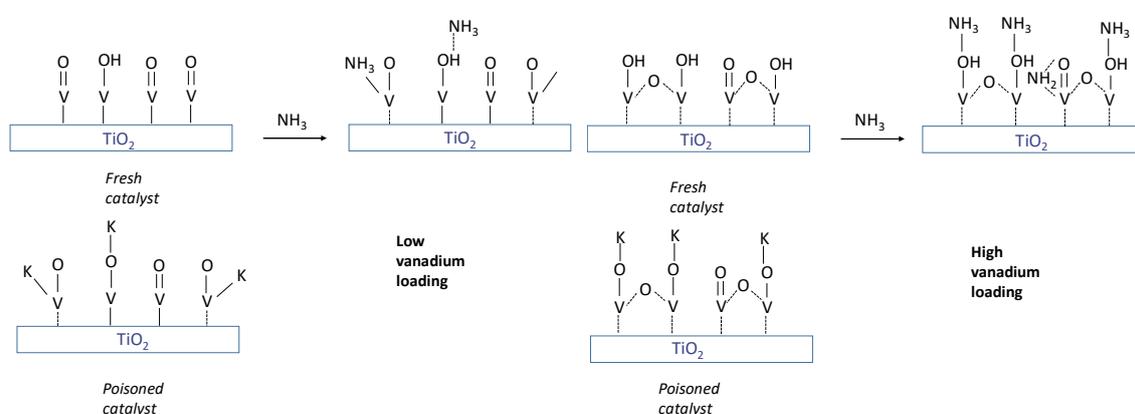
Another experience at the full-scale level was reported by Strege et al. [26] for a plant co-firing biomass and coal. They also found that pore blocking was one of the main causes of catalyst deactivation by alkali and alkaline earth metals mostly coming from the biomass that formed layers of sulfates where ash deposited near catalyst pores. Sulfates growth across pore openings significantly reduced catalyst activity. Even if the prevailing specie causing pore blockage was identified as calcium sulfate, it was suggested that a fraction of the sulfate material formed via ash alkali reaction with gas-phase sulfur oxides.

$V_2O_5$ / $TiO_2$  catalysts generally have a low vanadia content (ca. 1% by weight) to limit the catalytic oxidation of  $SO_2$ , largely present in the exhaust gas when fossil fuels are burnt. The total or partial substitution of fossil fuels for biomass releases the S-poisoning issue but raises new concerns for the large concentration of alkali and alkaline earth metals, which, on the contrary, is small for fossil fuels. As a consequence, an increase of the vanadium content in the catalysts can be used to contrast deactivation and increase the catalyst lifetime in biomass-fired plants [9].

Lisi et al. [16] investigated the poisoning effect of Na and K on the SCR activity of two commercial  $V_2O_5$ - $WO_3$ / $TiO_2$  monolith catalysts differing for their vanadium and tungsten loadings. They did not observe a reduction of surface area upon alkali poisoning, in agreement with Wu et al. [27], but only a marked reduction of surface acidity. This effect was much more pronounced for potassium with respect to sodium for the same level of alkali concentration on the catalysts. Moreover, strong acid

sites adsorbing ammonia at  $T > 350\text{ }^{\circ}\text{C}$  were identified as the preferential target for Na and K at low alkali concentration. On the other hand, at a high alkali concentration, weak and medium acid sites were also neutralized, resulting in a significant loss of activity. In particular, the authors reported a linear correlation between the reaction rate and the residual acid sites in the catalyst with a high vanadium load.

Kong et al. [28] increased the vanadium content of  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts from 1 to 5 wt.% to improve the K-tolerance. The authors found that monomeric vanadia species, containing  $\text{V}=\text{O}$  groups and responsible for the high-temperature SCR activity, prevailed at low  $\text{V}_2\text{O}_5$  loading, whereas at a higher loading, polymeric species were formed that promoted the low-temperature activity. Both  $\text{V}=\text{O}$  and  $\text{V}-\text{OH}$  are active sites for  $\text{NH}_3$  adsorption as well as for  $\text{K}^+$  binding, the former decreasing with increasing the vanadium content, as schematically shown in Figure 2 for low and high vanadium loading. In particular,  $\text{V}-\text{OH}$  is identified as the primary site for ammonia adsorption and  $\text{K}^+$  binding. Accordingly, the authors reported that an intermediate vanadia loading (3 wt.%) represents a good compromise, showing both a good catalytic activity and K resistance at  $300\text{ }^{\circ}\text{C}$  because of a favorable balance between monomeric and polymeric vanadia species.



**Figure 2.**  $\text{NH}_3$  adsorption on fresh catalysts with low (left) and high (right)  $\text{V}_2\text{O}_5$  loading. The same sites are poisoned by K, thus hindering  $\text{NH}_3$  adsorption. Adapted from Reference [28].

Yu et al. [29] were able to vary the fraction of polymeric vanadia species without changing the total vanadium amount using either wet or dry impregnation of the  $\text{TiO}_2$  support. The wet impregnation method promoted the formation of polymeric species, whereas dry impregnation favored the formation of isolated vanadia species. Since polymeric species provide a higher concentration of Brønsted acid sites, this contrasted the deactivating effect of potassium that adsorbs on acid sites decreasing the amount of ammonium coordinated to acid sites, responsible for the SCR activity. Therefore, the authors concluded that  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts prepared by wet impregnation were more tolerant to alkali poisoning than their counterparts with the same nominal composition but prepared via the dry impregnation method.

Xie et al. [17] made a kinetic investigation of the poisoning of commercial  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts exposed to flue gas from a coal-fired power plant to understand the deactivation behavior of both acid and redox sites. Their kinetic model was based on the kinetic variation of the activation energy of  $\text{NH}_3$  desorption,  $\text{NH}_3$  oxidation, and SCR reaction occurring on used catalysts. They concluded that alkali poisoning mostly takes place on vanadium sites rather than on titanium or tungsten and that polymeric vanadates are more alkali-resistant than monomeric vanadyl species. Furthermore, they found that the  $\text{deNO}_x$  activity and the  $\text{NH}_3$  adsorption capacity decline in the same way, and the decrease of all elementary steps is temperature-dependent.

In addition to biomass, some coals also show a high content of alkali metals, as reported by Du et al. [30], who also investigated the impact of different cations (K, Na, Ca) and anions (hydroxide, chloride, sulfate) reporting the following poisoning order for cation and anions, respectively:

$K^+ > Na^+ > Ca^{2+}$  and  $OH^- > Cl^- > SO_4^{2-}$ . Accordingly, Deng et al. [10], who investigated sodium and potassium salts with different anions (carbonates, sulfates, chlorides) from aerosols produced from the combustion of doped coal, found that potassium salts always displayed a stronger poisoning effect than the corresponding sodium salts with the same anion, and that the deactivating power decreased in the order chlorides > sulfates > carbonates. They also studied the combined effect of Na and K chlorides that was found in between that of the individual chlorides. The authors concluded that the chemical poisoning, related to the coordination of alkali salts to hydroxyl groups and the interaction with the oxygen of vanadium species limiting catalyst reducibility, prevailed upon the physical deactivation, associated with the decrease of surface area and masking of active  $V_2O_5$  sites.

Likewise, Chen et al. [31], investigating the effect of the addition of Na, K, Ca, and Mg on  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst with a nano-titania support, found that poisoning increased in the order  $K > Na > Ca > Mg$ . They further highlighted the modification of the reducibility in addition to the drop in the number and strength of Brønsted sites. They concluded that poisoning metals compete with surface oxygen species involved in the catalytic SCR cycle. In particular, they reported that the most negatively affected steps of the SCR mechanism are the formation of  $NH_4^+$  on the acid sites, its oxidation to  $NH_3$  via surface oxygen, and the oxidation of  $H-O-V^{4+}$  to  $V^{5+}=O$  by  $O_2$ .

Significant deposition of K, Mg and Ca on the surface of a commercial honeycomb  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst, in addition to a large sulfur deposition, was also reported by Yu et al. [32] for a coal-fired plant.

The combined effect of different cation-anion couples in the poisoning salt was investigated by Kröcher and Elsener [13]. According to their studies, calcium sulfate, the most common calcium salt found in aged catalysts, has a rather low deactivation potential, but calcium phosphate, carbonate, and borate are more poisonous. Magnesium sulfate has a stronger impact than  $CaSO_4$ . Very strong deactivation was reported for potassium sulfate, whilst it was less severe for  $KHSO_4$ . Furthermore, a strong deactivating effect of potassium was also found in combination with Ca, Zn, P, or B, as shown in Table 3. Unlike other metals, potassium strongly interacts with vanadium, forming potassium vanadates. As reported by many others, the authors found that upon alkali poisoning, ammonia adsorption was strongly inhibited. However, they asserted that not all adsorbed  $NH_3$  is directly involved in the SCR reaction, but it acts as a buffer providing fast replenishment of active SCR sites.

**Table 3.** The extent of deactivation of the  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts poisoned with 0.4 mol% (based on the sum of Ti, W and V) compounds reported in the first column (unless otherwise indicated) after calcination at 400 °C 5h. Adapted from Reference [13].

Poisons	Residual Activity (%)
Mg	77
Ca	46
$CaSO_4$	93
$MgSO_4$	92
Mg/P	91
Ca/P	79
Zn/ $CaSO_4$	78
K (0.1%)	73
K (0.2%)	32
K (0.4%)	4
$K_2SO_4$	5
$KHSO_4$	19
K/Ca	3
K/ $CaSO_4$	29

The role of alkali deposits on the neighboring tungsta and titania sites was better investigated in another work, focused on the characterization of the poisoned materials [33]. The authors concluded, based on XPS results of fresh and alkali-poisoned  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts, that K or Ca interact mainly with the oxygen in the vanadia phase rather than with the tungsta or titania support. The authors also explained the strong deactivating power of potassium: according to their model the poisoning agent is located in a non-atomic hole site of the (0 1 0)  $V_2O_5$  surface that blocks four active vanadium centers. The SCR reaction requires adjacent  $V^{5+}=O$  and Brønsted acid  $V-OH$  sites, the former stabilizing  $NH_3$  on the surface for the NO reduction and the formation of nitrosamide ( $NH_2NO$ ) specie, the latter favoring its fast decomposition. Therefore, it is sufficient that only one of the two vanadia centers is blocked to stop the whole reaction.

On the contrary, Wu et al. [27] reported the detrimental effect of KCl leading to the formation of potassium vanadate that shows a low activity and, at the same time, decreases the stability of ammonium ions coordinated to Brønsted acid sites. The authors also highlighted the main role of the cation compared to a minor role played by its counterion.

A study by Chen et al. [34] investigated the ability of tungsten in preserving to some extent vanadium from alkali poisoning. They compared catalysts consisting of  $V_2O_5$ / $TiO_2$ ,  $WO_3$ / $TiO_2$  and  $V_2O_5$ - $WO_3$ / $TiO_2$  and found that potassium reacts with tungsten, forming potassium tungstate. Thus, in the ternary catalytic system, tungsten acts as a K-scavenger or sacrificial agent, limiting the undesired formation of potassium vanadate and providing some alkali tolerance to the catalyst. In contrast, Xie et al. [17] reported that the preferential targets of alkali metals are always vanadium active sites such as  $V^{5+}-OH$  and/or  $V^{5+}=O$ , rather than sites associated with Ti and W.

Accordingly, Tian et al. [35] report that sodium, like potassium, reacts with  $V-OH$  groups, forming inactive  $Na-O-V$  species, strongly reducing the adsorption of ammonia, and affecting the formation of  $V^{4+}-NH_2$ , fundamental in the SCR mechanism. The poisoning effect of sodium is stronger if present as chloride rather than as oxide; this circumstance was attributed to the formation of new weak  $NH_3$  adsorption sites (promoted by the generation of HCl from NaCl) that do not selectively produce  $N_2$  and  $H_2O$ .

Although Yu et al. [36] agreed on the detrimental impact of K on vanadyl groups, they also reported a positive effect on the thermal stability of the catalyst. Indeed, they reported that the formation of potassium vanadyl hinders vanadia aggregation due to the condensation between surface hydroxyl groups and  $V-OH$ , which they considered the first step for sintering and rutilization of  $TiO_2$  support. Thus, quite surprisingly, they proposed the addition of small amounts of potassium to increase the thermal stability of SCR catalysts and to hinder an irreversible deactivation such as sintering, as opposed to the deactivation by alkaline poisoning, which is totally or partially reversible using regeneration methods.

Brandin and Ordebrand [6] evaluated the simultaneous effect of alkali metals and  $SO_2$ . They found that sulfur partially balanced the poisoning effect of alkali, replacing the neutralized acid sites with a new population of acid sites.

Conversely, Li et al. [37] reported that  $SO_2$  enhanced the deactivation of  $V_2O_5$ / $TiO_2$  catalysts due to KCl. Indeed, the presence of  $SO_2$  in the gas favors the formation of  $V_2O_5$ - $K_2S_2O_7$  eutectic already at a low K/V molar ratio (0.02–0.1); in turn, this negatively affects  $NH_3$  adsorption on Brønsted acid sites and weakens the oxidation ability of catalysts. Based on their experimental data collected on commercial  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts treating the exhaust gases from a waste incinerator plant, they developed an activation-deactivation model well predicting this particular behaviour. On the contrary, Lisi et al. [16] in their study on the combined effect of alkali and HCl in a SCR unit for a waste incinerator plant found that HCl can restore some surface acidity but, unfortunately, those new acid sites are not active for the SCR reaction.

Lei et al. [38] investigated the poisoning mechanism, selecting KCl as the model compound and comparing wet impregnation, solid diffusion, and vapor phase deposition methods to simulate in the lab the poisoning process under real-life conditions. The deactivation rate follows the order: vapor

phase deposition  $\gg$  solid diffusion  $>$  wet impregnation. In contrast to most other authors, they considered the effect on the acidity as playing a secondary role, whereas the formation of the eutectic  $V_2O_5$ - $K_2S_2O_7$  by vapor deposition of KCl strongly impacts the SCR activity because it reduces the surface area and increases the oxidation ability [37]. This eutectic was also formed by solid diffusion, but for higher levels of KCl deposited on the catalyst. On the other hand, the deposition of KCl via wet impregnation generated some  $V_2O_3$  species via the intimate contact between oxygen and potassium that leads to a limited loss of SCR activity.

Dahlin et al. [39] reported on the combined effects of different contaminants from bio-diesel on commercial  $V_2O_5$ - $WO_3$ / $TiO_2$  catalyst for Euro VI heavy-duty applications, namely alkali and alkaline earth metals with phosphorous, zinc and sulfur. After accelerated aging of the catalyst that was contacted with poisons in aqueous solution, they found that the interaction of P with the alkali metals and of S with Na resulted in a decreased poisoning effect compared to the single effects of Na and K due to the formation of phosphates and sulfates preventing the interaction of alkali metals with vanadium active sites.

Finally, two less-conventional studies can be mentioned that are not related to the application of the SCR process to exhaust gases from coal or biomass-fired plants.

An unusual investigation on the poisoning effect of alkali and alkaline earth bromides was reported by Chang et al. [40]. Bromides salts are used as additives to improve  $Hg^0$  oxidation on  $V_2O_5$ - $WO_3$ / $TiO_2$  catalysts. The order of deactivation they found is the same obtained for the other anions, i.e.,  $K > Na \approx Ca$ . Besides the conventional  $NH_3$ -TPD experiments aimed at testing the impact on surface acidity upon alkali and alkaline earth metals, the authors also studied the surface basicity through  $CO_2$ -TPD. They proposed that the enhancement of surface basicity related to the presence of KBr or NaBr affected the adsorption of NO species as nitrite or nitrate, improving their stability. Nevertheless, despite the enhanced NO adsorption capacity, the overall SCR activity decreased due to the simultaneous inhibition of the redox properties of the catalyst.

Sodium salts ( $Na_2O$  and  $NaOH$ ) together with  $Al_2O_3$  and  $Al(OH)_3$  represent the main compounds in the emission from the aluminum oxide hydrate calcining process in the aluminum production industry, and for this reason, Li et al. [41] investigated their impact on the VWT catalysts used in de $NO_x$  unit for this application. They found the following deactivation order:  $NaOH > Na_2O > Al_2O_3 \sim Al(OH)_3$ , which was roughly proportional to the decrease of ammonia adsorption detected by  $NH_3$ -TPD. Nevertheless, DRIFT analysis showed that Na compounds decreased both Brønsted and Lewis acid sites, while the main targets of Al species are the Lewis sites.

The effect of sodium on redox properties, in addition to that of the acid sites, is also reported by Tang et al. [42]. Those authors highlighted the key role of the oxidative dehydrogenation of adsorbed ammonia in the SCR mechanism since they found a good correlation between the decrease of reducibility of  $V_2O_5$ / $TiO_2$  catalysts and their loss of activity.

## 2.2. SCR Supported Catalysts Containing Metals Different from Vanadium

As already mentioned, vanadia-based catalysts are the most widely used systems in SCR units for both stationary and mobile applications. However, the promoting effect of  $V_2O_5$  on the catalytic oxidation of  $SO_2$  to  $SO_3$ , as well as the toxicity of vanadium, encouraged researchers to develop alternative catalysts containing environmentally friendly metals that can effectively operate in a lower temperature range, as in the case of tail-end SCR units that treat exhaust gases living the desulfurization unit [43].

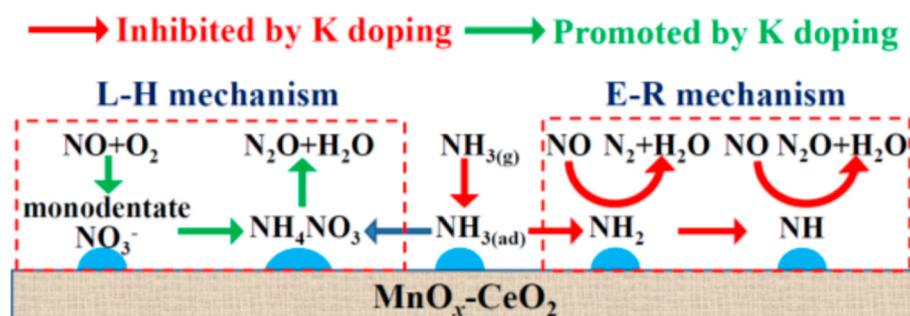
There are rather few studies on the alkali poisoning of non-vanadium catalysts. A recent review on Mn-based SCR catalysts [3] addresses the deactivation of this class of materials.

Manganese represents a good candidate as a vanadium substitute and it has been widely proposed for low-temperature SCR applications [20,43]. Nevertheless, alkali and alkaline metals also negatively impact Mn-based catalysts, although the redox properties and oxygen mobility seem to play a more significant role than the surface acidity, the main targeted property in the case of vanadia-based systems.

However, the poisoning order is similar to what is reported for  $V_2O_5$ -based catalysts. In particular, Fang et al. [44] concluded that K, Na, and Ca have a strong deactivating power decreasing in the order  $K > Na > Ca$ . On the contrary, Mg can even improve catalytic performance due to the appearance of a new  $MgMn_2O_4$  phase. As for  $V_2O_5$  based catalysts, the authors assert that  $NH_3$  adsorption on the acid site and redox properties of  $MnO_x$  are both affected by alkali and alkaline earth metals. They also attribute a significant role in the SCR reaction mechanism to the total amount of chemisorbed oxygen and of  $Mn^{3+}$  species in the catalyst, which are both reduced by the addition of K, Na, and Ca.

Guo et al. [43] identified two SCR mechanisms occurring on  $Mn/TiO_2$  catalysts: the Langmuir-Hinshelwood mechanism, taking place at  $T < 150$  °C, and the Eley-Rideal mechanism prevailing at  $T > 200$ °C due to the activation of adsorbed  $NH_3$  species promoted by the higher temperature. They analyzed the poisoning effects of Mg and K: at low temperatures, Mg inhibits the adsorption and oxidation of NO, whilst at high temperatures it only weakly inhibits the activation of  $NH_3$  adsorbed species. On the contrary, potassium seriously affects the activation of these species also at higher temperatures.

Xiong et al. [45] focused their transient reaction studies on the poisoning of  $MnO_x/CeO_2$  catalysts with special attention to the selectivity to the undesired formation of  $N_2O$ . In agreement with Guo et al. [43], they reported the occurrence of both the Eley-Rideal and the Langmuir-Hinshelwood mechanism, concluding that only the former mechanism contributes to  $N_2O$  formation over fresh  $MnO_x/CeO_2$  catalysts. The decrease of the SCR activity after K-poisoning was mainly attributed to the loss of acid sites and the reduction of the concentration of  $Mn^{4+}$  sites on the surface. At the same time, they measured an increased formation of  $N_2O$  over the K-poisoned  $MnO_x-CeO_2$  that probably occurred through the Langmuir-Hinshelwood mechanism, as shown in Figure 3.



**Figure 3.** The effect of K doping on the formation of  $N_2O$  by Langmuir-Hinshelwood and Eley-Rideal mechanisms. Reproduced from Reference [45].

The effect of the alkali counter-ions was also investigated for this class of low-temperature catalysts. Zhang et al. [46] addressed the problem of sub-micron and ultra-fine particles emitted by cement kiln that mostly contain potassium compounds, and they limited their study to  $KNO_3$ ,  $K_2SO_4$ , and  $KCl$ . They found that  $K^+$  with all anions deactivates the  $Mn/TiO_2$  catalyst, inducing textural modifications with a loss of surface area and pore volume. Besides,  $KNO_3$  possibly decomposes into  $K_2O$  or  $K_2O_2$ , and these oxides can react with acid sites, decreasing their reducibility.

The effect on the surface acidity was highlighted by Cimino et al. [20], who compared the performance at a low temperature of manganese oxide dispersed at various loads on  $TiO_2$  or ZSM-5, testing their tolerance to  $KCl$  as representative of poisoning compounds in marine diesel applications. For fresh catalysts,  $TiO_2$  is a superior support because it strongly promotes  $MnO_x$  dispersion and lattice oxygen mobility, which, however, is severely affected by  $KCl$  poisoning. On the other hand, the strong acid character of the ZSM-5 support enhances the catalyst tolerance towards  $KCl$  poisoning, the zeolite acting as a trap for the basic deactivating agent.

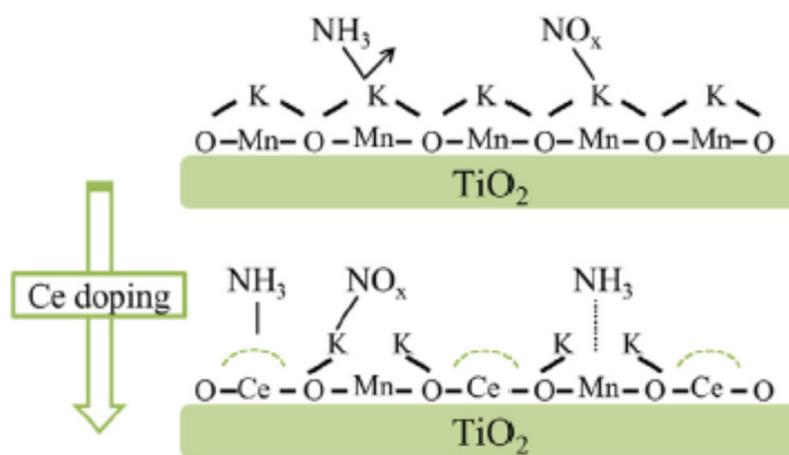
Cerium oxide has been proposed not only as a support but also as an active phase for the low-temperature SCR reaction, often in combination with manganese, because, just like manganese

oxides, it shows outstanding redox properties necessary to activate the reaction at low temperature, and also a high oxygen storage capacity [47–49].

As for supported  $\text{MnO}_x$  catalysts, Wang et al. [50] proposed a combination of the Eley-Rideal and the Langmuir-Hinshelwood mechanisms also for  $\text{Ce}/\text{TiO}_2$  catalysts. The addition of Na or K on  $\text{Ce}/\text{TiO}_2$  catalysts inhibits the adsorption of both  $\text{NH}_3$  and  $\text{NO}$ , but it also generates some new sites for the adsorption of  $\text{NO}_x$  species. They suggested that all the adsorbed  $\text{NH}_3$  species are involved in the SCR reaction, whereas the new  $\text{NO}_x$  adsorbed species are substantially inactive for the reaction as opposed to bridged nitrates.

The initial SCR activity of  $\text{Mn-Ce}/\text{TiO}_2$  catalysts was lowered by potassium ions due to the occupation of oxygen vacancy limiting the adsorption of oxygen on the surface and to the inhibition of the acid cycle [51]. Nevertheless, it was found that the addition of transition metals, such as Ni, can reduce the deactivation phenomenon, preserving to some extent a high surface area and oxygen mobility.

Peng et al. [52] reported that the addition of cerium to  $\text{MnO}_x/\text{TiO}_2$  catalysts promotes the formation of new Lewis acid sites for  $\text{NH}_3$  adsorption that are scarcely affected by K poisoning. The authors proposed a reaction mechanism occurring on the poisoned catalyst involving K bonding on active sites (mainly Mn cations), leading to the redistribution of Mn 3d orbitals. K also stabilizes inactive nitrites that do not react with adsorbed  $\text{NH}_3$ . Cerium addition promotes the formation of  $[-\text{O}-\text{Ce}-\text{O}-\text{Mn}-\text{O}-]$  active centers that pull K away from Ce, leaving good Lewis acid sites free to capture gaseous  $\text{NH}_3$ , as schematically shown in Figure 4.



**Figure 4.** A schematic of the promotion alkali resistance mechanism of Ce on Mn/Ti catalyst. Reproduced from Reference [52].

Zhou et al. [53] selected  $\text{Na}_2\text{SO}_4$  as a representative compound to investigate the combined effect of the alkali metal and  $\text{SO}_2$  in the flue gas on  $\text{Mn-Ce}/\text{TiO}_2$  catalysts. They observed an unusual fluctuating catalytic behavior due to the opposite effect on Lewis and Brønsted acid sites of Na and sulfates, respectively. As a consequence, the increase of Brønsted acid sites detected at higher  $\text{Na}_2\text{SO}_4$  contents determines a partial recovery of the original SCR catalytic activity depressed due to the loss of Lewis acid sites.

Interestingly, the choice of catalysts based on metals other than vanadium has been often proposed as a strategy to enhance the tolerance of SCR systems against alkali poisoning.

Based on the considerations that sulfates can have a positive effect on the SCR reaction, Wang et al. [54] proposed the use of  $\text{CeO}_2$  dispersed on sulfated titania nanotubes as a K-tolerant SCR catalyst. They identified an optimal  $\text{H}_2\text{SO}_4$  concentration for the sulfation of  $\text{TiO}_2$  and verified that the hollow multi-layer nanotube structure preserves many chemical and physical properties, such as surface area and the proportion of  $\text{Ce}^{3+}$  species, but it also increases the content of Brønsted acid sites with a positive effect on the SCR reaction. Furthermore, increasing the Brønsted acid sites,  $\text{K}^+$

is stabilized into the interlayer of the nanotubes, and this protects the active CeO<sub>2</sub>. In conclusion, the K-poisoned sulfated catalyst retained a better balance of acidity and basicity than its unsulfated counterpart, which is fundamental for the adsorption of NH<sub>3</sub> and NO<sub>x</sub>.

In another study on the deactivation of Ce/TiO<sub>2</sub> by Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> [55], the authors reported an additional negative effect of alkali and alkaline earth metals on the enlargement of CeO<sub>2</sub> nanoparticles, which they ascribed to a “molten salt flux” formed under real and simulated operating conditions. Sodium or calcium nitrate could form a molten salt flux on the surface of the Ce/TiO<sub>2</sub> catalyst, covering ceria nanoparticles and favoring their growth as well as decreasing the number of available oxygen vacancies, thus affecting the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycle involved in the SCR reaction.

Boxiong et al. [56] reported that Mn-CeO<sub>x</sub> supported on Zr-delaminated clays derived from montmorillonite can operate at a very low-temperature range (80–240 °C). Potassium and sodium nitrates severely affect the catalytic activity, and the poisoning impact is K > Na, as for vanadium-based catalysts. The deactivation is linearly proportional to the alkali content. Besides, alkali lower the reducibility of manganese oxide, stabilizing a less active form of the oxide, and reduce the surface acidity.

Combinations of conventional VWT catalysts and Ce-based catalysts have been proposed, where ceria represents either the main phase or dopant/promoter to the traditional catalyst. Peng et al. [57] studied the addition of WO<sub>3</sub> to CeO<sub>2</sub>/TiO<sub>2</sub> supported catalysts and investigated the resistance to sodium and potassium. As for the VWT counterpart, they confirmed the usual poisoning order (K > Na) at T < 200 °C. They demonstrated via DRIFT experiments that alkali mostly affect the amount of Brønsted acid sites, whilst Lewis acid sites are reduced only at a higher temperature. They also observed a decrease of reducibility upon alkali poisoning. Nevertheless, the CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst showed better tolerance to alkali poisoning than its commercial VWT counterpart.

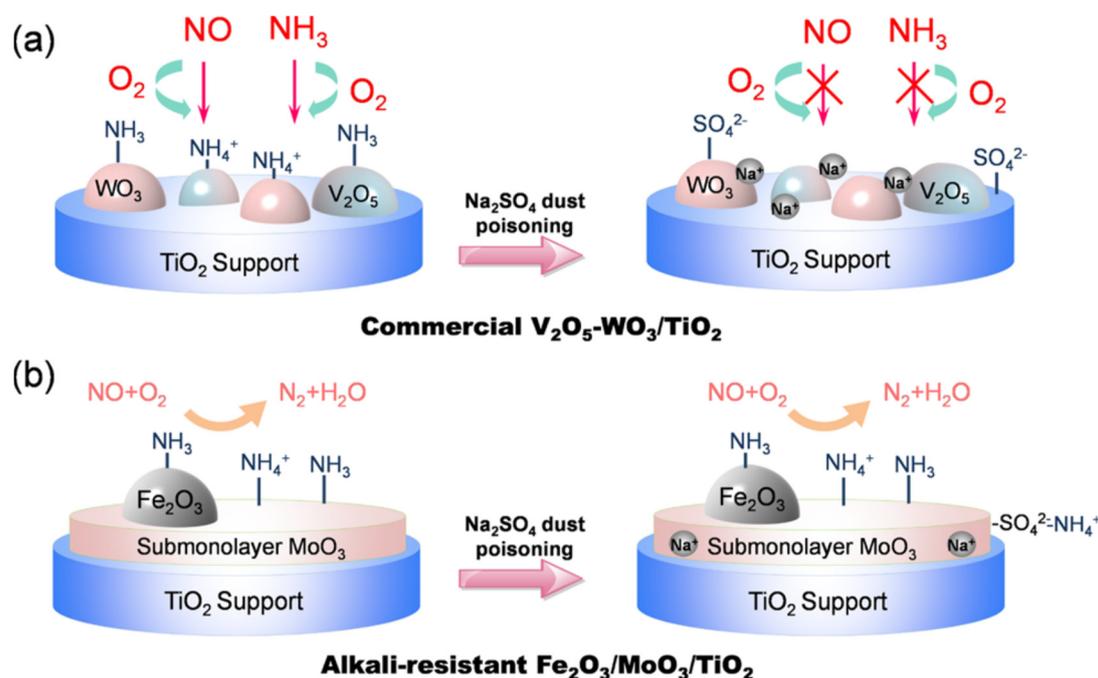
Likewise, Yan et al. [58] reported that the addition of cerium oxide to a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst can significantly increase its K-tolerance. Indeed, their Ce-promoted catalyst was able to retain 90% of its initial SCR activity at 350 °C at a K/V ratio as high as 4, whereas the unpromoted sample lost its activity under the same operating conditions. The authors confirmed that Brønsted acid sites represent the favorite target for potassium, whilst Lewis sites are relatively unaffected. A higher number of residual acid sites is preserved for Ce-promoted catalysts, which can be still involved in the SCR reaction in the poisoned material.

Other metals have been proposed in addition to manganese and cerium. Zeng et al. [59] reported that Cu/TiO<sub>2</sub> catalyst shows a better resistance than Ce/TiO<sub>2</sub> due to a higher surface acidity and a better dispersion of the active species.

Active copper sites were also well-preserved when copper oxide was dispersed onto the Ti<sub>2</sub>NbO<sub>x</sub> support. In this case, the preferential coordination of K to Nb–OH and Nb=O groups of the Ti<sub>2</sub>NbO<sub>x</sub> support preserves surface chemisorbed active oxygen and active isolated Cu<sup>2+</sup>, which can act as adsorption and redox sites during NH<sub>3</sub>-SCR reaction [60].

Furthermore, in a recent work, Zhang et al. [61] presented interesting results on a novel Fe<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/TiO<sub>2</sub> catalyst with a layered structure, where the intermediate MoO<sub>3</sub> phase traps and stabilizes the Na<sup>+</sup> poison from Na<sub>2</sub>SO<sub>4</sub> dust, preventing the neutralization of surface acid sites that generally occurs on the commercial VWT catalyst that results in 27% loss of NO conversion at high temperature, as represented in Figure 5.

Finally, a somewhat unexpected promoting effect of calcium on the SCR performance of a MnO<sub>x</sub>/TiO<sub>2</sub> catalyst was reported in Reference [62]: the authors found that Ca promotes better Mn dispersion through the formation of solid solutions, with Mn and Ti resulting in a higher surface area and pore volume. Moreover, they also reported that, though calcium decreases the total acidity of the catalyst, it tends to increase the number of active Brønsted acid sites.



**Figure 5.** Schematic illustration of Na-poisoning of commercial  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> catalyst showing blocking of active acid sites (a) and of  $Fe_2O_3$ /MoO<sub>3</sub>/TiO<sub>2</sub> catalyst showing Na trapping into MoO<sub>3</sub> layer (b). Reproduced from Reference [61].

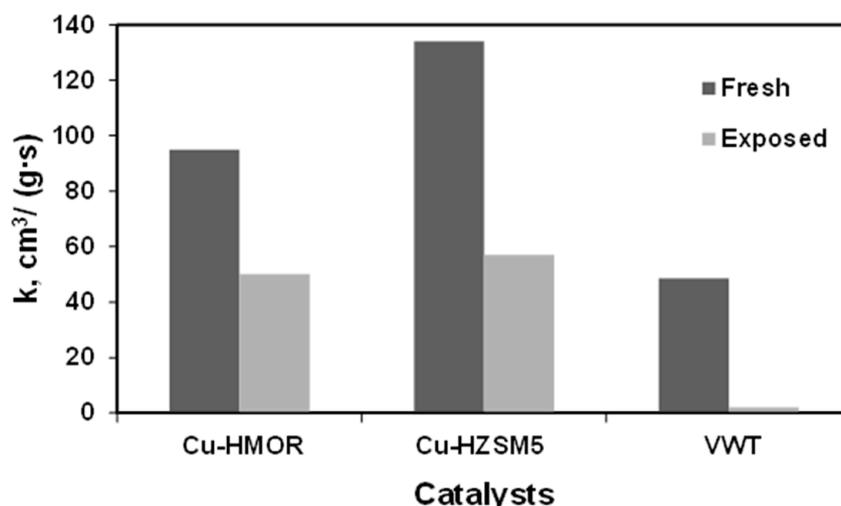
### 2.3. Zeolite-Type Catalysts

Cu- and Fe-zeolites with small to medium pore sizes are active and stable catalysts for the SCR process with  $NH_3$  to reduce  $NO_x$  from both stationary and mobile sources. Cu-zeolites generally provide better activity in the low-medium temperature range, whereas Fe-zeolites operate at higher temperatures [63]. Furthermore, due to their excellent hydrothermal stability, these catalysts are effectively used for diesel exhaust purification [64]. In some after-treatment systems, the SCR catalyst is coated onto the Diesel Particulate Filter (SCRf) [65]. In this location, the zeolite catalyst is exposed to higher alkali levels and, as a consequence, to a greater risk of deactivation [64]: even if zeolites have a higher alkali tolerance compared to vanadia-based catalysts [21] due to their higher surface area and stronger acidity, alkali poisoning still represents an issue.

Putluru et al. [66] compared the performance of two K-poisoned copper exchanged zeolites (ZSM-5 and MOR) with a standard  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> catalyst by exposing them to a KCl aerosol. They reported much better resistance to alkali poisoning for the two zeolite-type catalysts and attributed it to the large surface area and high acidity of these materials. Furthermore, the greater K/metal molar ratio they measured across the catalyst wall for  $V_2O_5$ - $WO_3$ /TiO<sub>2</sub> is also responsible for the almost total loss of SCR activity at 350 °C, as reported in Figure 6.

Deactivation by alkali and alkaline earth metals of copper-exchanged zeolites with a chabasite structure has been widely studied [67]. Both the surface acidity and reducibility of copper species in Cu/SAPO-34 are affected by potassium poisoning [68].

There is no general agreement on the poisoning order among alkali and alkaline earth metals. Zhu et al. [67] found  $K > Mg > Ca > Na$  for Cu-SSZ-39, whereas Fan et al. [69] reported the sequence  $Mg > Ca > Na > K$  for Cu-SSZ-13 catalyst. Wang et al. [70], based on their deactivation study by alkaline metals in the presence of water vapor at a high temperature under typical operating conditions for a SCRf system, reported that Na and K show the same poisoning mechanism, but the smaller diameter of hydrated potassium and its stronger binding ability allow for easy diffusion into the chabasite framework with the consequent exchange with acid sites.



**Figure 6.** The SCR activity of fresh and KCl aerosol exposed Cu-HMOR, Cu-HZSM5, and VWT catalysts. Reproduced from Reference [66].

Furthermore, it has been reported that sodium can also destroy the framework structure of a Cu/SSZ-13 catalyst [71].

It is generally accepted that, in addition to the more obvious effect on the acid properties, alkali and alkaline earth metals induce the transformation of isolated active  $\text{Cu}^{2+}$  ions into copper oxide and copper aluminate, thus lowering the SCR activity of Cu-SSZ-39 [67] and Cu-SAPO-34 [22]. In particular, Zhu et al. [67] reported the transformation of isolated  $\text{Cu}^{2+}$  ions into  $\text{CuO}_x$  and  $\text{CuAlO}_x$  species, with the simultaneous deterioration of the zeolite structure as a consequence of the addition of alkaline and alkaline earth metals.

Nevertheless, Albert et al. [22] found that this effect is negligible up to 0.5 mmol/g<sub>cat</sub> alkali or alkaline earth metal. In agreement, Zhu et al. [67] observed a significant deactivation at 1.0 mmol/g<sub>cat</sub> of alkali or alkaline earth metals on Cu-SSZ-39 catalyst, stronger for Na and K rather than for Ca and Mg [67]; Ma et al. [72] found that potassium contents >0.5% by weight greatly poison a Cu-SAPO-34 catalyst.

Liu et al. [64] investigated the effect of potassium as the most representative of alkali poisons from the ashes in a diesel exhaust: to this aim, they impregnated Cu-SSZ-13 catalysts with three different potassium salts (carbonate, sulfate and phosphate).  $\text{K}^+$  ions diffuse into the zeolite and exchange with both  $\text{H}^+$  and isolated  $\text{Cu}^{2+}$ , forming Si-O(K)-Al with a consequent decrease of both Brønsted acid sites and Lewis sites, respectively. They also reported that the degradation of the zeolite structure and the formation of copper oxide species at the expense of isolated  $\text{Cu}^{2+}$  active sites are somehow correlated. Indeed, the exchanged  $\text{Cu}^{2+}$  ions contribute to stabilizing the zeolite framework: thus, the extent of the partial degradation of the structure, estimated through the formation of penta-coordinated Al, corresponds to the loss of isolated  $\text{Cu}^{2+}$ , and it decreases in the order potassium carbonate > sulfate > phosphate. Furthermore, they observed that the stability of the products obtained by ion exchange when they impregnate with the different potassium salts, i.e., carbonates ( $\text{CuCO}_3/\text{H}_2\text{CO}_3$ ) < sulfates ( $\text{CuSO}_4/\text{H}_2\text{SO}_4$ ) < phosphates ( $\text{Cu}_3(\text{PO}_4)_2/\text{H}_3\text{PO}_4$ ), plays an important role in the poisoning process. Exchanged products with low stability promote the occupancy of  $\text{K}^+$  on the exchanged sites ( $\text{Cu}^{2+}$  or  $\text{H}^+$ ), thus leading to a more severe deactivation. At  $T < 350$  °C, the loss of isolated  $\text{Cu}^{2+}$  is the main cause of deactivation because the reaction mechanism mainly involves  $\text{NH}_3$  coordinated to Lewis acid sites (isolated  $\text{Cu}^{2+}$ ), while the Brønsted acid sites act as a reservoir. At higher temperatures, copper oxide (generated by carbonate), copper sulfate, and copper phosphate play a more complex role in catalyst deactivation. CuO promotes  $\text{NH}_3$  oxidation, decreasing the SCR selectivity, whereas copper sulfate and phosphate can promote the SCR reaction. The final balance is negative for  $\text{KCO}_3$  poisoning due to the simultaneous loss of Brønsted sites and the enhancement of the side reaction.

Among Fe-exchanged zeolites, Fe-MOR and Fe-ZSM5 show a higher K-tolerance than Fe-BEA, and this agrees well with the reported order of acidity for the pure zeolites: MOR > ZSM5 > BEA [21]. Notably, the order of acidity is preserved upon Fe exchange, which generally guarantees a further 20% acidity increase. Therefore, it is the high acidity of the support that makes these materials promising candidates for SCR applications requiring a high tolerance to alkali poisoning.

Du et al. [73] used HY zeolite as a support for the active Fe<sub>2</sub>O<sub>3</sub>. The role of HY was to protect iron oxide from sodium doping up to high loadings (1000 μmol/g), preserving both the redox properties and medium-strong acid sites of the catalyst, actually acting as a buffer. A similar buffering effect was also observed by Cimino et al. [20] for ZSM-5 used to support MnO<sub>x</sub>.

Eventually, Qi et al. [74] were able to model the decrease in the SCR rate constant over a Fe-ZSM-5 catalyst based on the type and amount of the poisoning cation, including Na, K and Mg, through experiments carried out under real conditions that were correlated with a chemical and physical analysis of the catalyst also in long-run tests.

### 3. Regeneration Strategies and Solutions to Improve Alkali Tolerance

In the SCR system, the catalyst accounts for 30–50% of the overall cost [75]. As a consequence, suitable regeneration strategies have been proposed to limit the costs related to catalyst substitution and disposal of the spent materials that are regarded as special wastes [5].

Most studies on the regeneration of poisoned catalysts are devoted to the widely used supported V<sub>2</sub>O<sub>5</sub> systems based on the vast experience matured on these catalysts across a large variety of applications.

The regeneration of SCR catalysts deactivated by SO<sub>2</sub>, arsenic, and heavy metals has been extensively explored in the past [76–81]. The regeneration of alkali- and alkaline-earth-poisoned catalysts has been less investigated due to the more recent application of these catalysts in units such as those treating exhaust gases from biomass-fired power plants involving a larger exposure to these poisoning agents.

The most widely used technique to regenerate commercial V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts is represented by water washing, eventually using acid addition (generally H<sub>2</sub>SO<sub>4</sub>). The acid solution quite effectively removes alkali, but some drawbacks have to be considered. It is reported that poisoned catalysts can be washed and regenerated by diluted sulfuric acid [75,82–85], but a low pH value can potentially decrease the mechanical stability of catalysts [86] and partially leach active components [84,87,88], thus imposing a subsequent replacement of these elements.

Table 4 summarizes the extent of recovery of the initial activity for (alkali/alkaline earth) poisoned VWT catalysts after regeneration by the main washing methods reported in the literature. In addition, it reports the fraction of alkali/alkaline earth metals removed by the specific regeneration treatment, as well as the amount of leached vanadium, which possibly needs to be replenished.

To limit vanadium and tungsten leaching, Wang et al. [89] proposed a washing solution containing 0.1 M ammonium persulfate in addition to 0.2 M sulfuric acid to regenerate commercial V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> honeycomb. They largely restored the original performance of the fresh catalyst by removing most of the alkali poisons and also provided longer stability in the presence of water and SO<sub>2</sub> and greater resistance to further alkali poisoning related to an enhanced surface acidity.

The same H<sub>2</sub>SO<sub>4</sub> concentration was used by Peng et al. [85] that removed about 90% potassium from deactivated V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> commercial catalysts. Nevertheless, the authors highlighted the simultaneous loss of a fraction (7%) of vanadium that must be replenished after the washing procedure.

Likewise, a 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution was proposed by Zheng et al. [15] for the regeneration of a V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst poisoned in a biomass-fired power plant. They verified that potassium was present in the washing solution, together with some vanadium and tungsten as well. Nevertheless, their results confirmed the presence of novel surface sulfates after potassium removal provided an enhanced activity at 300 °C.

On the other hand, Gao et al. [90] reported on the effectiveness of a washing treatment with deionized water or 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, eventually coupled with ultrasonic treatment, for the regeneration of their Na<sub>2</sub>O or K<sub>2</sub>O poisoned commercial VWT catalysts. Sulfuric acid is more effective than pure water for catalyst regeneration, even when the water-washing treatment is ultrasound-assisted. Once again, the results confirmed that sulfation of the catalyst surface by H<sub>2</sub>SO<sub>4</sub> was associated with activity improvement, especially in the case of ultrasonic-assisted acid treatment promoting the dispersion of sulfate groups.

**Table 4.** The extent of SCR activity recovery and the corresponding removal of specific elements from poisoned VWT catalysts following the specified regeneration method.

Regeneration Treatment	Poisons	Activity Recovery (%)	Removal Efficiency (%)				Ref.
			K	Na	Ca	V	
H <sub>2</sub> SO <sub>4</sub> (0.2 M) washing	K <sub>2</sub> NO <sub>3</sub> + As <sub>2</sub> O <sub>3</sub>	58	94			7	[85]
Electrophoresis	Na <sub>2</sub> O	32		99			[82]
Water washing		26		34			
Electrophoresis	K <sub>2</sub> O	51	96				
Water washing		26	40				
Water washing		0	60				
H <sub>2</sub> SO <sub>4</sub> (0.05 M) washing	K <sub>2</sub> O	67	60				[87]
H <sub>2</sub> SO <sub>4</sub> (0.5 M) washing		92	60				
Acetic acid (0.5 M) washing	K <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> SO <sub>4</sub> + PbNO <sub>3</sub> +As	96	92	100		2	[91]
Citric Acid (0.5 M) washing		70	92	100		46	
Oxalic Acid (0.5 M) washing		68	94			62	
H <sub>2</sub> SO <sub>4</sub> (0.5 M) washing		95	92	100		34	
Water washing	NaCl	90		47		9	[30]
Water washing	NaOH	15					
H <sub>2</sub> SO <sub>4</sub> (0.5 M) washing	NaOH	≈100				31	
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (0.5 M) washing	NaOH	≈100				21	
H <sub>2</sub> SO <sub>4</sub> (0.2 M) washing	Na <sub>2</sub> SO <sub>4</sub> + Na <sub>2</sub> CO <sub>3</sub> +NaCl	100		89		25	[89]
(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0.1 M) + H <sub>2</sub> SO <sub>4</sub> (0.2 M) washing		≥100		92		8	
H <sub>2</sub> SO <sub>4</sub> (1 wt.%) washing		40			66	63	[83]
alkylphenol polyoxyethylene ether (1 wt.%) washing	Ca(OH) <sub>2</sub>	74			78	12	
polyethyleneglycol mono-dodecyl ether (1 wt.%) washing		7			30	0	

Boxiong et al. [56] compared water and acid (10<sup>-3</sup> M H<sub>2</sub>SO<sub>4</sub>) washing of Mn-CeO<sub>x</sub>/Zr-delaminated-clay. They reported that both methods are rather effective for catalysts deactivated by low amounts of K, whereas for low Na content the acid washing provided a better recovery of the original activity. Nevertheless, the authors highlighted the dissolution of some of the Mn-CeO<sub>x</sub> active phase upon both washing treatments. They concluded that when the catalysts are mildly deactivated, regeneration by washing with water must be preferred because the dissolution of alkali salts by water overcomes that of Mn-CeO<sub>x</sub>.

An interesting study on the regeneration of alkali-poisoned V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> honeycomb catalysts using organic acids as an alternative to sulfuric acid was reported by Li et al. [91]. In particular, they tested acetic, citric, and oxalic acid solutions to wash the catalysts poisoned by Na, K, and Ca. Acetic acid provided the best regeneration efficiency while also preserving the vanadium oxide content

of the fresh catalyst which, on the contrary, is partially lost during  $\text{H}_2\text{SO}_4$  acid washing and needs to be replenished.

Diluted acid solutions are less effective at removing alkaline earth metals such as calcium because they are always associated with the presence of sulfates [2,84]. An alternative method is the treatment of the poisoned catalysts with solutions of nitrilotriacetic acid that attack calcium sulfate, forming soluble chelate complexes.

Cimino et al. [2] proposed both a thermal (400 °C) and a water washing treatment to remove soluble ammonium and calcium sulfates deposited on aged  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts that operated for a total of 18,000 h treating the exhaust gases of a municipal waste incinerator in a tail-end configuration. They found the water washing was more effective than the thermal method to restore initial activity since it was possible to remove most poisoning compounds with only limited leaching of soluble vanadia species.

Nie et al. [92] treated their K-poisoned  $\text{V}_2\text{O}_5\text{-Ce}(\text{SO}_4)_2/\text{TiO}_2$  catalyst with an  $\text{SO}_2/\text{O}_2/\text{N}_2$  flow in the temperature range 320–420 °C and compared the results with those obtained over a standard VWT system. They observed a good but not complete recovery of the original catalytic performance for the standard VWT system; at variance, an activity gain was measured for the  $\text{V}_2\text{O}_5\text{-Ce}(\text{SO}_4)_2/\text{TiO}_2$  system after treating it in the 320–370 °C temperature range and this effect was assigned to the formation of novel acidic Ti–OH groups from the conversion of surface sulfates on  $\text{TiO}_2$  to bidentate surface species.

Yu et al. [32] reported a detailed study on the effect of three different washing solutions for the regeneration of commercial  $\text{V}_2\text{O}_5\text{-WO}_3\text{-MoO}_3/\text{TiO}_2$  honeycomb catalysts exposed for a total of 37,000 h to exhaust gases from a coal-fired plant that contained large amounts of sulfur and alkali/alkaline metals. They used either diluted (0.2 M) solutions of NaOH and  $\text{HNO}_3$  or a combination of the two (first NaOH, then  $\text{HNO}_3$ ). All regeneration methods could remove the surface contaminants, increase the specific surface area (removing  $\text{Al}_2(\text{SO}_4)_3$  species), and recover the acid sites of the used catalyst, and hence reactivate the catalytic performance to some degree. However, active elements such as V, W, and Mo are also partially dissolved in the acid solution, while the alkaline solution shows a lower removal efficiency for poisons (but also for vanadium). The sequential alkali-acid combined treatment could overcome the drawbacks of single treatments.

Peng et al. [85] proposed a two-step regeneration of As and K poisoned commercial VWT catalysts. A diluted  $\text{H}_2\text{SO}_4$  solution was first used to remove potassium, and then an  $\text{H}_2\text{O}_2$  solution was used to remove arsenic. The regenerated catalyst recovered its original performance at high temperatures, although the high concentration of  $\text{H}_2\text{O}_2$  results in some leaching of vanadium being more aggressive than the 0.2 M  $\text{H}_2\text{SO}_4$  solution for this aspect.

A more complex method to deal with commercial spent catalysts poisoned by As and alkali metals was proposed by Li et al. [75]. They used an efficient and green advanced oxidation process (oxidative ammonium bicarbonate leaching) to detoxify and to almost completely extract V, W, As, Na, and K from the spent SCR materials. The leaching solution, containing  $\text{NH}_4\text{HCO}_3$ , 1.5 M  $\text{H}_2\text{O}_2$ , preserved the anatase structure of  $\text{TiO}_2$  so that the residual material could be re-utilized as a support to produce a new SCR catalyst after impregnation with proper amounts V and W.

A different regeneration technique was proposed by Peng et al. [82]. The authors proposed an electrophoresis method that effectively removed up to 95% K or Na ions, as opposed to the 30% removal of alkali metals obtained using a simple water treatment. In the case of  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  poisoned by 1% Na or K, it was reported that regeneration by electrophoresis restored ca. 32 and 51% of the initial  $\text{deNO}_x$  activity at 250 °C, respectively.

Apart from regeneration, the general approach to prolong the catalyst life-time is to use a special chemical formulation providing enhanced tolerance towards alkali poisoning.

The most common strategy to improve alkali tolerance is to increase the surface acidity using more acid supports that can potentially interact with the alkali metal, preserving the active acid sites to some extent.

In particular, the use of acid zeolites to support or exchange the active metals, already discussed in Section 2.3, can be regarded as a method to improve alkali tolerance.

Modification of  $\text{TiO}_2$  or  $\text{ZrO}_2$  supports by sulfation provides a method to enhance surface acidity. Surface sulphate groups exhibit strong acidity and act as attractive sites for potassium oxide [18]. Furthermore, the presence of  $\text{SO}_2$  in the reaction mixture was found to enhance the stability and activity of the  $\text{V}_2\text{O}_5$ /sulphated- $\text{ZrO}_2$ , probably due to a continuous regeneration mechanism of surface sulfated groups under reaction conditions. When K-poisoned, this catalyst keeps activity and stability up to 300 °C similar to that of the fresh catalyst; at variance, the possible formation of potassium sulfate-pyrosulfate species reacting with vanadium oxide markedly reduces the performance at 400 °C. For this reason, the authors proposed their catalytic formulation to realize alkali-tolerant systems operating at low temperatures in biomass-fired power plants.

The use of modified zirconia as a support to improve the K-tolerance of vanadia-based catalysts was also proposed by Due-Hansen et al. [93].  $\text{ZrO}_2$  surface acidity was enhanced by the dispersion of tungsten oxide with an optimal loading of 20% by weight. The authors also reported that a high degree of zirconia crystallinity, increasing with catalyst calcination temperature, ensures better performance for both fresh and K-poisoned catalysts.

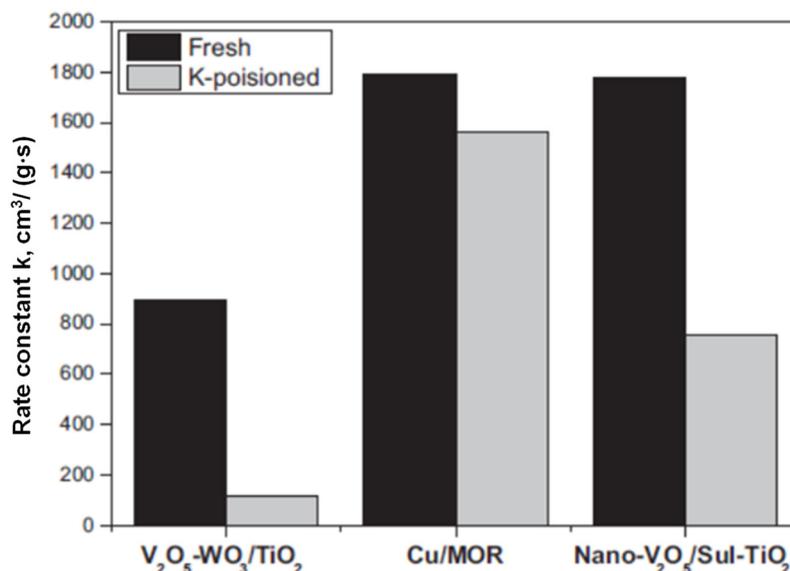
Putluru et al. [94] supported three different Keggin heteropolyacids ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) on  $\text{TiO}_2$  for the same purpose, before the dispersion of the  $\text{V}_2\text{O}_5$  active phase. These modified catalysts were compared to 3% $\text{V}_2\text{O}_5$ -7% $\text{WO}_3$ / $\text{TiO}_2$  commercial catalysts. The promoted catalysts showed excellent resistance to potassium poisoning, especially when the calcination temperature does not exceed 400 °C, so as to keep  $\text{WO}_3$  and  $\text{MoO}_3$  in the heteropolyacid matrix providing high stability and preserving great surface acidity.

In a more recent work [95] the same authors proposed to substitute the 10 wt.%  $\text{WO}_3$  added to traditional SCR catalysts with 15% heteropolyacid to increase the K tolerance of catalysts containing 3 or 5 wt.% vanadium operating at 225 °C. However, the stability of these new catalysts at temperatures beyond 300 °C has to be further investigated for their possible application in high dust configuration SCR units.

The same research group [19] identified three general approaches to contrast alkali deactivation, which are:

1. Increasing substrate acidity to promote a stronger interaction of alkali metals with the support rather than with vanadia.
2. Substituting vanadium oxide with other metal oxides having a higher number of Lewis sites with respect to Brønsted sites, representing the main target of alkali.
3. Improving the activity of  $\text{V}_2\text{O}_5$ / $\text{TiO}_2$  using more active nano-sized vanadia-particles dispersed on a high surface area of  $\text{TiO}_2$ , thus enhancing the catalyst lifetime.

In particular, the authors proposed more acid supports such as mordenite to replace  $\text{TiO}_2$ , the substitution of vanadium oxide with copper or iron oxides, a sol-gel method to deposit nano-sized vanadia particles on  $\text{TiO}_2$ . The highest alkali tolerance was obtained by coupling two of these approaches, as shown in Figure 7, where the activity of fresh or poisoned catalysts consisting of copper dispersed on acid mordenite or nano- $\text{V}_2\text{O}_5$  dispersed on sulfated  $\text{TiO}_2$  is compared with that of a conventional  $\text{V}_2\text{O}_5$ - $\text{WO}_3$ / $\text{TiO}_2$  catalyst.



**Figure 7.** The deNO<sub>x</sub> rate constant values at 400 °C over alternative SCR catalysts with high potassium loading: 250 μmol K/g for V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and Cu/MOR, and 280 μmol K/g for Nano-V<sub>2</sub>O<sub>5</sub>/Sul-TiO<sub>2</sub>. Reproduced from Reference [19].

A similar strategy was pursued in the work by Kustov et al. [96]. They compared potassium poisoning on vanadia-based catalysts with traditional carriers (TiO<sub>2</sub>, ZrO<sub>2</sub>) with that of sulfated systems, the former being deactivated even by small amounts of potassium oxide (K/V ratio < 0.5). Surface sulfate groups represent attractive sites for potassium oxide at temperatures below 400 °C due to their strong acidity. The K-tolerance of the catalysts correlates with the acidity of the corresponding supports and is maximum using sulfated-ZrO<sub>2</sub>. Nevertheless, at higher temperatures, potassium compounds become more mobile and are no longer bonded to sulfated groups of the support. As a consequence, they can migrate towards active sites responsible for the SCR reaction, causing a loss of activity. The use of alternative transition metals (Fe, Cu), which, unlike vanadium, show a prevailing Lewis acidity, can contribute to increasing the resistance towards alkali poisoning.

Also, in the case of Ce-based SCR catalysts, the main solution proposed to improve the alkali tolerance is to select supports with enhanced acid properties. In particular, Wang et al. [54] dispersed ceria on sulfated titania nano-tubes, finding a significantly larger content of Brønsted acid sites. Moreover, the stabilization of K<sup>+</sup> into the interlayer of the nanotubes appears to preserve CeO<sub>2</sub> from poisoning. Gao et al. [97] proposed a novel catalyst containing both vanadium and cerium (Ce:V = 1:1) dispersed on sulfated zirconia with high resistance against the simultaneous poisoning effect of alkali metals and SO<sub>2</sub>. The partial replacement of Ce for V limits the SO<sub>2</sub> adsorption and subsequent oxidation, thus inhibiting the formation of Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (responsible for the suppression of the Ce(IV)/Ce(III) redox cycle) and promoting the transformation of CeO<sub>2</sub> into CeVO<sub>4</sub>.

Similarly, Nie et al. [92] proposed a novel V<sub>2</sub>O<sub>5</sub>-Ce(SO<sub>4</sub>)<sub>2</sub>/TiO<sub>2</sub> catalyst showing better deNO<sub>x</sub> performance than a standard VWT catalyst after KCl deposition due to the superior oxidation properties of Ce<sup>4+</sup> and the acidity of SO<sub>4</sub><sup>2-</sup>.

Liu et al. [98] used Zr-doped TiO<sub>2</sub> support to improve the K-tolerance of their CeO<sub>2</sub> supported catalyst. The mixed TiZrO<sub>x</sub> support increased ceria dispersion and redox properties. Furthermore, their in-situ DRIFT studies showed that the Langmuir-Hinshelwood mechanism is accelerated on this catalyst.

A quite unusual solution to improve K-tolerance was proposed by Wang et al. [99]. The authors synthesized Nb-doped ceria nano-tubes that not only showed a superior deNO<sub>x</sub> activity but also a remarkable resistance to alkali metals, phosphorus, and lead compared to Nb-doped CeO<sub>2</sub> nano-particles. According to the authors, the nanotubular structure of the ceria nanotubes provides

a shell preventing the active phase from being poisoned. Furthermore, niobia doping is thought to increase acidic sites and to preserve the  $\text{Nb}^{5+}/\text{Nb}^{4+}$  and  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox cycles.

#### 4. Conclusions

The recent progressive transition from fossil fuels to biofuels in power plants and the use of bio-diesel in new vehicles has drawn research attention on novel issues related to the deactivation of SCR catalysts used in the de $\text{NO}_x$  units. In particular, alkali and alkaline earth metals, largely present in the raw biomass or deriving from bio-diesel production, are transported in various forms in the exhaust gases and accumulate on the surface of the SCR catalysts, acting as strong poisons by several different mechanisms.

This review critically analyzes recent literature data on the poisoning of SCR catalysts due to the main alkali and alkaline earth metals, in combination with various counterions or with the simultaneous presence of other poisoning elements/compounds. In particular, SCR catalysts have been divided into three main categories depending on the specific formulation and field of application.

Acid sites, mostly Brønsted type, are the favorite target of alkali poisons for the widely used  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts. Potassium is identified as the most poisoning element, and there is general agreement on the stronger deactivating power of alkali with respect to alkaline earth metals. Alkali metals bind to acid centers representing the adsorption sites for ammonia that will then react with either adsorbed (Langmuir mechanism) or gaseous (Eley-Rideal mechanism)  $\text{NO}$  depending on the reaction temperature (low or high, respectively). As a consequence, suppression of the initial  $\text{NH}_3$  adsorption step results in a dramatic loss of SCR activity.

Similarly, for zeolite-based catalysts, the surface acidity represents the key feature for the activation of the SCR reaction and also the main target of alkali and alkaline earth metal poisons.

For manganese or cerium oxide-based catalysts, in addition to the loss of surface acidity, the inhibition of the metal oxide reducibility also plays a significant role in the mechanism of deactivation, which is weaker for traditional  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts operating at higher temperatures. In particular, alkaline metals inhibit the transfer of surface oxygen required to activate adsorbed  $\text{NH}_3$  or  $\text{NO}_x$  species.

The review also focuses on the most common regeneration techniques proposed to restore the original performance of catalysts, this issue being very critical due to the high costs related to the replacement and disposal of spent SCR catalysts. Different washing (water or acid solution) treatments are analyzed, in addition to innovative methods, identifying the most effective practices to remove alkali while limiting the undesired leaching of the active components.

Finally, strategies to produce catalysts with enhanced tolerance to alkali poisoning are reviewed, with particular regards to the use of acid supports and modifications to the catalyst formulation aimed at promoting a larger formation of poorly affected Lewis acid sites rather than Brønsted sites.

**Author Contributions:** Conceptualization: L.L., S.C.; writing—original draft preparation: L.L.; writing—review and editing L.L., S.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflict of interest.

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