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Potassium Titanate Nanobelts: A Unique Support for Au and AuRh Nanoparticles in the Catalytic Reduction of NO with CO

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Abstract: The catalytic reduction of NO with CO was examined over monometallic Au and bimetallic AuRh nanoparticles supported on potassium titanate (K₂Ti₆O₁₇) nanobelts (KTN) and TiO₂. The highly crystalline KTN, prepared from TiO₂ by a hydrothermal process using KOH, were several μm long and ca. 8 nm wide. Both Au and bimetallic AuRh catalysts showed a striking enhancement of the catalytic performance with KTN as support, compared to corresponding TiO₂-supported catalysts. The reasons for this behavior could be traced back using in situ diffuse reflectance infrared Fourier transform spectroscopy in tandem with modulation excitation spectroscopy, which proved that the KTN support promotes the formation of surface nitrate (-NO₃⁻), carbonate (-CO₃²⁻), and isocyanide (-NCO) species. In particular, the combination of KTN with bimetallic AuRh nanoparticles results in the facile formation of isocyanide, which is a pivotal intermediate for producing dinitrogen molecules via the reaction with NO; NCO_(a) + NO_(a) → N₂ + CO₂.

Introduction

Anthropogenic emissions of nitric oxide and carbon monoxide are a serious threat to human health and ecosystems.^[1-3] Since both molecules can be co-reacted over noble metal-based catalysts^[4] or perovskite-type metal oxide materials^[5] into N₂ and CO₂, considerable efforts have been devoted to the development of suitable catalytic materials for the reduction of NO with CO. In the early stage, platinum catalysts were studied in terms of support effects^[6-9] and surface analysis using FT-IR.^[10] Later on, among the noble metals tested, Rh-based catalysts were found to outperform any other noble metals, such as Pt and Pd.^[11-14] The properties of Rh/Al₂O₃ catalysts have been well-summarized in a review article.^[15] Over the Rh-based catalysts, two reaction paths have been evidenced; (i) the direct reduction of NO to N₂, and (ii) the consecutive reduction mediated via N₂O, as follows:

The net reaction formula of path (ii) is identical to reaction 1 (path i). Therefore, in either path, an equal molar amount of CO is required to reduce NO. Reaction 3 proceeds rather slowly and is thus crucial in determining the selectivity to N₂.^[15] To enhance the selectivity to N₂ in the low-temperature range, alloying Rh with Pt or Pd was investigated.^[16-19] Gold nanoparticles are also reported to catalyze the NO reduction efficiently at low temperature, but Au itself is not active enough to promote reaction 3, leading to fairly poor selectivity to N₂.^[20, 21] The addition of metal oxides, such as FeO_x,^[22] and alloying of Au with Pd^[23] or Rh^[24], considerably improves the catalytic performance in terms of both activity and selectivity. The catalytic performances of alumina-supported Au, bimetallic AuRh, and Rh catalysts follows the order of Rh > AuRh > Au.^[24] In situ infrared spectroscopic studies demonstrated that CO and NO adsorb on the Au surfaces in different adsorption configurations; on-top Au⁰-CO, on-top Au^{δ+}-CO, bridged CO, Au⁰-NO, Au^{δ+}-NO, and bridged NO.^[20, 25-27] Their reactions afford isocyanate (-NCO) species on both Au and metal oxide support. The surface isocyanate species undergo further reaction with adsorbed NO to produce N₂ and CO₂:

Alloying of Au with Rh facilitates reaction 4 and enhances both conversion and selectivity.^[24]

Titanium oxide has been extensively employed in the selective catalytic conversion of NO_x (NO_x-SCR).^[28-32] To extend the scope of the catalytic properties of TiO₂, 2-dimensional (2D) nanostructures of TiO₂, such as nanobelts, nanowires, and

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nanotubes, have been evaluated for several heterogeneously catalyzed reactions due to their large surface areas,^[33] chemical and thermal stability.^[34] For improving the catalytic performance of 2D TiO₂ nanostructures, they are often decorated with monometallic noble metals to form heterostructures.^[35-37] Recently, 2D potassium titanate (K₂Ti₈O₁₇) with a nanobelt morphology (KTN), decorated with Pt nanoparticles, was shown to catalyze NO_x storage-reduction efficiently because of its large capacity for NO_x adsorption as potassium nitrate (KNO₃).^[38]

In this study, we explored the potential of KTN as support for monometallic Au and bimetallic AuRh catalysts in the reduction of NO with CO. Rh, which performed best in our previous study^[24] was not chosen because its behavior can be compromised by a strong metal support effect when supported on titania.^[39, 40] In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in combination with modulation excitation spectroscopy (MES) revealed a strong promotional effect of the KTN support on the generation of nitrate and isocyanate species and shed light on their relevance for high catalytic performance of the NO reduction by CO.

Results and Discussion

The TEM images and size distribution histograms of metal particles and EDS line scans are shown in Figure 1. Figures 1a-d demonstrate that with the simple hydrothermal treatment, nanoparticles of TiO₂ P-25 can be easily transformed into nanobelts with several micrometer length and ca. 8 nm width. As a result of this transformation, the BET surface area increased by a factor of ca. 4, as shown in Table 1. The histograms of the noble metal nanoparticles (Figures 1a,c,d) on Au/TiO₂, AuRh/TiO₂, and Au/KTN show that the majority of particles were in the size range 1-7 nm (> 97 %). An exception is Au/KTN (Figure 1b), where the majority of particles (> 94 %) was in the size range of 1-8 nm, beside some larger particles in the range 10-24 nm. Despite the significant difference in the BET surface area of the TiO₂- and KNT-supported catalysts, the metal particle sizes did not differ much. The energy-dispersive X-ray (EDS) line scans presented in Figures 1i and j show that the signals of Au and Rh components overlap with each other, hinting to the formation of AuRh alloy nanoparticles, in line with earlier reported results of similarly prepared AuRh catalysts.^[24]

Figure 1. TEM images, metal particle size distribution histograms and EDS line scans of (a, e) Au/TiO₂, (b, f) Au/KTN, (c, g, i) AuRh/TiO₂, (d, h, j) AuRh/KTN.

Table 1. Mean metal particle size and BET surface area of catalysts

Catalyst	Mean size of metal particles / nm	BET surface area / m ² g ⁻¹
Au/TiO ₂	4.7	42
Au/KTN	5.7	158
AuRh/TiO ₂	3.8	39
AuRh/KTN	3.4	162

XRD patterns of the catalysts after H₂ reduction at 300 °C are shown in Figure 2. Au/TiO₂ and AuRh/TiO₂ showed only reflections due to the crystalline phases of anatase and rutile. No diffraction patterns of Au and AuRh particles were discernible, indicating their well-dispersion. On the other hand, all reflections of the KNT samples can be assigned to a monoclinic phase of K₂Ti₈O₁₇ (space group C2/m(12), JCPDS 84-2057).^[41] The disappearance of the diffraction patterns of anatase and rutile evidenced the complete transformation of TiO₂ to KTN.

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Figure 2. X-ray diffraction patterns of TiO₂- and KTN-supported Au and AuRh catalysts.

Figure 3 presents the XPS spectra of Au 4f and Rh 3d. The Au 4f_{7/2} photoelectron peak located between 82.7 and 83.2 eV was assigned to metallic Au⁰ species.^[42] With the addition of Rh or dispersion on the nanobelts, the Au 4f_{7/2} binding energy (BE) showed a negative shift to 82.7 eV, suggesting the presence of negatively charged Au atoms. The formation of Au^{δ-} results from the intimate interaction between Au⁰ and surface Ti³⁺ centers at defects in the titania.^[43, 44] No appreciable change in the position of the Rh3d_{5/2} peak was recorded with the variation of supports. However, the Rh3d_{5/2} peak was located at 306.1 eV, which showed a negative shift by 0.9 eV from its most reduced state (307.0 eV), evidencing that the Rh atoms were also negatively charged.^[45] An electronic interaction between TiO₂ and the bimetallic particles was reported before, specified as electron donation from TiO₂ to gold, which in turn conveyed the electrons to Rh.^[45] Thus, the increased electron density of both Au and Rh can be explained by the electron transfer from the support materials.^[46]

Figure 3. XPS spectra of Au 4f and Rh 3d regions of Au and AuRh catalysts.

The NO conversion and N₂ selectivity for the reduction of NO by CO are presented in Figure 4. Au/TiO₂ showed extremely low performance in both NO conversion and N₂ selectivity; i.e. 14 % NO conversion and 0 % selectivity to N₂ even at 350 °C. The deposition of Au nanoparticles onto KTN dramatically enhanced the performance, in particular the selectivity, by facilitating reactions 1 and 3. Alloying Au with Rh further enhanced the catalytic performance. The best performance was achieved with AuRh/KTN; 100 % NO conversion and 100 % selectivity to N₂ at 300 °C, at which temperature Au/TiO₂ only showed 10.5 % NO conversion and 0 % selectivity to N₂.

Figure 4. NO conversion and N₂ selectivity in catalytic reduction of NO with CO; gas mixture: 2000 ppm NO, 2000 ppm CO, He balance, total flow rate: 150 mL/min, GHSV: 15,000 h⁻¹, reaction temperature: 50 – 400 °C.

Figure 5. Phase-domain (a, c, e, g) and time-domain (b, d, f, h) DRIFTS spectra during adsorption and desorption of 2000 ppm CO in He on (a, b) Au/TiO₂, (c, d) Au/KTN, (e, f) AuRh/TiO₂, (g, h) AuRh/KTN at 50 °C.

To gain deeper insights into the reason for the enhanced catalytic performance observed with the bimetallic AuRh particles deposited on the KTN support, we carried out in situ MES-DRIFTS experiments. Phase-domain (a, c, e, g) and time-domain (b, d, f, h) IR spectra during adsorption and desorption of 2000 ppm CO at 50 °C are shown in Figure 5. On the reference catalyst, Au/TiO₂ (Figure 5a), two intense bands at 2171cm⁻¹ and 2114cm⁻¹ were observed, assignable to CO on TiO₂ (Ti⁴⁺-CO) and on-top CO on metallic Au particles (Au_p⁰-CO), respectively.[22, 26, 27, 47] On Au/KTN (Figure 5c), the band of Ti⁴⁺-CO grew stronger. Notably, bands between 1250-1700 cm⁻¹ assigned to symmetric and asymmetric stretching vibrations of carbonate (CO₃²⁻) were also detected with an in-phase angle of 220 ° (phase-delay: 140 °).[48] Their formation was rather slow compared to Au_p⁰-CO, but this can be a key for the high catalytic performance with the KTN support. As in Figure 5e, three new bands emerged at 2063, 2029, and 1874 cm⁻¹ on AuRh/TiO₂. The band at 2063 cm⁻¹ belongs to on-top CO linearly bonded to the Rh_x clusters.[49] The band located at 2029 cm⁻¹ is attributed to on-top CO adsorbed on Rh⁰ sites of nano- or larger particles, while the band at 1874 cm⁻¹ is associated with bridged CO, i.e., (Rh)₂-CO.[50] The time-domain spectra in Figure 5f evidenced that on-top CO adsorbed on Rh takes a much longer time for its desorption compared to Au_p⁰-CO and Ti⁴⁺-CO. Similar to Au/KTN, AuRh/KTN also showed the bands originating from surface carbonate species. A major difference is the delayed CO adsorption and desorption as indicated by an in-phase angle of 290°. The in-phase angle analysis proved that CO adsorption occurred in the following sequence: firstly, on Au and KTN as linearly adsorbed CO, and secondly on Rh as on-top CO, and finally on KTN as carbonate species.

Figure 6. Phase-domain (a, c, e, g) and time-domain (b, d, f, h) DRIFTS spectra during adsorption and desorption of 2000 ppm NO in He on (a, b) Au/TiO₂, (c, d) Au/КТN, (e, f) AuRh/TiO₂, (g, h) AuRh/КТN at 50 °C.

Figure 6 presents phase-domain (a, c, e, g) and time-domain (b, d, f, h) IR spectra during adsorption and desorption of NO at 50°C. On Au/TiO₂ there was no NO adsorption detected. With the Au/KTN catalyst, three absorption bands at 1901, 1847 and 1651 cm⁻¹ appeared, which were absent on Au/TiO₂. The band at 1910 cm⁻¹ is assigned to a positively charged on-top NO species (-NO^{δ+}) as an Au-nitrosyl complex.^[51] The band at 1847 cm⁻¹ is ascribed to on-top NO with a neutral charge on metallic Au.^[52] The intense band at 1651 cm⁻¹ can be assigned to *adsorbed* NO₂, formed using oxygen atoms of the KTN support.^[20] Interestingly, there was a large gap of in-phase angles between Au-NO ($\varphi^{\text{PSD}} = 310^\circ$), and adsorbed NO₂ ($\varphi^{\text{PSD}} = 180^\circ$), indicating that the oxidative adsorption of NO on KTN proceeds slowly. With the same phase angle ($\varphi^{\text{PSD}} = 180^\circ$), nitrate (NO₃²⁻) species at 1300-1560 cm⁻¹ were also detected accompanied by the formation of adsorbed NO₂.^[53, 54] The XPS analysis evidenced that the KTN support contributes to enrichment of electrons on Au particles. Thus enhanced electron back-donation from the filled orbitals of Au to the vacant π^* orbital of NO might have accelerated the NO adsorption.^[55] On AuRh/TiO₂, a different band emerged at 1708 cm⁻¹, assigned to negatively charged on-top NO species (-NO^{δ-}) on Rh.^[56, 57] The Rh-NO^{δ-} has been reported to be an active precursor for NO dissociation to produce nitrile and adsorbed oxygen atoms, which is a key surface step for the reduction of NO with CO.^[56, 58]

On AuRh/KTN, this band shifted to 1689 cm^{-1} , as in Figure 6g (green line: $\varphi^{\text{PSD}} = 260^\circ$).^[56] The redshift indicates weakening of the N-O bond and strengthening of the Rh-N bond due to the electron transfer

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from Rh to the anti-bonding π^* orbital of the N-O bond, which leads to a higher propensity of this species to dissociate on reduced Rh surfaces.^[59-61] Note that the intensity of the band at 1647 cm^{-1} was doubled compared to that of AuRh/TiO₂. The formation of adsorbed NO₂ is much more facile and slightly rapid ($\varphi^{\text{PSD}} = 190^\circ$).

Figure 7. Time-domain (a, c, e, g) and phase-domain (b, d, f, h) DRIFTS spectra during CO-concentration modulation for the reduction of NO with CO; 2000 ppm CO and 2000 ppm NO in He balance (0 – 200 s), and following NO treatment; 2000 ppm NO in He balance (200 – 400 s) on (a, b) Au/TiO₂, (c, d) Au/KTN, (e, f) AuRh/TiO₂, (g, h) AuRh/KTN at 200 °C.

Figure 7 shows in situ DRIFT spectra during the reduction of NO with CO-concentration modulation at 200 °C. MES experiments were conducted by switching between two different effluent gases; (i) 2000 ppm CO and 2000 ppm NO in He balance (0 – 200 s), (ii) 2000 ppm NO in He balance (200 – 400 s). This MES experiments allowed to modulate reaction 4 (see Introduction section). On the Au/TiO₂ surface, there emerged only two bands at 2175 and 2110 cm^{-1} , assigned to $\text{Ti}^{4+}\text{-CO}$ and $\text{Au}^0\text{-CO}$, respectively. These two bands appeared with a delay ($\varphi^{\text{PSD}} = 354^\circ$) on Au/KTN. There was no NO adsorption confirmed for Au/KTN, whereas adsorbed NO₂ and nitrates emerged at an in-phase angle of 313° . This phenomenon seems to be the key for the high NO conversion observed with Au/KTN. However, at this reaction temperature (200 °C), the selectivity to N₂ remained at 0 % (see Figure 4), producing only N₂O via reaction 2. This lead us to assume that the formation of adsorbed NO₂ and nitrates only promotes reaction 2, resulting in high NO conversion at low N₂ selectivity. The most striking feature was observed for AuRh/KTN, as shown in Figures 7g and 7h. In addition to the above

described bands, a new band slowly emerged at 2202 cm^{-1} , assigned to isocyanate species on KTN (Ti-NCO).^[62] On the TiO₂-based catalysts (Figures 7a and 7e), the isocyanate species was not formed at all. The isocyanate species is known to be a pivotal reaction intermediate increasing the N₂ selectivity through reaction 4. The formation of the isocyanate species at low temperature is proposed to be the major factor for the high catalytic performance of the AuRh/KTN catalyst compared to AuRh/TiO₂. It seems likely that a similar enhancement of the catalytic performance can also be observed with other noble metals supported on KTN for this reaction.

Conclusion

The present work revealed a tremendous influence of the nature of the support (potassium titanate nanobelts (KTN) and TiO₂) on the catalytic performance of monometallic Au and bimetallic AuRh nanoparticles in the reduction of NO with CO. Catalysts based on KTN as support resulted in a compelling improvement of the activity and N₂ selectivity compared to corresponding titania-supported catalysts. The reasons for this enhancement were uncovered by in situ MES-DRIFTS. The combination of bimetallic AuRh nanoparticles and KTN as support dramatically lowers the temperature required for the formation of surface isocyanate (-NCO) species, which are at the origin of the high NO conversion and N₂ selectivity exhibited by the AuRh/KTN catalyst. On both supports the bimetallic AuRh nanoparticles showed enhanced adsorption of NO and the formation of adsorbed NO₂ species resulting in superior catalytic performance compared to the corresponding monometallic Au catalyst.

Experimental Section

Catalyst preparation

A commercially available titanium (IV) oxide (Sigma-Aldrich, P-25, a mixture of 70 % rutile and 30 % anatase, 99.5 % purity on the Ti metal basis) and potassium hydroxide (Kermel, > 85 %) were used to synthesize the nanowire support. Chloroauric acid (HAuCl₄, Energy Chemical, 98 %), and an ammonia solution (Aladdin, 25-28 %) was used for the deposition-precipitation (DP) method. The ammonia solution was diluted to 1 mol/L by adding deionized water. Rhodium (III) chloride trihydrate (RhCl₃·3H₂O, Damas-Beta, 98 %), PEG-2000 (polyethylene glycol, Energy Chemical), and NaBH₄ (Energy Chemical, 98 %) were used for the reduction of the cationic metal salts to metallic nanoparticles.

The KTN support was synthesized by a hydrothermal treatment using a suspension of solid TiO₂ powder and aqueous KOH as precursors.^[38] 1.5 g of TiO₂ was dispersed in 50 ml of 10 mol/L KOH aqueous solution. After stirring for 30 min, the resultant suspension was sealed into a Teflon-lined autoclave made of stainless-steel and heated to 130 °C, and kept at this temperature for 4 days. Then, the resulting precipitate was filtered and the residual KOH washed out with 2 L of deionized water. The obtained white-colored solid was placed in an oven and dried at 100 °C in air overnight.

3 wt% Au was dispersed onto KTN by a deposition-precipitation method.^[63] In brief, HAuCl₄·H₂O was dissolved in 100ml of deionized water and was heated to 70 °C. After adjusting the pH to 7.0 by adding aqueous solution of ammonia, dried KTN powder was added under stirring. The pH of the slurry was maintained at around 7.0 and aged for 1h. The resulting slurry was filtered and then washed with deionized water. The obtained

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material was dried at 60 °C overnight and then calcined at 300 °C in air for 1 h (ramping rate of 1 °C/min).

KTN-supported bimetallic AuRh catalysts were synthesized by reduction of corresponding Au and Rh salts with NaBH₄ at room temperature.^[64] In a typical synthetic procedure, 3.7 mL of deionized water, 200 µL of 80 mg/mL PEG-2000, and 1 mL of 50 mM solutions of HAuCl₄ and RhCl₃·3H₂O were mixed in a 20 mL glass vial. The molar ratio of Au to Rh was adjusted to 1:1 (total metal loading to a nominal value of 3 wt%). After stirring for 20 min, KTN powders were added to the solution. Afterward, 100 µL of 20 mg/mL NaBH₄ was added slowly and the slurry was aged for 1 hour. The obtained solid material was then separated by centrifugation and washed with ethanol several times. The obtained material was dried overnight at 60 °C. For comparison, Au/TiO₂ and AuRh/TiO₂ were also prepared in the same manner as reference catalysts.

Catalytic reaction

The performance of the different catalysts was evaluated using a fixed bed micro-flow reactor system. 300 mg of the catalyst was loaded into a stainless-steel tubular reactor (inner diameter of 8.2 mm). Before each reaction, the catalyst was pretreated in pure H₂ flow (100 mL/min) at 300 °C for 1 h (ramping rate, 5 °C/min). After H₂-reduction, the catalyst was kept at 300 °C for 10 min in pure He flow to remove gaseous H₂ and adsorbed H atoms on the catalyst surface. Then the reactor was cooled down to 50 °C in He flow. Subsequently, 2000 ppm of CO and 2000 ppm of NO in He balance was fed into the reactor at a total flow rate of 150 mL/min, which corresponds to a gas-hourly space velocity (GHSV) of 15,000 h⁻¹. The gaseous compositions were analyzed using a gas chromatograph (Fili, 9750 GC) equipped with a thermal conductivity detector (TCD) and a molecular sieve 5A column, and also with a NO_x analyzer (Thermo Scientific, 42i-HL). All the data at different temperatures were recorded after waiting for 30-70 min to reach steady-state conditions. Each experiment was measured at least twice to ensure the reproducibility of the data. A blank test without any catalyst did not indicate any activity of the walls of the stainless-steel tube reactor.

Catalyst Characterization

The specific surface areas of all catalysts after H₂ reduction at 300 °C were determined from nitrogen adsorption measurements at 77 K on an ASAP 2020 apparatus (Micromeritics) using the Brunauer-Emmett-Teller (BET) method. Before BET measurements, all samples were degassed at 250 °C for 4 h to eliminate adsorbed CO₂ and H₂O.

X-ray diffraction (XRD) measurements were carried out on a PANalytical X'Pert diffractometer using Pd-filtered Cu Kα radiation at 55 mA and 60 kV.

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi instrument to examine surface compositions and oxidation states of the catalyst surfaces. Al Kα radiation (1486.6 eV, 15 kV, 10.8 mA) was applied to excite photoelectrons at 50 eV of pass energy at an energy calibrated versus Ag 3d5/2 at 1 eV.

Transmission electron microscopy (TEM: FEI, Tecnai G² F30, 200kV~300kV) was employed to determine the particle size of Au and AuRh nanoparticles and to gain information about the morphology of the synthesized KTN. Electron dispersive spectroscopy (EDS) installed in the Tecnai G² F30 TEM was used to measure line profiles of the components of the bimetallic nanoparticles.

In situ IR measurements were recorded using a FT-IR spectrometer (Bruker Optics, Vertex 70) with a liquid N₂-cooled HgCdTe (MCT) detector. The optics settings employed were: spectral resolution, 4 cm⁻¹; scanning velocity, 60 kHz; aperture size, 8 mm. 20 mg of the samples was charged into a porous ceramic cup-shaped reactor through which gaseous molecules can pass. The ceramic cup was placed in a diffuse reflectance IR Fourier transform spectroscopy (DRIFTS) cell sealed with ZnSe

windows. The gas phase compositions were controlled by a 4-way valve (VICI AG International) and mass flow controllers (Azbil Control Solution Co., Ltd.). The sample compartment and all the IR beamlines were purged with dried air continuously supplied by an air compressor (EKOM) to remove the H₂O vapor, whose IR bands overlap with the IR fingerprint regions of our interest. Before each measurement, the samples were pretreated with pure H₂ (100 mL/min) for 1 h at 300 °C (ramping rate of 5 °C/min).

MES^[65, 66] experiments were carried out by changing between two gas mixtures: (i) 2000 ppm of CO in He balance (50 s) and pure He (50 s) at 50 °C for CO adsorption-desorption modulation; (ii) 2000 ppm of NO in He balance (50 s) and pure He (50 s) at 50 °C for NO adsorption-desorption modulation; (iii) 2000 ppm of CO and 2000 ppm of NO in He balance (200 s) and 2000 ppm of NO in He balance (200 s) for CO-concentration modulation during the reduction of NO with CO. The spectra obtained in the initial two modulation cycles were disposed to obtain stable and reproducible responses of IR absorption bands. We averaged five cycles into one cycle to enhance the time resolution and signal-to-noise (S/N) ratio. Phase-sensitive detection^[67] was applied to further remove the noise, which behaves in a different/random frequency and to evaluate kinetics of active species through phase-delay or in-phase angle. The phase-domain spectra were derived from the corresponding time-domain spectra by the following equation:

$$A_k(\varphi_k^{PSD}) = \frac{2}{T} \int_0^T A(t) \sin(k\omega t + \varphi_k^{PSD}) dt \quad (6)$$

where T is the length of a cycle, ω is the modulation frequency, φ_k^{PSD} is the demodulation phase angle, k is the demodulation index ($k = 1$ in this study), and $A(t)$ and A_k are the active species responses in the time and phase domains, respectively.

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Keywords: Bimetallic AuRh • potassium titanate nanobelts • NO reduction with CO • isocyanate • in situ IR spectroscopy

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FULL PAPER

Entry for the Table of Contents

Potassium titanate ($\text{K}_2\text{Ti}_8\text{O}_{17}$) nanobelts (KTN) are a unique support for Au and bimetallic AuRh nanoparticles showing strong enhancement of the catalytic reduction of NO with CO to N_2 . The KTN support facilitates the formation of surface nitrate, carbonate and isocyanide species, resulting in superior catalytic activity compared to corresponding TiO_2 -supported catalysts.