Pollutant Abatement of Nitrogen-Based Fuel Effluents over Mono- and Bimetallic Pt/Ru Catalysts

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Supporting Information

ABSTRACT: Mono- and bimetallic alloy Pt and Ru catalysts supported on γ-Al2O3 have been investigated for the reduction of pollutants (NOx, NH3, and CO) generated during the continuous combustion of an aqueous urea ammonium nitrate fuel. A Pt/Ru alloy with a Pt25/Ru75 atomic ratio has been found to have higher activity and selectivity than those of a 50/50 alloy and monometallic catalysts. Among monometallic catalysts, Ru was more selective toward N2 formation, whereas Pt showed a higher selectivity toward NH3 formation. For Ru, it was observed that the oxidizing atmosphere of NOx pollutants caused the formation of RuO2, whereas Ru in the Pt/Ru alloy was stable under these conditions. Temperature (250–500 °C) and pressure (1–8 MPa) studies over Ru and 25/75 Pt/Ru have concluded that the alloy catalyst at 400 °C and 5 MPa reduced the pollutants to a minimum level with high yields of N2 (99.7%) and CO2 (99.9%). It was also observed that the 25/75 Pt/Ru catalyst remained stable up to 100 h of thermal treatment at 400 °C. Minimal pollutants were obtained at a weight hourly space velocity = 11 822 h⁻¹. Characterization studies of the spent catalyst showed that metal particles were sintered over a period of time (8 h) and the γ-Al2O3 support was transformed into θ- and α-phases under the hydrothermal reaction conditions.

1. INTRODUCTION

Fossil fuels, formed during the course of hundreds of millions of years, are fundamental building blocks of our civilization. Nevertheless, their consumption at an ever rising rate has devastating effects on the environment and climate. The extraction and combustion of fossil fuels inevitably release tremendous amounts of CO2, NOx and volatile organic compound particles and other pollutants to the atmosphere. With increasing global greenhouse gas emission, there is urgency to pursue all measures to develop and deploy carbon-neutral energy technologies. Therefore, one of the most significant scientific challenges that our society must address is the development of a secure and sustainable energy economy. Hydrogen is often considered as a promising environmentally friendly fuel, but it cannot become the direct energy coin due to safety issues, low volumetric energy density, and costly infrastructure. A more favorable approach is to chemically store hydrogen in the form of more condensed compounds such as chemical fuels via carbon or nitrogen as the main hydrogen carriers. The carbon-based economy is well-established; however, the nitrogen-based analogue is not sufficiently studied. In such an economy, nitrogen-based fuels can be used as means of energy storage and production. Recently, a nitrogen-based fuel consisting of an aqueous solution of ammonium nitrate (AN) with urea as a reducing additive was suggested. The AN-based fuels (e.g., urea ammonium nitrate (UAN)) are monofuels because they contain the oxidizer (nitrate ion) as well as the reducer (ammonium ion and urea) in the same solution. Consequently, no external oxidizer such as atmospheric oxygen is required for their combustion. A recent study of aqueous UAN fuels was reviewed elsewhere. These fuels are nontoxic, nonflammable, nonexplosive, and chemically stable and hence safe to handle and transport. The aqueous UAN fuel has a volumetric energy density of 4.4 GJ m⁻³, which is equivalent to that of compressed natural gas at 10 MPa. Hence, aqueous UAN may be suitable for stationary power plant applications. The desired environmentally friendly combustion of aqueous UAN (reaction R1) produces H2O, N2, and small amounts of CO2. Noncatalytic steady-state experiments were carried out to investigate the fuel combustion at several flow rates and working pressures. It was observed that NOx emission (128 mg MJ⁻¹) from a UAN fuel at pressures above 15 MPa was lower than the regulation standard for power generation.

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\begin{align*}
\text{AN} + \text{urea} + 5.56\text{H}_2\text{O}(l) & \rightarrow 13.56\text{H}_2\text{O}(l) + 4\text{N}_2(g) + \text{CO}_2(g) \\
\Delta H_{\text{rxn}} &= -437 \text{ kJ mol}^{-1}
\end{align*}
\]

(R1)

Side reactions may release pollutants during UAN combustion such as nitrogen oxides (NO2, NO, and N2O) and CO, which can be a major cause for ozone depletion, acid rain, greenhouse effect, and photochemical smog. Nitrous oxide is a...
greenhouse gas with a life time of 150 years in the atmosphere and has a global warming potential (GWP) of 310 times that of CO2. Hence, further pollutant abatement (e.g., NOx, NH3, and CO) is required by a postcombustion catalytic process to ensure a green fuel operation. Therefore, it is essential to develop advanced technologies and seek better catalysts to guarantee low pollutant emission during UAN fuel combustion.

Catalytic reduction of NOx and CO on supported metal catalysts is an active field. In some cases, during NOx conversion, NH3 and N2O were found to form as undesirable byproducts. A large variety of catalysts were studied for the decomposition of N2O, including transition metals (Fe, Cu, Co, and Ni) and noble metals (Pd, Ru, and Rh). These catalysts are supported on metal oxides (SiO2, Al2O3, ZrO2, CaO, TiO2, CeO2, and Fe2O3), perovskites, hydrotalcites, zeolites (ZSM-5, USY, BEA, and ferrierite), and mesoporous materials (MCM-41 and SBA-15). The noble metals were preferred to other transition metals due to their superior activity and selectivity toward N2 formation. However, Ru has the disadvantage of getting oxidized in an oxidizing environment. Water also deactivates Ru catalysts; however, the activity can be restored at higher temperatures (>479 °C) by the desorption of water from the active sites. Among various formulations of catalysts including Pt, Ag, Pd, Au, Rh, Cu, Ni, and Co, Pt-based catalysts showed an excellent performance for NOx conversion to NH3 even at low temperatures and were less selective to N2 formation. Unfortunately, these catalysts had a narrow temperature operating window. Improving the catalyst stability and selectivity toward NOx and NH3 reduction requires the design of noble metal bimetallic catalysts.

Bimetallic catalysts were widely preferred over monometallic analogues due to their dual functionality. It has been reported that a bimetallic catalyst (PtRu/SiO2) improved the selectivity toward N2 formation. However, the Pt/Ru catalyst was used merely to study NO reduction.

One major drawback in most of the studies mentioned above is that catalysts were tested using models, standard mixtures of pollutants with known compositions. Hence, it becomes difficult to reproduce these results in actual fuel combustion with a highly complex composition compared to that of the model system.

The novelty in our work is the study of catalyst performance in a real system containing UAN postcombustion pollutants. The investigated system includes a complex mixture of effluents, such as NOx, NH3, and CO, which has to be converted into an environmentally friendly gas. It is very challenging to understand the behavior of these mixtures of components in the presence of a catalyst because they may exhibit a mutual interaction when reacting with the catalyst site. In addition, this system is characterized by high water content, which strongly influences the catalyst properties. Bimetallic Pt/Ru catalysts are promising candidates for solving the addressed problems. For support material, γ-Al2O3 was selected due to its high temperature stability and wear resistance, along with a high surface area (~200 m2 g⁻¹). The aim of the presented work is to investigate the activity of mono- and bimetallic Pt/Ru catalysts in the conversion of NOx, CO, and NH3 pollutants into H2O, N2, and CO2.

2. EXPERIMENTAL SECTION

2.1. Materials. Ammonium nitrate (≥99%, Sigma-Aldrich), urea (≥99.5%, Sigma-Aldrich), H2PtCl6 (8 wt % solution, Sigma-Aldrich), RuCl3·xH2O (Sigma-Aldrich), γ-Al2O3 pellets (1/8”, Alfa-Aesar), and Milli-Q ultrapure water were used for fuel and catalyst preparation.

2.2. Combustion and Catalytic Experiments. Aqueous UAN combustion was carried out in a continuous high-pressure reactor (Scheme 1). The fuel composition was as follows: 60% AN, 15% urea, and 25% water by weight. The fuel was fed at a flow rate of 10 mL min⁻¹ using a high-pressure pump (LC-20AP, Shimadzu) into a continuous SS310 reactor (634 mm long, 60 mm internal diameter). The temperature inside the reactor was monitored using a type-K thermocouple placed in a sleeve inside the reactor. The reactor was heated using a three-zone furnace (3210, Applied Test Systems) set to 550 °C at all zones. The pressure inside the reactor was controlled by a Programmable Logic Controller (PLC) via a pneumatic valve. The postcombustion catalyst chamber (15 cm long, 9.4 mm I.D.) made up of SS316L was connected in series with the outlet of the continuous reactor. The chamber was heated by heating tapes at temperatures varying between 250 and 500 °C. The pollutant-containing gas effluent was passed through the catalyst chamber packed with cylindrical pellets of catalysts.

Mono- and bimetallic Pt/Ru catalysts (2 wt %) were synthesized by impregnation (Supporting Information, Section 1.1.). Catalysts in the form of pellets of either 2 wt % Pt, Ru, Pt25Ru75, or Pt50Ru50 on γ-Al2O3 were placed in the chamber. The catalyst amount was varied among 6.75 g (0.135 g metal), 3.375 g (0.016875 g metal), 1.6875 g (0.03375 g metal) and 0.84375 g (0.0675 g metal). Effluents from the catalyst chamber flowed through a pneumatic valve and entered.
a heated gas receiver (11.5 L) at 180 °C, which was kept at a constant pressure of 0.2 ± 0.01 MPa. The sampled gas from the receiver was diluted by 99.995% N₂ at a 1:100 ratio using a gas dilution unit (M&C DIL-1/H). The diluted effluent gas was analyzed using a multicomponent online Fourier transform infrared (FTIR) gas spectrometer (Gasmet CX-4000O2). The spectrometer was calibrated using H₂O, CO, CO₂, NO, NO₂, N₂O, NH₃, HNO₃, and HNCO references. The FTIR sampling frequency was ∼10 Hz with an automatic averaging over 20 second segments. Subsequently, 15 consecutive data points were averaged. The lowest detection limit for all gases was 1−2 ppm.

Phase analysis via wide-angle X-ray diffraction (XRD) was performed for the bare supports and catalysts in the 2θ range of 5−90° at 4° min⁻¹. Continuous combustion of UAN fuel was conducted at various pressures (1−8 MPa) with a constant fuel flow rate (10 mL min⁻¹), to generate a steady gas output for the catalytic effluent abatement. Catalytic experiments for the pollutant reduction were performed at 250−500 °C. Blank experiments were performed using γ-Al₂O₃ pellets. Mono- and bimetallic noble-metal-supported catalysts, such as Pt/γ-Al₂O₃, Ru/γ-Al₂O₃, Pt₂₅Ru₇₅/γ-Al₂O₃, and Pt₅₀Ru₅₀/γ-Al₂O₃ were studied.

3. RESULTS AND DISCUSSION

Conversions, selectivity, and thermal and mechanical stabilities are the general parameters for the evaluation of supported metal catalysts. It is well known that the activity of supported metal catalysts is mainly dependent on the shape, size, distribution, and degree of agglomeration of the metal particles on the support. The morphology and properties of these catalysts were characterized before and after use. All of the catalysts were calcined at 400 °C for 2 h in air and reduced at 400 °C for 2 h in a 5% H₂/N₂ flow before characterization and catalytic testing.

3.1. Characterization of Mono- and Bimetallic Pt/Ru Catalysts. Structural and morphological features of the catalysts were characterized with XRD, high-resolution scanning electron microscopy (HR-SEM), N₂-sorption, and H₂-chemisorption analyses (Supporting Information, Section 1.2.) and correlated with the catalytic activity. Characteristic XRD peaks for all of the metals and support are shown in the diffractograms (Figure 1 and Figures S1−S4 in the Supporting Information). In some cases, because of high dispersion, the metal peaks were not clearly visible. After the reaction (8 h), the used catalysts were dried at 120 °C for 2 h and characterized. For the pure Al₂O₃ support, the formation of a poorly crystallized phase was evident from the broad peaks indexed for γ-Al₂O₃ in the obtained patterns (Figures S1−S4).

The characteristic features of γ-Al₂O₃ (2θ = 37.3, 45.93, 66.81°) (JCPDS 75-0921) can be noticed in all samples of the studied mono- and bimetallic Pt and Ru catalysts. The metallic phase of the active element (Pt or Ru) was confirmed by XRD. The crystallite size of metal nanoparticles was calculated using the Scherrer equation and was correlated with the size obtained from H₂ chemisorption and HR-SEM analyses (Table S2, Supporting information). It was observed that in the fresh catalyst (Figure S1) the Pt characteristic peaks were invisible (2θ = 39, 46, 67°) (JCPDS No. 01-1190) but became visible after the reaction (Figure S1). This indicated that the Pt nanoparticles grew during the reaction to 11 nm (calculated by the Scherrer equation). Similarly, the Ru catalyst (2θ = 38, 44, 58, 69, 78.5, 84.8, 86°) (JCPDS No. 06-0663) particle size increased from 15 to 25 nm (Figure S2). In addition, the bimetallic catalyst (Pt₂₅Ru₇₅) particle sizes of Pt and Ru were found to increase to 14 and 46 nm, respectively (Figure S3).

For monometallic Ru, it was observed that after the reaction some of the Ru was converted to RuO₂ (Figure S2) (2θ = 28, 39.6°) (JCPDS No. 00-43-1027) because of the highly oxidizing NO₃ species. However, Ru in the bimetallic Pt/Ru
catalyst was not oxidized. Another observation was that the $\gamma$-Al$_2$O$_3$ support transformed into $\theta$-Al$_2$O$_3$ (Figures S2 and S3) and $\alpha$-Al$_2$O$_3$ (Figure S3) because of the hydrothermal condition.\textsuperscript{52}

The diffractogram of the fresh and used bimetallic Pt$_{25}$Ru$_{75}$ and Pt$_{50}$Ru$_{50}$ catalysts does not show a XRD peak corresponding to alloy formation. This implies that the used bimetallic catalyst is either a disordered Pt/Ru alloy or a two-phase system with Ru-rich and Pt-rich phases with a non-bcc structure (common for alloy).\textsuperscript{50} Dispersion and crystallite size of the fresh and spent catalysts were calculated using H$_2$-chemisorption analysis (Table S2, Supporting Information). For the Pt catalyst, the initial crystallite size was found to be 3 nm, which increased to 10 nm after the reaction, which is quite similar to XRD data. The dispersion of the Pt catalyst also decreased from 38 to 10% during the course of the reaction. For the Ru catalyst, the crystallite size was found to decrease from 27 to 19 nm, which is against the trend observed from XRD and HR-SEM. The dispersion changed from 3 to 5%.

For Pt$_{25}$Ru$_{75}$, the crystallite size increased from 2 to 18 nm, whereas for Pt$_{50}$Ru$_{50}$ it increased from 4 to 18 nm, after the reaction. Hence, obviously, dispersion of these catalysts reduced from 40 to 5% for Pt$_{25}$Ru$_{75}$ and from 24 to 5% for the Pt$_{50}$Ru$_{50}$ catalyst after the reaction (Table S2, Supporting Information).

The morphologies of fresh and spent catalysts are shown in the HR-SEM data (Figures 2 and S5–S8), where only Ru particles were clearly visible in the fresh samples. The HR-SEM results were generally in agreement with XRD and H$_2$-chemisorption analyses and support the fact that the metal particle size increased during use of the catalysts. In the case of fresh Pt/Al$_2$O$_3$ and Pt$_{25}$Ru$_{75}$/Al$_2$O$_3$ catalysts, the nanoparticles were too small to be seen by HR-SEM (Figures S5a and S7a). However, in the spent catalysts, the particles’ size increased due to sintering, making the particles sufficiently large to be seen (Figures S5b and S7b). In spent Pt/Al$_2$O$_3$ and spent Pt$_{25}$Ru$_{75}$/Al$_2$O$_3$, the particle size was 20 and 25–50 nm, respectively. For Ru/Al$_2$O$_3$, the particle size range increased from 11–20 to 25 nm. Similarly, for Pt$_{50}$Ru$_{50}$/Al$_2$O$_3$, the size increased from 20–25 to 25–50 nm (Figures S6 and S8). N$_2$-adsorption analysis determined the high Brunauer–Emmett–Teller surface area of the $\gamma$ phase (Table S1). The lower surface area of the supported catalysts (195–202 m$^2$ g$^{-1}$) is due to the metal loading on the support (Table S1).

### 3.2. Evaluation of Catalytic Activity of Mono- and Bimetallic Pt/Ru Catalysts

The catalytic activity of mono-
and bimetallic Pt and Ru catalysts for UAN combustion effluent pollutant reduction was measured. Previous work on non-catalytic continuous combustion of UAN showed that pollutant concentrations can be reduced by increasing the pressure up to 15 MPa.\textsuperscript{\text{53,54}} At lower pressures, significant pollutant levels can exist in the effluent stream. Therefore, a catalyst can help in reducing leftover CO, NO, and NH\textsubscript{3} pollutants in the effluent gas, especially at lower pressures. The complete noncatalytic UAN combustion effluent composition as a function of pressure is provided in the Supporting Information (Figure S9).

3.2.1. Activity of Pt Catalysts. Initially, the Pt/Al\textsubscript{2}O\textsubscript{3} catalyst was tested because of its expected activity and stability described elsewhere.\textsuperscript{\text{41,55–57}} In this work, the catalytic activity of Pt was studied initially at 250 °C\textsuperscript{\text{58,59}} and pressures of 1, 2.5, and 5 MPa (Figure S10). The effluent pollutant concentrations introduced into the catalysts changed with the reactor combustion pressure. The Pt catalyst became active at 5 MPa, eliminating NO and CO, reducing the amounts of N\textsubscript{2}O (0.2 mmol ANmol\textsuperscript{-1}) and NO\textsubscript{2} (1.5 mmol ANmol\textsuperscript{-1}), and achieving a N\textsubscript{2} yield of 96%. However, the concentration of NH\textsubscript{3} increased from 37.4 to 108 mmol ANmol\textsuperscript{-1} following the catalytic process. This behavior for Pt was also observed by other researchers.\textsuperscript{\text{44,59,60}} Our catalyst does not suffer deactivation due to CO poisoning. In our case, H\textsubscript{2} can be possibly generated by the water gas shift reaction (WGS) of CO and H\textsubscript{2}O (water vapor) present in the pollutant gas (R2).

\begin{equation}
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\end{equation}

Marcleod showed that Al\textsubscript{2}O\textsubscript{3} support increases the formation of NH\textsubscript{3} in the presence of NO, CO, and H\textsubscript{2}O.\textsuperscript{\text{61}} During this step, hydrolysis of isocyanate groups (–NCO) also occurs, which is a well-known route for NH\textsubscript{3} formation.\textsuperscript{\text{62}} The –NCO group requires a catalytic site for hydrolysis to happen (e.g. –Pt) (reactions R3–RR6)

\begin{align*}
\text{Pt-NCO} + \text{H}_2\text{O} &\rightarrow \text{Pt-OH} + \text{HNCO} \\
\text{HNCO} + \text{H}_2\text{O} &\rightarrow \text{NH}_3 + \text{CO}_2 \\
\text{Pt} - \text{NCO} + \text{H}_2\text{O} &\rightarrow \text{Pt} - \text{NH}_2 + \text{CO}_2 \\
\text{Pt} - \text{NH}_2 + \text{H}_2\text{O} &\rightarrow \text{Pt} - \text{OH} + \text{NH}_3
\end{align*}

To reduce the NH\textsubscript{3} effluent concentration with Pt catalysts, we performed the reactions at 300 and 400 °C at 5 MPa (Figure S11). At 300 °C, there was no effect on the NH\textsubscript{3} concentration, but there was a slight decrease in N\textsubscript{2}O. At 400 °C, the NH\textsubscript{3} concentration decreased from 108 to 11 mmol ANmol\textsuperscript{-1} and NO\textsubscript{2} also decreased from 1.5 to 0.5 mmol ANmol\textsuperscript{-1}. However, the NO\textsubscript{2} pollutants increased. For example, NO and N\textsubscript{2}O increased from 0 to 13 mmol and from 0.2 to 7.9 mmol ANmol\textsuperscript{-1}, respectively. Therefore, monometallic Pt/Al\textsubscript{2}O\textsubscript{3} catalysts are not sufficiently effective in postcombustion reduction of UAN emission levels.

3.2.2. Activities of Ru and Pt\textsubscript{25}Ru\textsubscript{75} Catalysts. 3.2.2.1. Effect of Temperature. According to the literature, Ru/Al\textsubscript{2}O\textsubscript{3} is more selective to N\textsubscript{2} formation compared with the Pt/Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{\text{45,50}} The higher selectivity to N\textsubscript{2} of the Ru catalyst in the steady-state reaction at a higher temperature was correlated with a high coverage of the catalyst surface with nitrogen- and oxygen-containing adsorbrates, keeping the coverage of adsorbed atomic hydrogen (H) low, thus suppressing the NH\textsubscript{3} formation. In our system, atomic hydrogen was generated from NH\textsubscript{3} (reducer) present in the fuel effluent mixture. With the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst, we observed a drastic reduction in the NH\textsubscript{3} concentration from 45.8 mmol ANmol\textsuperscript{-1} (at 250 °C, 5 MPa) to 0.4 mmol ANmol\textsuperscript{-1} (at 400 °C, 5 MPa), consistent with the trend in the literature. Hence, N\textsubscript{2} formation was dominant over NH\textsubscript{3} with the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst.

Although Ru is highly selective to N\textsubscript{2} formation, it can be deactivated by oxidation to RuO\textsubscript{2} under the atmosphere of NO\textsubscript{2} pollutants. In an attempt to resolve this problem, we prepared bimetallic Pt/Ru catalysts, hypothesizing that when the two metals are intimately mixed, the oxidation resistance of Pt could protect the Ru from getting oxidized. Compositions of Pt\textsubscript{75}Ru\textsubscript{25}/Al\textsubscript{2}O\textsubscript{3} and Pt\textsubscript{25}Ru\textsubscript{75}/Al\textsubscript{2}O\textsubscript{3} were selected for testing.

The reaction temperature and pressure were varied to evaluate the optimal operating conditions of these catalysts. The Ru/Al\textsubscript{2}O\textsubscript{3} and Pt\textsubscript{25}Ru\textsubscript{75}/Al\textsubscript{2}O\textsubscript{3} catalysts were tested initially at 1 MPa and temperatures of 200 and 250 °C (Figure S12). Interestingly, it was observed that even at 200 °C the Pt\textsubscript{25}Ru\textsubscript{75} catalyst reduced the pollutants more efficiently compared with Ru. For instance, the concentrations of pollutants over the bimetallic catalyst (in mmol ANmol\textsuperscript{-1}) were NO = 6.7, N\textsubscript{2}O = 7, CO = 0, and NH\textsubscript{3} = 2.2 compared to those over Ru, NO = 347, N\textsubscript{2}O = 11.8, CO = 30.5, and NH\textsubscript{3} = 193.3. Both reduced the pollutant concentrations considerably below those achieved without a catalyst (Figure S12).

To reduce pollutants further, tests were performed at 250 °C, which showed that Ru catalysts reduced the pollutants to even lower values: NO = 8, N\textsubscript{2}O = 3.5, CO = 0, and NH\textsubscript{3} = 1.2 mmol ANmol\textsuperscript{-1}. The higher temperature also increased the N\textsubscript{2} yield from 79 to 99% for Ru. It was found that during combustion at 1 MPa, the reaction of the larger amount of ammonia and NO\textsubscript{2} effluent in the catalytic chamber produced a large amount of heat. Consequently, the temperature difference (ΔT) over the catalyst chamber was 240–280 °C. To avoid such large temperature variation across the catalyst bed, further reactions with Pt\textsubscript{25}Ru\textsubscript{75}/Al\textsubscript{2}O\textsubscript{3} at 1 MPa and higher temperatures were not performed. Similar studies were performed with Ru and Pt\textsubscript{25}Ru\textsubscript{75} catalysts at 2.5 MPa and temperatures of 250, 300, and 350 °C (Figure S13). Unexpectedly, at 250 °C, the Ru catalyst released a higher amount of NO and NH\textsubscript{3} when compared with reference, noncatalytic reactions (NO = 261.6 vs 156.2, N\textsubscript{2}O = 1.5 vs 6.7, CO = 4.8 vs 12.1, NH\textsubscript{3} = 154.8 vs 115.4 mmol ANmol\textsuperscript{-1}). At 300 °C, there was a slight improvement in the results in comparison to those at 250 °C (NO = 163.2, N\textsubscript{2}O = 7.4, CO = 6.9, NH\textsubscript{3} = 116.1 mmol ANmol\textsuperscript{-1}). When the catalyst temperature was raised to 350 °C, there was a higher N\textsubscript{2} yield of 99.4% and the pollutants were reduced drastically (NO = 1.5, N\textsubscript{2}O = 6.1, CO = 0, NH\textsubscript{3} = 0.8 mmol ANmol\textsuperscript{-1}). Studies at higher temperatures with the Ru catalyst at 2.5 MPa were not performed due to a temperature rise of 102 °C over the catalyst. This would translate to an outlet temperature above 500 °C, damaging the experimental system. With the Pt\textsubscript{25}Ru\textsubscript{75} catalyst (Figure S13), there was not a significant effect on the pollutant concentrations at 250 °C. However, at 300 °C, much smaller concentrations of pollutants were emitted (NO = 0, N\textsubscript{2}O = 6.3, CO = 0, NH\textsubscript{3} = 1.1 mmol ANmol\textsuperscript{-1}), with an improved N\textsubscript{2} yield of 99.5%. Increasing the temperature to 350 °C led to higher pollutant concentrations (NO\textsubscript{2} = 0.2, NO = 4.3, N\textsubscript{2}O = 8.6, CO = 0, NH\textsubscript{3} = 4 mmol ANmol\textsuperscript{-1}); hence, studies at higher temperatures were not conducted.

The Pt\textsubscript{25}Ru\textsubscript{75} catalyst facilitated low pollutant concentrations at 50 °C lower than the other catalysts, reducing high-temperature damage to the catalyst and equipment. It is worth noting that NO\textsubscript{2} measurements were close to zero at all tests.
performed at $P = 1$–2.5 MPa and were therefore omitted from the text (the data can be viewed in Figures S12a and S13a).

On the basis of our previous experience,$^8$ the most optimized noncatalytic reaction pressures for UAN combustion with minimal pollutant emission were 15–25 MPa. The challenge is to obtain such low pollution concentrations at lower pressures, which will greatly simplify the reactor design. In our blank experiments, at 5 MPa (without catalyst), we observed the following pollutant emission (in mmol AN$^{-1}$) at a $N_2$ yield of 95.9%: NO$_2$ = 0.9, NO = 69.2, N$_2$O = 0.3, CO = 3.3, and NH$_3$ = 37.4. Tests were performed with Ru and Pt$_{25}$Ru$_{75}$ as postcombustion catalysts at $T = 250$–500 °C (Figures 3 and 4).

For the Ru catalyst, at 250 °C, the pollutant levels were not reduced much (NO$_2$ = 0.2, NO = 92.9, N$_2$O = 0, CO = 0.3, NH$_3$ = 45.8 mmol AN$^{-1}$) compared to those in the noncatalytic experiments. In fact, with the Ru catalyst, the concentrations of NO and NH$_3$ increased relative to those in the blank experiments. At 300 °C, NO$_2$, NO, and NH$_3$ were converted, whereas N$_2$O and CO were generated (NO$_2$ = 1.5, NO = 52.8, N$_2$O = 1.4, CO = 1.8, NH$_3$ = 37 mmol AN$^{-1}$). At 350 °C, CO and NO$_2$ were converted and NO, N$_2$O, and NH$_3$ were generated (NO$_2$ = 1, NO = 59, N$_2$O = 4.9, CO = 0,

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Figure 3. Concentration of (f) CO$_2$ and major combustion pollutants: (a) NO$_2$, (b) NO, (c) N$_2$O, (d) NH$_3$, and (e) CO formed in noncatalytic and Ru/Al$_2$O$_3$- and Pt$_{25}$Ru$_{75}$/Al$_2$O$_3$-catalyzed reactions at $P = 5$ MPa, $T = 200$–500 °C, and WHSV = 5911 h$^{-1}$. 

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NH\textsubscript{3} = 40.8 mmol ANmol\textsuperscript{-1}). The final temperature studied for the Ru catalyst at 5 MPa was 400 °C, which was found to be optimal for pollutant emission (NO\textsubscript{2} = 0.2, NO = 0, N\textsubscript{2}O = 5, CO = 0, NH\textsubscript{3} = 0.5 mmol ANmol\textsuperscript{-1}). Unfortunately, N\textsubscript{2}O is a relatively stable compound, as it decomposes at about 800 °C. According to the literature, a catalyst (Ru/Al\textsubscript{2}O\textsubscript{3} and Ru/MgO) can help reducing N\textsubscript{2}O at 600 °C in the presence of H\textsubscript{2}. However, it is also reported that the catalytic activities of the Ru/Al\textsubscript{2}O\textsubscript{3} catalysts decrease with time and the conversion of N\textsubscript{2}O is linearly dependent on the amount of metallic Ru. In our studies, we observed that the Ru/Al\textsubscript{2}O\textsubscript{3} catalyst was undergoing oxidation to RuO\textsubscript{2} during the reaction, suppressing the activity of the catalyst to convert N\textsubscript{2}O into N\textsubscript{2}. Literature reviews show that the presence of moisture and oxygen in the feed stream can also slightly decrease the Ru catalyst activity, probably due to the competitive adsorption between these species with N\textsubscript{2}O on the catalytic sites. Similar to this case, in our system, the catalyst is subjected to an oxidizing environment and excess of H\textsubscript{2}O during the reaction. Therefore, even higher temperatures of 500 °C did not promote N\textsubscript{2}O to N\textsubscript{2} conversion significantly. Hence, for the Ru catalyst, 400 °C and 5 MPa were the best conditions to reduce the pollutant levels.

A similar temperature study was performed for the Pt\textsubscript{25}Ru\textsubscript{75} catalyst. As shown in Figure 3, at 250 °C, the pollutant levels (in mmol ANmol\textsuperscript{-1}) were below the noncatalytic results (NO\textsubscript{2} = 0.5, NO = 25.1, N\textsubscript{2}O = 4.8, CO = 0, NH\textsubscript{3} = 20.8). However, at 300 °C, the pollutant levels were higher than those at 250 °C (NO\textsubscript{2} = 0.7, NO = 35.3, N\textsubscript{2}O = 11.5, CO = 0, NH\textsubscript{3} = 31.3). A further increase in temperature to 350 °C reduced the pollutants drastically (NO\textsubscript{2} = 0.2, NO = 0.9, N\textsubscript{2}O = 5.1, CO = 0, NH\textsubscript{3} = 1.5). The optimal condition for the Pt\textsubscript{25}Ru\textsubscript{75} catalyst was 400 °C (NO\textsubscript{2} = 0.2, NO = 0.3, N\textsubscript{2}O = 3.5, CO = 0, NH\textsubscript{3} = 0.2 mmol ANmol\textsuperscript{-1}), with a N\textsubscript{2} yield of 99.7% (Figure 4). To completely eliminate the pollutants, tests at temperatures of 450 °C (NO\textsubscript{2} = 0.2, NO = 1.7, N\textsubscript{2}O = 3.3, CO = 0, NH\textsubscript{3} = 0) and 500 °C (NO\textsubscript{2} = 0, NO = 3.3, N\textsubscript{2}O = 2.3, CO = 0.4, NH\textsubscript{3} = 0.5) were also conducted. However, the NO\textsubscript{2}, NH\textsubscript{3}, and CO levels started to rise with increased temperature. The above temperature studies at different pressures with Ru and Pt\textsubscript{25}Ru\textsubscript{75} catalysts concluded that the bimetallic Pt\textsubscript{25}Ru\textsubscript{75} catalyst is preferable at 400 °C and 5 MPa.

### 3.2.2.2. Effect of Catalyst Content and TOF Calculation.

Additional experiments were performed to find the minimal amount of catalyst required to achieve the lowest pollutant levels (Figure S14). We performed the tests with catalyst (active metal) weights equal to 0.0675, 0.03375, and 0.016875 g, which are exactly 1/2, 1/4, and 1/8 the weight of the catalyst used in the above reactions (0.135 g). This way, the WHSV value was actually increased by sequent factors of 2. It was observed that the minimum amount of pollutants in mmol ANmol\textsuperscript{-1} (NO\textsubscript{2} = 0, NO = 0.3, N\textsubscript{2}O = 3.5, CO = 0, NH\textsubscript{3} = 0.5 at a N\textsubscript{2} yield = 99.5%) could be achieved with 1/2 of the catalyst weight (0.0675 g) used in the previous tests. Further lowering the catalyst quantity (equivalent to increasing WHSV) led to a decrease in the conversion activity of the catalyst. Hence, a catalyst amount of 0.0675 g (active metal), with a WHSV = 1182 h\textsuperscript{-1}, was used in further studies with the Pt\textsubscript{25}Ru\textsubscript{75} catalyst.

The turnover frequency (TOF) was calculated for both mono- and bimetallic Pt/Ru catalysts (Table S3, Supporting Information). It was calculated at T = 400 °C and P = 5 MPa by considering the total moles of the reactants (NO, NO\textsubscript{2}, NH\textsubscript{3} and CO). Nitrous oxide was neglected from the calculation because it was formed, rather than converted by these catalysts. The TOF was found to be in the order Ru > Pt\textsubscript{50}Ru\textsubscript{50} > Pt > Pt\textsubscript{25}Ru\textsubscript{75}. It was observed that the total number of pollutant moles converted is similar for all of the catalysts (0.09–0.11 mol ANmol\textsuperscript{-1}). Thus, the TOF depended mainly on the dispersion of these catalysts (Table S3).

#### 3.2.2.3. Effect of Pressure.

A pressure study was performed using the Pt\textsubscript{50}Ru\textsubscript{50} catalyst (0.0675 g) at a pressure range of 1–7.5 MPa and a temperature of 400 °C (Figure S15). At 5 MPa and 400 °C, the pollutant levels (in mmol ANmol\textsuperscript{-1}) were as follows: NO\textsubscript{2} = 0, NO = 0.3, N\textsubscript{2}O = 3.5, CO = 0, and NH\textsubscript{3} = 0.5. Raising the pressure to 7.5 MPa increased most of the pollutant levels (NO\textsubscript{2} = 0.1, NO = 1.5, CO = 0, NH\textsubscript{3} = 0.7), whereas only N\textsubscript{2}O decreased from 3.5 to 2.6 mol ANmol\textsuperscript{-1}.

#### 3.2.2.4. Effect of Pt/Ru Atomic Ratio.

Catalytic pollutant abatement was additionally conducted with a higher-Pt-content bimetallic catalyst (Figure S16). A Pt\textsubscript{50}Ru\textsubscript{50} catalyst was prepared to compare its activity to that of Pt\textsubscript{25}Ru\textsubscript{75} at 400 °C at 5 MPa. This catalyst showed excellent activity in reducing the CO and NO\textsubscript{2} levels. However, the emission of NO\textsubscript{2}, NO, and NH\textsubscript{3} was slightly higher than that obtained with the Pt\textsubscript{25}Ru\textsubscript{75} catalyst. Hence, a bimetallic catalyst with the Pt\textsubscript{25}Ru\textsubscript{75} atomic ratio was preferred in our studies.

#### 3.2.2.5. Catalyst Stability.

The stability of the Pt\textsubscript{25}Ru\textsubscript{75} catalyst was tested by heating a spent catalyst to 400 °C for 100 h under N\textsubscript{2} flow. After this treatment, the catalyst was used again to treat the effluent combustion gases at 400 °C and 5 MPa. We found that the catalyst was completely stable and retained its original activity even after this prolonged thermal treatment.

Overall, using bimetallic Pt\textsubscript{50}Ru\textsubscript{50}/Al\textsubscript{2}O\textsubscript{3} catalysts at the optimal conditions (T = 400 °C, P = 5 MPa, WHSV = 11 822 h\textsuperscript{-1}) reduced the levels of NO, CO, and NH\textsubscript{3} by 99, 100, and 99%, respectively. Monometallic Pt and Ru and even bimetallic PtRu catalysts were unable to completely eliminate the NH\textsubscript{3} and N\textsubscript{2}O generated during UAN fuel combustion. Instead of using these catalysts individually, it may be more productive to use a one-pot catalyst reactor with a ternary mixture of Pt, Ru, and Pt\textsubscript{25}Ru\textsubscript{75} catalysts arranged in series for complete catalytic decomposition of NH\textsubscript{3} and N\textsubscript{2}O. A Ru catalyst plug can reduce most of the pollutants except N\textsubscript{2}O. The next plug could be a Pt catalyst, which can convert the N\textsubscript{2}O to NH\textsubscript{3}. Finally, a third plug with a Pt/Ru bimetallic catalyst could convert the generated NH\textsubscript{3} into N\textsubscript{2}.
Future studies can be extended to using other noble metals (e.g., Rh\textsuperscript{16,65,66} and Pd\textsuperscript{58}). Furthermore, to improve the catalyst stability, either supports like zeolites\textsuperscript{67} or additives such as Ba, La, Si, Li, or Re\textsuperscript{67} can be used to increase the thermal stability of the Al\textsubscript{2}O\textsubscript{3} support.

4. SUMMARY

The central theme of this project is that the UAN fuel can serve as a future state-of-the-art energy storage and energy carrier material. However, to become such a candidate, it must be a clean-burning and nonpolluting fuel.

In summary, the catalytic activity, selectivity, and stability of mono- and bimetallic Pt/Ru-based catalysts were demonstrated for the pollutant abatement of the UAN fuel postcombustion effluent. The novelty in our work is the study of catalyst performance in a real system with a complex mixture of effluents such as NO\textsubscript{x}, NH\textsubscript{3}, and CO. We have synthesized mono- and bimetallic Pt and Ru catalysts by impregnation on a γ-Al\textsubscript{2}O\textsubscript{3} support. The monometallic Pt/Al\textsubscript{2}O\textsubscript{3} catalyst reduced the levels of NO\textsubscript{x}, NO, N\textsubscript{2}O, and CO and showed higher selectivity toward NH\textsubscript{3} than N\textsubscript{2} formation. On the other hand, the monometallic Ru/Al\textsubscript{2}O\textsubscript{3} catalyst reduced pollutants, such as NO\textsubscript{x}, NO, CO, and NH\textsubscript{3}, but was unable to decrease the N\textsubscript{2}O sufficiently by converting it into N\textsubscript{2}. The multifunctionality of the bimetallic Pt\textsubscript{25}Ru\textsubscript{75} catalyst enabled higher activity and selectivity compared to those of Pt, Ru, and Pt\textsubscript{50}Ru\textsubscript{50} catalysts. Temperature (250–500 °C) and pressure (1–7.5 MPa) studies concluded that the bimetallic Pt\textsubscript{25}Ru\textsubscript{75} catalyst at 400 °C and 5 MPa (WHSV = 11 822 h\textsuperscript{−1}) reduced the pollutants to a minimal level, with a high yield of N\textsubscript{2} (99.7%) and CO (99.9%). This study clearly demonstrates that Pt is more selective toward NH\textsubscript{3} formation, whereas Ru is more selective toward N\textsubscript{2} formation. The Ru species were partially oxidized under the reactor’s oxidizing atmosphere. However, the active species of the Pt\textsubscript{25}Ru\textsubscript{75} catalyst were highly stable under the reaction conditions. The γ-Al\textsubscript{2}O\textsubscript{3} support phase transformed into the θ-phase and α-phase due to the large steam content in the effluent gas.

The previous catalytic studies on pollutant reduction were mainly focused on individual components. Our work is indeed significantly more general using a complex mixture of real effluents (NO\textsubscript{x}, NH\textsubscript{3}, CO) from UAN combustion because these pollutants can have mutual effects on each other in the presence of a catalyst. Until now, the reduction of pollutants (NO\textsubscript{x}, NH\textsubscript{3}, CO) formed during combustion of nitrogen-based fuels was achievable only at pressures above 15 MPa. The addition of a postcombustion catalyst reduced the NO\textsubscript{x}, NH\textsubscript{3} and CO emission even further, giving rise to much lower emission (99–100% reduction) at a considerably lower pressure (5 MPa). Use of bimetallic Pt\textsubscript{25}Ru\textsubscript{75} catalysts at lower pressures along with an improved reactor design will reduce the capital cost of future reactors. Therefore, this work opens new opportunities and a new frontier for UAN high-pressure postcombustion catalyzed pollution abatement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01344.

Full detail on catalyst preparation and characterization, N\textsubscript{2}-sorption results, dispersion and crystallite/particle sizes, XRD patterns, HR-SEM images, and combustion pollutant and product concentrations (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the generous support from Ed Satell NHAF laboratory, the Nancy and Stephen Grand Technion Energy Program (GTEP), the I-CORE Program of the Planning and Budgeting Committee and The Israel Science Foundation (Grant No. 152/11), the Russell Berrie Nanotechnology Institute (RBNI), the Adelis Foundation, the Committee for Planning and Budgeting of the Council for Higher Education under the framework of the KAMEA program, and the Arturo Gruenbaum Chair in Material Engineering.

ABBREVIATIONS

AN, ammonium nitrate; FTIR, Fourier transform infrared; GPW, global warming potential; HR-SEM, high-resolution scanning electron microscopy; PLC, programmable logic controller; TOF, turnover frequency; UAN, urea ammonium nitrate; VOC, volatile organic compound; WGS, water gas shift; WHSV, weight hourly space velocity; XRD, X-ray diffraction

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