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Insights into the poisoning mechanisms of zinc species on V_2O_5-WO_3/TiO_2 catalyst for NH_3-SCR: effect of the anion species

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Abstract

V_2O_5-WO_3/TiO_2 is commercial catalyst for controlling NO_x emissions from municipal solid waste incineration by NH_3 Selective Catalytic Reduction (NH_3-SCR). However, the flue gas contains a large amount of zinc compounds, which would lead to the deactivation of the catalyst. Therefore, in this work we studied the effect of different zinc species ($ZnSO_4$, ZnO and $ZnCl_2$) on a V_2O_5-WO_3/TiO_2 catalyst, investigating the deactivation mechanism. The different compounds negatively affected the activity in the order $ZnCl_2$>ZnO>$ZnSO_4$, indicating an important influence of the anions. The characterization results points to the evidence that Zn^{2+} would interact with the active V-OH and O=V structure, reducing the content of active Brønsted acid sites and influencing the $V^{5+}\rightleftarrows V^{4+}$ redox cycle, as well as inhibiting the activation of NH_3. Cl^- would interact with V-OH, possibly forming V-Cl and also suppress the formation and mobility of surface adsorbed oxygen, which further exacerbates the negative effect. On the other hand, SO_4^{2-} would weaken the poisoning effect of Zn^{2+} by a strong anion/cation interaction and likely form V-O-SO_3OH by reaction with V-OH, which is proposed to be an active Brønsted acid site able to active NH_3 in the NH_3-SCR reaction. Finally, the introduction of Zn^{2+} increased the adsorption of NO_x species to form a stable and inactive nitro species, the formation of which is inhibited by the presence of SO_4^{2-}.

Keywords: V_2O_5 -WO_3/TiO_2; Zinc salts; Poisoning mechanism; Structure-activity relationship.

1 Introduction

A large amount of nitrogen oxides (NO_x) is generated by anthropogenic activities, particularly in O_2-rich combustion processes *i.e.*, in stationary plants and transportation. The release of NO_x in atmosphere can cause serious environmental pollution, such as photochemical smog, acid rain and haze, with a negative impact on human health and related social costs [1-3]. The Selective Catalytic Reduction with ammonia (NH_3-SCR) technology is one of the most effective ways for the abatement of NO_x by municipal solid wastes incineration plants (MSWI), and the choice of the catalyst is crucial for an optimal performance [4, 5]. The most common catalyst used in NH_3-SCR technology in MSWI plant is based on a vanadium active phase supported on TiO_2, with tungsten as promoter to improve stability, (V_2O_5-WO_3/TiO_2 with typical composition of 3 wt% V_2O_5 and 5 wt%WO_3) [6, 7]. While, the flue gas from MSWI is still contains amount of alkali metals, alkaline earth metals, heavy metals, and acid gases (SO_2, HCl, etc.), even after the treatment. These substances pause a serious problem of catalyst deactivation.

The influence of alkali metals, alkaline earth metals and SO_2 on V_2O_5-WO_3/TiO_2 catalyst has been extensively studied. It was found that the alkali or alkaline earth metals would bind to the active species and promoters (V_2O_5 and WO_3), thereby reducing the surface acidity and reducibility of the catalyst, resulting in a decrease in the activity [8-10]. SO_2 could lead to the generation of ammonium sulfate (bisulfate) salts, which can block the pores of catalyst resulting in physical deactivation [11-14] . For heavy metals, most of the research has focused on the effect of As and Pb [15-18]. Kong et al. [19] found that As_2O_3 would be oxidized to As_2O_5 on the surface of V_2O_5-WO_3/TiO_2 catalyst, forming a dense surface layer which would prevent NH_3 adsorption and active sites recovery. Moreover, Friderike [15] and Peng [16] et al. found that As_2O_3 would form As-OH groups on the V_2O_5-WO_3/TiO_2 catalyst surface, which had quite low activity at high temperature. Miao et al. [20] proposed that PbO would react with the active sites of V_2O_5-WO_3/TiO_2 catalyst, decreasing the surface acidity and activity. A more detail description of the interaction of Pb with

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V_2O_5-WO_3/TiO_2 was obtained by Density Functional Theory (DFT) calculation. Indeed, Wu et al. [21] showed that Pb can interact with V=O groups and form a stable V-O-Pb structure, changing the electronic structures of V=O sites and inhibiting the adsorption of NH_3, resulting in a decrease in NH_3-SCR performance. On the other hand, relatively few studies have been reported on the effect of zinc on the catalytic activity of V_2O_5-WO_3/TiO_2 catalyst. According to the literature [22], the content of zinc in fly ash is usually much higher than that of other heavy metals (Pb, Cr, As, etc.), so that its influence on the performance of NH_3-SCR catalyst cannot be ignored. Additionally, the flue gas from MSWI also contains a high concentration of SO_4^{2-} and Cl^-.

Concerning zinc poisoning, most of the research has been focused on non-vanadium based catalysts. According to literature [23, 24], it was found that Zn species had a great influence on the NH_3-SCR activity of the catalysts when the load reached 2 wt%. Zhu et al. [23] studied the effect of zinc on the Mn-Fe/Ni SCR catalyst, and found that zinc reduced surface acidity and the amount of high-valence metal elements (Fe^{3+} and Mn^{4+}) with consequent decrease in the catalyst reducibility. Wang et al. [25] studied the structural effect of iron spinel oxides doped with Mn, Co, Ni, and Zn on the NH_3-SCR activity, and found that Zn doping favors the catalytic oxidation of NH_3 to NO. Moreover, Wang et al. [24] compared the effect of different zinc species (ZnO, $ZnSO_4$, and $ZnCl_2$) on Sb-$CeZr_2O_x$ catalysts, and found that the deactivation rate of these zinc species was in the order of $ZnCl_2$ > $ZnSO_4$ > ZnO. They reported that ZnO decreased the reducibility of the catalyst, SO_4^{2-} would suppress oxygen mobility, and Cl^- would replace O in the Ce-O-Sb structure. However, the effect of zinc species on V_2O_5-WO_3/TiO_2 catalyst are rarely reported.

Based on the above considerations, in this work we have investigated the effect of different zinc species poisoning ($ZnSO_4$, ZnO and $ZnCl_2$) on the *de*NO_x activity of V_2O_5-WO_3/TiO_2 catalysts. These three precursors were selected also in relation to the potential poisoning effect of SO_4^{2-} and Cl^-, which are present in a high concentration in flue gas from MSWI. The catalysts were fully characterized in relation to their structural and textural properties, reducibility and surface sites

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nature and distribution, with the general aim to draw structure-activity correlations and investigate the interaction of the different zinc compounds with the surface active species.

2 Experimental section

2.1 Preparation of the catalysts

The impregnation method was chosen to prepare the V_2O_5-WO_3/TiO_2 catalyst, and the details were described as in our previous work [38], and the sample was labeled as VWTi.

The zinc poisoned catalysts were prepared by impregnation of VWTi using a $ZnSO_4$, $Zn(NO_3)_2$ or $ZnCl_2$ solution with a salts of concentration of 3.06×10^{-4} mol/g, corresponding to a mass fraction of Zn of 2.0 wt%. ICP measurements indicated a Zn amount around 1.7-1.8 wt% (Table S1 in Supporting Information). The solvent was evaporated at 90 ^oC in a water bath with continuous stirring and the remaining solid calcined in air at 400 ^oC for 5 h. After this treatment we can assume that $Zn(NO_3)_2$ is decomposed, leaving on the surface of the catalysts only the metal ions (dispersed or in the form of ZnO), while it is not possible to exclude the presence of SO_4^{2-} (or other sulfur species) and Cl^- in the other two cases. Accordingly, the obtained samples were labeled as $ZnSO_4$-VWTi, ZnO-VWTi and $ZnCl_2$-VWTi, respectively.

2.2 Catalysts characterization and the test of NH_3-SCR activity

The samples were characterized by inductively coupled plasma (ICP), X-ray diffraction (XRD), N_2-physisorption, Raman spectroscopy, NH_3 temperature-programmed desorption (NH_3-TPD), H_2 temperature-programmed reduction (H_2-TPR), electron paramagnetic resonance (EPR), X-ray photoelectron spectra (XPS), *in situ* fourier transform infrared spectroscopy *(in situ* FTIR) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) technologies. The characterization details and the test of NH_3-SCR activity are listed in the Supporting information.

3 Results and discussion

3.1 NH_3-SCR activity

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The effect of different zinc species ($ZnSO_4$, ZnO, and $ZnCl_2$) on the NH_3-SCR activity of VWTi catalyst has been investigated in the temperature range of 100-300 ^oC, relevant for applications in MSWI plants (Fig. 1). The NO_x conversion of VWTi catalyst exceeded 85% above 225 ^oC, and reached about 99% at 300 ^oC. After introducing the zinc species, the NO_x conversion decreased, in the order of $ZnSO_4$-VWTi >ZnO-VWTi>$ZnCl_2$-VWTi. The activity of $ZnSO_4$-VWTi is only slightly lower than that of VWTi catalyst, reaching about 92% NO_x conversion at 300 ^oC. However, the activity of ZnO-VWTi and $ZnCl_2$-VWTi was significantly reduced, reaching only 83% and 67% conversion at 300 ^oC, respectively. No effect on selectivity was observed, in that 100% selectivity to N_2 was found for all samples, without N_2O production (Fig. S1).

Wang et al. [25] found that the Zn doped iron spinel oxides led to the catalytic oxidation of NH_3 to NO. To further investigated whether the same situation exists on VWTi catalyst, NH_3 oxidation experiments were carried out. A mixed gas with 1000 ppm NH_3, 11 vol.% O_2, and balance N_2 was used to explore the formation of NO_x caused by NH_3 over-oxidation on these catalysts and pure zinc compounds ($ZnSO_4$, ZnO, and $ZnCl_2$). However, we did not find NO generation during the whole reaction for all samples (not reported), which indicates that Zn doping did not lead to the over-oxidation of NH_3 on VWTi catalysts.

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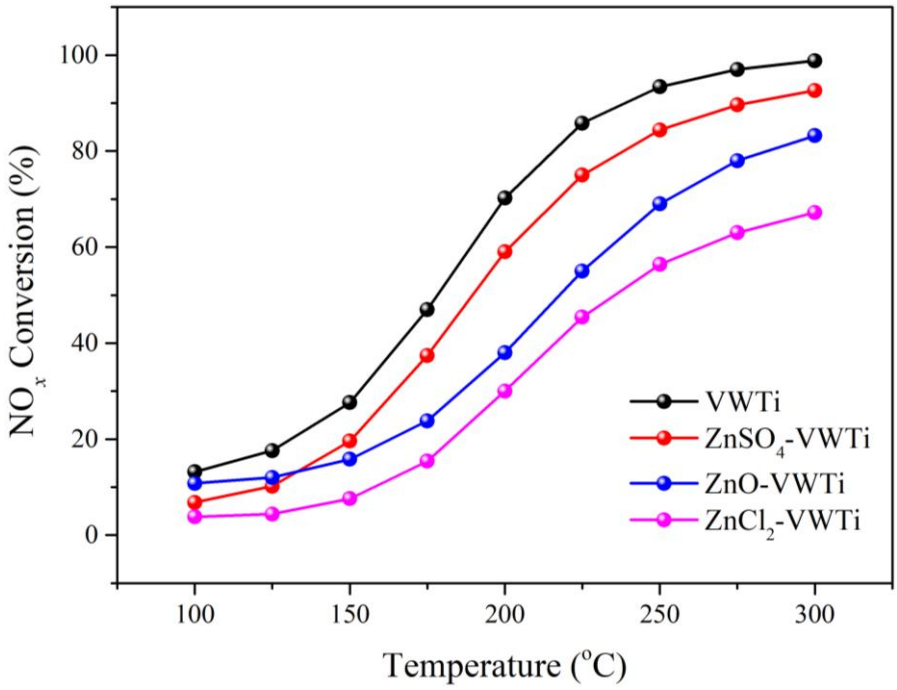

Fig. 1 The effect of different zinc species on NH_3-SCR performance on VWTi catalyst.

3.2 Physical properties (*XRD and BET*)

The XRD was chosen to explore the effect of impregnation of Zn from different zinc precursors on the crystal structure of VWTi catalyst, as shown in Fig. S2. It was found that all catalysts only displayed diffraction patterns of TiO_2 anatase phase [PDF-ICDD-1272]. The absence of extra phases is in line with the low loading of the V_2O_5-WO_3 active phase and of the zinc species used for the poisoning, and generally indicate a good dispersion of both active phase and pollutant. As expected, impregnation with Zn precursors does not affect the crystal structure of VWTi catalyst.

Table 1 shows the BET specific surface area, total pore volume and mean pore diameter of the fresh and Zn-poisoned catalysts. The BET specific surface area of VWTi, $ZnSO_4$-VWTi, ZnO-VWTi and $ZnCl_2$-VWTi catalysts were 79, 60, 82 and 84 m^2/g, respectively. The small increase in surface area in the ZnO-VWTi and $ZnCl_2$-VWTi catalysts (accompanied by a very small decrease of pore volume and increase of pore diameter) is within the 5% error of the method. On the other hand, a decrease in surface area from 76 to 60 m^2/g in $ZnSO_4$-VWTi is outside this confidence

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interval and indicates a small effect of the pollutant on the textural properties of the catalyst, including porosity. Since the catalytic activity of $ZnSO_4$-VWTi is definitely higher than that of the other two poisoned catalysts, we can conclude that the textural properties are not the major factor affecting the activity in this experimental system.

Table 1 Textural properties of the investigated catalysts.

Sample	BET specific surface area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
VWTi	79	0.36	9.1
$ZnSO_4$-VWTi	60	0.29	8.6
ZnO-VWTi	82	0.34	9.2
$ZnCl_2$-VWTi	74	0.34	11.7

Moreover, we calculated the surface density (expressed in at/nm^2) of the active phase (V), promoters (W) and pollutants according to the measured values of surface area of each catalyst, and the results are listed in Table 2. The surface density of V was between 2 and 3 at/nm^2 in these catalysts, with values between 4 and 5.5 at/nm^2 for V+W, respectively. These values are below the theoretical monolayer for V_2O_5 (between 6 and 8 at/nm^2 following classical literature and more recent reports) [26, 27] and close to the proposed monolayer for WO_3 (4.5 W at/nm^2) [28]. These results indicate that the active phase and promoter were good dispersed on the surface of TiO_2 support, which in line with the XRD results.

The surface density of the zinc species in the order of ZnO < $ZnCl_2$ < $ZnSO_4$ (with value between 2.2 and 3.1 at/nm^2), which does not reflect the observed trends in NO_x conversion. This indicates that in this work the observed effect of the pollutants on the catalytic activity cannot be correlated to their nominal surface density but needs to be described in terms of a chemical specificity.

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Table 2 Surface density of active phase, promoter and pollutants of the studied catalysts.

Sample	V (at/nm^2)	W (at/nm^2)	V+W (at/nm^2)	ZnX (at/nm^2)	Total (at/nm^2)
VWTi	2.5	1.6	4.1	-	4.1
$ZnSO_4$-VWTi	3.3	2.2	5.5	3.1	8.6
ZnO-VWTi	2.4	1.6	4.0	2.2	6.2
$ZnCl_2$-VWTi	2.7	1.8	4.5	2.5	8.0

3.3 Structure of VO_x species (*Raman*)

The Raman spectra on the studied samples are shown in Fig. 2. All the samples displayed a series of peaks assigned to the $E_{g(1)}$ (143 cm^{-1}), $B_{1g(1)}$ (395 cm^{-1}), A_{1g}+$B_{1g(2)}$ (515 cm^{-1}), and $E_{g(2)}$ (619 cm^{-1}) vibration modes of anatase TiO_2 [29]. Three very weak bands appeared at 1032 cm^{-1}, 1015 cm^{-1} and 1009 cm^{-1} over VWTi catalyst, which are related to the V=O stretching mode of the vanadyl species in di/oligomeric O=$V^{5+}O_3$, and to W=O stretching modes of di/oligomeric and isolated tungstenyl species, respectively [27, 30-32]. A very weak and broad band around 975 cm^{-1} would be ascribed to V-O-V/V-O-W vibrations in the oligomeric structure. And crystalline V_2O_5 (sharp band at 998 cm^{-1}) and WO_3 phases (sharp band at 800 cm^{-1}) are not observed, which indicates that the active phases are good dispersed on the surface of the support.

After introducing zinc species, the bands related to the vanadyl and tungstenyl groups disappeared in samples ZnO-VWTi and $ZnCl_2$-VWTi, while a band remains at 1024 cm^{-1} in $ZnSO_4$-VWTi, related to V=O stretching in isolated O=VO_3 species. A broad band with maxima around 984 and 970 cm^{-1} appeared in all samples, with higher intensity on ZnO-VWTi and $ZnCl_2$-VWTi. This is the typical range for V-O-V/V-O-W vibrations, similar to what observed in hydrated VWTi catalyst, which indicates that V-O-V and V-O-W group are perturbed by the presence of zinc species [33, 34]. According to the literature [27, 35], the oligomeric VO_x species are the main active species,

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which can promote the NH_3-SCR reaction. These results indicate that $ZnSO_4$ has a weaker influence on the surface active VO_x species than Zn from ZnO and $ZnCl_2$, which is in line with the results of the activity.

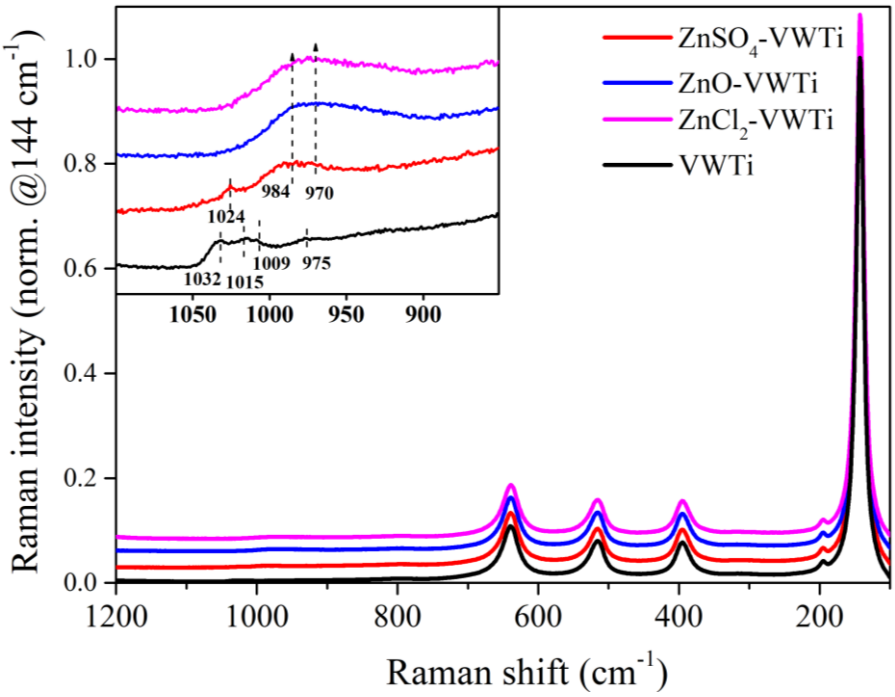

Fig. 2 Raman spectra of VWT and different zinc poisoned catalysts.

3.3 The surface acidity (*NH_3-TPD and in-situ DRIFTS of NH_3*)

The effect of zinc species on the surface acidity of VWTi catalyst was tested by NH_3-TPD, and the results are shown in Fig. 3. The profiles of the fresh and poisoned catalysts can be deconvoluted into three peaks, resulting from desorption of chemisorbed NH_3 on weak, medium, and medium-strong acid sites, respectively [36, 37]. Interestingly, unlike alkali or alkaline-earth metals poisoning [8, 38], the amount of desorbed NH_3 increased after introducing zinc species (see Table 3). The amount of desorbed NH_3 on $ZnSO_4$-VWTi catalyst is 537 μmol/g, which is larger than those of ZnO-VWTi (319 μmol/g) and $ZnCl_2$-VWTi (357 μmol/g) catalysts, and more than double with respect to VWTi (246 μmol/g). Moreover, it was found that the desorption temperature is shifted to higher temperature by a similar amount after ZnO and $ZnCl_2$ poisoning, and to lower temperature

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for $ZnSO_4$-VWTi. These results indicate that the introduction of zinc species enhanced the surface acidity of VWTi catalyst, and again $ZnSO_4$-VWTi show a different trend with respect to the other two samples. In general, NH_3 sorption capacity of the catalyst is a good indicator for their a NH_3-SCR activity. However, in this case we observe that neither the amount of adsorbed NH_3, nor the strength of the involved surface sites can be directly correlated to the performance of the catalysts in NO_x conversion in the considered temperature range.

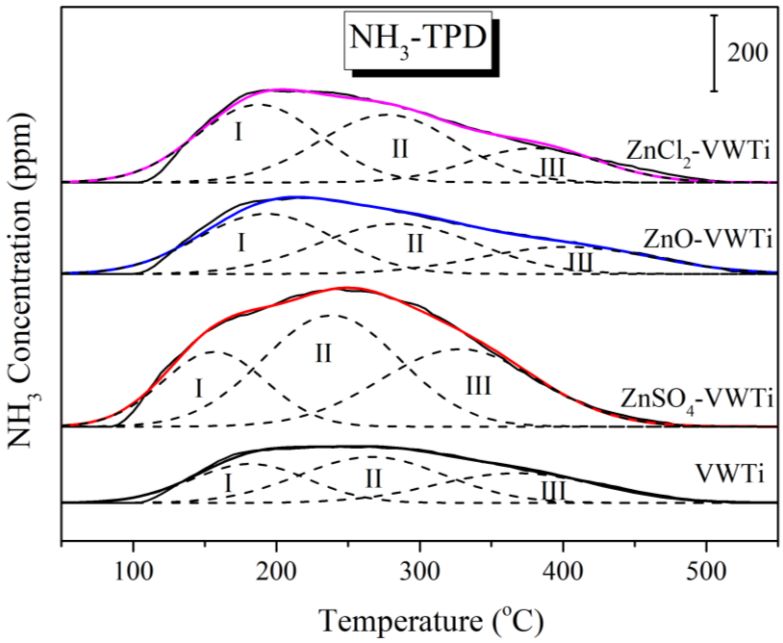

Fig. 3 NH_3-TPD profiles of VWTi and different zinc poisoned catalysts.

Table 3 Quantitative data of NH_3-TPD profiles over these catalysts

Sample	Peak temperature (°C)			Acid amount (μmol)			Acid amount (μmol)
	T_1	T_2	T_3	S_1	S_2	S_3	$S_1+S_2+S_3$
VWTi	179	269	369	70	102	74	246
$ZnSO_4$-VWTi	154	239	329	118	233	186	537
ZnO-VWTi	194	284	403	124	122	73	319
$ZnCl_2$-VWTi	189	279	379	146	142	69	357

To further investigate the effect of zinc species on Brønsted (B) and Lewis (L) acid sites as well as the process of NH_3 adsorption over VWTi catalyst, *in-situ* DRITFS of NH_3 adsorption

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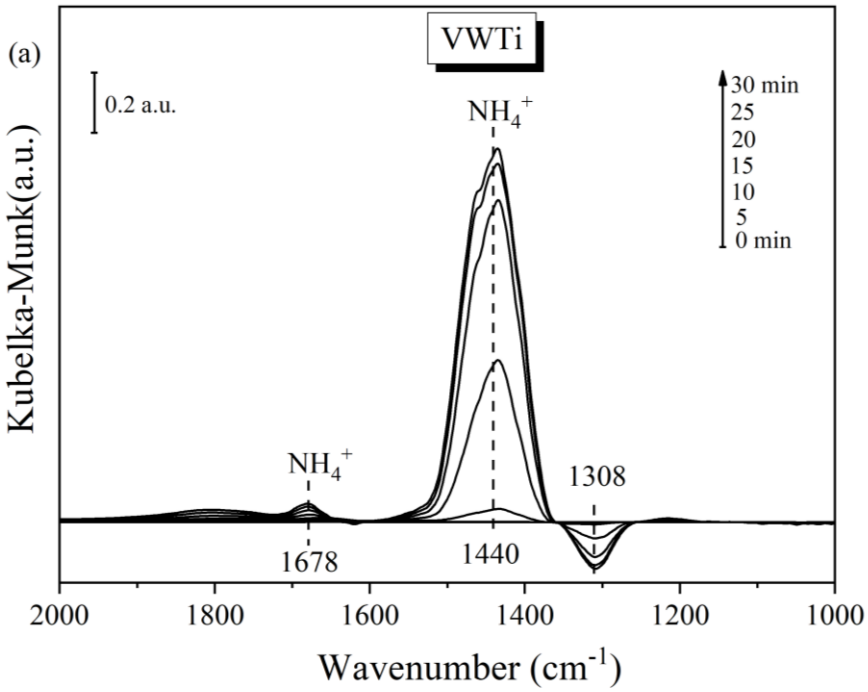
experiments were carried out at 50 ºC, and the results are shown in Fig. 5. Two bands assigned to the bending modes of NH_4^+ species (δNH_4^+) formed by reaction of NH_3 with B acid sites were observed at 1440 cm^{-1} and 1678 cm^{-1} on VWTi catalyst [9, 39-41]. The negative band at 1308 cm^{-1} is explained as surface impurity deriving from the oxalate precursor used in the impregnation process, which is displaced by NH_3 adsorption. After introducing Zn from ZnO and $ZnCl_2$, two new bands appeared at 1615 cm^{-1} and 1227 cm^{-1}, which are assigned to NH_3 species adsorbed on L acid sites (labeled as NH_3* in the Fig. 4, antisymmetric and symmetric bending modes δ_{as} and δ_{sym}, respectively) [1, 42, 43]. These can be reasonably assigned to the interaction of NH_3 with Zn^{2+} sites with Lewis character. On the other hand, the amount of NH_3 adsorbed on Lewis sites on $ZnSO_4$-VWTi catalyst is quite small, and only the more intense antisymmetric mode at 1615 cm^{-1} can be appreciated.



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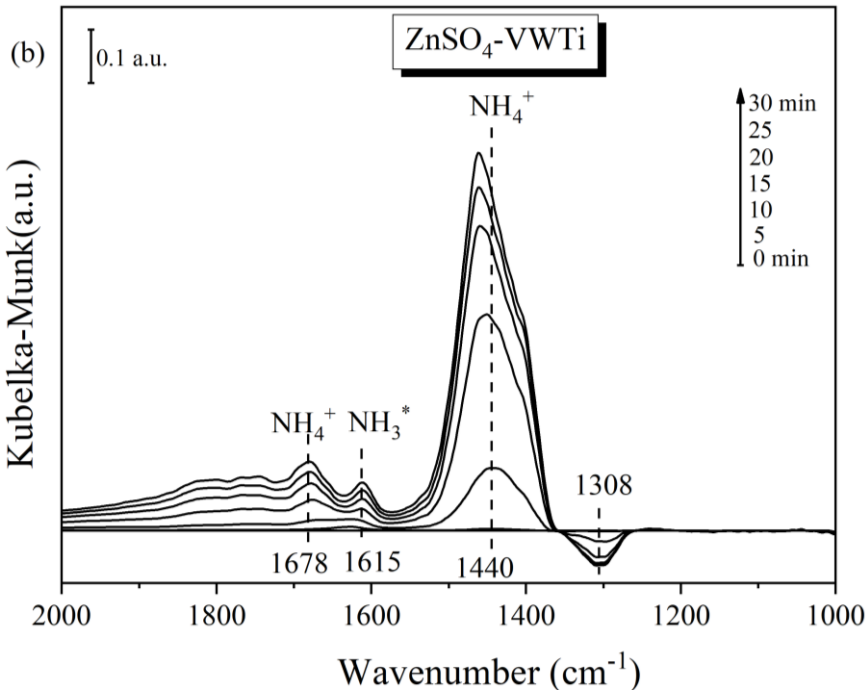

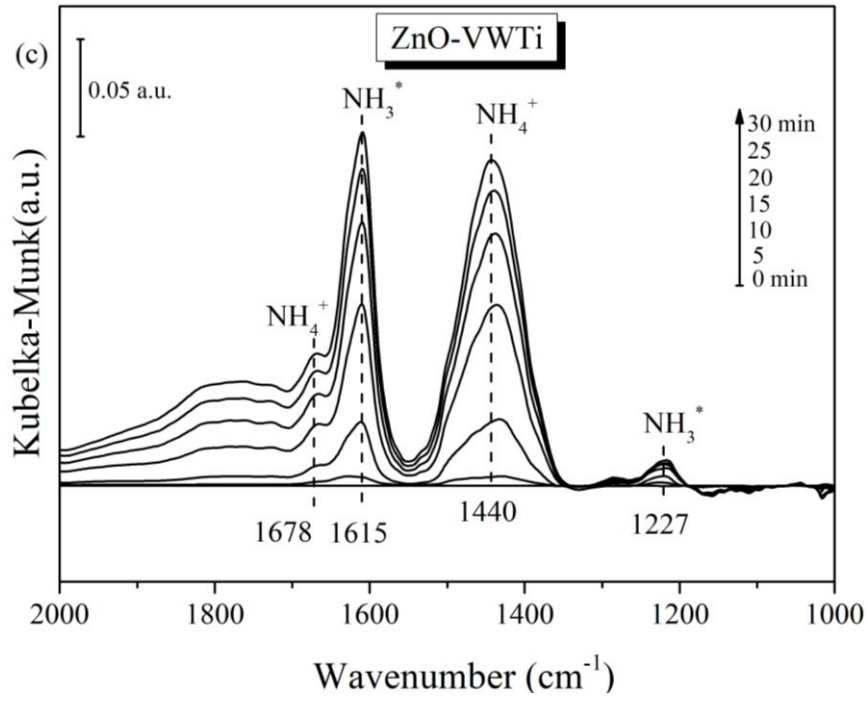

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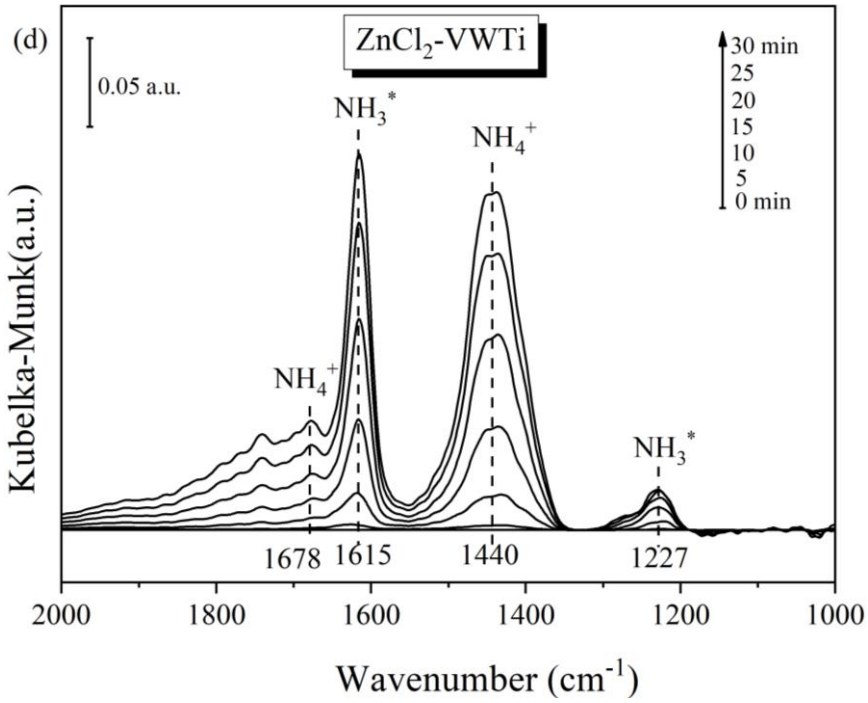

Fig. 4 *In-situ* DRIFTS spectra of NH_3 adsorption over VWTi and different zinc poisoned catalysts at 50 ^oC.

For easier comparison, the relative intensity of the NH_3 δ_{as} band at 1615 cm^{-1} and that of the δNH_4^+ mode at 1440 cm^{-1}, measured after NH_3 saturation at 50 ^oC, has been plotted for the four catalysts in Fig. S3. No quantitative consideration can be made about the ratio of B and L sites in the catalysts, but some trends can be observed. Only B acid site exist on the VWTi catalyst. After introducing zinc species, the ratio of the $\delta NH_4^+ / (\delta NH_4^+ + NH_3\ \delta_{as})$ is significantly reduced for both ZnO-VWTi and $ZnCl_2$-VWTi catalysts, which indicates an important effect of the pollutants on the nature of acid surface sites of the catalysts. It is clear that addition of Zn from ZnO and $ZnCl_2$ results in a similar increase of surface Lewis sites, which would indicate the presence of surface Zn^{2+} ions not particularly influenced by the possible presence of chloride anions. On the other hand, this effect is not observed when Zn is impregnated on the catalysts starting from a $ZnSO_4$ precursor.

According to literature [44], B acid sites on VWTi catalyst are more active than L acid sites in the NH_3-SCR reaction. The observed decrease of B site on ZnO-VWTi and $ZnCl_2$-VWTi catalysts

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suggests a reaction of Zn^{2+} ions with V-OH groups to form V-O-Zn (and possibly V-Cl) structures, where Zn ions are coordinatively unsaturated (have L acid character). On the other hand, SO_4^{2-} can react with V-OH to form V-SO_3OH structures, with B acid character and/or remain coordinated to Zn^{2+} so that they do not display Lewis character.

3.4 Reducibility of the catalysts (*EPR* and *H_2-TPR*)

H_2-TPR experiments were used to study the effect of zinc from different precursors on the redox performance of VWTi catalyst, and the results are displayed in Fig. 5. Two peaks appeared at 471 and 528 °C on VWTi catalyst, which are assigned to the reduction of V^{5+} to V^{3+} and W^{6+} to W^{4+}, respectively [17, 45]. After introducing $ZnSO_4$, a very intense reduction peak with slightly higher maximum position (479 °C) is observed, which can be related to the reduction of SO_4^{2-} overlapping to the reduction of V^{5+} and W^{6+}, in agreement with the results of Wang [24]. However, for ZnO-VWTi and $ZnCl_2$-VWTi catalysts, the reduction temperature shifted to a lower temperature. Considering that Zn^{2+} will not be reduced at low temperature, this change of reduction temperature indicates an electronic effect of Zn on the vanadium reducibility. Moreover, the total H_2 consumption also increased. This may be due to the fact that Zn^{2+} and Cl^- affect the electronic properties of O=V groups to negatively influence the $V^{5+}\rightleftarrows V^{4+}$ active redox cycle, resulting in an increase of V^{5+}. These formed V^{5+} species could be reduced by H_2 to V^{3+}, but could not be able to activate NH_3 with a V^{5+}/V^{4+} reduction. Therefore, the total H_2 consumption increased but the NH_3-SCR activity reduced after zinc species poisoned.

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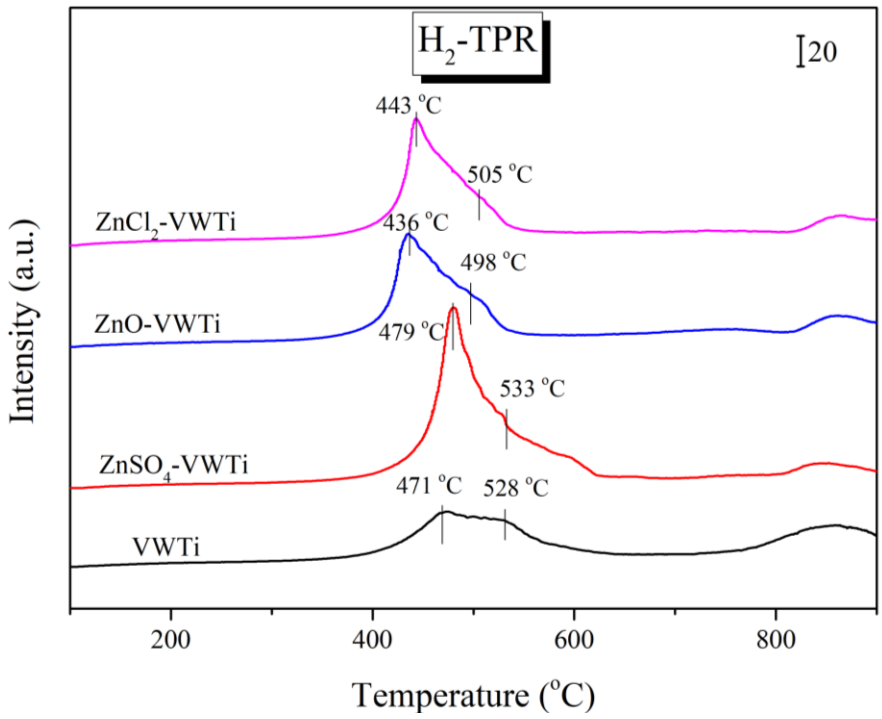

Fig. 5 H_2-TPR profiles of VWTi and different zinc poisoned catalysts.

Fig. 6 shows the EPR spectra of these fresh and Zn-poisoned catalysts recorded after a mild reduction treatment with NH_3 at 150 °C, necessary to reduce a (small) fraction of $O=V^{5+}O_3$ species to EPR active a $O=V^{4+}O_2$. The spectra are characterized by a set of a complex overlap of different spectral line arising from the anisotropy of both g and A tensors of $O=V^{4+}O_2$ groups. Two species (indicated with A and B in Fig. 6) with slightly different spin-Hamiltonian parameters can be identified over VWTi catalyst, which were recently assigned to V^{4+} species on the (001) and (101) exposed facets of TiO_2, respectively [46]. Interestingly, specie A disappeared after introducing Zn from ZnO and $ZnCl_2$, while this does not occur on $ZnSO_4$-VWTi catalyst. Some researchers compared the activity of VO_x/TiO_2 catalysts with differently exposed crystal-planes of TiO_2, and found that VO_x/TiO_2(001) has a higher activity than VO_x/TiO_2(101) [47].

The amount of surface V^{4+} formed in the catalysts after a mild reducing treatment in NH_3, has been evaluated by the double integration of the EPR spectra. This corresponds to 3.14×10^{19} V^{4+} atoms on VWTi catalyst, which is very similar to what measured for $ZnSO_4$-VWTi (2.85×10^{19}). On

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the contrary, ZnO-VWTi and $ZnCl_2$-VWTi show a lower V^{4+} amount (9.24×10^{18} and 8.34×10^{18} spins, respectively), meaning that in these samples the introduction of Zn affects the reducibility of $O=V^{5+}O_3$ to $O=V^{4+}O_2$, which is a crucial step for the NH_3-SCR cycle.

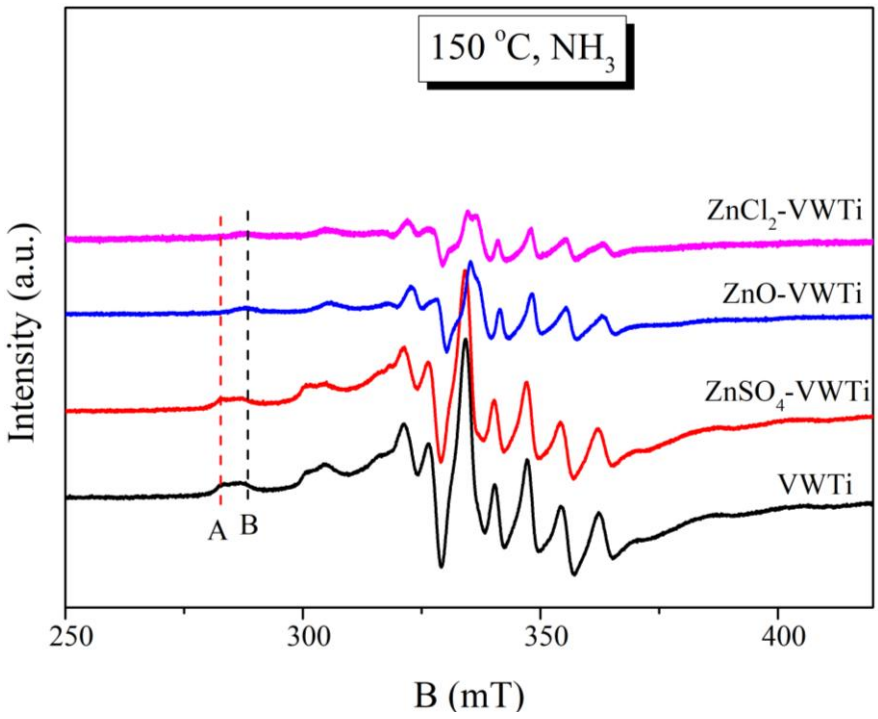

Fig. 6 EPR spectra of VWT and different zinc poisoned catalysts.

3.5 Surface compositions (*XPS*)

Fig. S4(a) shows Ti 2p XPS results of these fresh and Zn-poisoned catalysts. The binding energy of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ of all samples were centered at 464.4 eV and 458.7 eV, respectively [48]. These results show that Ti mainly existed on the surface of these catalysts as Ti^{4+}. The corresponding W 4f XPS spectra are presented in Fig. S4(b). These catalysts displayed two bands assigned to surface W^{6+} species at 37.3 eV and 35.2 eV, hardly affected by poisoning [12].

Fig. 7 shows the O 1s XPS spectra of these fresh and Zn-poisoned catalysts. All samples displayed two bands at 529.9 eV (labeled as O_β) and 531.3 eV (labeled as O_α), which were related to lattice oxygen (O^{2-}) and surface adsorbed oxygen (O_2^{2-} and O^-), respectively [49-51]. As we known, the surface adsorbed oxygen is usually formed in the oxide defects, which can promote the

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activation of adsorbed NH_3 and NO_x species owing to its high mobility, thereby improving the activity [52, 53]. Therefore, we calculated the ratio of O_α (*i.e.*, (O_α/ (O_α+ O_β)) over these fresh and Zn-poisoned catalysts (Table 4). It can be seen that the ratio of O_α decreased from 42.4% to 39.6%, 30.0%, and 26.1% after introducing $ZnSO_4$, ZnO, and $ZnCl_2$, respectively. These results indicate that Zn-poisoning reduced the availability of reactive surface oxygen, weakening the activation of the reactant molecules. Interestingly, the O_α peak is more defined in sample $ZnSO_4$-VWTi, suggesting a contribution from surface sulphates.

The V $2p_{3/2}$ XPS spectra of these fresh and Zn-poisoned catalysts are shown in Fig. 7(b). The spectra can be divided into three energy around 517.3, 516.6 and 515.7 eV, which are assigned to V^{5+}, V^{4+} and V^{3+}, respectively [54, 55]. The ratio of $V^{5+}/(V^{5+}+V^{4+}+V^{3+})$ was calculated, and it was found that the V^{5+} ratio of VWTi catalyst was 30.4%. After introducing zinc species, the V^{5+} ratio slightly increased, in the order of $ZnSO_4$-VWTi (30.9%) < ZnO-VWTi (31.5%) < $ZnCl_2$-VWTi (32.4%). Given the different pre-treatment conditions of the used techniques, these results are in agreement with the increased H_2 consumption in TPD experiments after poisoning and with EPR results obtained after mild reduction in NH_3.

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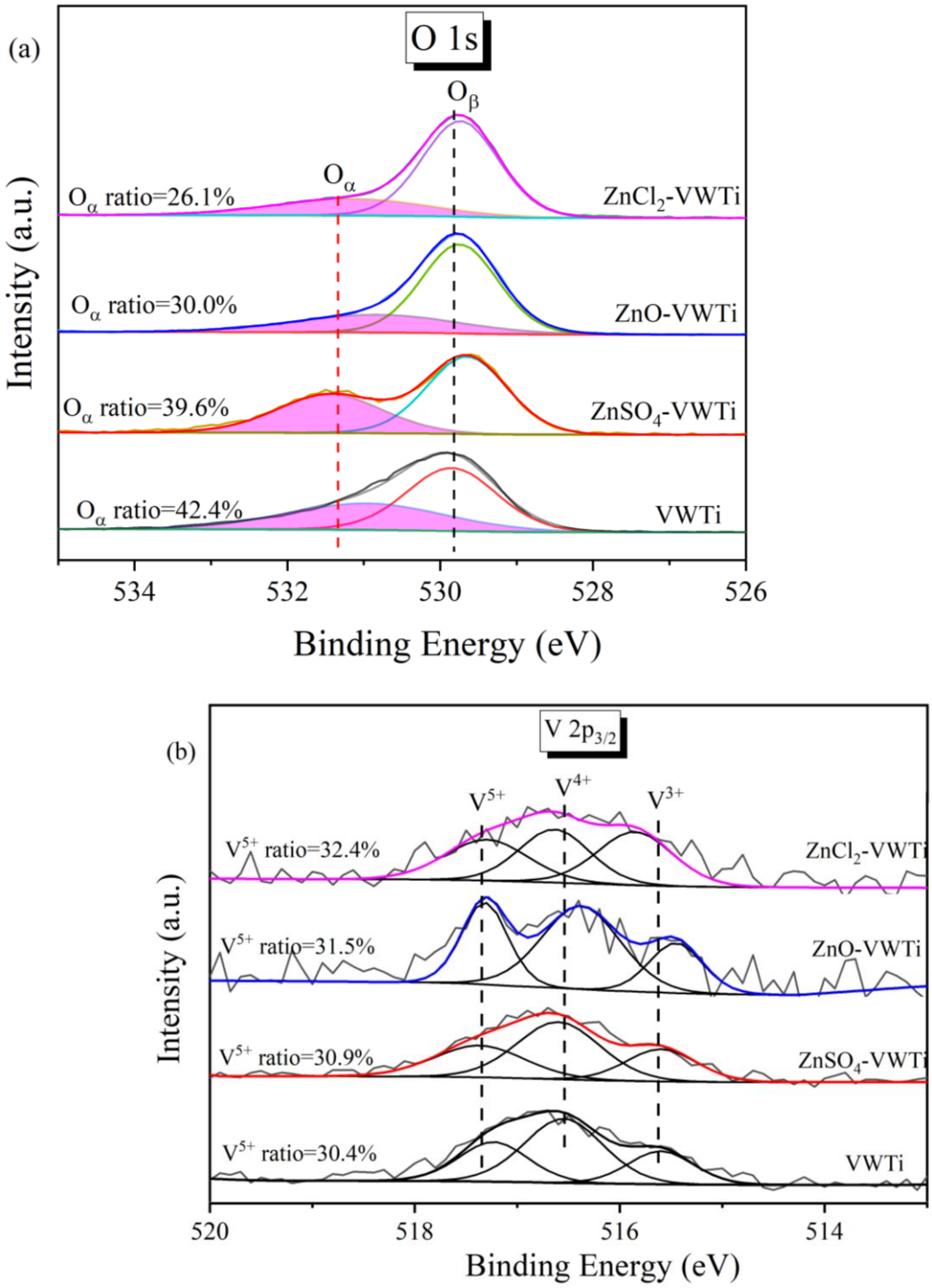

Fig. 7 O 1s (a) and V2$p_{3/2}$ (b) XPS spectra of VWTi and different zinc species poisoned catalysts.

Table 4 Surface composition and atomic ratio of these catalysts.

Sample	V	W	Ti	O	Zn	S	Cl	O_α

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								ratio
VWTi	3.67%	4.68%	22.41%	69.24%	/	/	/	42.4%
$ZnSO_4$-VWTi	3.25%	4.38%	21.54%	67.93%	1.88%	1.02%	/	39.6%
ZnO-VWTi	3.37%	4.33%	21.26%	69.11%	1.93%	/	/	30.0%
$ZnCl_2$-VWTi	3.21%	4.28%	21.87%	67.27%	1.84%	/	1.53%	26.1%

3.6 Study of adsorbed surface species (*in-situ FTIR*)

3.6.1 *In-situ FTIR study of CO adsorption*

Fig. S5 shows CO adsorption spectra of VWTi and Zn-poisoned catalysts at liquid nitrogen temperature with different CO pressure. Three peaks appeared at 2193 cm^{-1} (moving at 2198 cm^{-1} at low CO coverage), 2169 and 2142 cm^{-1} on VWTi catalyst, which are related to the so-called 'liquid-like', CO interacting with V-OH groups and with W^{x+} ions (X=5 or 6), respectively [27]. After introducing zinc, a new band assigned to CO interacting with coordinatively unsaturated Zn^{2+} ions appeared at 2216/2213 cm^{-1}, which is slightly weaker on $ZnSO_4$-VWTi with respect to the other two samples [56, 57]. Moreover, the intensity of the bands assigned to CO interacting with V-OH groups decreased, suggesting that introduction of zinc species reduced the amount of V-OH structure on the surface of catalysts, in the order $ZnCl_2 \backsimeq ZnO > ZnSO_4$, which in line with the *in-situ* DRIFTS of NH_3 results.

3.6.2 *In-situ DRITFS of NO+O_2 adsorption*

The effect of different zinc species on NO+O_2 adsorption process over VWTi catalyst at 50 °C is presented in Fig. 8. One broad band appeared at 1627 cm^{-1} with a very weak peak around 1577 cm^{-1} on VWTi catalyst, which are assigned to adsorbed NO_2 species and chelating bidentate nitrates, respectively [40, 58]. For ZnO-VWTi and $ZnCl_2$-VWTi catalysts, a new band assigned to nitro species appeared at 1522 cm^{-1} [59]. According to literature [36, 60], this nitro species is stable, and does not play a role in the NH_3-SCR reaction. However, this band does not appear on the $ZnSO_4$-VWTi catalyst, where adsorbed NO_2 is the main observed species. These results indicate that the

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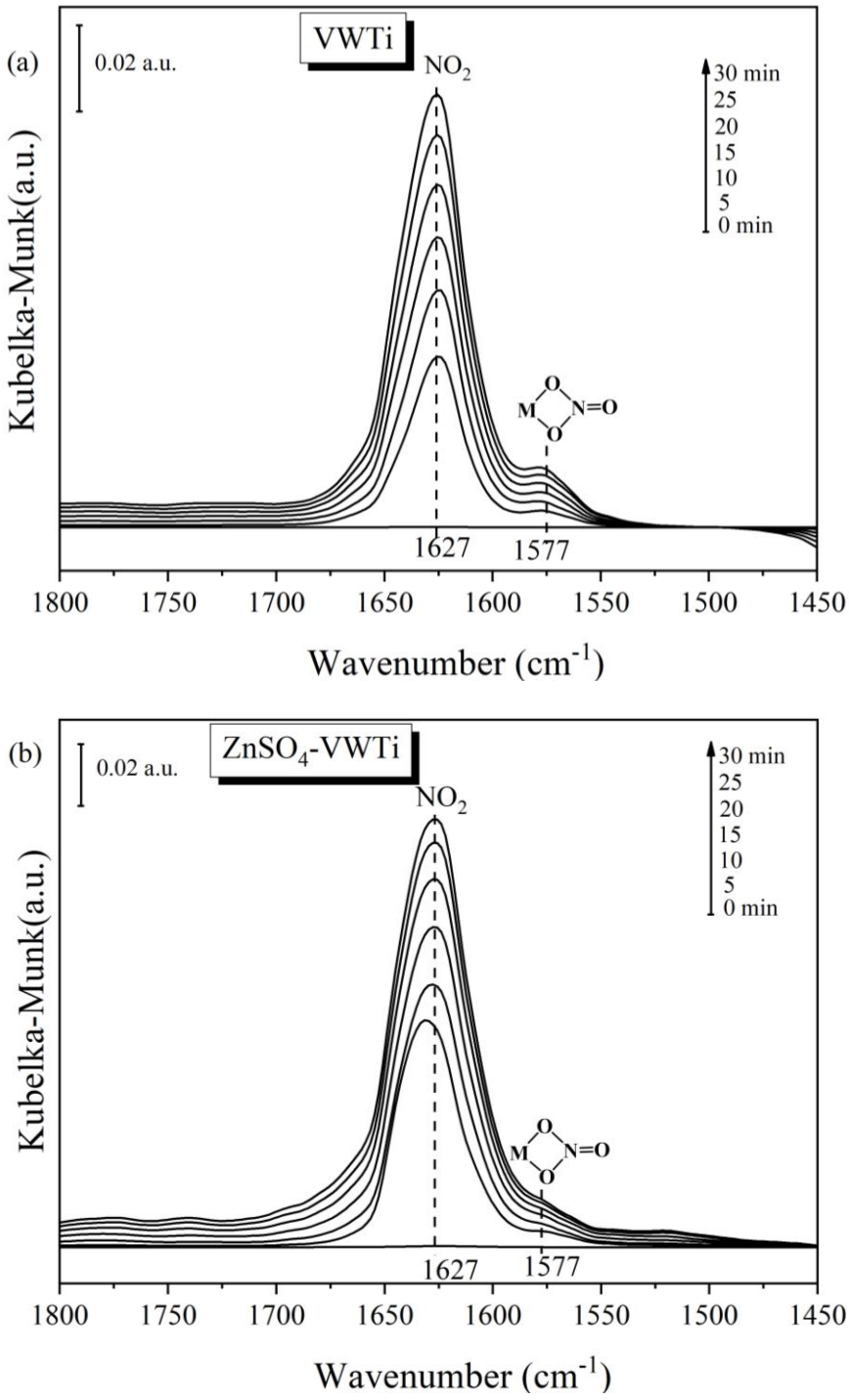
introduction of Zn^{2+} increased the NO_x adsorption sites to form stable nitro species, while SO_4^{2-} would inhibit the formation of the stable nitro species by Zn^{2+}.



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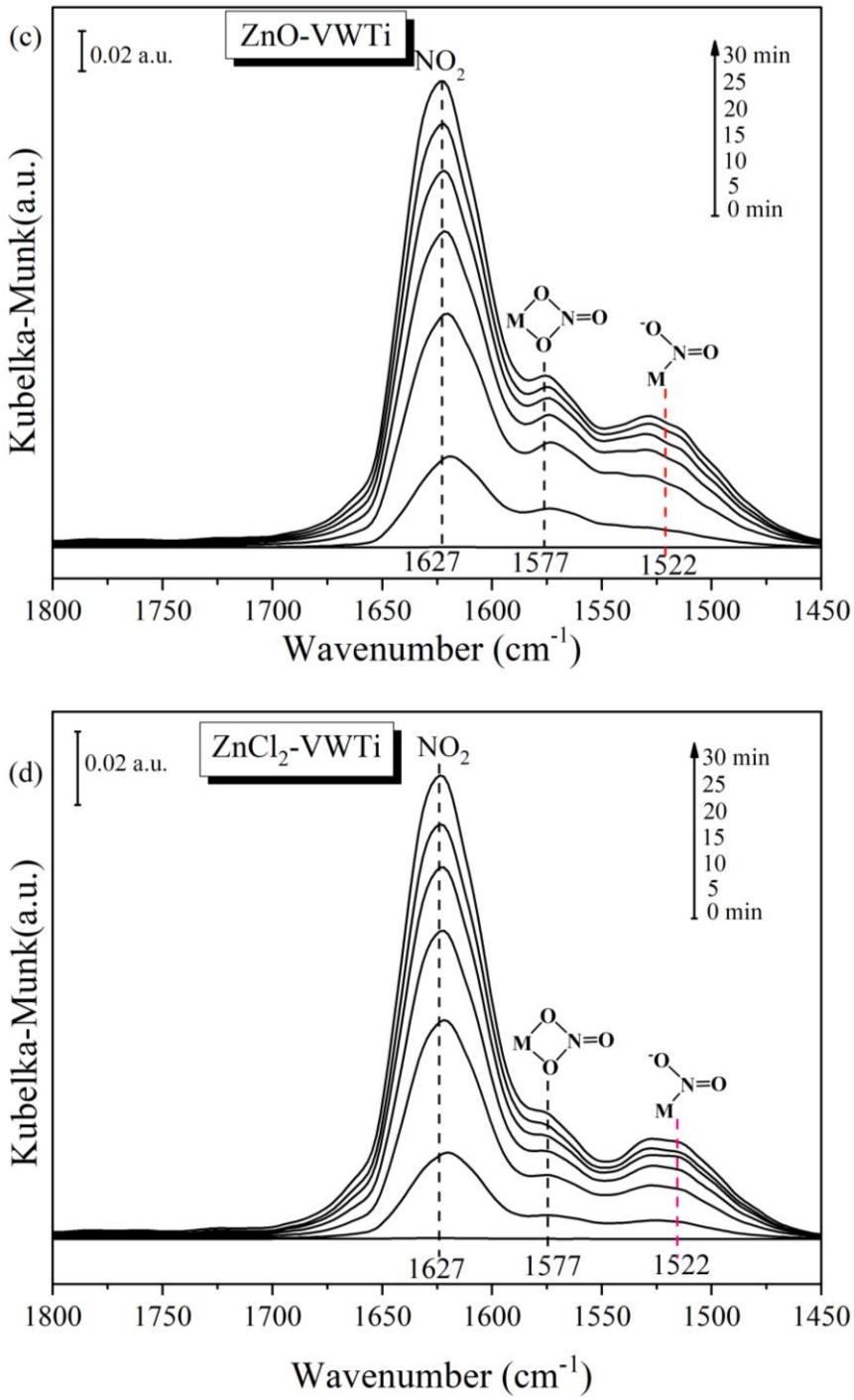

Fig. 8 *In-situ* DRIFTS spectra of $NO+O_2$ adsorption over VWTi and different zinc poisoned catalysts at 50 ^oC.

3.6.3 In-situ DRITFS of $NO+O_2$ reaction with pre-adsorption of NH_3

The DRIFT spectra measured upon $NO+O_2$ interaction at 200 ^oC after NH_3 pre-adsorption are shown in Fig. 9. For comparison, the spectra obtained by $NO+O_2+NH_3$ co-adsorption are reported

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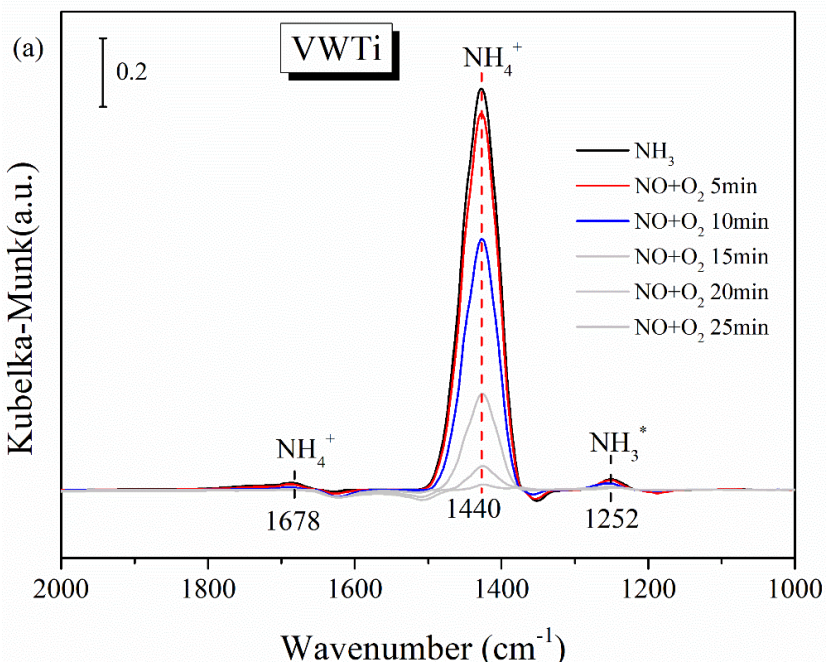
in Figure S6. Apart from some differences in the bands intensity, these can be roughly described as the sum of those obtained dosing on the samples NO/O_2 and NH_3 separately (Figures 4 and 8), with the bands related to NO/O_2 (nitrates and nitro species) appearing first, followed by the growth of the bands related to NH_4^+ and to NH_3 on Lewis sites.

In the step-wise experiment described in this section (Fig. 9), the spectra obtained after introducing NH_3 for 60 min are similar to those reported in Fig. 4 (30 minutes NH_3 exposure) and discussed in Section 3.3, apart from some difference in the bands intensity. When $NO+O_2$ is introduced on VWTi, the band due to NH_4^+ (1440 cm^{-1}) rapidly decreases and adsorbed NO_x species are not observed, at variance with the co-adsorption experiment (Fig. S6). This indicates the reaction between adsorbed NH_4^+ and $NO+O_2$ and suggests an Eley-Rideal mechanism. Interestingly, for the poisoned catalysts, a small increase in the intensity of the NH_4^+ band is observed within 10 min after introducing $NO+O_2$. This could be explained by the transformation of Lewis coordinated NH_3 to NH_4^+ species in the presence of H_2O, which is formed by the reaction of NH_4^+ with $NO+O_2$ [27, 61]. These results suggest that the Brønsted acid sites on VWTi catalyst are more important than Zn^{2+} Lewis acid sites coordinating NH_3, which needs to be converted into NH_4^+ species before reacting with $NO+O_2$.



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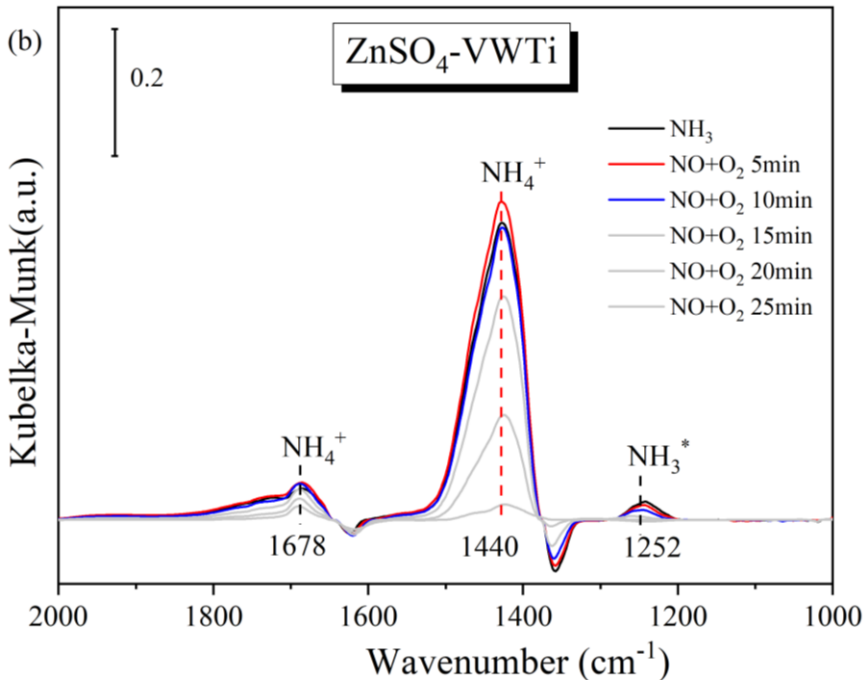

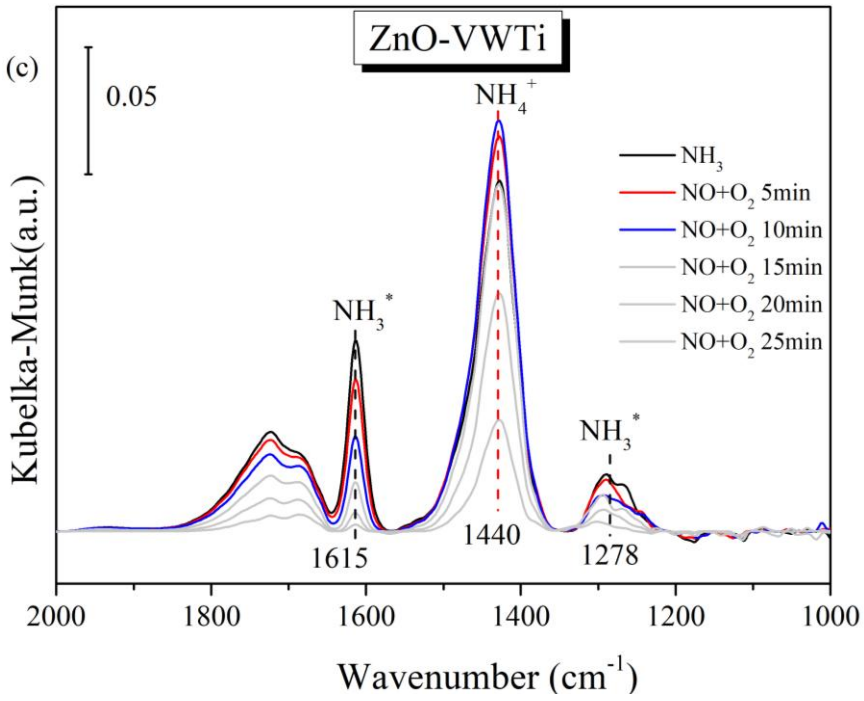

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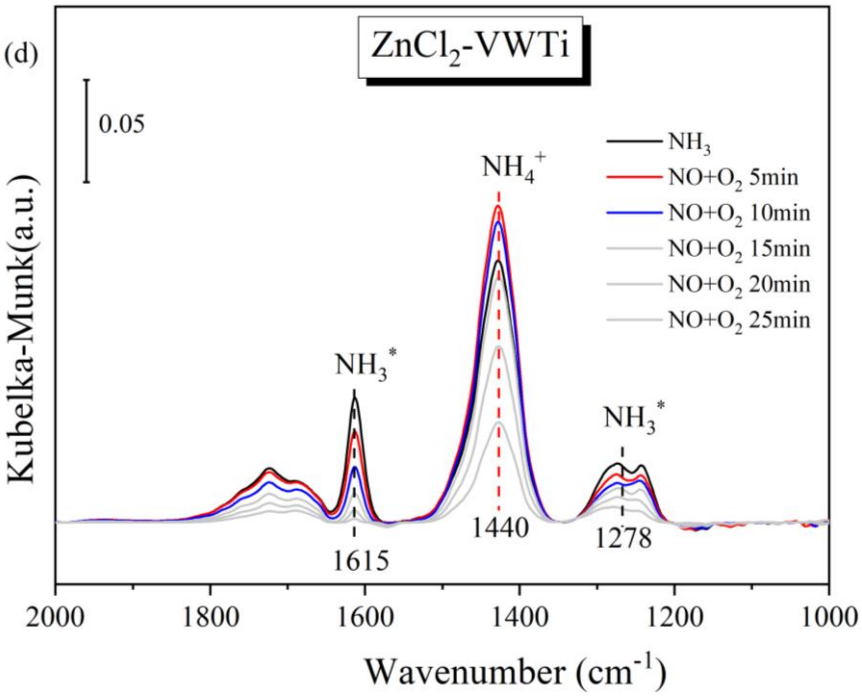

Fig. 9 *In-situ* DRIFTS spectra of $NO+O_2$ adsorption over VWTi and different zinc poisoned catalysts pre-adsorbed NH_3 at 200 °C.

3.7 Deactivation mechanism of different zinc species

According to literature [62], the NH_3-SCR reaction can be explained by a two sites mechanism, involving a V-OH Brønsted sites and a vicinal $O=V^{5+}$ involved in a reversible $V^{5+}\rightleftarrows V^{4+}$ redox cycle. The former would adsorb NH_3 as NH_4^+, while the latter would activate it forming some intermediates which can directly react with gaseous NO and O_2 to generate N_2 and H_2O.

Our work shows that Zn^{2+} can decrease the amount of Brønsted V-OH sites, as testified by the infrared spectra of adsorbed NH_3 and CO (Figures 4, S4 and S5), while increasing the Lewis acidity of the catalysts. This is coherent with the reaction of Zn^{2+} with V-OH to form V-O-Zn, where Zn is coordinatively unsaturated (i.e., has L acid character). Moreover, Zn^{2+} could also react/interact with O=V to form Zn-O-V/Zn··O=V, which could inhibit the activation of NH_3 and influence the $V^{5+}\rightleftarrows V^{4+}$ redox cycle. This is particularly evident on samples ZnO-VWTi and $ZnCl_2$-VWTi, which do not show the typical Raman bands of V=O groups, and show an effect on the reducibility of

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vanadium (H_2-TPR and EPR). These two catalysts show similar features in terms of reducibility, surface acidity and B/L distribution, which can be mainly ascribed to the role of Zn^{2+} as Lewis sites in V-O-Zn and Zn-O-V/Zn··O=V structures. However, the catalytic activity of $ZnCL_2$-VWTi is lower in the whole temperature region than that of ZnO-VWTi (Figure 1), indicating a negative role of the Cl^- anion on reactivity. This sample is characterized by the lowest O_α ratio (estimated by XPS) and by slightly lower B/L ratio with respect to ZnO-VWTi (NH_3 DRIFT, Figure 4). We can thus propose a double role of Cl^- ions. On one hand they could interact with defective surface sites suppressing the formation and mobility of adsorbed oxygen, which could play a role in the formation of reaction intermediates. Moreover, we cannot exclude an exchange with V-OH groups, influencing the activation of adsorbed NH_3 in the catalytic cycle.

On the other hand, the negative effect of Zn^{2+} on the catalytic activity and surface properties of the catalysts is mitigated by the presence of SO_4^{2-} anions. This could be due to the fact that the SO_4^{2-} anions are strongly coordinated to the Zn^{2+} ions, reducing their Lewis activity and reactivity towards V-OH and O=V groups. Moreover, we cannot exclude the possibility that SO_4^{2-} can react with V-OH to form V-O-SO_3OH, with strong Brønsted character. NH_3 adsorbed on V-O-SO_3OH could be activated by O=V active structures, and react directly with NO+O_2 to generate N_2 and H_2O.

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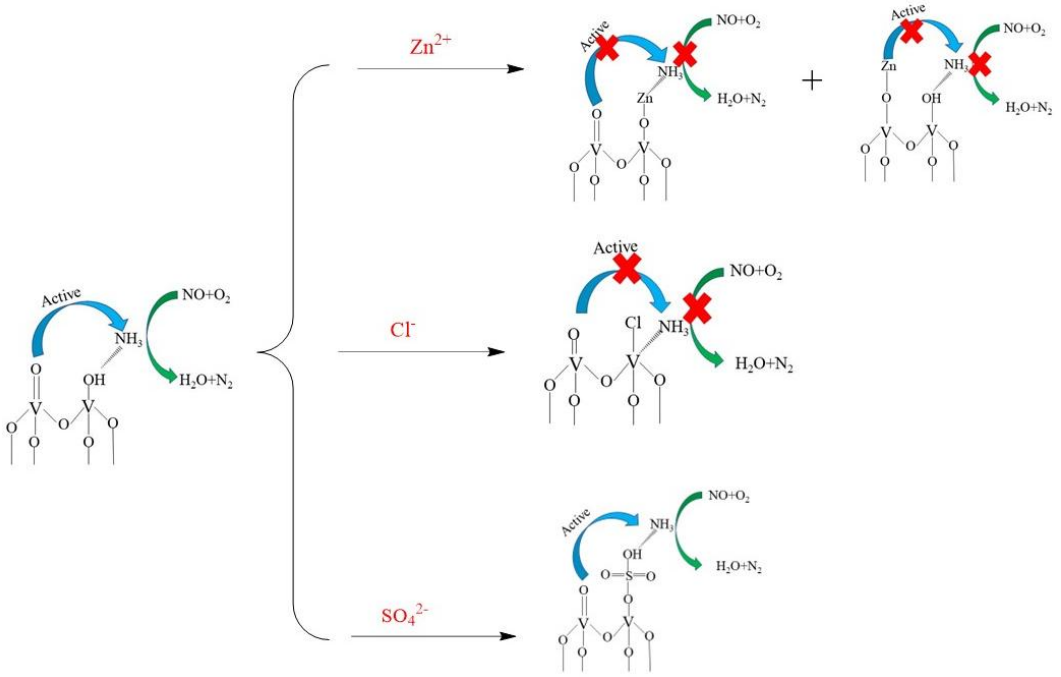

Scheme 1 Possible deactivation mechanism of different zinc compounds on VWTi catalyst during the NH_3-SCR reaction.

4. Conclusions

In this work, the effect of different zinc species ($ZnSO_4$, ZnO and $ZnCl_2$) on V_2O_5-WO_3/TiO_2 catalyst was investigated. It was found that these zinc species would reduce the NH_3-SCR activity, in the order of $ZnCl_2$>ZnO>$ZnSO_4$. A series of characterization results showed that Zn^{2+} would interact with active V-OH group to form V-O-Zn structure. In these structures, Zn^{2+} would be coordinatively unsaturated (i.e., with Lewis acid character and low activity) and prevent the activation of adsorbed NH_3 by V-OH groups, blocking its reaction with $NO+O_2$. However, the presence of SO_4^{2-} would limit this effect: on one side this could be simply due to its strong interaction with Zn^{2+} ions, thus limiting the interaction of the cation with surface active sites. The important increase in Brønsted sites in this catalyst points to the formation of acidic V-O-SO_3OH groups, which could be able to activate adsorbed NH_3 to react with $NO+O_2$ and generate N_2 and H_2O products. Additionally, Zn^{2+} also affected the electronic properties of O=V groups, negatively

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influencing the $V^{5+} \rightleftarrows V^{4+}$ active redox cycle. The poisoning effect was worsened by the presence of Cl^- ions, which could suppress the formation and mobility of the surface adsorbed oxygen and further affect the reactivity of V-OH groups, possibly by forming V-Cl structure.

Acknowledgments

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