NO reduction with CO on low-loaded platinum-group metals (Rh, Ru, Pd, Pt, and Ir) atomically dispersed on Ceria

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Abstract

Low-loaded platinum-group single-atom catalysts on CeO₂ (M₁/CeO₂) were synthesized via hightemperature atom trapping (AT) and tested for the NO + CO reaction under dry and wet condition. The activity of these catalysts for NO+CO reaction follows the order Rh > Pd \approx Ru > Pt > Ir. For Rh, Ru, and Pd single-atom catalysts, the N₂O byproduct is formed but not clearly observed on Ir and Pt cases, which may result from the higher reaction temperature (> 200°C) required for Pt and Ir catalysts. The presence of water can promote the activity of these M₁/CeO₂ catalysts for NO + CO reaction. Under wet conditions, significant NH₃ formation occurred during the reaction, which is due to the co-existence of water-gas-shift reaction on these catalysts. Compared with Pt, Pd and Ir, the Rh and Ru single-atom catalysts show higher selectivity to NH₃ species, resulting from the more hydride species on the surface. Among all tested catalysts, Ru₁/CeO₂ shows the highest production of ammonia and highest CO conversion due to excellent water-gas-shift activity, whereas Pd₁/CeO₂ shows lowest ammonia production.

Introduction

Platinum-group metals (PGMs) such as Pt, Pd, and Rh are known to be efficient catalysts for the NO reduction by CO (NO+CO)¹⁻⁴, which is a key reaction in three-way catalysts (TWCs)^{5, 6}. The recent challenges in this field mainly involve i) improving the utilizing effectivity of noble atoms⁷⁻⁹; ii) controlling the product distribution (N₂O, NH₃ and N₂)^{10, 11}. Single-atom catalysts due to the 100% metal dispersion and distinct isolated atom properties were shown to be active for catalytic CO oxidation^{12, 13}, water gas shift (WGS)^{14, 15} and NO reduction reaction¹¹. Ceria (CeO₂) is a commonly used component in automotive exhaust catalysts¹⁶. The Ce_xM_yO_z solid solution catalysts (M represents Pd, Rh and Pt) with ionically dispersed metal ions had been found the high performance for NO+ CO reaction¹⁷⁻¹⁹. The full conversion of NO and 100% selectivity to N₂ could be achieved on Ce_xPd_yO_z catalyst at ~175 °C, whereas slightly lower selectivity for Rh and Pt cases was observed¹⁸⁻²⁰. In contrast, for Al₂O₃ supported Pd particles, the full conversion of metal atoms and the special surface of the support. The possible disadvantage of these solid solution catalysts is that part of the metal single atoms was trapped in bulk structure, which is inactive for catalytic reaction resulting in the lower utilization effectivity.

Recently, our group reported the direct evidence that Rh(I) single atoms dispersed on CeO₂ via atom trapping method²², are the highly active and stable species for low-temperature NO+CO reaction¹. Notably, the low-temperature activity of Rh₁/CeO₂ was promoted due to the presence of H₂O with observable amounts of ammonia (NH₃) generated, which was related to the water-gas shift reaction (WGS). We also suggested that rhodium nanoparticles were significantly less active in the low-temperature regime for NO reduction: only at higher temperature they can catalyze NO reduction. These findings naturally raise a question whether other platinum-group metal single-atom catalysts could be active for NO + CO reaction? Their low loading (<0.5 wt%) is especially relevant considering the volatility of PGM prices in the current economy (for example, Rh with price for ounce reaching about 20000 USD recently²³). In this study, we have synthesized and systematically explored the performance of these single-atom-based catalysts for NO + CO under dry and wet conditions, filling in the existing gap in the literature. The metal activity sequence for NO reduction and production distribution (N₂O, NH₃ and N₂) were investigated. Spectroscopic studies with probe molecules aided in understanding nuclearity of the active structures.

Results and discussion

Influence of synthesis method and loading on performance of NO + CO reaction

Taking Rh_1/CeO_2 as an example, we have studied the influence of the synthesis methods and Rh loadings on catalytic performance for NO + CO reaction (Figure 1). Compared to co-precipitation method (0.5 wt%Rh-CeO₂-CP, Experimental section), the 0.5wt%Rh_1/CeO₂ synthesized via high-temperature atom trapping (0.5 wt% Rh/CeO₂-AT) with single atom site¹ shows higher performance (Figure 1A). The full NO conversion temperature greatly decreased from 360 to 157 °C. Corresponding maximum N₂O formation temperature shifted from 181 to 101 °C (Figure 1B). The different behavior of Rh₁/CeO₂ for NO + CO reaction with different methods (CP vs AT) originated from the different percentages of exposed Rh atoms. For 0.5 wt% Rh/CeO₂-AT, the Rh can be fully dispersed on the CeO₂ surface, unlike 0.5 wt% Rh/CeO₂-CP, where part of the atoms may be encapsulated in CeO₂ bulk.

Furthermore, the effect of Rh loading (0.02 to 0.5 wt%) on performance was studied (Figure 1). We have reported the 0.1 and 0.5 wt% cases before¹ and the activity is very similar but lower selectivity to N₂O for 0.1wt%Rh₁/CeO₂-AT. When the Rh loading further decreased to 0.02wt%, the NO full conversion temperature shifted a lot (~385 °C). Corresponding maximum N₂O formation temperature needs ~ 193 °C, much higher than 0.1wt%Rh₁/CeO₂-AT sample of ~85 °C. Based on these results, we can conclude i) AT method is an effective way to synthesize the high active Rh single-atom catalysts; ii) 0.1 wt% Rh on CeO₂ has the optimized catalytic performance. Now, another question arises regarding the performance of the other platinum-group metal single-atom catalysts (Ir, Pt, Ru, Pd) for NO + CO reaction? We focus on that in the next sections.



Figure 1. Activity and selectivity of Rh/CeO₂ with different Rh loading (0.02-0.5 wt%) and synthesis methods (Atom trapping (AT) and Mixed precursor (MP)) under dry NO+CO reaction conditions. (A), NO concentration versus temperature; (B), N₂O concentration versus temperature. Conditions: 120 mg catalysts. Total flow 300 mL/min. Concentrations: 460 ppm NO, 1750 ppm CO, balanced with N₂. GHSV= ~150 L/(g.h), ramp rate 2 °C/min.

Performance of different noble metal single-atom on CeO₂ under dry NO + CO condition

We started by first synthesizing other platinum-group metal single-atom catalysts on CeO₂ via AT. After 800°C calcination in air, the as-prepared materials, labeled as M_1/CeO_2 (M= Rh, Ru, Ir, Pt, and Pd) show significantly higher surface area (Table 1) than bare CeO₂ support (11 m²/g)¹ calcined at same temperature, indicating that theses noble metal cations can stabilize CeO₂ nanoparticles against sintering, which is in agreement with our recent report²⁴. As shown in Figure 2(A-D), these M_1/CeO_2 presented the clean surface and clear (111) lattice spacing (~0.32nm) of polyhedral CeO₂ with no trace of NPs or large clusters.



Figure 2. High-resolution transmission electron microscopy (HRTEM) images of M₁/CeO₂ (M= Ru, Ir, Pt, and Pd). (A), Ir₁/CeO₂; (B), Pt₁/CeO₂; (C), Pd₁/CeO₂; (D), Ru₁/CeO₂.

Samples	Special surface area (m ² /g)	Average pore Diameter (nm)	Pore volume (cm ³ /g)
Ir ₁ /CeO ₂	38.2	14.7	0.14
Pt ₁ /CeO ₂	38.6	13.7	0.13
Ru ₁ /CeO ₂	38.7	13.2	0.13
Pd ₁ /CeO ₂	30.2	13.6	0.10
Rh ₁ /CeO ₂	37.3	14.2	0.13

 Table 1 The physical property of various synthesized samples

Subsequently, the performance of NO + CO reaction under dry condition on different noble metal singleatom catalysts were tested (Figure 3). The Rh₁/CeO₂ shows the highest activity, where the full NO conversion was achieved at ~100 °C. Compared the Rh or Pd single-atom catalysts, the Ir and Pt show relatively poor performance, where the light-off starts above 200 °C and can be not fully eliminated before 350 °C. The activity sequence of single-atoms for NO+CO reaction is Rh > Pd > Pt > Ir. The lower activity of Pt or Ir may be due to the strong adsorption of CO, which inhibits the NO dissociation²⁵.

In terms of selectivity, the Pt₁/CeO₂ and Ir₁/CeO₂ show very low selectivity to N₂O with ~10% selectivity ~320 °C. N₂ appears in the effluent at ~200°C, which is in agreement with the NO conversion temperature, indicating N₂ is the primary product. Measurable amounts of N₂O byproduct were produced on Rh and Pd single atoms catalysts. N₂O concentration versus temperature for Pd and Rh single-atom catalysts shows volcanic curve. As the temperature increased, the N₂O formation rate increased on Pd and Rh and got the maximum at 188 and 84°C, respectively. Extrapolating the initial rates to low conversions, N₂O is the primary product and the corresponding N₂ is secondary product. The origin of N₂O formation on Rh supported on CeO₂ may be related to the special oxidation state (+1). The low N₂O selectivity on Pt and Ir single-atom catalysts may be related to the high reaction temperature², at which N₂O is known to decompose to N₂. Another possible explanation may be due to the different reaction pathways on these catalysts²⁶.



Figure 3. Gas concentration versus temperature for dry (NO+CO) reaction. (A), Ir_1/CeO_2 ; (B), Pt_1/CeO_2 ; (C), Pd_1/CeO_2 ; (D), Rh_1/CeO_2 . Conditions: 120 mg catalysts. Total flow 300 mL/min. Concentrations: 460 ppm NO, 1750 ppm CO, balanced with N₂. GHSV= ~150 L/(g.h), ramp rate 2 °C/min.

CO abatement activity was further analyzed and is summarized in Figure 4. In the reaction equation (CO + NO = N₂ + CO₂), the molar ratio of NO/CO approaches 1, if no N₂O is formed. Therefore, relative to NO concentration (~460 ppm), the CO concentration (~1750 ppm) is excessive, which cannot be fully converted before 350 °C. By arbitrarily choosing the temperature of 20% CO conversion (T₂₀) as an activity indicator, we have listed the T₂₀ in Table 2 and the CO activity sequence of single-atoms is the same to the NO activity (Rh > Pd > Pt > Ir). In general, the dissociation of adsorbed NO molecules occurred on metal atom surface with the formation of N* and O*. The N* can further react with adsorbed NO or N* to form N₂O or N₂ molecules. The role of CO is believed to remove adsorbed O* species on the metal surface. Therefore, the theoretically residual CO concentration should be ~1280 ppm. The lower concentration of CO in Figure 2 may result from the surface reaction with O from CeO₂ support¹⁶.



Figure 4. Reactant CO concentration versus temperature for wet (NO+CO) reaction on M_1 /CeO₂ (M= Rh, Ru, Ir, and Pd). Conditions: 120 mg catalysts. Total flow 300 mL/min. Concentrations: 460 ppm NO, 1750 ppm CO, balanced with N₂. GHSV= ~150 L/(g.h), ramp rate 2 °C/min.

Performance of different noble metal single-atom on CeO₂ under wet NO + CO condition

Under real engine conditions, water is always present in the engine gas stream, so we tested the activity of this sample in the presence of ~3% water vapor (~30,000 ppm) which is industrially relevant. The light-off curves are summarized in Figure 4. We studied the catalytic reactivity of CO+NO reaction in the presence of steam on different noble metal single atom catalysts. By arbitrarily choosing the temperature of 50% NO conversion (T_{50}) as an activity indicator (Figure 5A), the activity sequence on these catalysts was Rh > Pd \approx Ru > Pt > Ir. The Rh₁/CeO₂ can fully convert NO at ~126 °C, which is the best among these catalysts. The poorest activity is Ir₁/CeO₂, which cannot fully convert NO before 400°C. Compared to the dry condition, the presence of water can promote the activity of NO and greatly decrease the T₅₀ (Table 2) for these single-atom catalysts, which is in agreement with previous observation of Rh₁/CeO₂¹.

Just like the NO activity, the presence of water can also promote the activity of CO conversion (Figure 5B and Table 2). For example, the T_{20} drops from 206 to 152° C on Pd₁/CeO₂ catalyst. Unlike under dry condition, the CO can potentially be fully converted under wet condition, which may because CO participates in the WGS (CO+H₂O) reaction. The contribution of CO conversion includes two reactions (NO+CO and CO+H₂O), where there is a synergistic effect (Table2).



Figure 5. Reactant NO (A) and CO (B) concentration versus temperature for wet (NO+CO) reaction on M_1 /CeO₂ (M= Rh, Ru, Ir, and Pd). Conditions: 120 mg catalysts. Total flow 300 mL/min. Concentrations: 460 ppm NO, 1750 ppm CO, approximately 2.6% H₂O, balanced with N₂. GHSV= ~150 L/(g.h), ramp rate 2 °C/min.

Table 2	Temperatures	for ~ 5	0% NO	(T_{50}) and	1~20%	$CO(T_{20})$) conversion	on d	lifferent	noble	metal	catalysts	with
differen	t reaction cond	itions											

Samples	Dry co	ndition	Wet condition			
	T ₅₀ (NO)	T ₂₀ (CO)	T ₅₀ (NO)	T ₂₀ (CO)		
Ir ₁ /CeO ₂	~304	~327	~268	~253		
Pt ₁ /CeO ₂	~287	~287	~203	~199		
Ru ₁ /CeO ₂			~155	~166		
Pd ₁ /CeO ₂	~183	~206	~138	~152		
Rh ₁ /CeO ₂	~82	~89	~73	~78		

Figure 6 shows the selectivity of N₂O and N₂ on these single-atom catalysts. Compared to the Ir and Pt cases, the Rh, Ru, and Pd produce more N₂O by-products. Pd₁/CeO₂ will produce the largest amounts of N₂O among these single-atom catalysts. The maximum N₂O formation temperature sequence is Rh< Ru \approx Pd < Pt < Ir. For the N₂ selectivity, as the temperature increases, the N₂ gradually produces and achieves the maximum at ~300°C except for Pt and Ir. For Pt and Ir cases, the N₂ concentration can achieve the maximum (~160 ppm) at 350°C but a gap occurs compared with the Rh/Ru/Pd cases (~230 ppm). This gap in formation is related to the NH₃ formation during reaction under wet conditions.



Figure 6. Product N₂O (A) and N₂ (B) concentrations versus temperature for wet (NO+CO) reaction on M_1 /CeO₂ (M= Rh, Ru, Ir, and Pd). Conditions: 120 mg catalysts. Total flow 300 mL/min. Concentrations: ~460 ppm NO, ~1750 ppm CO, ~2.6% H₂O, balanced with N₂. GHSV= ~150 L/(g.h), ramp rate 2 °C/min.



Figure 7. Product NH₃ concentration versus temperature for wet (NO+CO) reaction on M_1 /CeO₂ (M= Rh, Ru, Ir, and Pd). Conditions: 120 mg catalysts. Total flow 300 mL/min. Concentrations: 460 ppm NO, 1750 ppm CO, approximately 2.6% H₂O, balanced with N₂. GHSV= ~150 L/(g.h), ramp rate 2 °C/min.

The NH₃ concentration versus temperature on these single-atom catalysts was plotted in Figure 7. For the optimal Rh₁/CeO₂, the NH₃ starts generating at ~60 °C and the amounts gradually increase to the maximum at ~116 °C. For Pt and Ir cases, the amounts of NH₃ can maintain a high concentration (~150 ppm) before 400°C, which can well explain why there is a gap in N₂ concentration between these catalysts (Figure 5B). Among these single-atoms catalysts, the largest amounts of NH₃ can be achieved on Ru₁/CeO₂.

Our previous work demonstrated that NH₃ formation correlates with WGS activity of the material and we detected the formation of Rh hydride species spectroscopically. Therefore, we infer that these single-atom catalysts have different catalytic activity for WGS, which results in the difference in forming NH₃ amounts during NO+CO reaction under wet condition.



CO_DRIFTS on different noble metal single-atom on CeO₂ after CO reduction at 350°C

Figure 8 In situ CO_DRIFTS over M_1 /CeO₂ (M= Rh, Ru, Ir, and Pd) under atmospheric pressure at 125°C (red), after flowing 0.5% CO (50 ml/min) from 125 to 350°C and cooled down to 125°C in 0.5% CO (blue).

Infrared spectroscopy using CO as the probe has been employed to identify supported PGM species, including single-atom, clusters, and nanoparticles due to the characteristic absorption of the metal-carbonyl complex. Herein, in situ CO-DRIFTS at 125°C was used to probe the surface species of these catalysts after CO-TPR. Exposing Ir_1/CeO_2 sample to CO yields the two range of peaks (Figure 8A, red line) including 2000 to 2100 cm⁻¹ and 1850 to 1950 cm⁻¹. After CO-TPR at 350°C (blue line), the peak at ~1900 cm⁻¹

disappeared and generated the new peak at ~1989 cm⁻¹, which may be due to the agglomeration of the cluster to nanoparticles. The dominant peaks from 2000 to 2100 cm⁻¹ still exist and become much stronger, indicating that more cationic Ir species was reduced to nanoparticles on the surface²⁷. For Ru₁/CeO₂ treated under CO at 125°C, the CO adsorption spectra are characterized by four bands, at ~2116, ~2060, ~2050, and ~1980 cm⁻¹ (Figure 8B). CO adsorption on Ru₁/CeO₂ produces lack of metallic CO bands for Ru and reveals the presence of Ru(CO)₂ and Ru(CO)₃ complexes (Ru⁸⁺-(CO)_x) on the surface²⁸. Even under CO condition after 350°C, the main peaks can be maintained. Figure 8C shows Pd₁/CeO₂ catalyst after reduction at 350°C exhibited CO adsorption in the range of 2150-2050 cm⁻¹, and 2000-1900 cm⁻¹ which are attributed to linear (Pd⁰-CO), and bridged (Pd₂-CO) configurations, respectively¹³. As shown in Figure 8D, no metallic Rh signatures could be established and the ~2079 and ~2013 cm⁻¹ doublets observed in the CO-DRIFTS spectra during CO adsorption, correspond to CO stretching frequencies of symmetric and asymmetric CO stretches in the di-carbonyl Rh(CO)₂ complexes¹. Among these M₁/CeO₂ catalysts, only Rh₁/CeO₂ catalysts, the single atoms can be partially or fully reduced under CO reduction at 350°C. For the other M₁/CeO₂ catalysts, the single atoms can be partially or fully reduced under CO condition at 350°C. For the other M₁/CeO₂ catalysts, the single atoms can be partially or fully reduced under CO condition at 350°C. For the other M₁/CeO₂ catalysts, the single atoms can be partially or fully reduced under CO condition at 350°C. For the other M₁/CeO₂ catalysts, the single atoms can be partially or fully reduced under CO condition at 350°C. For the other M₁/CeO₂ catalysts, the single atoms can be partially or fully reduced under CO condition at 350°C. For the other M₁/CeO₂ catalysts, the single atoms can be partially or fully reduce

Conclusion

In summary, these M_1/CeO_2 single-atom catalysts (M = Rh, Ru, Pd, Pt, and Ir) were synthesized via atom trapping with atomically dispersed on CeO₂. The activity sequence of these M_1/CeO_2 catalysts for NO+CO reaction is Rh > Pd \approx Ru > Pt > Ir, regardless of the dry or wet conditions. The Ir₁/CeO₂ and Pt₁/CeO₂ produce less N₂O by-product compared to the more active Rh, Ru and Pd cases. The activity of these singleatom catalysts for NO + CO was enhanced with the presence of water. NH₃ formation occurs simultaneously with excellent WGS activity of these single-atom catalysts which may be due to the M-H complex formation during the reaction. Among these M₁/CeO₂ catalysts, only Rh₁/CeO₂ and Ru₁/CeO₂ can sustain the singleatom structure before and after the reaction.

Experimental section

NO reduction with CO experiments were conducted in a plug-flow reactor system with powder samples (120 mg, 60–80 mesh) loaded in a quartz tube, using a synthetic gas mixture containing 460 ppm of NO and 1,750 ppm CO balanced with N_2 at a flow rate of 310 sccm (corresponding to GHSV 150 L/g*hr). Wet experiments were performed in the presence of 2.6 % water vapor. All the gas lines were heated to over 100 °C. Concentrations of reactants and products were measured by an online MKS Multi-Gas 2030 FTIR gas analyzer with a gas cell maintained at 191 °C. Two four-way valves were used for gas switching between the reactor and the bypass.

Preparation of catalysts

Synthesis of M₁/CeO₂. Cerium nitrate hexahydrate was purchased from Sigma with purity of 99.999%. Ceria nanoparticles were prepared from it by heating in a regular muffle furnace under static conditions at 350 °C for 5 hours. Metal precursors (Iridium(III) acetylacetonate, Tetraammineplatinum(II) nitrate, Ruthenium(III) nitrosyl nitrate solution, Palladium(II) nitrate dihydrate, Rhodium(III) nitrate hydrate) were respectively impregnated on CeO₂ powder by incipient wetness impregnation, with the calculated M loadings of 0.2wt%Ir, 0.2wt%Pt, 0.1Ru, 0.1wt%Pd and 0.1wt%Rh (keep the same mole amount). After impregnation, the samples were dried at 100 °C for 12 h, followed by calcination at 800 °C in air for 1 h to yield M_1 /CeO₂ catalyst ((M= Ir, Pt, Ru, Pd, and Rh), respectively.

Synthesis of Rh_1/CeO_2 -AT with different loadings. The same synthesis process was conducted to M_1/CeO_2 -AT except for the loadings (0.02wt%Rh, 0.1wt%Rh and 0.5wt%Rh). The formed samples are designated as 0.02wt%Rh_1/CeO_2-AT, 0.1wt%Rh_1/CeO_2 and 0.5wt%Rh_1/CeO_2-AT

Synthesis of Rh-CeO₂-CP. Cerium nitrate hexahydrate and Rhodium(III) nitrate hydrate $(0.5wt\%Rh/CeO_2)$ were simultaneously dissolved in deionized water at room temperature. Under stirring, ammonia was added dropwise. The obtained sample was washed with H₂O followed by ethanol and then dried. Finally, the sample was calcined at 800 °C in air for 1h. The resulting sample is designated as $0.5wt\%Rh-CeO_2$ -CP.

Characterizations

Specific Surface areas were conducted on a Micromeritics ASAP-2000 instrument with Ar as the adsorbate. Prior to analysis, the samples were dehydrated under vacuum for 3 hours at 250 °C.

High-resolution transmission electron microscopy (HRTEM) images were performed with a probe corrected FEI Titan 80-300 electron microscope operated at 300 kV. The sample preparation involved an

initial meshing through a 100 mesh No. grid. Then, a small amount of powder was thoroughly dissolved in ethanol and further deposited on a 200 mesh Lacey Carbon Cu grid, where the ethanol was fully evaporated before imaging.

In situ CO-DRIFTS spectra were recorded on a Nicolet iS50R FTIR spectrometer with an MCT-B detector cooled by liquid nitrogen at 2 cm⁻¹ resolution. The catalyst powder was packed into the DRIFTS cell whereafter it was immediately connected to the gas manifold and exposed to flowing dry He. Spectra were referenced to a KBr background and 64 scans were averaged in each spectrum. Samples were pretreated at 300 °C for 30 min and cooled down to 125°C under He condition, then were exposed to the flow of 0.5% CO (50 ml/min) until the spectra did not change anymore. The resulting spectra were recorded. After that, the CO temperature-programmed reduction (CO-TPR) experiments were conducted from 125°C to 350°C and the corresponding spectra were recorded. Finally, the samples were cooled down to 125°C under 0.5% CO (50 ml/min) condition and the corresponding spectra were collected.

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PGM single-atom on CeO_2 (M₁/CeO₂)

TOC