

Article

“PdO vs. PtO”—The Influence of PGM Oxide Promotion of Co_3O_4 Spinel on Direct NO Decomposition Activity

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Abstract: Direct decomposition of NO into N_2 and O_2 ($2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$) is recognized as the “ideal” reaction for NO_x removal because it needs no reductant. It was reported that the spinel Co_3O_4 is one of the most active single-element oxide catalysts for NO decomposition at higher reaction temperatures, however, activity remains low below 650 °C. The present study aims to investigate new promoters for Co_3O_4 , specifically PdO vs. PtO. Interestingly, the PdO promoter effect on Co_3O_4 was much greater than the PtO effect, yielding a 4 times higher activity for direct NO decomposition at 650 °C. Also, Co_3O_4 catalysts with the PdO promoter exhibit higher selectivity to N_2 compared to PtO/ Co_3O_4 catalysts. Several characterization measurements, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), H_2 -temperature programmed reduction (H_2 -TPR), and *in situ* FT-IR, were performed to understand the effect of PdO vs. PtO on the properties of Co_3O_4 . Structural and surface analysis measurements show that impregnation of PdO on Co_3O_4 leads to a greater ease of reduction of the catalysts and an increased thermal stability of surface adsorbed NO_x species, which contribute to promotion of direct NO decomposition activity. In contrast, rather than remaining solely as a surface species, PtO enters the Co_3O_4 structure, and it promotes neither redox properties nor NO adsorption properties of Co_3O_4 , resulting in a diminished promotional effect compared to PdO.

Keywords: direct NO decomposition; PGM oxide promotion; PdO vs. PtO; in-situ FT-IR; NO adsorption properties; redox properties

1. Introduction

Nitrogen oxides (NO_x) formed by combustion from fixed and mobile sources cause severe detrimental environmental problems, such as acid rain and photochemical smog [1–3]. Effectively controlling the emission of NO_x is the topic of much research and has led to the introduction of many new catalyst technologies, such as three-way catalysts (TWC), NO_x storage-reduction (NSR), and selective catalytic reduction (SCR) for NO_x gas removal from mobile sources, and SCR and selective non-catalytic reduction (SNCR) for NO_x gas removal from fixed sources [4–6]. Among various deNO_x strategies, direct decomposition of NO ($\text{NO} \rightarrow 1/2\text{O}_2 + 1/2\text{N}_2$) has been considered to be the most desirable method because this reaction is thermodynamically favorable at low temperatures and does not need any reductants, such as NH_3 , H_2 , CO, or hydrocarbons. However, kinetic studies have indicated that the reaction needs to overcome a large activation energy ($\sim 335 \text{ kJ mol}^{-1}$) barrier [4–15]. Accordingly, there is an apparent need for a suitable catalyst to decompose NO_x at a given temperature, and therefore, significant research has been undertaken towards development of active and stable catalysts.

Since the pioneering work of Jellinek on the catalytic decomposition of NO in 1906, much research has been reported on NO direct decomposition over several materials, including perovskites, rare earth

oxides, and Cu-zeolites [2–7]. Numerous metal oxides have also been examined as candidates for NO decomposition catalysts [16] and Co_3O_4 is often recognized as a significant component in many active catalysts at higher reaction temperatures [17–21]. However, Haneda et al. recently reported that NO decomposition takes place slowly, if at all, over pure Co_3O_4 at temperatures below 650 °C [18]. They reported that the presence of small amounts of alkali metals were essential to activate NO decomposition over Co_3O_4 oxide by enhancing NO adsorption [18–20]. This interesting effect of alkali metals, particularly Na, was also reported by Kung et al. [21], but dependence on alkali metals is not feasible for practical applications due to their volatile nature at temperatures above 600 °C.

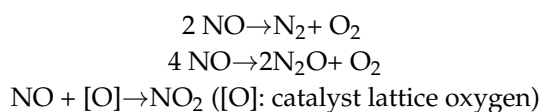
Metal oxide supported platinum group metals (PGM metals) were also one of the earliest types of NO decomposition catalysts studied, and the results have been widely reported; mainly Au, Pt, Pd, and Ir at temperatures higher than 700 °C [22,23]. Suzuki et al. [24] synthesized a porous $\text{CaZrO}_3/\text{MgO}/\text{Pt}$ composite and found that this catalyst could obtain a NO conversion rate of about 52% at 900 °C in the absence of O_2 . Haneda et al. [25] found that the addition of Pt improved the direct NO decomposition performance of rare earth oxides. They [26,27] also compared the activity of $[\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$, $\text{Pd}(\text{CH}_3\text{COO})_2$, and $(\text{NH}_4)_2[\text{PdCl}_4]$ as palladium precursors for NO decomposition in a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst at 700 °C, and the activity was found to decrease in the order of $\text{Pd}(\text{NO}_3)_2 > [\text{Pd}(\text{NH}_3)_4](\text{NO}_3)_2 > \text{Pd}(\text{CH}_3\text{COO})_2 \gg (\text{NH}_4)_2[\text{PdCl}_4]$. Almusaiteer et al. [28] reported that compared to $\text{Pd}/\text{Al}_2\text{O}_3$, the Pd/C (activated carbon) catalyst was found to be more beneficial for O_2 desorption, but both have similar activity. Oliveira et al. [29] investigated the catalytic performance of palladium and copper catalysts loaded in mordenite (MOR) and found that these catalysts were more active for NO decomposition than alumina supported catalysts. However, the reports on supported PtO catalysts for direct NO decomposition at temperatures below 700 °C are very limited in the literature. Similarly, metallic Pd catalysts always deactivate over time due to oxidation of Pd metal to PdO at temperatures below 650 °C [30].

To the best of our knowledge, Co_3O_4 supported PGM catalysts have never been explored for direct NO decomposition, likely due to the inactivity of the individual components at lower temperatures. However, the need for enhanced NO adsorption on Co_3O_4 suggests that the addition of PGM promotion can lead to increased low temperature activity. Hence, the present study aims to investigate the promotional effect of PdO vs. PtO on the Co_3O_4 for direct NO decomposition. The activity measurements show that the optimum PdO/ Co_3O_4 catalyst exhibits 4 times higher activity than PtO/ Co_3O_4 catalysts. Several characterization techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), H_2 -Temperature programmed reduction (H_2 -TPR), and *in situ* FT-IR are employed to understand the influence of PdO and PtO on the structural and surface properties of Co_3O_4 .

2. Results and Discussion

2.1. Direct NO Decomposition Activity Measurements

To qualify as direct NO decomposition, the catalyst must decompose NO into just two products: N_2 and O_2 . The possibility for unwanted N_2O and NO_2 formation as side products cannot be neglected during the analysis of this reaction. Therefore, high NO conversion is desired, but not sufficient; it is also very important to maximize selectivity towards N_2 rather than N_2O or NO_2 . Considering all possible products, the reaction can be written as:



The selectivity to N_2 can be defined as:

$$\text{N}_2 \text{ selectivity (\%)} = 2 \times [\text{N}_2] / (2 \times [\text{N}_2] + 2[\text{N}_2\text{O}] + [\text{NO}_2])$$

Also, when NO dissociates on the catalyst surface, it is possible for N₂ production to occur, but without simultaneous release of the stoichiometric amount of the O₂ product. This situation can occur quite frequently and is the topic of a previous study from some of us [30]. Rather than desorb as the O₂ product, oxygen atoms either remain strongly adsorbed on the surface or chemically react with catalyst material, oxidizing both surface and bulk, and changing the catalyst composition. In either case, the catalyst deactivates over time. Hence, it is very important to confirm that the catalyst releases both N₂ and O₂ as products.

Direct NO decomposition measurements were performed over the pure spinel oxide Co₃O₄ and over the PdO- and PtO-promoted Co₃O₄ catalysts, denoted PdO/Co₃O₄ and PtO/Co₃O₄, respectively. Activity was measured for 2 h at 400, 450, 550, and 650 °C. The direct NO decomposition activity to N₂ of PdO/Co₃O₄ and PtO/Co₃O₄ with varying PGM loading is presented in Figure 1 as a function of temperature and compared to the pure Co₃O₄ spinel. All numeric values of NO conversion and N₂, N₂O, NO₂ ppm product concentrations of the Co₃O₄, PdO/Co₃O₄, and PtO/Co₃O₄ catalysts at various reaction temperatures are presented in Tables S1 and S2. The raw NO conversion profiles (NO converted to all the products) of Co₃O₄, 3PdO/Co₃O₄, and 4 PtO/Co₃O₄ during the steady state direct NO decomposition obtained from FT-IR detector in the temperature region 400 to 650 °C are presented in Figure S1. High values for NO conversion at lower temperatures may seem counterintuitive, however, most of the NO conversion at low temperature is simply due to thermodynamically favorable NO oxidation to NO₂. For example, as shown in Table S1, the NO conversion values of Co₃O₄, 3 PdO/Co₃O₄, and 3 PtO/Co₃O₄ are 3.15, 2.92, and 7.66, respectively, giving the impression that 3 PtO/Co₃O₄ is the most active catalyst at 400 °C. However, for 3 PtO/Co₃O₄, the NO conversion specifically to N₂ is lower than that of 3 PdO/Co₃O₄ because most of the NO conversion is due to NO oxidation. Hence, for NO decomposition to N₂, it is more instructive to consider NO converted into N₂ rather than total NO conversion. The activity values were calculated in this manner and are presented in Figure 1 in units of micromoles of NO converted to N₂ per gram per second.

NO and Ar partial pressure values obtained by mass spectrometry (MS) during the steady state measurements are presented in Figure S2 and compared with data obtained in the absence of the catalyst, which serves as a baseline. Inert Ar gas was introduced as a tracer to monitor for potential systematic variation in signal intensity during the experiment. As shown in Figure S2, no change in Ar signal intensity was observed during the experiment, however, the intensities of NO signal changed based on catalyst identity and reaction temperature. These measurements confirm the change in the NO signal is due to catalytic conversion of NO and not due to artifacts. Also, the MS signal for NO ($m/z = 30$) tracks with the conversion reported by the FT-IR measurements (Figure S1). Figures S3–S5 present the MS partial pressure values of the N₂, N₂O, and NO₂ products, respectively, during direct NO decomposition and are also compared to the MS partial pressures obtained in the absence of the catalyst. As shown in Figure S3, the N₂ and O₂ signal intensities are higher compared to the background signals, which confirms the simultaneous release of N₂ and O₂ as expected for NO decomposition. Furthermore, the MS intensity of the N₂ signal qualitatively tracks with the N₂ concentrations calculated by nitrogen mass balance from the FTIR measurements (Tables S1 and S2), lending additional confidence in the activity results. Similarly, good correlation between the FT-IR detection of N₂O and NO₂ and the MS signals was observed (compare Tables S1 and S2 to Figures S3 and S4). Finally, the release of oxygen as a product (Figure S3) and stable NO conversion (Figures S1 and S2) during the steady state measurements suggest that the catalysts were not poisoned by the irreversible chemical adsorption of oxygen. Thus, the good correlation between the FT-IR data and MS signals suggests that the calculation of N₂ production from the FT-IR is reliable and can be used for the calculation of activity from NO conversion to N₂. As shown in Figure 1b, NO decomposition activity to N₂ increases slightly with temperature up to 550 °C for the pure Co₃O₄ catalyst. Further increase in the temperature to 650 °C results in decreased activity. This result suggests that the Co₃O₄ spinel is not a good catalyst for NO decomposition at temperatures below 650 °C, as indicated by Hamada et al. [21]. The addition of PdO and PtO to the Co₃O₄ spinel improves the direct NO_x decomposition activity of

Co₃O₄. Direct NO_x activity increases with temperature for all palladium and platinum loadings, but unlike the pure Co₃O₄, deactivation was not observed above 550 °C for the any of PdO or PtO catalysts.

The direct NO decomposition activity of PdO/Co₃O₄ and PtO/Co₃O₄ to N₂ at various temperatures is presented as a function of the weight percent loading of the respective PGMs in Figure 2. For PdO/Co₃O₄, activity increases with palladium loading up to 3 wt%, but further increase in the palladium loading leads to decreased activity (Figure 2a). For PtO/Co₃O₄, activity increases with PtO loading up to 4 wt%, however, the overall effect on activity is significantly diminished compared to PdO/Co₃O₄ (Figure 2b). The optimum loading of each PGM was found to be 3 wt% PdO/Co₃O₄ and 4wt% PtO/Co₃O₄. Interestingly, PdO-promoted catalysts exhibit higher activity than the PtO-promoted catalysts. At 650 °C, the optimum PdO/Co₃O₄ catalyst exhibits 4 times higher activity compared to the optimum PtO/Co₃O₄ catalyst.

To confirm the reaction is indeed direct NO decomposition to N₂ rather than the unwanted production of N₂O or NO₂, the selectivity to N₂ was calculated. The N₂ selectivity is presented as a function of PGM loading from 400–650 °C for PdO/Co₃O₄ and PtO/Co₃O₄ in Figure 3a,b, respectively. As expected, pure Co₃O₄ (0 wt% PGM loading) exhibited relatively low selectivity to N₂ (<20%) at 400 and 450 °C. The N₂ selectivity increased to 80% at 550 °C and to 100% at 650 °C. Formation of N₂O was not observed and only N₂ and NO₂ products are detected during direct NO decomposition over the PtO- and PdO-promoted Co₃O₄ catalysts (Tables S1 and S2). Thus, the product distribution measurements suggest NO oxidation (NO₂ formation) is more favorable at lower reaction temperatures (<450 °C), and at higher reaction temperatures, NO decomposition (N₂ formation) is predominant. Remarkably, the addition of 1 wt% PdO to the Co₃O₄ improves the N₂ selectivity from 1 to 40% at 400 °C and from 21 to 70% at 450 °C. The N₂ selectivity further increased to 50% at 400 °C and 75% at 450 °C with increasing PdO loading to 3 wt%. Increasing the PdO loading from 3 wt% to 4 wt% lead to only a slight decrease in the N₂ selectivity. When also considering the activity measurement in Figure 2, the N₂ selectivity measurements confirm 3 wt% PdO as the optimum loading on Co₃O₄ for direct NO decomposition.

Regarding N₂ selectivity as a function of PtO loading (Figure 3b), the addition of 1 wt% PtO yielded less improvement at 400 °C (1 to 16%) compared to the addition of 1 wt% PdO (1 to 40%). Furthermore, the N₂ selectivity decreases with increasing PtO loading, dropping to 9% for the 4wt% PtO/Co₃O₄ catalyst. Moreover, there is no improvement in the selectivity observed at reaction temperatures at and above 450 °C. Therefore, the direct NO decomposition measurements show that the addition of PdO to Co₃O₄ improves the decomposition activity and N₂ selectivity and 3wt% is the optimum Pd loading over Co₃O₄, whereas PtO loaded on Co₃O₄ leads to only slight improvement in the activity and almost no influence on the N₂ selectivity.

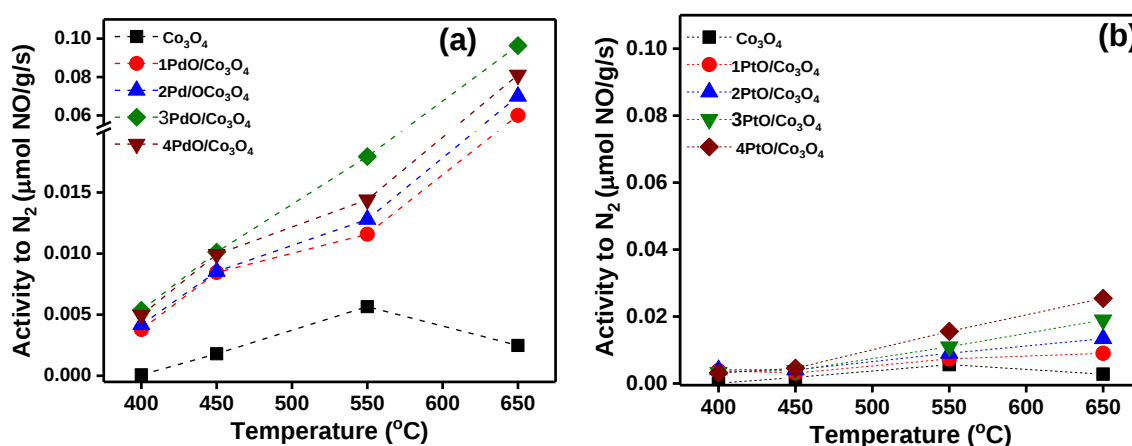


Figure 1. Direct NO decomposition activity to N₂ as a function of reaction temperature for (a) PdO- and (b) PtO-promoted Co₃O₄ catalysts with varying PGM loading. The pure Co₃O₄ support is included for comparison. (Gas hourly space velocity (GHSV) = 2100 h^{−1}, 1% NO/He).

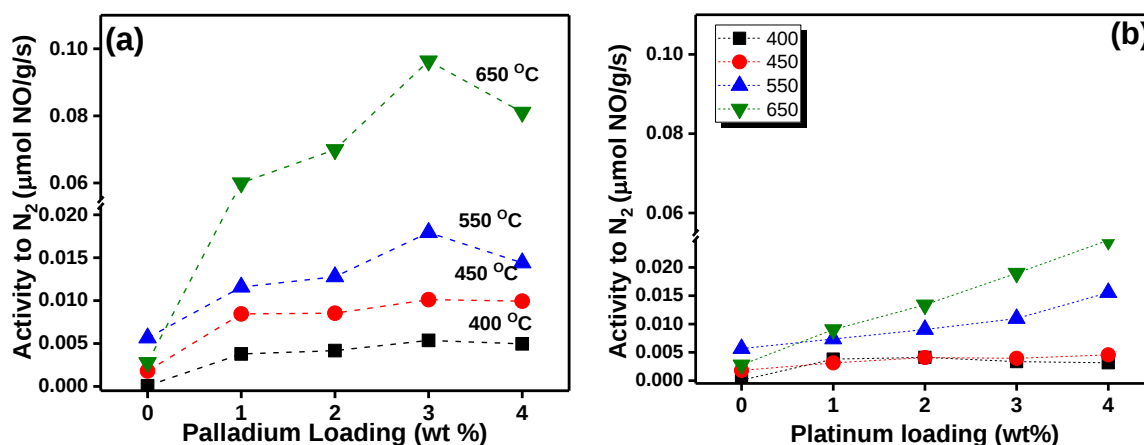


Figure 2. Direct NO decomposition activity to N_2 as a function of Pd and Pt loading for (a) PdO- and (b) PtO-promoted Co_3O_4 catalysts at varying temperature. The pure Co_3O_4 support is included for comparison. (GHSV = 2100 h^{-1} , 1% NO/He).

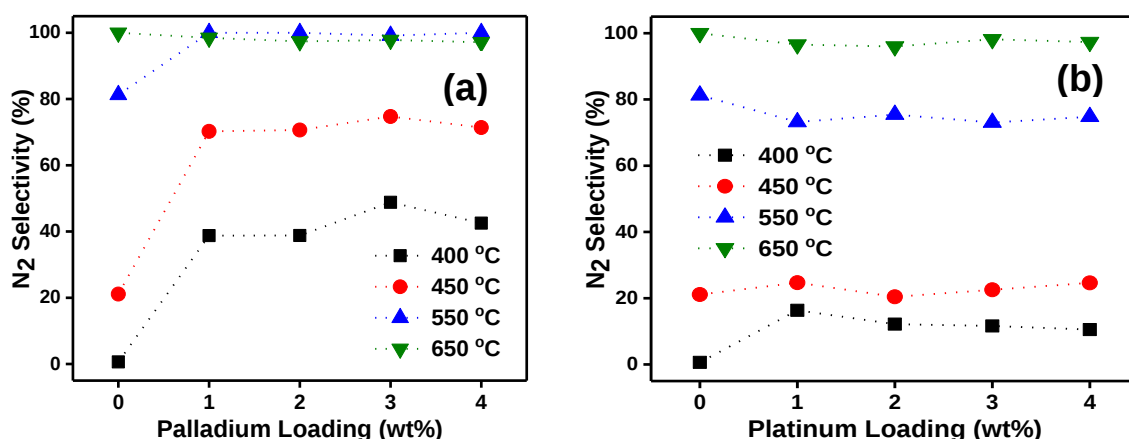


Figure 3. N_2 selectivity as a function of PdO and PtO loading for (a) PdO- and (b) PtO-promoted Co_3O_4 catalysts at varying temperature. The pure Co_3O_4 support is included for comparison. (GHSV = 2100 h^{-1} , 1% NO/He).

2.2. Catalyst Characterization

2.2.1. Structural and Textural Properties

These catalysts have been evaluated using several characterization techniques, like XRD, XPS, H_2 -TPR, BET surface area, and *in-situ* FT-IR during NO adsorption, to understand the influence of PdO and PtO on the structural and surface properties of Co_3O_4 and to explain the greater promoter effect of PdO on Co_3O_4 compared to PtO during NO decomposition. The palladium and platinum loadings of the studied catalysts prepared by impregnation were verified with XRF spectrometry. For the nominal 1.0, 2.0, 3.0, and 4.0 wt% of PdO, the experimental values were 0.83, 1.94, 2.80, and 4.15, respectively (Table 1). The experimental values for PtO doped Co_3O_4 catalysts were 0.93, 2.12, 3.23, and 4.02, respectively. Differences may be due to surface heterogeneity or incomplete precursor dispersion during the impregnation procedure or the inherent uncertainty related to the employed XRF method, which did not utilize a standard material to aid the data analysis.

The BET surface area values of PdO/ Co_3O_4 and PtO/ Co_3O_4 catalysts and the pure Co_3O_4 are presented in Table 1. The pure Co_3O_4 catalyst exhibits a BET surface area of $36 \text{ m}^2/\text{g}$. Little change in the surface area is observed after impregnating Co_3O_4 with 1, 2, and 3 wt% Pd. However, increasing Pd loading from 3 to 4 wt% on to Co_3O_4 lead to a decrease in the surface area from 33 to $26 \text{ m}^2/\text{g}$. These values suggest that PdO dispersed very well on the surface of Co_3O_4 until 3wt% and further

increase in the loading to 4wt% likely leads to surface agglomeration, which can block access to the active surface. The BET surface area measurements are corroborated by the activity measurements, which showed that the activity of Co_3O_4 increases with increasing palladium doping only until 3 wt%. Further increase in the Pd loading to 4 wt% lead to a decrease in the activity. Little change in surface area was observed for the Co_3O_4 with platinum impregnation (Table 1), as only a slight decrease in the surface area was observed at the highest loading. As suggested above, the blockage of the active surface may be the cause of the decrease in the activity for the 4 wt% $\text{PdO}/\text{Co}_3\text{O}_4$ catalyst. It is hypothesized that the formation of PdO crystallites is responsible for this behavior, and this hypothesis will be investigated below.

Table 1. Co/M (M = Pd, Pt) and BET surface area values of $\text{PdO}/\text{Co}_3\text{O}_4$ and $\text{PtO}/\text{Co}_3\text{O}_4$ catalysts.

Catalyst Loading	PGM Loading (wt%) *		BET Surface Area (m^2/g)	
	Pd wt%	Pt wt%	$\text{PdO}/\text{Co}_3\text{O}_4$	$\text{PtO}/\text{Co}_3\text{O}_4$
0	-	-	36	36
1	0.83	0.93	36	35
2	1.94	2.12	35	39
3	2.8	3.23	33	34
4	4.15	4.02	26	33

* As measured by XRF.

The X-ray diffraction (XRD) patterns of the fresh $\text{PdO}/\text{Co}_3\text{O}_4$ and $\text{PtO}/\text{Co}_3\text{O}_4$ catalysts are shown in Figure 4a,b, with the pattern of the pure Co_3O_4 for reference. The X-ray diffraction lines characteristic of the cubic cobalt spinel structure were indexed within the $\text{Fd}3\text{m}$ space group (JCPDS card no. 01-080-1533) in the case of the pure Co_3O_4 catalyst [31]. As shown in Figure 4a, all the $\text{PdO}/\text{Co}_3\text{O}_4$ catalysts exhibit peaks due to Co_3O_4 . The diffractograms provide evidence that the spinel structure was preserved after Pd impregnation, revealing no observable structural changes compared to the pure Co_3O_4 carrier. Diffraction peaks related to Pd or PdO were not detected on samples up to a nominal Pd loading of 3 wt%. For the 4 wt% Pd sample, a low-intensity diffraction peak indicative of tetragonal PdO (0 0 2) (JCPDS card no. 75-584) was visible at 2θ of 33.6° [32]. These measurements suggest that PdO is well-dispersed on the Co_3O_4 support up to 3 wt%, and above this loading, crystalline PdO forms on Co_3O_4 surface. As stated above, the BET surface decreases from 33 to $26 \text{ m}^2/\text{g}$ with increasing Pd loading from 3 wt% to 4 wt%. XRD measurements confirm that the decrease in the surface area is due to the formation of crystalline PdO on the surface of Co_3O_4 and blocking of the active surface. The X-ray diffraction patterns of $\text{PtO}/\text{Co}_3\text{O}_4$ catalysts are shown in Figure 4b and only peaks due to Co_3O_4 are present at all Pt loadings, suggesting the absence of bulk metallic Pt or PtO with long-range order. However, unlike $\text{PdO}/\text{Co}_3\text{O}_4$, the XRD peaks of the $\text{PtO}/\text{Co}_3\text{O}_4$ samples were shifted to higher values relative to the pure Co_3O_4 spinel for all Pt loadings. The shift in the peak position to higher values indicates that Pt is likely incorporating into the Co_3O_4 spinel structure in contrast to $\text{PdO}/\text{Co}_3\text{O}_4$, where the absence of the peak shift indicates that Pd remained dispersed on the Co_3O_4 surface.

Figure 5a,b display X-ray diffraction patterns of the spent $\text{PdO}/\text{Co}_3\text{O}_4$ and $\text{PtO}/\text{Co}_3\text{O}_4$ catalysts after direct NO decomposition. As shown in Figure 5a, the spent Co_3O_4 exhibits only peaks due to spinel structure. There are no peaks due to either CoO or metallic Co, suggesting the Co_3O_4 spinel is structurally stable during direct NO decomposition. In addition to the Co_3O_4 spinel peaks, the spent $\text{PdO}/\text{Co}_3\text{O}_4$ catalysts with 1, 2, and 3 wt% Pd loading also exhibit peaks at 2θ values of 40.3 , 46.79 , and 68.4° . These peaks are due to the (1 1 1), (2 0 0), and (2 2 0) facets of Pd metal (JCPDS no: 46-1043). The XRD measurements of the spent catalysts show that the dispersed PdO reduced to Pd metal during direct NO decomposition. Similar to the XRD pattern for the fresh 4 wt% $\text{PdO}/\text{Co}_3\text{O}_4$, the spent XRD pattern also exhibits peaks due to PdO along with the Pd metal and Co_3O_4 peak, which suggests that the crystalline PdO remains even after direct NO decomposition. The X-ray diffraction patterns of the spent $\text{PtO}/\text{Co}_3\text{O}_4$ catalysts after direct NO decomposition are displayed in Figure 5b. The spent

PtO/Co₃O₄ catalysts exhibit peaks due only to Co₃O₄ after direct NO decomposition. In contrast to the metallic phase observed in the spent PdO/Co₃O₄ catalysts, there are no peaks due to metallic Pt observed in the spent PtO/Co₃O₄ catalysts.

The XRD measurements show that in the case of PdO/Co₃O₄ catalysts, the PdO reduced to metallic Pd during direct NO decomposition and promotes the activity of Co₃O₄ catalysts. On the other hand, no metallic Pt formation occurred in the PtO/Co₃O₄ catalysts, leading to a greatly diminished promoter effect compared to the PdO/Co₃O₄ catalysts. Also, the NO decomposition measurements show that the catalytic activity decreases with increasing Pd loading from 3 wt% to 4 wt%. The formation of crystalline PdO and decrease in the surface area (blocking of the active surface) explains the lower activity of 4 wt% sample compared to 3 wt% sample. Hence, XRD and BET surface area measurements corroborate with the activity measurements. The spent PtO/Co₃O₄ catalysts also exhibit a shift in the peak positions to higher 2θ values compared to the pure Co₃O₄ catalyst, which suggests the incorporation of Pt into the Co₃O₄ spinel structure even after direct NO decomposition.

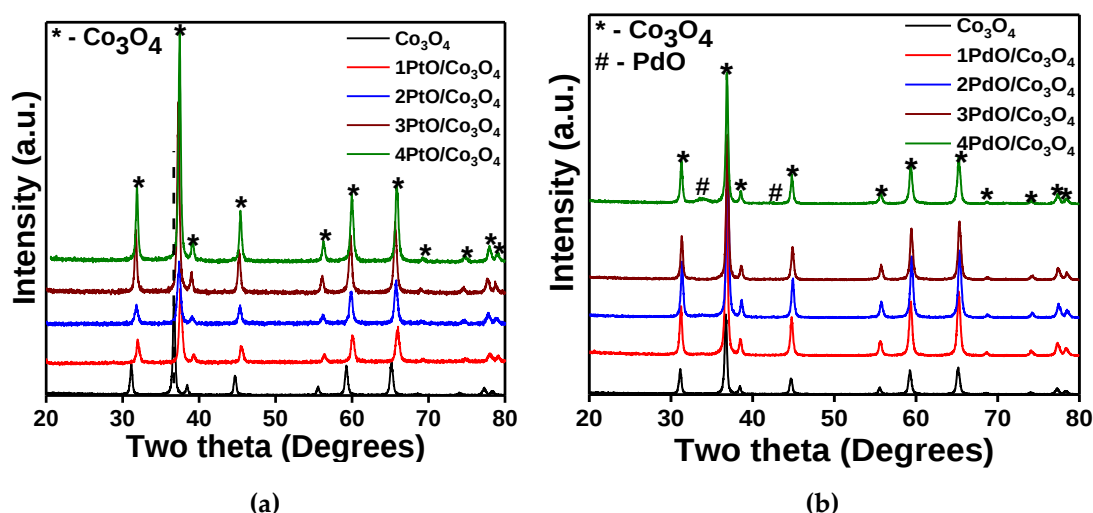


Figure 4. X-ray diffraction patterns of fresh (a) PdO- and (b) PtO-promoted Co₃O₄ catalysts. The pattern for the fresh pure Co₃O₄ support is included for reference.

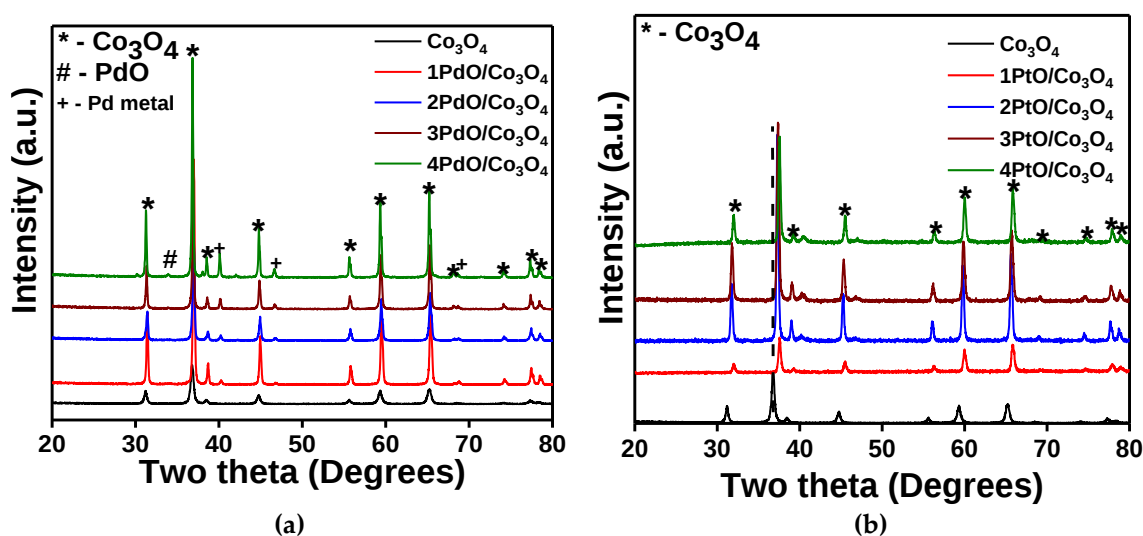
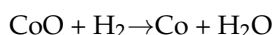
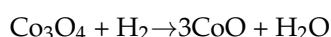


Figure 5. X-ray diffraction patterns of spent (a) PdO- and (b) PtO-promoted Co₃O₄ catalysts. The pattern for the spent pure Co₃O₄ support is included for reference.

2.2.2. Redox Properties

The influence of PdO and PtO on the redox properties of Co₃O₄ are investigated using H₂-temperature programmed reduction (H₂-TPR) measurements. The H₂-TPR profiles of PdO/Co₃O₄ and PtO/Co₃O₄ catalysts are presented in Figure 6a,b, along with that of the pure Co₃O₄ for comparison. Several authors reported that the reduction behavior of Co₃O₄ is strongly dependent on the preparation method, catalyst composition, and dispersion on a support [33,34]. The reduction behavior of Co₃O₄ was widely accepted as a stepwise process, including the reduction of Co³⁺ to Co²⁺ and Co²⁺ to metallic Co. There are three well-defined reduction peaks in the TPR profile of Co₃O₄ (Figure 6). The peak at 235 °C is attributed to the reduction of surface oxygen species. The other two peaks are for the stepwise reduction of Co₃O₄ to metallic cobalt. According to the literature, the second reduction peak centered at 275 °C is due to the reduction of Co₃O₄ to CoO, and the third peak at the region of 305 °C is due to the reduction of CoO to metallic cobalt [33,34].



The addition of 1 wt% PdO to the Co₃O₄ leads to a drastic change in the redox profile of Co₃O₄ (Figure 6). No peaks were observed in the 250–310 °C temperature region. Both PdO and Co₃O₄ were reduced at much lower temperature and all reduction events completed below 150 °C. These measurements show that PdO promotes the reduction of Co₃O₄. Two reduction peaks were observed in the 1 wt% PdO/Co₃O₄ H₂-TPR profile at 79 and 104 °C. The first reduction peak at 79 °C is due to the reduction of PdO to metallic Pd and the second reduction peak is due to the reduction of Co₃O₄. The H₂-TPR profiles for 1, 2, and 3 wt% PdO/Co₃O₄ were all very similar (Figure 6). The promotion of Co₃O₄ reduction by Pd observed in H₂-TPR is possibly ascribed to hydrogen spillover and the synergistic effect between Pd species and Co₃O₄. The synergistic effect can weaken the Co-O bond. Chen et al. [35] also reported a similar promotional effect for PdO impregnated on Co₃O₄ catalysts with different morphologies, and the synergistic effect between Pd and Co existed, regardless of Co₃O₄ morphology. In the present study, the intensity of the first reduction peak increases with increasing PdO loading from 1 to 3 wt%, and the increase is accompanied by a slight shift in the peak temperature from 79 to 85 °C. This may be due to the increase in the PdO loading on the Co₃O₄ surface. The reduction profile of 4 wt% PdO/Co₃O₄ is slightly different from the PdO promoted catalysts of lower loading. Along with the peaks due to Co₃O₄ and PdO, a small additional peak is observed at 220 °C. Given the identification of crystalline PdO in the XRD pattern of the 4 wt% PdO/Co₃O₄, it is reasonable to assign this peak to reduction of crystalline PdO.

The H₂-TPR profiles of PtO/Co₃O₄ catalysts are presented in Figure 6b. Two types of reduction features were observed in the case of PtO promoted Co₃O₄ catalysts, one from 130 to 190 °C and another from 200 to 325 °C. The first feature corresponds to reduction of PtO to metallic Pt and the second is reduction of Co₃O₄. Unlike PdO/Co₃O₄, little to no shift in the Co₃O₄ reduction temperature of PtO/Co₃O₄ catalysts was observed relative to the pure Co₃O₄. The reduction of Co³⁺ to Co²⁺ occurred in the 260–275 °C temperature region for Co₃O₄ and PtO/Co₃O₄ catalysts, irrespective of PtO loading, and the reduction of PtO occurred separately at a distinctly lower temperature. Yang et al. [36] observed similar behavior for Pt promoted Co₃O₄/Al₂O₃ catalysts, wherein both PtO and Co₃O₄ reduced separately in distinct temperature regions. Even though the Co₃O₄ reduction shifted to slightly lower temperatures at higher Pt loadings in their study, a synergistic effect, similar to Pd and Co in PdO/Co₃O₄, was not observed between Pt and Co. This lack of synergistic effect by Pt on the reduction of Co₃O₄ is consistent with the smaller promotional effect of Pt on direct NO decomposition activity compared to Pd promotion. Conversely, the decreased reduction temperature of Co₃O₄ observed in H₂-TPR measurements of PdO/Co₃O₄ illustrates how Pd can promote direct NO decomposition by enhancing the reducibility of the catalyst.

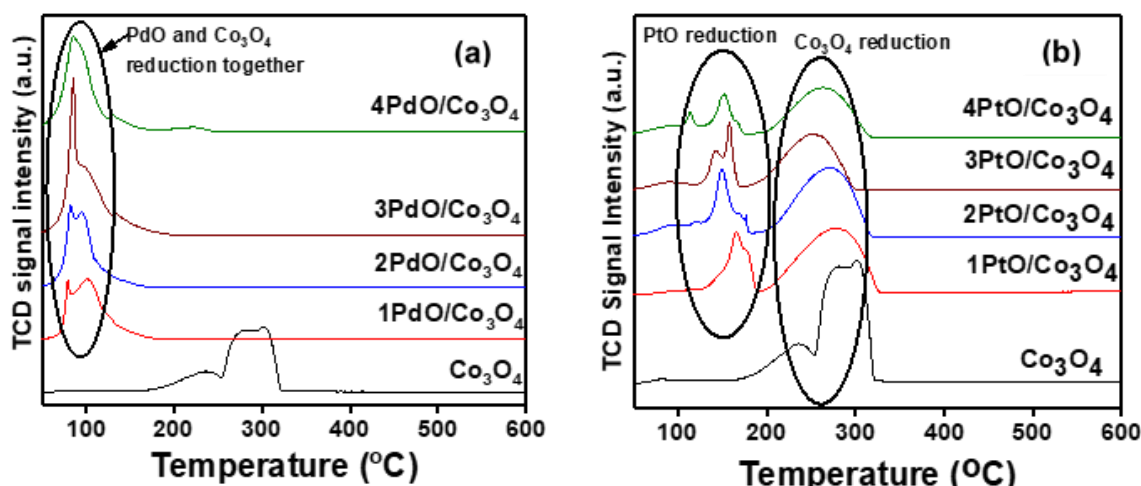


Figure 6. H₂- Temperature programmed reduction profiles of fresh (a) PdO- and (b) PtO-promoted Co₃O₄ catalysts. The pure Co₃O₄ profile is shown for comparison.

2.2.3. Surface Properties

The X-ray photoelectron spectroscopy (XPS) was used to investigate the surface elemental compositions, metal oxidation states, and adsorbed oxygen species of the as-prepared and spent samples. The O1s XPS spectra of fresh PdO- and PtO-promoted Co₃O₄ catalysts are presented in Figure 7, with that of the pure Co₃O₄ for comparison. The pure Co₃O₄ exhibits two peaks in the O1s spectra. The large peak at lower binding energy (BE = 530.2–530.7 eV) is attributed to the surface lattice oxygen in Co₃O₄ (denoted as O_{lat}) [37]. The shoulder at higher BE (532.0–532.7 eV) is associated with oxygen atoms present as surface adsorbed oxygen or surface hydroxyl groups or defect oxide (denoted as O_{ad}). The PdO- and PtO-promoted Co₃O₄ samples also exhibit two peaks in their O1s spectra due to the O_{lat} and O_{ad} species., however, little difference in the peak energies is observed. This is may be due to lower loadings of promoters.

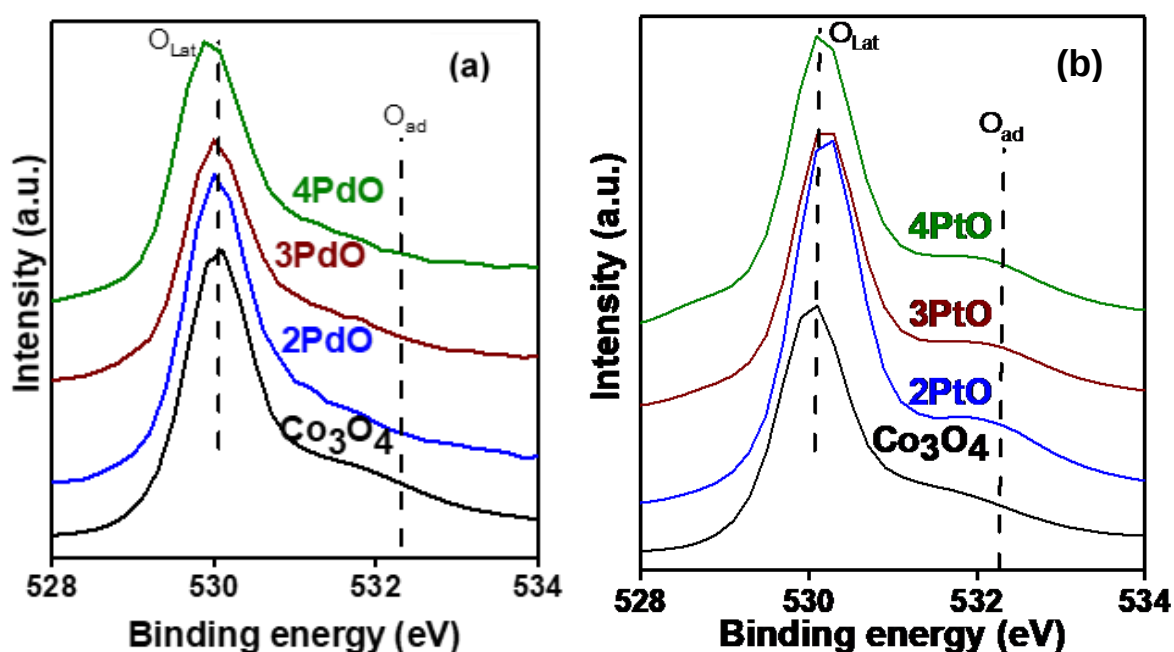


Figure 7. O1s XPS spectra of fresh (a) PdO- and (b) PtO-promoted Co₃O₄ catalysts. Co₃O₄ spectrum is shown for reference.

The fitted $\text{Co}2p$ XPS spectra of the fresh PdO- and PtO-promoted Co_3O_4 catalysts are presented in Figure 8, with that of the pure Co_3O_4 for comparison. In the pure Co_3O_4 XPS spectrum, the main peak in the BE range of 780.7–782.2 eV is assigned to $\text{Co}2p_{3/2}$, and the shoulder at 795.9–797.9 eV is attributed to $\text{Co}2p_{1/2}$. Pure Co_3O_4 exhibits peaks due to both Co^{3+} and Co^{2+} and their satellites. The main $\text{Co}2p_{3/2}$ feature can be further resolved into two components, with BE values centered at 778.7–780.4 eV and 779.8–781.6 eV, and corresponding to Co^{3+} and Co^{2+} , respectively [38]. Furthermore, the presence of the satellite peaks also confirms the presence of Co^{2+} in the catalysts. As expected for samples containing Co_3O_4 spinel, all catalysts exhibited peaks and satellites due to both Co^{3+} and Co^{2+} , irrespective of Pd or Pt promoter loading. Also, no significant change in the position of the peaks was observed upon impregnation of Co_3O_4 with PdO or PtO. The spent catalysts also exhibit peaks due to the Co^{3+} and Co^{2+} ions, irrespective of promoter identity or loading. The $\text{Co}2p$ XPS measurements show that the Co_3O_4 spinel is very stable during direct NO decomposition, which agrees with XRD measurements.

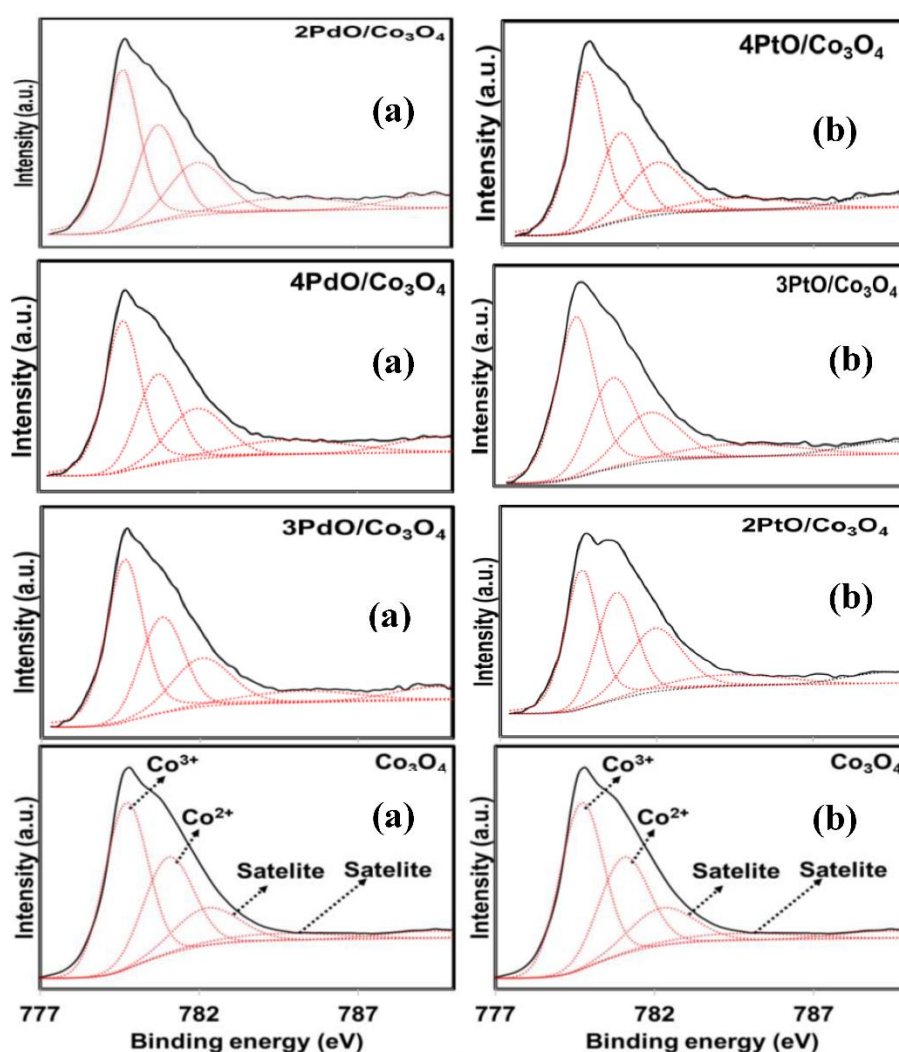


Figure 8. $\text{Co}2p$ XPS profiles of fresh (a) PdO- and (b) PtO-promoted Co_3O_4 . The pure Co_3O_4 spectra is presented for reference.

The $\text{Pd}3d$ XPS spectra of the fresh and spent 2, 3, and 4 wt% PdO/ Co_3O_4 are presented in Figure 9a,b. In general, Pd may exist as Pd^0 (335.1–335.4 eV [39]), Pd^{2+} (336.8.1–337.2 eV or 336.3–336.8 eV [40–44]), Pd^{4+} (337.8–339.3 eV), or a combination thereof. All the PdO/ Co_3O_4 catalysts exhibit peaks due to the Pd^{2+} and Pd^{4+} after calcination at all PdO loadings. However,

XRD measurements show no peaks corresponding to PdO or PdO₂ up to 3 wt% loading, which indicates that the PdO present on Co₃O₄ is in amorphous form and dispersed very well on the surface. In agreement with the above XRD analysis of the spent samples (see Figure 6a), XPS indicates PdO/Co₃O₄ catalysts exhibit peaks due to PdO and metallic Pd after direct NO_x decomposition. These results suggest that some of the PdO reduced to metallic Pd during direct NO_x decomposition, which corroborates the evidence from H₂-TPR and XRD of the promotional effect of Pd on the activity of Co₃O₄ spinel catalysts. The intensity of the metallic Pd increases with increasing PdO loading from 2 to 3 wt%, however, the intensity of the metallic Pd peak decreases drastically with further PdO loading from 3 to 4 wt%. This is due to the formation of the separate bulk PdO phase in the spent 4 wt% PdO/Co₃O₄ sample, which is clearly observed in the spent 4 wt% PdO/Co₃O₄ Pd3d spectrum. The formation of a separate PdO phase leads to less reduction of PdO to metallic Pd during direct NO_x decomposition and is the likely cause of the lower activity compared to the 3 wt% PdO/Co₃O₄ catalyst. These results agree with the conclusions made based on the spent XRD patterns (see Figure 5a), further strengthening the evidence that 3 wt% Pd is the optimum loading for promoting activity.

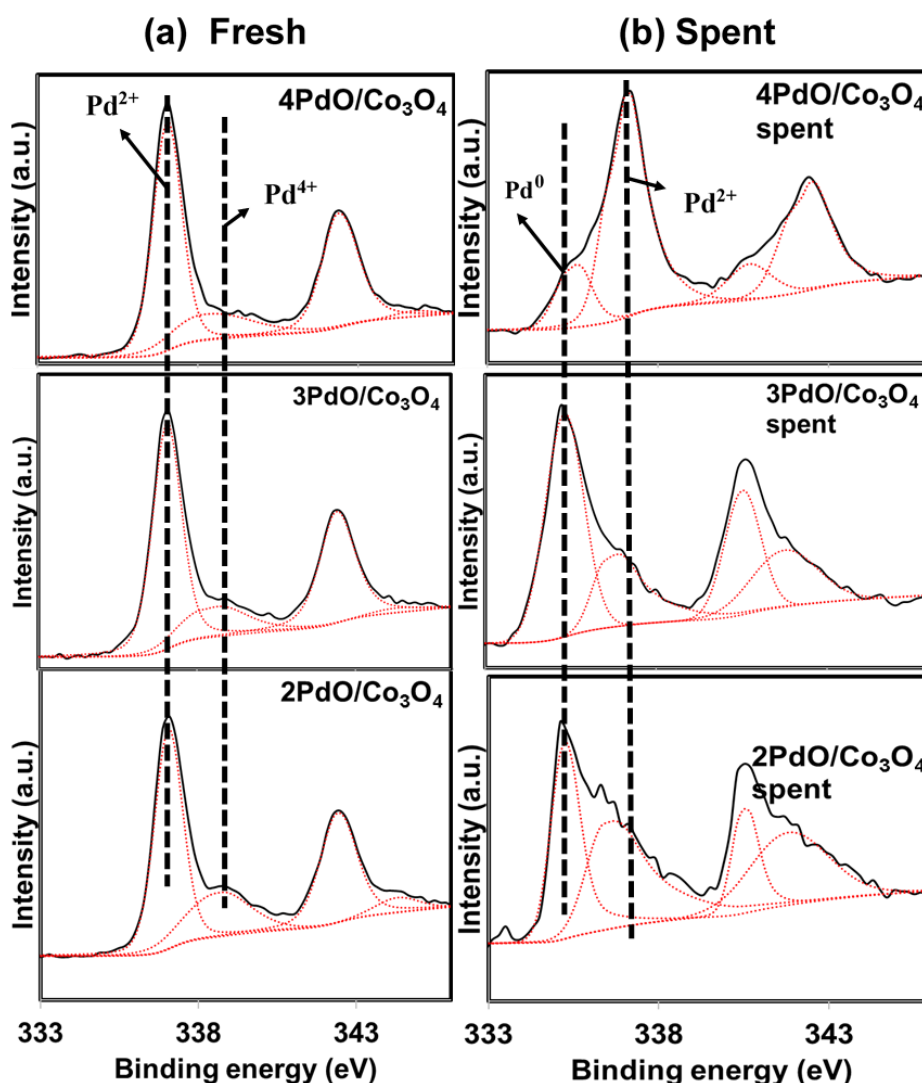


Figure 9. Pd3d XPS spectra of (a) fresh and (b) spent PdO-promoted Co₃O₄ catalysts.

Figure 10a,b present the Pt4f XPS spectra of the fresh and spent 2, 3, and 4 wt% PdO/Co₃O₄. All fresh and spent PtO/Co₃O₄ catalysts only exhibit peaks due to Pt²⁺ (72.3, 74.1 eV) at all Pt loadings [45]. There are no observed peaks due to either Pt⁴⁺ or metallic Pt⁰ in contrast to the

PdO/Co₃O₄ catalysts, wherein the PGM underwent significant changes in oxidation state with exposure to reaction conditions. Overall, XPS measurements show that the support Co₃O₄ is very stable during the promoter impregnation, as well as during the direct NO decomposition. PdO reduced to metallic Pd during the direct NO decomposition and improves the direct NO decomposition activity of Co₃O₄. On the other hand, PtO stays in an oxidized state (no metallic Pt formation) during the direct NO decomposition and exhibits less promotional effects compared to PdO.

2.2.4. NO Adsorption Properties

The adsorption of NO and formation of surface intermediates is essential to establishing activity for direct NO decomposition. In situ FT-IR spectroscopy was performed on pure Co₃O₄ and the PdO- and PtO-promoted Co₃O₄ catalysts to understand the interaction of NO with the catalyst during adsorption. In situ FT-IR measurements were collected during NO adsorption over the catalysts at 300 °C. Before NO adsorption, all the catalysts were pretreated at 350 °C in the presence of 10% O₂ in a helium balance and cooled to 300 °C in the presence of helium. All the spectra collected were normalized with respect to the gas phase NO peak at 1874 cm⁻¹. The in situ FTIR spectra of Co₃O₄, PdO- and PtO-promoted Co₃O₄ catalysts during NO adsorption are presented in Figure 11a,b. As shown in Figure 11a, little to no NO adsorption occurs over the pure Co₃O₄ spinel oxide at 300 °C, as no clear peaks were present relative to the noise level. Interestingly, impregnating PdO over Co₃O₄ leads to a formation of chelating surface nitrate intermediates (1577 and 1254 cm⁻¹) during the NO adsorption [46]. The intermediate formation was observed for all the catalysts irrespective of loading and the intensity of the peak increases with PdO loading. On the other hand, PtO-promoted Co₃O₄ catalysts do not produce spectroscopically relevant amounts of intermediates during the NO adsorption and exhibit spectra similar to the pristine Co₃O₄ catalyst. The catalysts in the current study exhibit activity at temperatures ≥400 °C, however, at these temperatures, no spectroscopically relevant surface NO_x species were observed by in situ FTIR (not shown). This observation indicates that neither the surface chelating nitrate nor any other surface NO_x species is the most abundant reactive intermediate in the direct NO decomposition mechanism. The in situ FTIR results at 300 °C are, therefore, interpreted as a probe of the affinity of the NO reactant molecule to interact with the catalyst surface. In this interpretation, it is concluded that the presence of PdO improves the affinity of the catalyst to interact with NO compared to PtO or the pure Co₃O₄ support.

The direct NO decomposition measurements show that PdO promotes direct NO decomposition activity of Co₃O₄ much better compared to the PtO. The Co₃O₄ is a normal spinel with AB₂O₄ formula, where A (T_d) sites are occupied by Co²⁺ ions and B (Oh) sites are occupied by Co³⁺ ions. According to the general mechanism proposed by Haneda et al. [18], initially NO adsorbs on the surface and decomposes into N and O. The oxygen atoms adsorb on Co²⁺ ions and are oxidized to Co³⁺. Then, Co³⁺ ions reduce back to Co²⁺ upon release of the oxygen as a product. Hence, NO adsorption and oxygen release (redox) properties are very important for direct NO decomposition. The *in-situ* FT-IR results reveal that PdO increases the affinity of the catalyst to form surface NO_x species compared to PtO or a pure Co₃O₄ support. The H₂-TPR studies in our work show that the Co₃O₄ reduction temperature is significantly decreased by the presence of dispersed PdO, thus suggesting a more facile reduction of Co³⁺ to Co²⁺ to release O₂ during direct NO_x decomposition is possible. The improvement in the NO_x adsorption properties and ease of cobalt reduction explains the better direct NO decomposition activity of PdO catalysts compared to PtO catalysts.

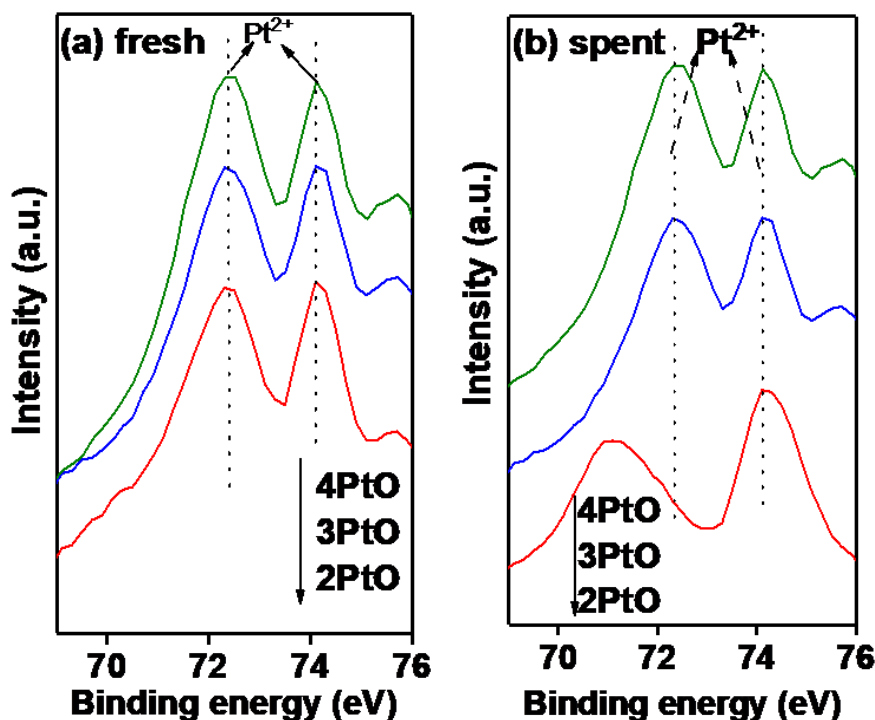


Figure 10. Pt4f XPS profiles of (a) fresh and (b) spent PtO-promoted Co_3O_4 catalysts.

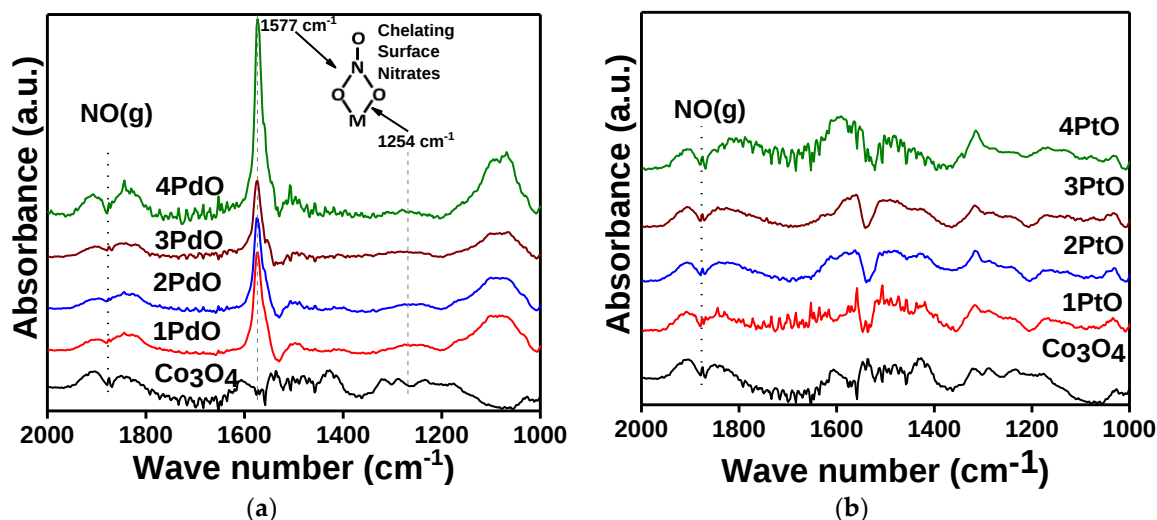


Figure 11. In-situ FT-IR spectra of Co_3O_4 , PdO (a), and PtO (b) promoted Co_3O_4 catalysts during NO adsorption at 300 °C.

3. Materials and Methods

3.1. Catalyst Synthesis

Palladium and platinum promoted Co_3O_4 catalysts were synthesized using the wet impregnation method. Commercial Co_3O_4 was purchased from Sigma-Aldrich (St. Louis, MO, USA) (99.5% trace metal basis) and used as received without any further modification for the synthesis. In a typical synthesis procedure, 5 g of commercial Co_3O_4 were mixed with 50 mL of water. Then, the required quantity of palladium nitrate hydrate (Sigma-Aldrich), or tetraamine platinum (II) nitrate (Sigma-Aldrich, 99.995% trace metal basis) was dissolved separately in deionized water and combined with the Co_3O_4 suspension. The mixture was heated to 80 °C with continuous stirring. The obtained powder was then dried in an oven at 120 °C for 12 h under air. Finally, the catalyst was calcined

at 400 °C for 4 h with a 1 °C/min ramp. Different loadings of palladium and platinum on Co₃O₄ (nominally 1 to 4 wt%) catalysts were prepared by varying the amount of palladium nitrate or platinum nitrate. For reference, the commercial Co₃O₄ support was also calcined at 400 °C for 4 h.

3.2. Catalyst Characterization

X-ray diffraction: X-ray powder diffraction (XRD) patterns were obtained using a Rigaku SmartLab X-ray diffractometer (Rigaku, The Woodlands, TX, USA) using Cu K α radiation (1.5405 Å). A glass holder was used to support the sample. The scanning range was from 10 to 80° (2 θ) with a step size of 0.02° and a step time of 1 s. The XRD phases present in the samples were identified with the help of ICDD-JCPDS [31] data files.

BET Surface Area Measurements: The surface area of the PdO and PtO promoted Co₃O₄ materials were measured using a Micromeritics 3Flex surface characterization instrument (Micromeritics, Atlanta, GA, USA). N₂ physisorption isotherms was conducted at −196 °C, and the surface area was measured by the BET method. Prior to the analyses, the samples were outgassed at 300 °C under vacuum (5×10^{-3} Torr) for 3 h.

X-ray Fluorescence Measurements: XRF was collected using a Rigaku ZSX, primus II X-ray spectrometer (Rigaku, The Woodlands, TX, USA). Impurities in the crystals were gained by X-ray fluorescence in operation of spectrometer in standard fewer modes with coverage of a full element. The amount of any elements and oxides particles was detected by the XRF experiment.

H₂-Temperature Programmed Reduction (H₂-TPR) Measurements: The redox properties of the PtO/Co₃O₄ and PdO/Co₃O₄ catalysts were studied using H₂ temperature programmed reduction (H₂-TPR) experiments. H₂-TPR experiments were performed using a Micromeritics 3Flex surface characterization instrument (Micromeritics, Atlanta, GA, USA) equipped with a thermal conductivity detector. Before the experiment, the catalysts were preheated to 300 °C in the presence of 20% O₂/He (30 mL/min). After the pretreatment, the temperature was decreased to 50 °C. The H₂-TPR measurements were performed by heating the catalyst from 50 to 600 °C in the presence of 10% H₂/Ar (30 mL/min).

X-ray Photo Electron Spectroscopy: The XPS measurements were performed using a PHI 5000 Versa Probe II X-ray photoelectron spectrometer (Physical Electronics, East Chanhassen, MN, USA) using an Al K α source. Charging of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C1s) to 284.6 eV [47]. The XPS analysis was performed at ambient temperature and at pressures typically on the order of 10^{−7} Torr. Prior to the analysis, the samples were outgassed under vacuum for 30 min.

In Situ FTIR Spectroscopy Measurements during NO Adsorption: The NO adsorption properties were measured using in situ Fourier transform infrared (FTIR) spectroscopy. The Harrick High Temperature Cell with environmental (gas flow) and temperature control was used for in situ diffuse-reflectance FTIR spectroscopy. Spectra were recorded using a Thermo Scientific Nicolet 8700 Research FT-IR Spectrometer (Thermo Scientific Fidher, Waltham, MA USA) equipped with a liquid N₂ cooled MCT detector. Spectra were obtained with a resolution of 2 cm^{−1} and by averaging 64 scans. In situ diffuse-reflectance FTIR spectra were collected during NO adsorption at 300 °C. Prior to NO adsorption, the sample was first pretreated at 350 °C in 30 mL/min of 10% O₂/He. The background spectrum (64 scans) was of the catalyst after cooling to 300 °C in 30 mL/min UHP He. Adsorption of NO was achieved by flowing 30 mL/min of 10,000 ppm NO over the catalyst for 25 min. Adsorption of NO proceeded for 25 min, while spectra were obtained every minute using a series collection. To compare peak intensities among different catalyst samples, the adsorption spectra were normalized to the NO gas phase peak at ~1876 cm^{−1}.

3.3. Direct NO Decomposition Measurements

Direct NO decomposition measurements were performed in a fixed bed flow reactor. A gas mixture of ~1% NO in helium balance was used with a gas hourly space velocity of ~2100 h^{−1} and in

the temperature region of 450–650 °C. Before the reaction, catalysts were pretreated at 500 °C in the presence of 20% O₂/He. After pretreatment, the bed temperature was decreased to 400 °C and direct NO decomposition measurements were collected. The measurements were performed at 400, 450, 550, and 650 °C, with 2 h of steady state at each temperature. The NO, N₂O, and NO₂ concentrations were analyzed with a FTIR detector (CAI 600 SC FTIR California Analytical Instruments, Inc., Orange County, CA, USA). The N₂ concentration was calculated by mass balance of the total nitrogen species. The raw NO conversion (NO converted to all the products) during the steady state measurements are presented in Figure S1 of the supporting information and activity to N₂ was reported in Figure 1 of the manuscript. The steady state direct NO decomposition measurements were also performed in a reactor, which was equipped with the mass spectroscopy (MKs, Cirrus 2). The changes in the NO, N₂, O₂, N₂O, and NO₂ signal intensities were monitored during the reaction (Figures S2–S5). The inert Ar gas was introduced as a tracer to monitor for potential systematic variation in signal intensity during the experiment (Figure S2).

4. Conclusions

The direct NO decomposition measurements show that PdO promotes the activity of Co₃O₄ and is 4 times more active compared to PtO at 650 °C. Also, the activity increases with increasing PdO loading until 3 wt% and further increase in the loading leads to a decrease in the activity. On the other hand, only a slight increase in the activity was observed with increasing PtO loading up to 4 wt%. Surface area measurements indicated that both PdO and PtO have little to no influence on the surface area of Co₃O₄, except for a decrease in surface area for 4 wt% PdO/Co₃O₄. The X-ray diffraction measurements show that Pt incorporated into the Co₃O₄ structure during the synthesis and PdO stays mostly on the surface. The diffraction measurements also suggested that PdO is in an amorphous form up to 3 wt% over Co₃O₄ surface and crystalline PdO forms at 4 wt% loading, whereas PtO mostly stays as amorphous form or incorporated into Co₃O₄ structure until 4 wt%. Due to the synergistic effect between Pd species and Co₃O₄, an improvement in the redox properties of Co₃O₄ was observed in the case of PdO/Co₃O₄ catalysts. Conversely, PtO do not have any influence on the redox properties of Co₃O₄. The X-ray photo electron spectroscopic measurements reveal that PdO reduced to Pd metal during the direct NO decomposition reaction and Pt was in 2+ oxidation state before and after the direct NO decomposition reaction. In situ NO adsorption measurements show that PdO improve the NO adsorption properties of Co₃O₄ by forming the nitrate ion intermediates, whereas PtO/Co₃O₄ do not form any intermediates during the NO adsorption at 300 °C. Overall, PdO ease the redox properties of Co₃O₄ and forms surface adsorbed species during NO adsorption and improves the direct NO decomposition activity of Co₃O₄. On the other hand, PtO do not have any influence on the redox or NO adsorption properties of Co₃O₄ and exhibits lesser promotional effects compared to PdO. For PdO/Co₃O₄ catalysts, the PdO remains in amorphous form until 3PdO/Co₃O₄ and improves the activity of Co₃O₄ with loading. However, further increase in the loading to 4 wt% leads to formation of crystalline PdO, which reduces separately during H₂-TPR and inhibits the PdO reduction to metallic Pd during direct NO decomposition and exhibits lesser activity compared to 3 wt% PdO/Co₃O₄.

Supporting information: The NO conversion, and N₂, N₂O, and NO₂ ppm values of various PdO/Co₃O₄ and PtO/Co₃O₄ catalysts are presented in Tables S1 and S2. The total NO conversion profiles of the Co₃O₄, 3PdO/Co₃O₄, and 4PtO/Co₃O₄ calculated from the FT-IR detector during the steady state direct NO decomposition measurements are presented in Figure S2. NO, Ar, N₂, O₂, N₂O, and NO₂ partial pressure values (obtained from mass spectroscopy) of Co₃O₄, 3 wt% PdO/Co₃O₄, and 3 wt% PtO/Co₃O₄ during steady state direct NO decomposition in the 400 to 650 °C temperature region are presented in Figures S3 and S4.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/1/62/s1>. Table S1: NO conversion, N₂, N₂O, NO₂ ppm values of the Co₃O₄ and various PdO/Co₃O₄ catalysts in the temperature region 400–650 °C. Table S2: NO conversion, N₂, N₂O, NO₂ ppm values of the Co₃O₄ and various PtO/Co₃O₄ catalysts in the temperature region 400–650 °C. Figure S1: Steady state NO conversion values of

the Co_3O_4 , $3\text{PdO}/\text{Co}_3\text{O}_4$, and $4\text{PtO}/\text{Co}_3\text{O}_4$ catalysts during the direct NO decomposition in the temperature region 400 to 650 °C. Figure S2: NO and Ar M.S. partial pressures of the (a) Co_3O_4 , (b) $3\text{PdO}/\text{Co}_3\text{O}_4$, and (c) $3\text{PtO}/\text{Co}_3\text{O}_4$ catalysts during the steady state direct NO decomposition in the temperature region 400 to 650 °C. Figure S3: N_2 and O_2 M.S. partial pressures of the (a) Co_3O_4 , (b) $3\text{PdO}/\text{Co}_3\text{O}_4$, and (c) $3\text{PtO}/\text{Co}_3\text{O}_4$ catalysts during the steady state direct NO decomposition in the temperature region 400 to 650 °C. Figure S4: N_2O M.S. partial pressures of the (a) Co_3O_4 , (b) $3\text{PdO}/\text{Co}_3\text{O}_4$, and (c) $3\text{PtO}/\text{Co}_3\text{O}_4$ catalysts during the steady state direct NO decomposition in the temperature region 400 to 650 °C. Figure S5: NO_2 M.S. partial pressures of the (a) Co_3O_4 , (b) $3\text{PdO}/\text{Co}_3\text{O}_4$, and (c) $3\text{PtO}/\text{Co}_3\text{O}_4$ catalysts during the steady state direct NO decomposition in the temperature region 400 to 650 °C.

Author Contributions: This study was conducted through contributions of all authors. G.K.R. Reddy designed the study, performed the experiments, and wrote the manuscript. T.C.P. was involved in performing the experiments. C.A.R. checked and corrected the manuscript.

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References

- Irfan, M.F.; Goo, J.H.; Kim, S.D. Effects of NO_2 , CO, O_2 , and SO_2 on oxidation kinetics of NO over $\text{Pt-WO}_3/\text{TiO}_2$ catalyst for fast selective catalytic reduction process. *Int. J. Chem. Kinet.* **2006**, *38*, 613–620. [\[CrossRef\]](#)
- Masui, T.; Uejima, S.; Tsujimoto, S.; Nagai, R.; Imanaka, N. Direct NO decomposition over C-type cubic $\text{Y}_2\text{O}_3\text{--Pr}_6\text{O}_{11}\text{--Eu}_2\text{O}_3$ solid solutions. *Catal. Today* **2015**, *242*, 338–342. [\[CrossRef\]](#)
- Hong, Z.; Wang, Z.; Li, X.B. Catalytic oxidation of nitric oxide (NO) over different catalysts: An overview. *Catal. Sci. Technol.* **2017**, *7*, 3440–3452. [\[CrossRef\]](#)
- Imanaka, N.; Masui, T. Advances in direct NO decomposition catalysts. *Appl. Catal. A* **2012**, *431–432*, 1–8. [\[CrossRef\]](#)
- Haneda, M.; Hamada, H. Recent progress in catalytic NO decomposition. *C. R. Chim.* **2016**, *19*, 1254–1265. [\[CrossRef\]](#)
- Locci, C.; Vervisch, L.; Farcy, B.; Domingo, P.; Perret, N. Selective Non-Catalytic Reduction (SNCR) of nitrogen oxide emissions: A perspective from numerical modeling. *Flow Turbul. Combust.* **2018**, *100*, 301–340. [\[CrossRef\]](#)
- Jellinek, K. About decomposition rate of nitric oxide and dependence of the same on the temperature. *J. Inorg. Chem.* **1906**, *49*, 229–276.
- Glick, H.S.; Klein, J.J.; Squire, W. Single-Pulse Shock Tube Studies of the Kinetics of the Reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ between 2000–3000 °K. *J. Chem. Phys.* **1957**, *27*, 850–857. [\[CrossRef\]](#)
- Zhu, J.; Thomas, A. Perovskitetype mixed oxides as catalytic material for NO removal. *Appl. Catal. B* **2009**, *92*, 225–233. [\[CrossRef\]](#)
- Royer, S.; Duprez, D.; Can, F.; Courtois, X.; Batiot-Dupeyrat, C.; Laassiri, S.; Alamdari, H. Perovskites as Substitutes of Noble Metals for Heterogeneous Catalysis: Dream or Reality. *Chem. Rev.* **2014**, *114*, 10292–10368. [\[CrossRef\]](#)
- Tofan, C.; Klvana, D.; Kirchnerova, J. Direct decomposition of nitric oxide over perovskite-type catalysts: Part I. Activity when no oxygen is added to the feed. *Appl. Catal. A* **2002**, *223*, 275–286. [\[CrossRef\]](#)
- Yokoi, Y.; Uchida, H. The influence of palladium on the structure and catalytic activity of lanthanum based mixed oxide. *Catal. Today* **1998**, *42*, 167–174. [\[CrossRef\]](#)
- Zhao, Z.; Yang, X.G.; Wu, Y. Comparative study of Nickel-based perovskite-like mixed oxide catalysts for direct decomposition of NO. *Appl. Catal. B* **1996**, *8*, 281–297. [\[CrossRef\]](#)
- Zhu, J.J.; Xiao, D.H.; Li, J.; Yang, X.G.; Wu, Y. Effect of Ce on NO direct decomposition in the absence/presence of O_2 over $\text{La}_{1-x}\text{Ce}_x\text{SrNiO}_4$ ($0 \leq x \leq 0.3$). *J. Mol. Catal. A Chem.* **2005**, *234*, 99–105. [\[CrossRef\]](#)
- Zhu, J.J.; Xiao, D.H.; Li, J.; Yang, X.G.; Wu, Y.; Wei, K. Effect of Ce and MgO on NO decomposition over $\text{La}_{1-x}\text{Ce}_x\text{--Sr--Ni--O}/\text{MgO}$. *Catal. Commun.* **2006**, *7*, 432–435. [\[CrossRef\]](#)
- Winter, E.R.S. The catalytic decomposition of NO by metallic oxides. *J. Catal.* **1971**, *22*, 158. [\[CrossRef\]](#)

17. Boreskov, G.K. Forms of oxygen bonds on the surface of oxidation catalysts *Discuss. Faraday Soc.* **1966**, *41*, 263. [[CrossRef](#)]
18. Haneda, M.; Kintaichi, Y.; Bion, N.; Hamada, H. Alkali metal-doped cobalt oxide catalysts for NO decomposition. *Appl. Catal. B* **2003**, *46*, 473–482. [[CrossRef](#)]
19. Haneda, M.; Kintaichi, Y.; Hamada, H. Reaction mechanism of NO decomposition over alkali metal-doped cobalt oxide catalysts. *Appl. Catal. B* **2005**, *55*, 169–175. [[CrossRef](#)]
20. Haneda, M.; Nakamura, I.; Fujitani, T.; Hamada, H. Catalytic Active Site for NO Decomposition Elucidated by Surface Science and Real Catalyst. *Catal. Surv. Asia* **2005**, *9*, 207–215. [[CrossRef](#)]
21. Park, P.W.; Kil, J.K.; Kung, H.H.; Kung, M.C. NO decomposition over Na promoted cobalt oxide. *Catal. Today* **1998**, *42*, 51–60. [[CrossRef](#)]
22. Amirnazmi, A.; Benson, J.E.; Boudart, M. Oxygen inhibition in the decomposition of NO on metal oxides and platinum. *J. Catal.* **1973**, *30*, 55–65. [[CrossRef](#)]
23. Behm, R.J.; Brundle, C.R. Decomposition of NO on Ag(111) at low temperatures. *J. Vac. Sci. Technol. A* **1984**, *2*, 1040–1041. [[CrossRef](#)]
24. Suzuki, Y.; Hwang, H.J.; Kondo, N.; Ohji, T. In Situ Processing of a Porous Calcium Zirconate/Magnesia Composite with Platinum Nanodispersion and Its Influence on Nitric Oxide Decomposition. *J. Am. Ceram. Soc.* **2001**, *84*, 2713–2715. [[CrossRef](#)]
25. Haneda, M.; Kintaichi, Y.; Hamada, H. Surface reactivity of prereduced rare earth oxides with nitric oxide: new approach for NO decomposition. *Phys. Chem. Chem. Phys.* **2002**, *4*, 3146–3151. [[CrossRef](#)]
26. Haneda, M.; Kintaichi, Y.; Nakamura, I.; Fujitani, T.; Hamada, H. Comprehensive study combining surface science and real catalyst for NO direct decomposition. *Chem. Commun.* **2002**, *21*, 2816–2817. [[CrossRef](#)]
27. Haneda, M.; Kintaichi, Y.; Nakamura, I.; Fujitani, T.; Hamada, H. Effect of surface structure of supported palladium catalysts on the activity for direct decomposition of nitrogen monoxide. *J. Catal.* **2003**, *218*, 405–410. [[CrossRef](#)]
28. Almusaiteer, K.; Krishnamurthy, R.; Chuang, S.S.C. In situ infrared study of catalytic decomposition of NO on carbon-supported Rh and Pd catalysts. *Catal. Today* **2000**, *55*, 291–299. [[CrossRef](#)]
29. De Oliveira, A.M.; Crizel, L.E.; da Silveira, R.S.; Pergher, S.B.C.; Baibich, I.M. NO decomposition on mordenite-supported Pd and Cu catalysts. *Catal. Commun.* **2007**, *8*, 1293–1297. [[CrossRef](#)]
30. Reddy, G.K.; Ling, C.; Peck, T.; Jia, H. Understanding the chemical state of palladium during the direct NO decomposition—Influence of pretreatment environment and reaction temperature. *RSC Adv.* **2017**, *7*, 19645–19655. [[CrossRef](#)]
31. Klug, H.P.; Alexander, L.E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed.; Wiley: New York, NY, USA, 1974.
32. Ercolino, G.; Grzybek, G.; Stelmachowski, P.; Specchia, S.; Kotarba, A.; Specchia, V. Pd/Co₃O₄-based catalysts prepared by solution combustion synthesis for residual methane oxidation in lean conditions. *Catal. Today* **2015**, *257*, 66–71. [[CrossRef](#)]
33. Bahlawane, N.; Rivera, E.F.; Höfinghaus, K.K.; Brechling, A.; Kleineberg, U. Characterization and tests of planar Co₃O₄ model catalysts prepared by chemical vapor deposition. *Appl. Catal. B* **2004**, *53*, 245. [[CrossRef](#)]
34. Lin, H.Y.; Chen, Y.W. The mechanism of reduction of cobalt by hydrogen. *Mater. Chem. Phys.* **2004**, *85*, 171. [[CrossRef](#)]
35. Chen, Z.; Wanga, S.; Dinga, Y.; Zhanga, L.; Lva, L.; Wanga, M.; Wanga, S. Pd catalysts supported on Co₃O₄ with the specified morphologies in CO and CH₄ oxidation. *Appl. Catal. A Gen.* **2017**, *532*, 95–104. [[CrossRef](#)]
36. Yang, H.; Deng, J.; Liu, Y.; Xie, S.; Xu, P.; Dai, H. Pt/Co₃O₄/3DOM Al₂O₃: Highly effective catalysts for toluene combustion. *Chin. J. Catal.* **2016**, *37*, 934–946. [[CrossRef](#)]
37. Voogt, E.H.; Mens, A.J.M.; Gijzeman, O.L.J.; Geus, J.W. XPS analysis of palladium oxide layers and particles. *Surf. Sci.* **1996**, *350*, 21–31. [[CrossRef](#)]
38. Zhang, C.; Zhang, L.; Xu, G.C.; Ma, X.; Li, Y.H.; Zhang, C.; Jia, D. Metal organic framework-derived Co₃O₄ microcubes and their catalytic applications in CO oxidation. *New J. Chem.* **2017**, *41*, 1631–1636. [[CrossRef](#)]
39. Gnanamani, M.K.; Jacobs, G.; Hamdeh, H.H.; Shafer, W.D.; Liu, F.; Hopps, S.D.; Thomas, G.A.; Davis, B.H. Hydrogenation of Carbon Dioxide over Co–Fe Bimetallic Catalysts. *ACS Catal.* **2016**, *6*, 913–927. [[CrossRef](#)]
40. Brun, M.; Berthet, A.; Bertolini, J.C. XPS, AES and Auger parameter of Pd and PdO. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *104*, 55–60. [[CrossRef](#)]

41. Suhonen, S.; Valden, M.; Pessa, M.; Savimäki, A.; Harkonen, M.; Hietikko, M.; Pursiainen, J.; Laitinen, R. Characterization of alumina supported Pd catalysts modified by rare earth oxides using X-ray photoelectron spectroscopy and X-ray diffraction: Enhanced thermal stability of PdO in Nd/Pd catalysts. *Appl. Catal. A Gen.* **2001**, *207*, 113–120. [[CrossRef](#)]
42. Mirkelamoglu, B.; Karakas, G. The role of alkali-metal promotion on CO oxidation over PdO/SnO₂ catalysts. *Appl. Catal. A Gen.* **2006**, *299*, 84–94. [[CrossRef](#)]
43. Mucalo, M.R.; Cooney, R.P.; Metson, J.B. Platinum and palladium hydrosols: Characterisation by X-ray photoelectron spectroscopy and transmission electron microscopy. *Colloids Surf.* **1991**, *60*, 175–197. [[CrossRef](#)]
44. Kibis, L.S.; Titkov, A.I.; Stadnichenko, A.I.; Koscheev, S.V.; Boronin, A.I. X-ray photoelectron spectroscopy study of Pd oxidation by RF discharge in oxygen. *Appl. Surf. Sci.* **2009**, *255*, 9248–9254. [[CrossRef](#)]
45. Hegde, M.S.; Bera, P. Noble metal ion substituted CeO₂ catalysts: Electronic interaction between noble metal ions and CeO₂ lattice. *Catal. Today* **2015**, *253*, 40–50. [[CrossRef](#)]
46. Hadjiivanov, K.I. Identification of Neutral and Charged N_xO_y Surface Species by IR Spectroscopy. *Catal. Rev. Sci. Eng.* **2000**, *42*, 71–144. [[CrossRef](#)]
47. Wagner, C.D.; Riggs, W.M.; Davis, L.E.; Moulder, J.F. *Handbook of X-ray Photoelectron Spectroscopy*; Muilenberg, G.E., Ed.; Perkin-Elmer Corp.: Waltham, MA, USA, 1978.



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