

Thermal Decomposition of Metal Nitrates in Air and Hydrogen Environments

Shanmugam Yuvaraj,[†] Lin Fan-Yuan,[†] Chang Tsong-Huei,[‡] and Yeh Chuin-Tih*,[†]

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan, R.O.C., and
Department of Chemical Engineering, Minghsin University of Science and Technology,
Hsinchu, Taiwan, R.O.C.

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The decomposition of metal nitrates in air has been systematically studied by thermogravimetry. Observed temperatures of decomposition (T_d) have been inversely correlated to the charge densities (CD) of the metal cations. Due to a back-donation of electronic cloud from the nitrate to an unfilled d-orbital of transition and noble metals, their nitrates generally exhibited lower T_d s (<700 K) than those of the base metals (>850 K). The thermal stability/reducibility of metal nitrates in an hydrogen atmosphere has also been studied by temperature-programmed reduction (TPR). Observed reduction temperatures (T_r) for nitrates of the base metals and the noble metals are lower than their T_d , i.e., $T_r < T_d$. The lowering of T_r might be attributed to a spillover of hydrogen to a nitrate moiety through heterolytic (ionic) and homolytic (atomic) dissociation of hydrogen on the respective base and noble metals. The stoichiometry of hydrogen consumption, quantitatively measured from TPR, varied with the group of metal cations. According to the stoichiometry, the end product in the TPR reduction was NH_3 ($\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-} \sim 4.4$) and N_2 ($\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-} \sim 2.4$) for nitrates of the noble and base metals, respectively. The T_r s for nitrates of the transition metals are often ~ 20 K higher than their T_d s, and the ratio $\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-}$ varies widely between 0.7 and 3.2. Their reduction may be triggered by thermal decomposition.

1. Introduction

Transition and noble metals are widely used as active components in industrial metal catalysts.¹ In the preparation of metal-dispersed catalysts, metal salts are generally employed as precursors and may be dispersed on porous supports. Metal nitrates, because of their high solubility in water and their low-contamination of the final catalysts, are generally preferred precursors over other inorganic salts such as sulfates and halides. The dispersed metal nitrates are converted to metal oxides and then activated to metal through sequential pretreatments of calcination and reduction.¹ In practice, operational temperatures for calcination (T_c) and reduction (T_r) pretreatments have been optimized by experience to prevent detrimental effects—fouling of supports, sublimation of noble metal oxides, and sintering of dispersed-metal.

The calcination pretreatment is to eliminate extraneous material, such as volatile components in the precursor (e.g., NO_x in nitrates) and binders in supports. The decompositions of several nitrates have been studied,^{2–10} but most of them were studied under either N_2 or vacuum conditions, primarily to focus on academic interests of kinetics and thermodynamics. Nitrates of catalytically active metals are thermally unstable^{1,11} and decompose at $T_d < 700$ K (see Table 1 for transition metal nitrates) into metal oxides, NO_x (NO , NO_2 , etc.), and O_2 . Hence, $T_c \leq 750$ K is severe enough to get nitrate-free metal catalysts and, in practice, a $T_c \leq 750$ K is generally employed. On the other hand, sulfate and halide ions usually remain as contaminants in catalysts upon the same calcination pretreatment.^{12–14}

The reduction pretreatment in catalyst preparation further activates the decomposed metal oxide to metal through



The required activation temperature, T_a , varies with the nature of the metal cations, their oxidation states, and the location of their oxides in the support. A high T_a is as detrimental to a final catalyst as a high T_c and, hence, T_a optimization is also vital for reduction pretreatment. In this regard, the temperature-programmed reduction (TPR) technique, can be employed to find the minimum T_a temperature for metal catalysts.^{13–18} Values of T_r for metal nitrates have been sought in the literature but, surprisingly, could not be found.

Solid metal catalysts and semiconductor oxides are, in general, prepared from the thermal decomposition of nitrates of various transition and base metals. The current article is focused on the temperatures required for the decomposition (T_d) and the reduction (T_r) of metal nitrates. Thermogravimetry was employed to find T_d values in air while T_r values in hydrogen were obtained from TPR experiments. The experimental values of T_d and T_r are discussed in terms of a theoretical approach and a correlation between T_d and T_r values is also drawn.

2. Experimental Section

In this work, the thermal stabilities of finely powdered ACS grade metal nitrates (Merck and Riedel de Haën) were studied under air and hydrogen environments. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded using a Seiko TG/DTA 300 thermal analyzer under flowing air at a rate of 100 mL min^{-1} . About 1×10^{-2} g of sample was placed in a sample pan and heated gradually from 298 to 1200 K at 10 K min^{-1} . For temperature-programmed reduction (TPR) studies, about 5×10^{-3} g of sample was inserted in a U-shaped TPR cell and the sample was reduced in a flow of 10% H_2 in N_2 by gradually raising the system temperature to 1000 K at 5 K min^{-1} .

* Author to whom correspondence should be addressed. Fax: 886-3-5711082 and 886-3-5726047. E-mail: ctyeh@mx.nthu.edu.tw.

[†] National Tsing Hua University.

[‡] Minghsin University of Science and Technology.

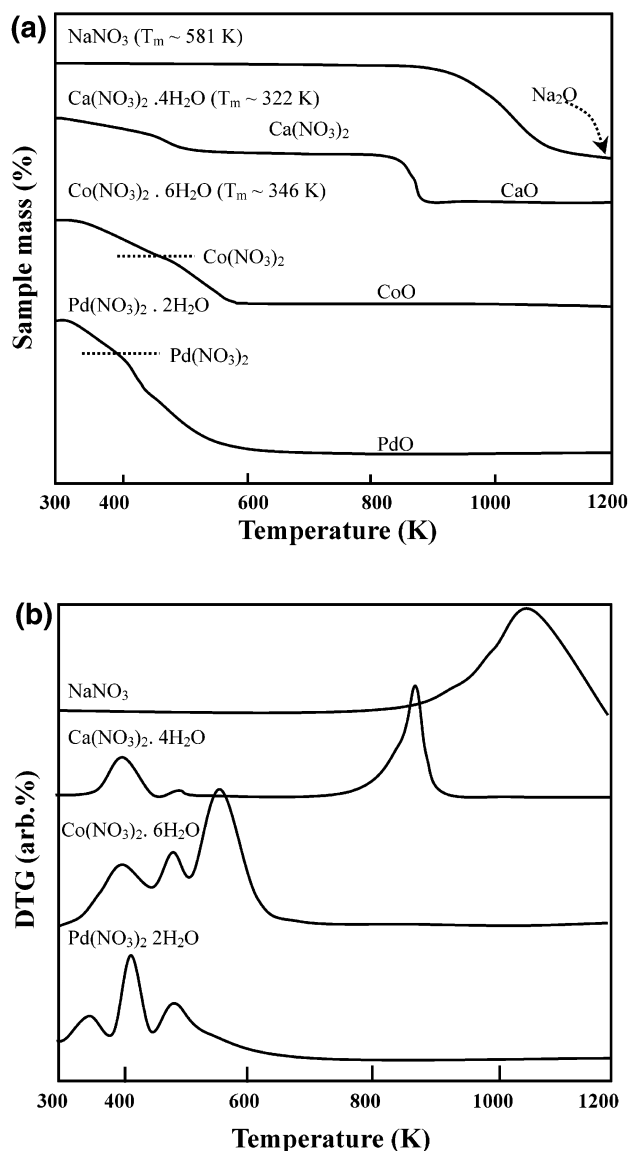
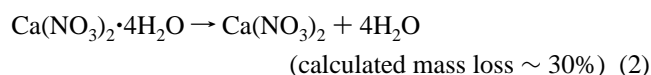


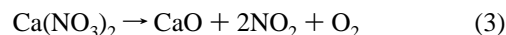
Figure 1. (a) Thermogravimetric (TG) curves are recorded from 296 to 1200 K (heating rate: 10 K min⁻¹) under air (flow rate: 100 mL min⁻¹) atmosphere: (top to bottom) NaNO₃, Ca(NO₃)₂·4H₂O, Co(NO₃)₂·6H₂O, and Pd(NO₃)₂·2H₂O. (b) Differential thermogravimetric (DTG) curves of TG spectra shown in Figure 1a: (top to bottom) NaNO₃, Ca(NO₃)₂·4H₂O, Co(NO₃)₂·6H₂O, and Pd(NO₃)₂·2H₂O.

3. Results and Discussion

3.1. Decomposition of Metal Nitrates in Air. Figure 1a presents the thermogravimetric (TG) profiles for four metal nitrates recorded under air atmosphere and their corresponding differential thermogravimetric curves (DTG) are presented in Figure 1b. Among them, NaNO₃ is an anhydrous sample while the other three [Ca(NO₃)₂·4H₂O, Pd(NO₃)₂·2H₂O and Co(NO₃)₂·6H₂O] are hydrates. NaNO₃ decomposed (*T_d* ~ 1020 K) in a single stage in the molten state (*T_m* ~ 582 K). The base metal hydrate, Ca(NO₃)₂·4H₂O, showed two successive mass losses after melting (*T_m* ~ 322 K): a preliminary dehydration (~ 500 K, 29% mass loss),



and then decomposition of the anhydrous nitrate (~ 875 K, 46% mass loss):

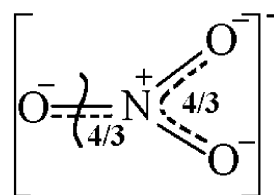


Nitrates of the transition metals, i.e., Pd(NO₃)₂·2H₂O and Co(NO₃)₂·6H₂O lose their water of hydration below 450 K and successively decomposed (*T_d* ~ 450 and 515 K, respectively) in multiple stages. Possibly, the decomposition might occur through an intermediate nitrite and/or through oxide species with variable valence for metal ions. From Figure 1, it is evident that the decomposition temperatures (*T_d*) of anhydrous metal nitrates vary with the inherent nature of the metal ions and showed a trend: Pd(NO₃)₂ < Co(NO₃)₂ < Ca(NO₃)₂ < NaNO₃. The wide range (450–1020 K) observed for *T_d*s under air set off a further investigation on *T_d* values for commonly used metal nitrates.

In general, in case of the base metal nitrates, the preliminary dehydration under air did not have any noticeable influence on the resultant anhydrous nitrate except magnesium nitrate, (Mg(NO₃)₂·6H₂O), whose decomposition might be influenced by the hydrolysis of the salt. This is in agreement with the literature on the decomposition of the base metal nitrates under other environments such as nitrogen and vacuum conditions.¹⁰ In the case of the nitrates of the transition and noble metals, the dehydration (<450 K) is subsequently followed by the decomposition (~ 450–550 K) of their anhydrous nitrates. The successive stage of decomposition might be influenced by the preliminary dehydration and led the decomposition to occur in multiple stages.

Tables 1 and 2 summarize the experimental *T_d*s observed in this study for nitrates of transition and base metals, respectively. *T_d* values are generally <700 K for transition metal nitrates (Table 1). Therefore, calcination at this temperature is severe enough to cause thermal decomposition of these nitrates. However, the *T_d*s of base metal nitrates (Table 2) are generally well above the conventional calcination temperature, *T_c* ~ 750 K. Hence, nitrates of base metals should remain intact with catalysts during the calcination pretreatment.

Thermal decomposition of a nitrate may be initiated through dissociation of the N–O bond.^{6,10,11} As a consequence, *T_d* should increase with the strength of the N–O bond and its bond order. Molecular orbital theory predicts that the nitrate anion, with 24 valence electrons, will have a bond order of 4/3.^{20, 21} The bond



order can be decreased primarily by two factors: (1) through polarization of the electronic cloud of the nitrate ion by the high charge density of the metal ion, and (2) through the back-donation of the nitrate electron cloud to a vacant d-orbital of the metal ion.

The polarization is induced by the charge density (CD) of a metal ion. The CD of a metal ion, by definition, is the ratio of its effective charge to its volume. Theoretically, a metal ion may be presumed to be a sphere and its CD is given by $e/(4/3)\pi r^3$, where e and r (taken from ref 21) are the charge and the radius (in nm) of a metal ion, respectively. The theoretically calculated CD is plotted against experimental *T_d* in Figure 2 for nitrates of transition and main group metals.

Figure 2 shows that the *T_d*s of the base metal nitrates, in general, are inversely related to the calculated CD values of the metal ions. In accordance with Fajan's rule,²¹ metal ions with high CDs, such as Al³⁺, Ga³⁺, and Mg²⁺, can effectively

TABLE 1: A Comparison between the Literature-Reported (in parentheses) and the Experimental Decomposition Temperature (T_d) and Reduction Temperature (T_r) (in hydrogen) Found in This Study for the Nitrates of Transition Metals

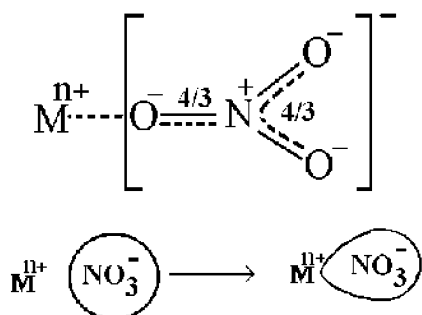
sample	10^3 charge density (e/nm^3)	T_d (K)	T_r (K)	$(N_{H_2}/N_{NO_3^-})^b$
Mn(NO ₃) ₂	1.18	(473) ^a 480 ± 20	510 ± 15	
Fe(NO ₃) ₃	2.18	440 ± 20	465 ± 20	0.7
Co(NO ₃) ₂	1.28	(543) ^a 515 ± 30	515 ± 20	3.4
Ni(NO ₃) ₂	0.83	(573) ^a 580 ± 25	585 ± 15	3.1
Cu(NO ₃) ₂	1.33	(563) ^a 520 ± 30	550 ± 15	3.2
Zn(NO ₃) ₂	2.21	(610) ^a 590 ± 50	630 ± 25	2.9
ZrO(NO ₃) ₂	1.73	465 ± 50	475 ± 20	
Ce(NO ₃) ₃	0.66	570 ± 30	585 ± 20	
Gd(NO ₃) ₃	0.57	640 ± 30	665 ± 20	
Pd(NO ₃) ₂	1.01	450 ± 30	375 ± 20	4.2
Pt(NH ₃) ₄ (NO ₃) ₂	1.13	510 ± 15	450 ± 20	4.4
Rh(NO ₃) ₃	1.37		470 ± 10	
AgNO ₃	0.15	723 ± 25	600 ± 10	4.1

^a Ref 10. ^b Moles of hydrogen consumed per mole of nitrate.**TABLE 2: A Comparison between the Literature (in parentheses) and the Observed Decomposition Temperature (T_d) and the Reduction Temperature (T_r) (in hydrogen) for Nitrates of the Base Metals**

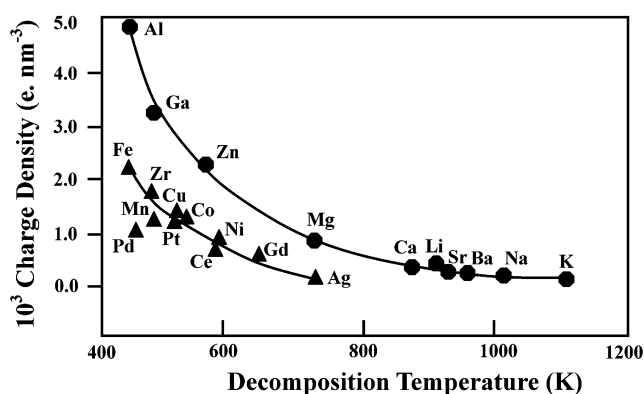
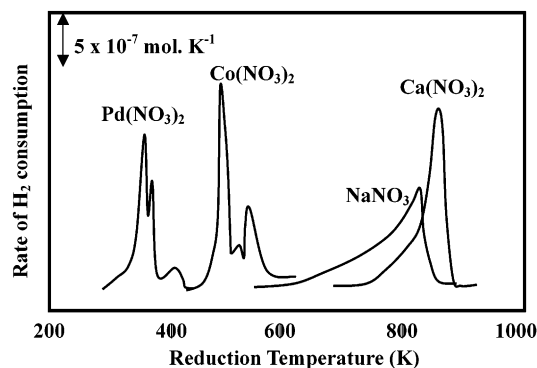
sample	10^3 charge density (e/nm^3)	T_d (K)	T_r (K)	$(N_{H_2}/N_{NO_3^-})^c$
LiNO ₃	0.33	913 ± 100	790 ± 50	4.1
NaNO ₃	0.15	(1023) ^a 1013 ± 120	830 ± 60	2.4
KNO ₃	0.07	(1123) ^a 1113 ± 150	890 ± 40	2.4
Mg(NO ₃) ₂	0.75	(723) ^b 723 ± 50	735 ± 25	
Ca(NO ₃) ₂	0.32	(848) ^b 875 ± 30	855 ± 25	2.6
Sr(NO ₃) ₂	0.21	(908) ^b 925 ± 30	875 ± 35	2.4
Ba(NO ₃) ₂	0.14	(948) ^b 960 ± 30	950 ± 35	2.4
Al(NO ₃) ₃	4.81	440 ± 25	465 ± 30	
Ga(NO ₃) ₃	3.15	475 ± 25	480 ± 25	

^a Ref 19. ^b Ref 10. ^c Moles of hydrogen consumed per mole of nitrate.

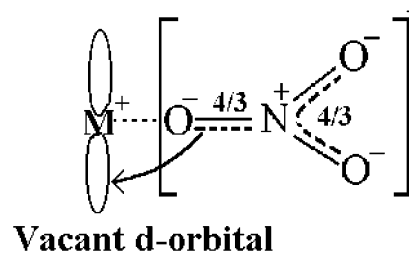
polarize the nitrate ions. The polarization of these metal ions establishes a sort of covalence between M and O and, as a result, these metal ions tend to share their valence electron cloud with the nitrate ion. Conceivably, the bond order of N–O in the nitrate ion could decrease from 4/3 and lead to decomposition at a low T_d .



In contrast, K^+ , Na^+ , and Ba^{2+} cations have low CD values and are ineffective in polarizing the nitrate ion. In these metal nitrates, the bonds between M^{n+} and NO_3^- ions are quite strong and remain ionic. Further, the oxides of these metals are strongly basic in nature and tend to react with acidic gases such as NO_x and are generally utilized to scrub acidic gases in industry. This tendency may help to keep the nitrate moiety intact at low temperature until the thermal force overcomes the ionic force and leads to decomposition.

**Figure 2.** Variation of nitrate decomposition temperature (T_d) with metal charge density plotted for base metals (top curve) and transition metals (bottom curve).**Figure 3.** Temperature-programmed reduction profiles are obtained in a flow of 10% H_2 in N_2 with a flow rate of 30 mL min^{-1} by gradually raising the system temperature from ambient to 1000 K at a rate of 5 K min^{-1} : (left to right) $Pd(NO_3)_2$, $Co(NO_3)_2$, $NaNO_3$, and $Ca(NO_3)_2$.

In a similar manner, the T_d s of transition and inner-transition metal nitrates showed an inverse relation to their CDs in Figure 2. However, the nitrates of transition metals generally exhibited lower T_d s than those of base metal nitrates with similar CD values. The observed difference in T_d s is attributed to back-donation^{20,21} of the π -electronic cloud in nitrate ions to the unfilled d-orbitals in transition metals. The so-called back-donation



decreases the bond order of the N–O bond from 4/3 and consequently, decreases the T_d s of the transition metal nitrates.

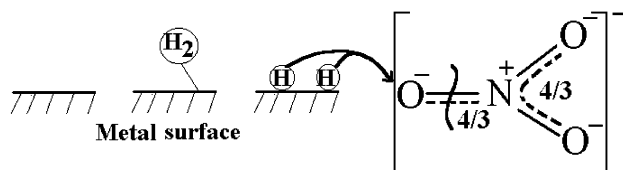
3.2. Reduction of Metal Nitrates. Figure 3 illustrates TPR traces of four metal nitrates, whose TG profiles are shown in Figure 1. These nitrates are reduced in TPR between 375 and 855 K. As seen, the hydrogen reduction of transition metal nitrates $Pd(NO_3)_2$ and $Co(NO_3)_2$ proceeds in multiple stages through sequential reduction of different oxide species formed during decomposition. Nitrates of the base metals, $NaNO_3$ and $Ca(NO_3)_2$, showed a single-step reduction process. The experimental reduction temperatures (T_r s) of the common metal nitrates are given in Tables 1 and 2. For transition metal nitrates in Table 1, the experimental T_r values are slightly higher (~ 25

K) than the observed T_d values. This suggests that the hydrogen reduction of these metal nitrates might be triggered by their thermal decomposition. Hence, the hydrogen may act on the decomposed products (NO_x , MO). However, $T_r < T_d$ is observed for the nitrates of the alkali, alkaline, and noble metals.

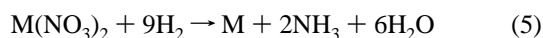
It is known that the noble metal ions (Pt, Pd, and Rh) in their metal oxides are reduced at temperatures less than 373 K.^{13–18} Hence, it is presumed that the noble metal ions in their nitrates can be reduced at low temperatures,



and then the reduced metal dissociatively adsorbs hydrogen.²² The adsorbed hydrogen subsequently reduces nitrate ion to ammonia through the spillover mechanism

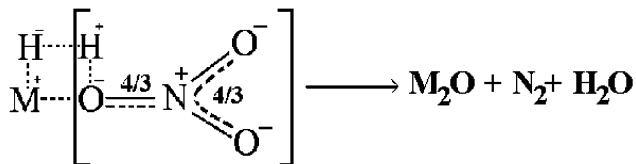


and the overall reaction is given by

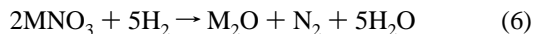


The calculated hydrogen consumption for the above reaction agrees well with the observed TPR hydrogen consumption ($\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-} \sim 4.4$).

For the alkali and alkaline metal nitrates, an ionic hydrogen adsorption mechanism (heterolytically dissociated hydrogen), prior to thermal decomposition of the nitrate, may occur at the surface between M and O as shown below:



The T_r s shown in column 4 of Table 2 indicate that the ionic adsorption of hydrogen mechanism might apply to the nitrates of the alkali and alkaline metals that have low CD ($< 350 \text{ e nm}^{-3}$) values. As pointed out in the previous section, metal ions with a low CD value are bound with nitrate ions mainly through strong ionic forces. The ionic nature probably induces a charge separation in an approaching hydrogen molecule and, consequently, the M–O bond dissociatively adsorbs the molecular hydrogen. Tanabe et al.^{23,24} and Hightower et al.²⁵ also proposed an ionic adsorption of hydrogen mechanism over MgO and ThO_2 . The amount of hydrogen consumed ($\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-} \sim 2.4$) in TPR for the metal nitrates listed in column 4 of Table 2 suggested the following reduction reaction:



However, the high ratio ($\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-} \sim 4.1$) found with lithium nitrate indicates that the reduction product may be NH_3 rather than N_2 . The ratio $\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-}$ for transition metal nitrates is found to be between 2.5 (leading to N_2) and 4.5 (leading to NH_3). An intermediate $\text{N}_{\text{H}_2}/\text{N}_{\text{NO}_3^-}$ ratio might result from the partial reduction of nitrates to lower valent nitrogen oxides (NO_x) or

the reduction might take place on the decomposition products (NO_x) from the nitrates.

4. Conclusions

The thermal decomposition of metal nitrates has been studied in atmospheres of air and hydrogen by thermogravimetry and temperature-programmed reduction. The following salient features have been noted:

1. The experimental decomposition temperatures (T_d) of metal nitrates are inversely correlated with the charge density (CD) of the metal cations. However, the T_d s for the nitrates of the transition metals were generally decreased by a back-donation of electrons from the nitrate ions to an unfilled d-orbital in the metal cations.

2. Most of the metal nitrates (with the exception of the nitrates of the alkali and alkaline earth metals) decompose into metal oxides during calcination at $T_c \sim 750 \text{ K}$.

3. Reduction of the transition metal nitrates is triggered by an initial decomposition of the nitrate. However, the reduction of the nitrates of the noble, alkali, and alkaline metals ($T_r < T_d$) is significantly promoted by a spillover of adsorbed hydrogen.

4. The extent of reduction of nitrates varies with the group of metal cations. The complete reduction (oxidation state of +5 for nitrogen in nitrate goes to –3 in NH_3) of the nitrates of the noble metals are observed, but nitrates of base metals are reduced to zerovalent nitrogen. In the case of the transition metals, the nitrates may be partially reduced to lower valent nitrogen oxides (NO_x).

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