

Article

Catalysts Promoted with Niobium Oxide for Air Pollution Abatement

Wendi Xiang ², **Xiaochen Han** ¹, **Jennifer Astorsdotter** ³ and **Robert Farrauto** ^{1,*}

¹ Earth and Environmental Engineering Department, Columbia University, New York, NY 10027, USA; xh2271@columbia.edu

² Chemical Engineering Department, Columbia University, New York, NY 10027, USA; xiang.wendi@columbia.edu

³ Chemical Engineering for Energy and the Environment Department, KTH Royal Institute of Technology, 10044 Stockholm, Sweden; jennifer.astorsdotter@gmail.com

* Correspondence: rf2182@columbia.edu; Tel.: +1-212-854-6390

Academic Editor: Morris D. Argyle

Received: 31 March 2017; Accepted: 4 May 2017; Published: 8 May 2017

Abstract: Pt-containing catalysts are currently used commercially to catalyze the conversion of carbon monoxide (CO) and hydrocarbon (HC) pollutants from stationary chemical and petroleum plants. It is well known that Pt-containing catalysts are expensive and have limited availability. The goal of this research is to find alternative and less expensive catalysts to replace Pt for these applications. This study found that niobium oxide (Nb_2O_5), as a carrier or support for certain transition metal oxides, promotes oxidation activity while maintaining stability, making them candidates as alternatives to Pt. The present work reports that the orthorhombic structure of niobium oxide (formed at 800 °C in air) promotes Co_3O_4 toward the oxidation of both CO and propane, which are common pollutants in volatile organic compound (VOC) applications. This was a surprising result since this structure of Nb_2O_5 has a very low surface area (about 2 m²/g) relative to the more traditional Al_2O_3 support, with a surface area of 150 m²/g. The results reported demonstrate that 1% $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$ has comparable fresh and aged catalytic activity to 1% Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 1% Pt/ Nb_2O_5 . Furthermore, 6% $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$ outperforms 1% Pt/ Al_2O_3 in both catalytic activity and thermal stability. These results suggest a strong interaction between niobium oxide and the active component—cobalt oxide—likely by inducing an oxygen defect structure with oxygen vacancies leading to enhanced activity toward the oxidation of CO and propane.

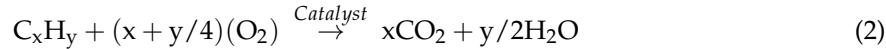
Keywords: cobalt on Nb_2O_5 catalyst; CO and propane oxidation; promoting effects of Nb_2O_5

1. Introduction

Carbon monoxide (CO) is produced by incomplete combustion of carbon-containing fuels. When this deadly toxic gas combines with hemoglobin in blood, oxygen (O₂) cannot be delivered to vital organs essential for life. Propane (C₃H₈) is produced during the process of combusting liquefied petroleum gas, but can also be considered a model of volatile organic compounds (VOCs). An active low-temperature oxidation catalyst has attracted immense attention to meet ever-changing stringent environmental regulations for oxidation of volatile organic compounds in chemical plants, petroleum refineries, pharmaceutical plants, automobile manufacturing, etc. [1,2].

Volatile organic compounds are toxic and mainly contribute to the formation of photochemical smog with a negative impact on air quality [3]. Catalytic oxidation is a main technology used

commercially in their reduction [4,5]. The basic catalytic oxidation reactions of CO (1) and hydrocarbon (C_xH_y) (2) are shown as follows [2]:



Many environmental abatement catalysts are precious metals, such as Pt and Pd, due to their excellent performance and superior life in abating real exhausts. However, their high price is a disadvantage, and therefore alternative materials are always being sought. However, this is very challenging. For low temperature applications, such as VOCs removal in indoor air, transition metal oxides have been proposed as replacements for precious metals [6]. Among transition metal oxides, cobalt oxide (Co_3O_4) shows very high CO oxidation activity in CO/O_2 mixtures even at ambient temperature [7]. Co_3O_4 is also highly effective for the total oxidation of propane under conditions relevant for VOC emission control [8]. Moreover, the elusive “holy grail” for catalytic applications is a precious metal-free catalyst for three-way automobile gasoline exhaust catalysts [9].

It is essential to disperse the catalytic components on a carrier with a high surface area, such as Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , or $SiO_2-Al_2O_3$, in order to maximize active sites available for reactants. Furthermore, supported catalysts are deposited (as washcoats) on high cell density monoliths (ceramic and metal) to minimize pressure drop and volume relative to packed beds [2]. Niobium pentoxide (Nb_2O_5) has been reported to show strong metal support interaction (SMSI) with certain metals [1,10,11]. However, no commercial VOC applications that include Nb_2O_5 are known.

The goal of this study was to investigate Nb_2O_5 's promoting effects on base metal catalysts for CO and propane oxidation. Nb_2O_5 has the ability to form defect structures with oxygen vacancies when combined with base metal oxide materials to enhance catalytic activity [12,13]. The active oxidation state for cobalt is +3 in Co_3O_4 and has been reported to be a prime candidate for precious metal replacement in VOC applications due to its high catalytic activity [14,15]. Retaining Co in the active +3 state will enhance its thermal stability. The current study was designed to further explore the performance of Co supported on Nb_2O_5 and to investigate whether other transition metal oxides combined with Nb_2O_5 could also have a beneficial effect for VOC applications. This feasibility study compared the oxidation performance of Co_3O_4/Nb_2O_5 with traditional Co_3O_4/Al_2O_3 . Furthermore, the study expanded to evaluate other base metal oxides such as iron oxide (Fe_2O_3), copper oxide (CuO), and nickel oxide (NiO), all of which were deposited on Nb_2O_5 relative to Al_2O_3 with the aim to broaden the understanding of the promoting effects of Nb_2O_5 in VOC applications. Finally, the catalytic performance of Co_3O_4/Nb_2O_5 was compared to that of $Pt/\gamma-Al_2O_3$.

The catalytic protocols used in establishing performance characteristics were fresh and aging activity tests. Thermal gravimetric analysis (TGA) was used to establish minimum time and temperature necessary for complete decomposition of precursor to the respective oxides.

2. Result and Discussion

2.1. TGA Results for Precursor of Cobalt (Co)

Thermal gravimetric analysis (TGA) measures the weight change of a material upon heating in various gaseous environments. Figure 1 shows the TGA results of three samples: the precursor $Co(NO_3)_2 \cdot 6H_2O$, the impregnated precursor on carriers, 6% $Co(NO_3)_2/Nb@800$ (the term $Nb@800 =$ pre calcination temperature of Nb_2O_5 at 800 °C in air for 2 h), 6% $Co(NO_3)_2/Al@800$ (pre calcination of Al_2O_3 in air for 2 h). The precursor $Co(NO_3)_2 \cdot 6H_2O$ decomposes completely to Co_3O_4 at about 300 °C where no additional weight loss occurs [16] upon continued heating as shown in Figure 1. The impregnated catalysts also achieve constant weight at 300 °C. Thus, all impregnated catalysts were calcined at 300 °C. The cobalt oxide content was 6% by weight on supported carriers.

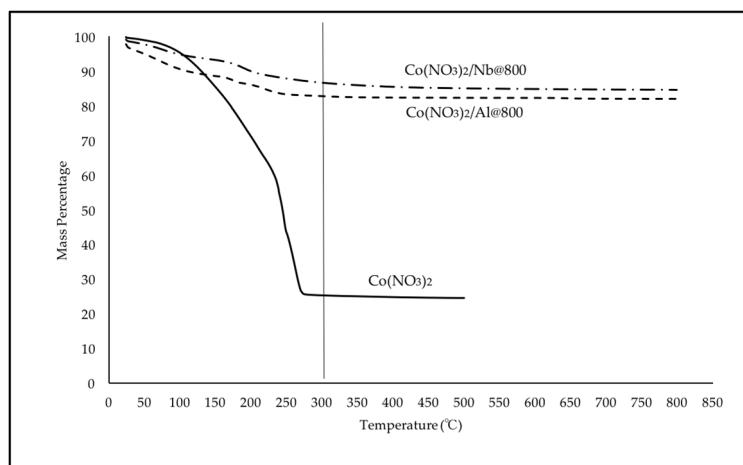


Figure 1. Thermal gravimetric analysis (TGA) tests for the decomposition of the $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and impregnated catalysts $\text{Co}(\text{NO}_3)_2/\text{Nb}@800$ and $\text{Co}(\text{NO}_3)_2/\text{Al}@800$. Both Nb_2O_5 and Al_2O_3 were pre-calcined at $800\text{ }^\circ\text{C}$ for 2 h in air. The supported catalysts were prepared to give 6% cobalt oxide.

2.2. Preparative Details of Co/Nb and Co/Al

2.2.1. Pre-Calcination Temperature of Carriers Nb_2O_5 and Al_2O_3

Nb_2O_5 has different crystal phases at different temperature [17]. The pre-calcination temperature affects the crystal phase of Nb_2O_5 , which in turn affects the chemical and physical properties of Nb_2O_5 . The structure of Al_2O_3 is similarly affected. The monohydrate and tri-hydrate alumina structures change as a function of the temperature ($^\circ\text{C}$) in air [18]. The impact of pre-calcination temperature on carriers and final catalysts were therefore explored.

All carriers were pre-calcined at specified temperatures for 2 h in air. After pre-calcination of the carriers, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was deposited on each carrier and calcined at $300\text{ }^\circ\text{C}$ in air for 2 h to give 6% Co@300/Nb and 6% Co@300/Al. This nomenclature indicates 6% cobalt oxide calcined at $300\text{ }^\circ\text{C}$ after deposited on Nb_2O_5 or Al_2O_3 .

Table 1 demonstrates catalytic performances of fresh catalysts of 6% Co/Nb with different pre-calcination temperatures of Nb_2O_5 . In Table 1, all carriers were Nb_2O_5 pre-calcined from $500\text{ }^\circ\text{C}$ to $900\text{ }^\circ\text{C}$. T_{20} , T_{50} and T_{90} values (temperature for 20%, 50% and 90% conversion) are compared. T_{20} and T_{50} are indicative of chemical kinetic control, while T_{90} often reflects some pore diffusion control. It is clear that Co on Nb@700 and Nb@800 show better catalytic performance of CO oxidation with the Nb@800 showing the best performance.

Table 1. Six percent Co@300/Nb with the number following @ = pre-calcination temperatures of the carrier for CO oxidation.

Catalyst	T_{20} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)	T_{90} ($^\circ\text{C}$)
6% Co@300/Nb@500	190	200	220
6% Co@300/Nb@700	150	155	160
6% Co@300/Nb@800	130	145	160
6% Co@300/Nb@900	130	155	185

Table 2 provides catalytic results of fresh 6% Co/Al with different pre-calcination temperatures of Al_2O_3 . The T_{20} , T_{50} and T_{90} indicate that Al@800, pre-calcined at $800\text{ }^\circ\text{C}$, yielded the best results.

Table 2. Six percent Co/Al with @ = pre-calcination temperatures of the carrier for CO oxidation.

Catalyst	T ₂₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
6% Co@300/Al@500	205	225	245
6% Co@300/Al@700	200	215	-
6% Co@300/Al@800	185	205	240
6% Co@300/Al@900	215	240	270

One can conclude that the optimal pre-calcination temperature for both Nb₂O₅ and Al₂O₃ was 800 °C. Therefore, both Nb₂O₅ and Al₂O₃ were pre-calcined at 800 °C for all experiments conducted henceforth.

Further, Figure 2 compares the activity of cobalt catalysts as a function of the pre-calcination temperature of the two carriers. Clearly, 6% Co@300/Nb@800 yielded the best performance of all for CO oxidation.

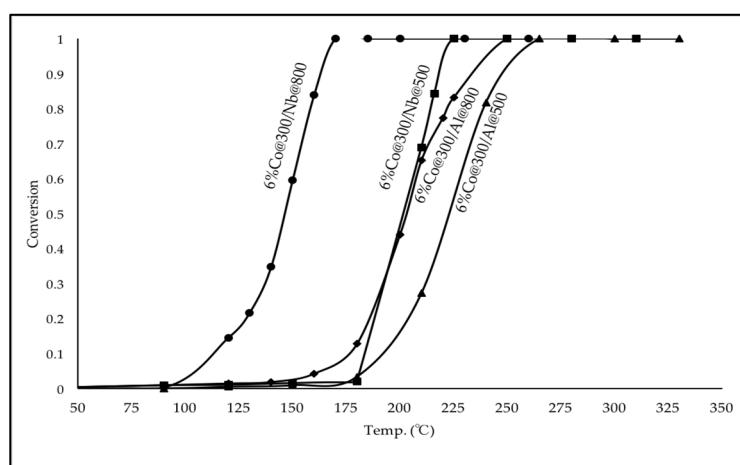


Figure 2. Six percent Co@300/Nb@800, 6% Co@300/Nb@500, 6% Co@300/Al@800 and 6% Co@300/Al@500 for CO oxidation. Both Nb@800 and Al@800 were pre-calcined at 800 °C for 2 h in air, and both Nb@500 and Al@500 were pre-calcined at 500 °C for 2 h in air. All four impregnated catalysts were calcined at 300 °C for 2 h in air. Gas composition: CO 1.5 vol %; O₂ 14.5 vol %, N₂ 84 vol %. Catalysis volume: 0.1 mL; GHSV: 64,800 (h⁻¹).

To further quantify the advantages offered by fresh 6% Co@300/Nb@800 relative to fresh 6% Co@300/Al@800 turn over frequencies (TOF) are presented in Table 3 for different temperatures.

$$T = \frac{(\text{gram of CO}) \cdot (\text{fractional conversion of CO})}{\text{gram of } \text{Co}_3\text{O}_4}$$

Table 3. Turnover Frequencies (TOF) for CO oxidation for fresh 6% Co@300/Nb@800 relative to fresh 6% Co@300/Al@800.

Catalyst	TOF@150 °C (h ⁻¹ × 10 ⁵)	TOF@170 °C (h ⁻¹ × 10 ⁵)	TOF@190 °C (h ⁻¹ × 10 ⁵)	TOF@210 °C (h ⁻¹ × 10 ⁵)
6% Co@300/Nb@800	897.8	1508	1508	1508
6% Co@300/Al@800	53.48	129.9	496.6	1241

2.2.2. Catalytic Performance of Fresh and Aged Co Catalysts for CO Oxidation

Based on the data in Tables 1–3, the pre-calcination temperature of carriers was set at 800 °C with the precursor decomposition at 300 °C for 2 h in air.

Figure 3 shows that fresh 6% Co@300/Nb@800 outperforms fresh 6% Co@300/Al@800 for CO oxidation over the entire conversion-temperature profile including the kinetic control regime up to fractional conversion approaching of 1.0 (100% conversion). Catalytic performance of each catalysts aged at 400 °C for 12 h in reaction gases is also shown in this figure. This temperature is approximately the maximum experienced in abating VOC from some stationary chemical plants. Clearly, 6% Co@300/Nb@800 outperformed its counterpart however, both catalysts suffered some deactivation after aging. Six percent Co@300/Nb@800 seemed to experience some reaction rate limited by pore diffusion (slightly lower slope at T₅₀ region), while the chemical kinetic control region (T₂₀) was not affected. For 6% Co@300/Al@800 both kinetic control (T₂₀ region) and pore diffusion control (T₅₀ region) were negatively affected as evidenced by the large shift to higher temperature and the decrease in their respective slopes. One can speculate that the shift to higher temperature and a slightly lower slope reflects a loss of accessibility to the Co active sites due to its reaction rate limited by pore diffusion.

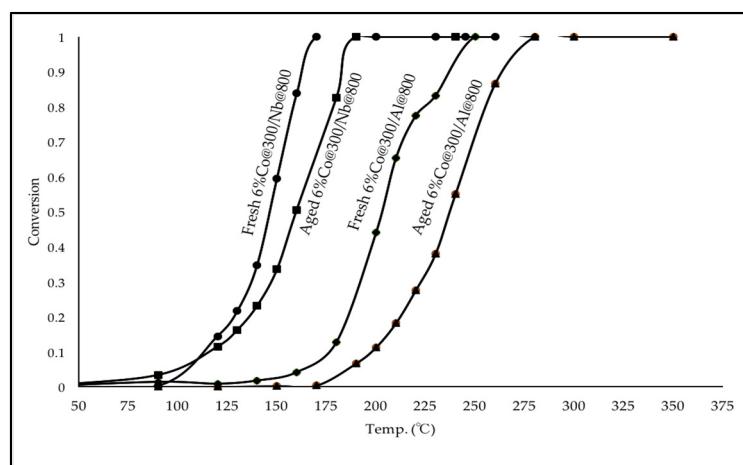


Figure 3. Fresh 6% Co@300/Nb@800, aged 6% Co@300/Nb@800, fresh 6% Co@300/Al@800 and aged 6% Co@300/Al@800 for CO oxidation. Aging was conducted at 400 °C for 12 h with reaction gases flowing. Gas composition: CO 1.5 vol %; O₂ 14.5 vol %, N₂ 84 vol %. Catalysis volume: 0.1 mL; GHSV: 64,800 (h⁻¹).

2.3. Various Loadings of Co₃O₄ Supported on Nb₂O₅

2.3.1. Catalysts with Various Co₃O₄ Loadings: Propane Oxidation

Various Co₃O₄ loadings were studied to optimize Co₃O₄ content. The oxidation of propane was used as the metric because it is more difficult to oxidize than CO. In Figure 4 (left), three fresh catalysts with cobalt contents, 1%, 3%, and 6% are compared. All three completed propane oxidation up to 400 °C. Not surprisingly 6% Co@300/Nb@800 shows the best catalytic performance. The sensitivity of performance to cobalt loading confirms that the activity is in the kinetic regime suitable for activity comparison.

In Figure 4 (right), all cobalt oxides on niobium oxide were aged at 400 °C for 12 h in reaction propane gas.

Detailed information of these Co@300/Nb@800 are provided in Table 4. It is clear that 6% Co@300/Nb@800 presents the lowest T₂₀, T₅₀, and T₉₀ over the entire conversion profile.

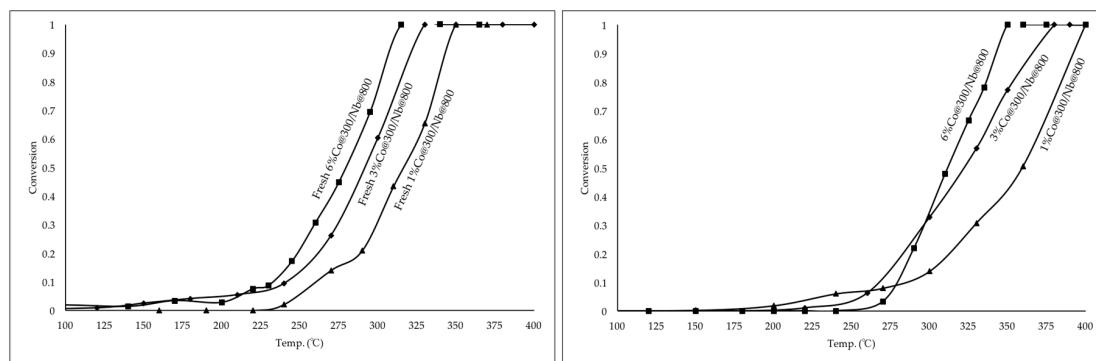


Figure 4. Fresh Co@300/Nb@800 with loadings of 1%, 3%, and 6%, for propane oxidation (**left**); aged Co@300/Nb@800 for propane oxidation (**right**). Aging was conducted at 400 °C with reaction gases for 12 h. Gas composition: C₃H₈ 0.1 vol %, O₂ 18.9 vol %, N₂ 81 vol %. Catalysis volume: 0.1 mL, GHSV: 64,800 (h⁻¹).

Table 4. Co@300/Nb@800 with various cobalt loadings for propane oxidation: fresh and aged.

Catalyst	T ₂₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
Fresh 6% Co@300/Nb@800	250	280	305
Aged 6% Co@300/Nb@800	290	310	340
Fresh 3% Co@300/Nb@800	260	270	310
Aged 3% Co@300/Nb@800	285	320	360
Fresh 1% Co@300/Nb@800	290	315	345
Aged 1% Co@300/Nb@800	315	355	390

2.3.2. Propane Oxidation with and without Moisture

Results for both fresh 6% Co@300/Nb@800 and 6% Co@300/Al@800, are presented in Figure 5. Once again, the superiority of fresh 6% Co@300/Nb@800 relative to the baseline 6% Co@300/Al@800 is demonstrated.

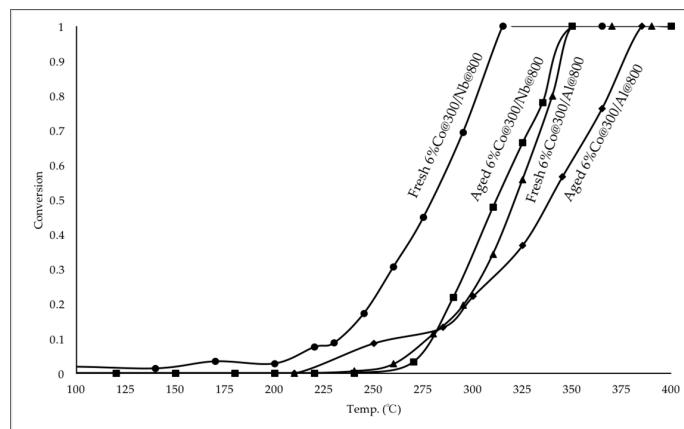


Figure 5. Fresh and aged 6% Co@300/Nb@800 and 6% Co@300/Al@800 for propane oxidation. Aging was conducted at 400 °C with reaction gases for 12 h. Gas composition: C₃H₈ 0.1 vol %, O₂ 18.9 vol %, N₂ 81 vol %. Catalysis volume: 0.1 mL, GHSV: 64,800 (h⁻¹).

Moisture (from upstream combustion) is always present and typically has a poisoning or inhibiting effect on the performance of the catalyst. Tests were conducted with a feed containing 5% H₂O (steam) for both 6% Co@300/Nb@800 and 6% Co@300/Al@800. In Figure 6, fresh and aged 6% Co@300/Nb@800 and 6% Co@300/Al@800 are compared for propane oxidation with 5% H₂O

present. 6% Co@300/Nb@800 retains much of its activity, and is far more resistant to deactivation than 6% Co@300/Al@800. However, moisture does inhibit 6% Co@300/Nb@800, but far less than for the 6% Co@300/Al@800.

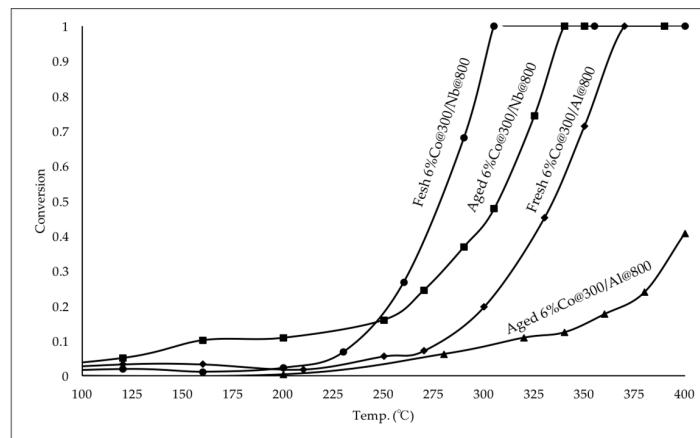


Figure 6. Fresh and aged 6% Co@300/Nb@800 and 6% Co@300/Al@800 for propane oxidation with moisture. Aging test was conducted at 400 °C with reaction gases for 12 h. Gas composition with H₂O 5 vol %, C₃H₈ 0.1 vol %, O₂ 17.85 vol %, N₂ 77.05 vol %. Catalysis volume: 0.1 mL, GHSV: 64,800 (h⁻¹).

This figure also demonstrates the obvious advantage of 6% Co@300/Nb@800 over 6% Co@300/Al@800 when both catalysts were aged for 12 h in feed gas containing H₂O at 5 vol %. The aged 6% Co@300/Al@800 lost the majority of its active sites achieving only about 40% (0.4) conversion at 400 °C. Aged 6% Co@300/Nb@800 showed significant catalytic activity even after being aged in steam containing reaction gas at 400 °C for 12 h.

2.4. Comparison of Co₃O₄ and Pt for Propane Oxidation

The state of the art catalyst used in VOC abatement is typically 1% Pt/Al₂O₃. For the purpose of a practical application, the behavior of 1% Co@300/Nb@800 and 6% Co@300/Nb@800 was compared with 1% Pt/Nb@800 and 1% Pt/Al@800 for propane oxidation. The result shown in Figure 7 (left) indicates that 6% Co@300/Nb@800 shows a performance advantage over 1% Pt@500/Nb@800 and 1% Pt@500/Al@800. Some advantage for 1% Co@300/Nb@800 is noted at both low and higher conversions however, diffusional effects may be operative. 1% Pt@500/Nb@800 shows no advantage over 1% Pt@500/Al@800. Figure 7 (right) shows results of 1% Co@300/Nb@800, 6% Co@300/Nb@800 and 1% Pt@500/Nb@800 subjected to aging test at 400 °C for 12 h in air. The 6% cobalt system suffers slightly, relative to the Pt system, at light off but recovers its performance advantage as 100% conversion is approached. From these encouraging results, monolith-supported catalysts will be prepared in the future and comparison extended closer to an actual system.

Tables 5 and 6 exhibit T₂₀, T₅₀, and T₉₀ of Co catalysts and Pt catalysts showed in Figure 7. The advantages 6% Co@300/Nb@800 over 1% Pt@500/Nb@800 are clear to see.

Table 5. T₂₀, T₅₀, and T₉₀ of fresh Co catalysts and Pt catalysts for propane oxidation.

Catalysts	T ₂₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
6% Co@300/Nb@800	250	280	305
1% Co@300/Nb@800	290	315	345
1% Pt@500/Nb@800	275	325	370
1% Pt@500/Al@800	275	340	370

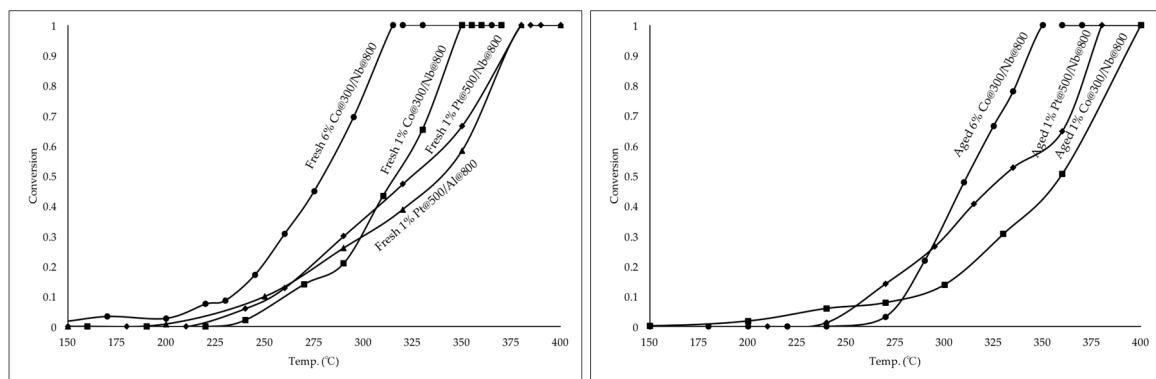


Figure 7. Fresh cobalt oxide catalyst and fresh platinum catalyst for propane oxidation (**left**); aged cobalt oxide and aged platinum on niobium oxide for propane oxidation (**right**). Impregnated platinum catalysts were calcined at 500 °C. Aging was conducted at 400 °C with reaction gases for 12 h. C₃H₈ 0.1 vol %, O₂ 18.9 vol %, N₂ 81 vol %. Catalysis volume: 0.1 mL; GHSV: 64,800 (h⁻¹).

Table 6. T₂₀, T₅₀, and T₉₀ of aged Co catalysts and Pt catalysts for propane oxidation.

Catalysts	T ₂₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)
6% Co@300/Nb@800	290	310	340
1% Co@300/Nb@800	315	355	390
1% Pt@500/Nb@800	290	335	375

2.5. Other Base Metal Oxides for Propane Oxidation

Based on the encouraging results with 6% Co@300/Nb@800 for both CO and C₃H₈ the study was expanded to include nickel (Ni), copper (Cu) and iron (Fe) each deposited on Nb@800 and Al@800. A comparison is shown in Figure 8 (left) for propane oxidation. All four base metal oxides were prepared with a loading of 6% on Nb@800. It is clear that Co₃O₄ on Nb₂O₅ has lowest light-off and full oxidation performance. Aging for 12 h at 400 °C in reacting gases also showed the superiority of the cobalt system. Figure 8 (right) shows results that Nb₂O₅ has a much greater promoting effects on Co₃O₄ than on NiO.

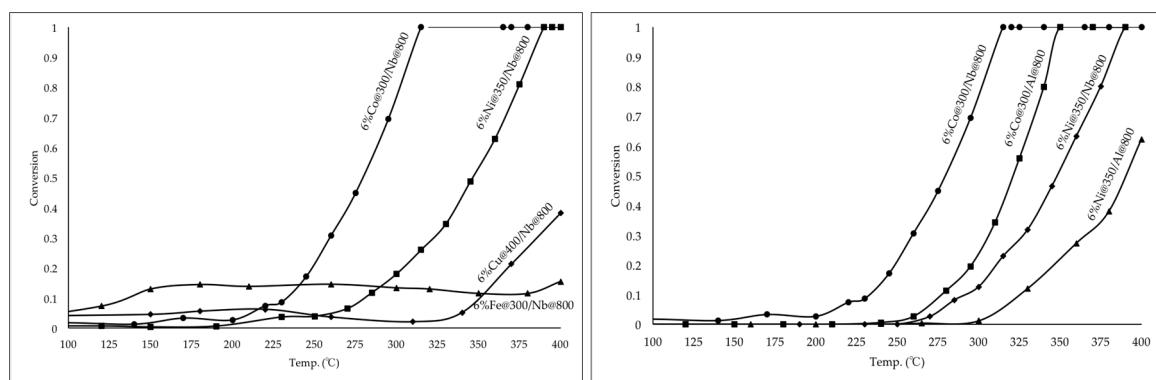


Figure 8. Different metal oxides (6%) on Nb@800 for propane oxidation (**left**); 6% Co₃O₄ and 6% NiO on different carriers for propane oxidation (**right**). The iron catalysts were calcined at 300 °C, impregnated nickel catalysts were calcined at 350 °C, and impregnated copper catalysts were calcined at 400 °C. C₃H₈ 0.1 vol %, O₂ 18.9 vol %, N₂ 81 vol %. Catalyst volume: 0.1 mL; GHSV: 64,800 (h⁻¹).

2.6. Cobalt Oxide Catalyst Characterization

BET Tests for Catalysts and Carriers

Surface area of the carrier is among the most fundamentally important properties in catalysis because the active sites are present or dispersed throughout the internal surface through which reactants and products are transported [2]. Quantachrome ChemBET Pulsar TPR/TPD is used to measure surface area of Al_2O_3 and Nb_2O_5 .

A 50 mg sample is used for Al_2O_3 and 6% $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$; 200 mg sample is used for Nb_2O_5 and 6% $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$. Figure 9 shows that Nb_2O_5 pre-calcined at 500 °C has a surface area of $53 \text{ m}^2/\text{g}$. When pre-calcined at 700 °C, Nb_2O_5 has a surface area decrease to $5 \text{ m}^2/\text{g}$, while at 800 °C it, decreased to $2 \text{ m}^2/\text{g}$. Meanwhile, Al_2O_3 has a 100 times larger surface area than Nb_2O_5 . After pre-calcined at 800 °C Al_2O_3 still has a surface area of about $120 \text{ m}^2/\text{g}$. Nb_2O_5 has no surface area stability advantages over Al_2O_3 , indicating some other interaction of Nb_2O_5 and Co_3O_4 gives rise to the enhancement of activity. In Figure 10 (left), when 6% Co_3O_4 is impregnated onto Nb_2O_5 , the total surface area increases. But the final surface area is still very small compared to the surface area of Al_2O_3 . Figure 10 (right) shows no change in surface area after Co impregnation.

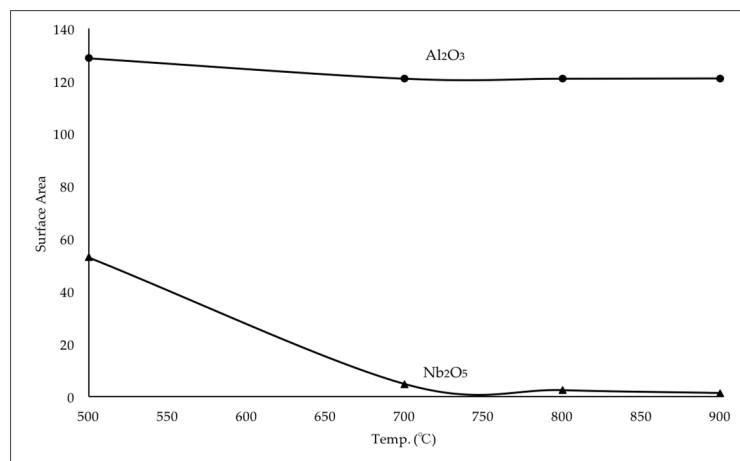


Figure 9. Surface area of Al_2O_3 and Nb_2O_5 pre-calcined at different temperatures. BET test was conducted on Quantachrome ChemBET Pulsar TPR/TPD carrier gas is 30% N_2/He .

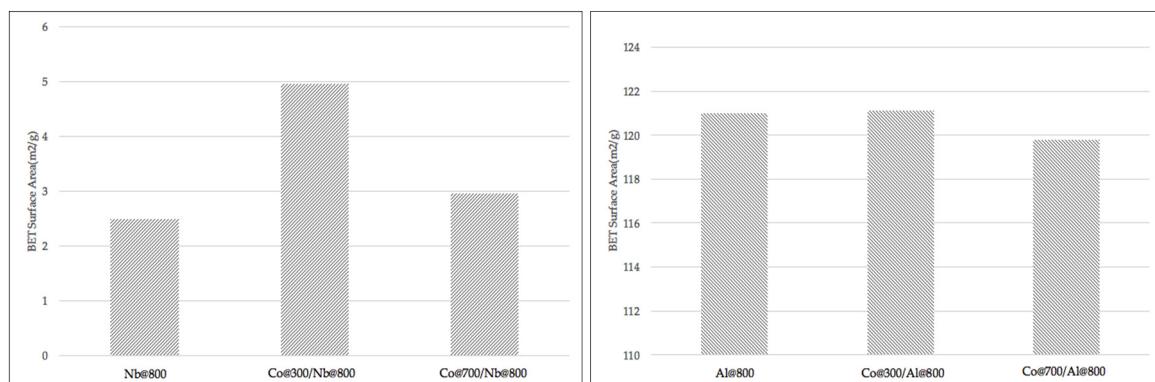


Figure 10. Comparison between $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$ and Nb_2O_5 (left); comparison between $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ and Al_2O_3 (right). BET test was conducted on Quantachrome ChemBET Pulsar TPR/TPD, carrier gas is 30% N_2/He .

3. Materials and Methods

3.1. Carrier Preparation

Niobium Oxide Hydrate ($\text{Nb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$) was received from CBMM Brazil (Sao Paolo, Brazil). Alumina (gamma- Al_2O_3) was provided by BASF (Iselin, NJ, USA). Both Nb_2O_5 and Al_2O_3 were pre-calcined at various temperatures prior to deposition of cobalt nitrate hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$).

3.2. Catalyst Preparation

Incipient wetness was used for metal impregnations. In order to determine the required volume to fill the pores, water was slowly added to the calcined carrier until saturation was achieved. The precursor salt was dissolved in this precise amount of water, which was then added to the carrier. It was dried in air at 130 °C for one hour and then calcined in air to various temperatures as shown in the Results and Discussion section.

3.2.1. Co-Containing Catalyst Preparation

The cobalt nitrate impregnated catalyst was dried at 130 °C for 1 h in air to remove all the water and then calcined at 300 °C in air to completely decompose the precursor salt for 2 h. The heating rate was 10 °C/min. Cobalt catalysts were prepared with loadings from 1%, 3% to 6% on both carriers. Percentages are based on the metal oxide component.

3.2.2. Pt-Containing Catalysts Preparation

A water soluble platinum amine salt, which is alkali and halide free, provided by BASF (Iselin, NJ, USA), was used for preparation of the Pt catalyst using incipient wetness. 1% Pt/ Nb_2O_5 and 1% Pt/ Al_2O_3 were prepared with the 800 °C pre-calcined carriers. Drying was accomplished 130 °C in air and the final calcination at 500 °C for 2 h in air at a heating rate of 10 °C/min.

3.3. Reactor Test

3.3.1. Reactor Preparation

The 0.1 mL (about 0.08–0.09 g) of finished catalyst was uniformly mixed with about 0.75 g of diluent quartz to maintain the bed temperature approximately constant. Air and propane (1% C_3H_8 in N_2) were introduced into the reactor. The reactor quartz tubing was 10.5 mm (ID) × 12.75 mm (OD) with a length of 50 cm with XC-course quartz frit provided by Quartz Scientific, Inc. Harbor, OH, USA to support the catalyst.

3.3.2. Reactor Gas Flow Rate

The volume of catalyst used for all experiments was 0.1 mL and the total volumetric flow rate was 108 mL/min. Thus the GHSV was set at 64,800 h^{-1} .

$$\text{GHSV} = \frac{\text{Flow Rate (STP)}}{\text{Catalyst Volume}} = \frac{108 \text{ mL/min}}{0.1 \text{ mL}} = 1080 \text{ min}^{-1} = 64,800 \text{ h}^{-1}$$

Reactor Gas Flow without Steam for CO Oxidation

21% O_2/N_2 with flow rate 75 mL/min and 4.94% CO/N_2 with flow rate 33 mL/min was used as reactant gases. Flow rates are measured at room temperature of 25 °C and pressure of 1 atm. The GHSV here is: 64,800 h^{-1} . Rotameters were calibrated with a soap film bubble meter and used to control flow rates.

Reactor Gas Flow without Steam for Propane Oxidation

21% O₂/N₂ at flow rate of 97.2 mL/min and 1% C₃H₈/N₂ at a flow rate of 10.8 mL/min was used as reactant gases giving C₃H₈ = 0.1% C₃H₈ or 1000 ppm. All flow rates were measured at room temperature of 25 and pressure of 1 atm. The GHSV here was: 64,800 h⁻¹. Rotameters were calibrated with a soap film bubble meter and used to control flow rates.

Reactor Gas Flow with Steam for Propane Oxidation

Twenty-one percent O₂/N₂ at a flow rate of 91.8 mL/min, 1% C₃H₈/N₂ at a flow rate of 10.8 mL/min and H₂O (steam) was introduced giving a flow rate of 5.4 mL/min. This gives 0.1% C₃H₈ with 5% steam and balance air. Liquid water was injected into the reactor connected into a heated transfer line. The heating tape was set at 150 °C; sufficiently high to generate a homogenous gaseous mixture. The GHSV here is 64,800 h⁻¹. Rotameters were calibrated with a soap film bubble meter and used to control flow rate.

3.4. Data Management

3.4.1. Data Acquisition

Catalytic oxidations were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. A cold trap was placed at the outlet to condense water produced during the reaction prior to entering the gas chromatography (GC). Effluent gases of O₂, CO, CO₂, C₃H₈ and N₂ were analyzed by the micro GC. The temperature of the catalyst bed was measured by a K-type thermocouple and controlled by Omega CN7800 series temperature controller. An INFICON 3000 Micro GC, East Syracuse, NY, USA was used to analyze gas composition. Five single runs were conducted at each temperature. The GC was calibrated using 4 different certified standard gases before measurement.

3.4.2. Data Processing

Raw data from the GC was managed and analyzed in Excel to obtain plots of conversion as a function of temperature. The inlet catalyst temperature was increased and held until steady conversion was achieved. The temperature was controlled by a thermocouple located inside the reactor immediately above the catalyst inlet and connected to the MELLEN TEMPERATURE CONTROLLER. The temperature was increased in increments of 10 °C and the conversion measured.

Conversion of CO and C₃H₈ oxidation at each temperature point is as follows:

$$CO(Conversion)\% = \frac{CO_{(initial)} - CO_{(exit)}}{CO_{(initial)}} \times 100\% \quad (3)$$

$$C_3H_8(Conversion)\% = \frac{C_3H_8_{(initial)} - C_3H_8_{(exit)}}{C_3H_8_{(initial)}} \times 100\% \quad (4)$$

The oxidation reaction of CO and C₃H₈ to CO₂ is as follows:



3.5. Aging Test

The aging temperature was maintained at 400 °C for 12 h in the reactant gases, followed by the generation of a conversion vs. temperature profile.

4. Conclusions

The pre-calcination temperature of the Nb_2O_5 carrier of 800 °C with cobalt calcined at 300 °C gives the best fresh and aged performance for both CO and propane oxidation. Nb_2O_5 shows a significant advantage over Al_2O_3 as the carrier. Six percent Co@300/Nb@800 has better fresh catalytic performance, higher thermal stability and greater resistance to steam than its counterpart, 6% Co@300/Al@800. $\text{Co}_3\text{O}_4/\text{Nb}_2\text{O}_5$ demonstrates increasing catalytic performance with Co_3O_4 loading from 1% to 6%. 6% Co@300/Nb@800 outperforms 1% Pt@500/Nb@800 for both fresh and aged states. Nb_2O_5 promotes Co_3O_4 and fresh NiO. However there is no advantage for CuO and Fe_2O_3 compared to the traditional Al_2O_3 carrier. Additionally, 6% Ni@350/Nb@800 has poor thermal stability relative to 6% Co@300/Nb@800. Therefore, 6% Co@300/Nb@800 is a viable candidate for replacing 1% Pt@500/Al@800 even though some small decrease in GHSV may be necessary to insure equal performance. However, this will not negatively affect the cost advantage of Co_3O_4 compared to Pt-containing catalysts. Naturally, candidate catalysts must be deposited on monolith and subjected to real VOC feed streams before a definitive recommendation can be made regarding replacement for Pt.

Acknowledgments: The authors are indebted to CBMM, San Paolo, Brazil, for their financial support. The authors especially want to thank Rogerio Ribas of CBMM and Robson Monteiro of Catalysis Consultoria Ltda for valuable contributions throughout these studies.

Author Contributions: Wendi Xiang designed the experiments under instruction of Robert J. Farrauto. Xiaochen Han conducted most of the propane experiments, and Jennifer Astorsdotter conducted most of the CO experiments. Both Wendi Xiang and Xiaochen Han analyzed the data and prepared this paper. Robert J. Farrauto is the only advisor for this research and contributed substantially to the editing of this paper.

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

References

1. Leung, E.; Shimizu, A.; Barmak, K.; Farrauto, R. Copper oxide catalyst supported on niobium oxide for CO oxidation at low temperatures. *Catal. Commun.* **2017**. [[CrossRef](#)]
2. Heck, R.M.; Farrauto, R.J.; Gulati, S.T. *Catalytic Air Pollution Control: Commercial Technology*, 3rd ed.; John Wiley and Sons: Hoboken, NJ, USA, 2012.
3. Liotta, L.F. Catalytic oxidation of volatile organic compounds on supported noble metals. *Appl. Catal. B Environ.* **2010**, *100*, 403–412. [[CrossRef](#)]
4. Spivey, J.J. Complete catalytic oxidation of volatile organics. *Ind. Eng. Chem. Res.* **1987**, *26*, 2165–2180. [[CrossRef](#)]
5. Duprez, D.; Cavani, F. *Handbook of Advanced Methods and Processes in Oxidation Catalysis “from Laboratory to Industry”*; Imperial College Press: London, UK, 2014; Chapters 1–8.
6. Busca, G.; Daturi, M.; Finocchio, E.; Lorenzelli, V.; Ramis, G.; Willey, R.J. Transition metal mixed oxides as combustion catalysts: Preparation, characterization and activity mechanisms. *Catal. Today* **1997**, *33*, 239–249. [[CrossRef](#)]
7. Thormahlen, P.; Thormählen, P.; Skoglundh, M.; Fridell, E.; Andersson, B. Low-Temperature CO Oxidation over Platinum and Cobalt Oxide Catalysts. *J. Catal.* **1999**, *188*, 300–310. [[CrossRef](#)]
8. Solsona, B.; Vázquez, I.; Garcia, T.; Davies, T.E.; Taylor, S.H. Complete oxidation of short chain alkanes using a nanocrystalline cobalt oxide catalyst. *Catal. Lett.* **2007**, *116*, 116–121. [[CrossRef](#)]
9. Glisenti, A.; Pacella, M.; Guiotto, M.; Natile, M.M.; Canu, P. Largely Cu-doped $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ perovskites for TWC: Toward new PGM-free catalysts. *Appl. Catal. B Environ.* **2016**, *180*, 94–105. [[CrossRef](#)]
10. Tauster, S.J.; Fung, S.C.; Baker, R.T.; Horsley, J.A. Strong interactions in supported-metal catalysts. *Science* **1981**, *211*, 1121–1125. [[CrossRef](#)] [[PubMed](#)]
11. Hu, Z.; Nakamura, H.; Kunimori, K.; Asano, H.; Uchijima, T. Ethane hydrogenolysis and hydrogen chemisorption over niobia-promoted rhodium catalysts: A new phase by a strong rhodium-niobia interaction. *J. Catal.* **1988**, *112*, 478–488. [[CrossRef](#)]
12. Leung, E.; Lin, Q.; Farrauto, R.J.; Barmak, K. Oxygen storage and redox properties of Nb-doped $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3$ solid solutions for three-way automobile exhaust catalytic converters. *Catal. Today* **2016**, *277*, 227–233. [[CrossRef](#)]

13. Sasaki, K.; Zhang, L.; Adzic, R.R. Niobium oxide-supported platinum ultra-low amount electrocatalysts for oxygen reduction. *Phys. Chem. Chem. Phys. PCCP* **2008**, *10*, 159–167. [[CrossRef](#)] [[PubMed](#)]
14. Sun, Y.; Lv, P.; Yang, J.Y.; He, L.; Nie, J.C.; Liu, X.; Li, Y. Ultrathin Co₃O₄ nanowires with high catalytic oxidation of CO. *Chem. Commun.* **2011**, *47*, 11279–11281. [[CrossRef](#)] [[PubMed](#)]
15. Xie, X.; Li, Y.; Liu, Z.-Q.; Haruta, M.; Shen, W. Low-temperature oxidation of CO catalysed by Co₃O₄ nanorods. *Nature* **2009**, *458*, 746–749. [[CrossRef](#)] [[PubMed](#)]
16. Ehrhardt, C.; Gjikaj, M.; Brockner, W. Thermal decomposition of cobalt nitrate compounds: Preparation of anhydrous cobalt (II) nitrate and its characterisation by Infrared and Raman spectra. *Thermochim. Acta* **2005**, *432*, 36–40. [[CrossRef](#)]
17. Yan, L.; Rui, X.; Chen, G.; Xu, W.; Zou, G.; Luo, H. Recent advances in nanostructured Nb-based oxides for electrochemical energy storage. *Nanoscale* **2016**, *8*, 8443–8465. [[CrossRef](#)] [[PubMed](#)]
18. Wefers, K.; Misra, C. *Oxides and Hydroxides of Aluminum*; Alcoa Laboratories: East Saint Louis, IL, USA, 1987.



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).