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COMMUNICATION

Ammonium formate decomposition over Au/TiO₂: A unique case of preferential selectivity against NH₃ oxidation†

Manasa Sridhar,‡[a] Daniel Peitz,‡[a] Jeroen Anton van Bokhoven[a,b] and Oliver Kröcher[a,c]*

The unique selectivity of Au/TiO₂ for converting ammonium formate to CO₂ in the presence of excess O₂ and H₂O without oxidising NH₃ up to 300 ºC is reported. The catalyst is highly stable and selective even after severe hydrothermal aging.

The advent of stringent measures curbing NO_x emissions has increased the demand for improved technologies for the selective catalytic reduction (SCR) of NO_x in both stationary and mobile applications.[1,2] Currently, urea is the most widely used NH_3 source implemented in mobile SCR. Immense interests in replacing this material with alternative NH_3 precursors, such as concentrated guanidinium formate, ammonium formate (AmFo) and methanamide solutions, that are more thermally stable, freeze at lower temperatures, have higher NH_3 storage capacities, and decompose more selectively have grown recently.[3] One challenge is identifying highly active and robust dedicated hydrolysis catalysts that selectively hydrolyse the precursors and release NH_3 without oxidation.[4–6] Of the aforementioned precursors, AmFo is experimentally the simplest choice to study the activity and behaviour of the hydrolysis catalysts towards selective NH_3 release and side product suppression under realistic conditions.[7]

In this work, analogous to the extraordinary selectivity of finely dispersed Au for preferential CO oxidation (PROX) in H_2-rich stream[8–11], we highlight another phenomenological observation, wherein, Au supported on TiO₂ catalysts are found to show absolute selectivity for AmFo decomposition in the presence of excess O₂, yielding 100% NH_3 without any NH_3 oxidation up to temperatures as high as 300 °C. Anatase Au/TiO₂ catalysts synthesised via a facile modified incipient wetness impregnation method[12] were coated onto 400 cpsi cordierite monoliths[13] and tested in a laboratory reactor setup to study the decomposition of liquid NH_3 precursor compounds under spray conditions with precise temperature control.[5,14] Fig. 1 illustrates the CO₂, CO, NH_3, formic acid, methanamide and NO_x (NO+NO₂) yields released upon the complete decomposition of 40% AmFo over 0.5 wt% Au/TiO₂.
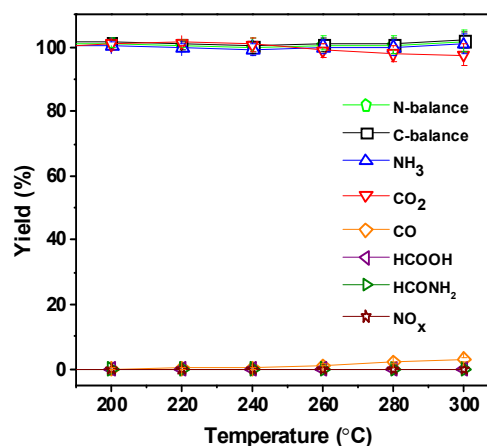
Fig. 1 Product yields during AmFo decomposition over 0.5% Au/TiO₂ (100 g·L⁻¹ washcoat loading, GHSV = 19,490 h⁻¹; feed gas: 5% H₂O, 10% O₂, 85% N₂ and 0.05 mL·min⁻¹ liquid spray of 40 wt% AmFo) showing nearly 100% NH_3 and CO₂ yields between 200 °C and 300 °C.

The carbon and nitrogen balances were closed using the molar feed and reactor outlet concentrations as quantified by FT-IR spectroscopy.[15] Washcoat loading refers to the amount of the catalyst deposited on the monolith per unit volume.[16] At a 100 g·L⁻¹ washcoat loading, which is approximately two-thirds of the typical catalyst loadings in automobiles, Au/TiO₂ reliably converted AmFo into NH_3, and CO₂ with 10% O₂ and 5% H₂O present in the feed. NH_3 did not react under such conditions rendering negligible NO_x and methanamide yields, the latter being a side-product arising from the reaction between formic acid and NH_3.[7] Methanamide may dehydrate further to form HCN; however, under these reaction conditions, no HCN was formed over Au/TiO₂. To determine the stability of the catalysts at partial conversion, the washcoat loading was reduced by 99.5% and tested under identical conditions of
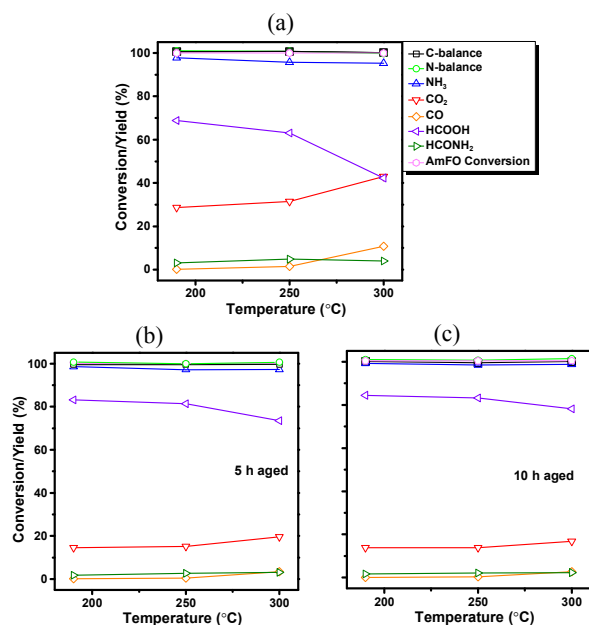
Fig. 2 Product yields and AmFo conversion during AmFo decomposition over (a) fresh (b) 5 h aged, and (c) 10 h aged 0.5% Au/TiO_2 catalysts (0.5 g·L^{-1} washcoat loading, GHSV = 19,490 h^{-1}; feed gas: 5% H_2O, 10% O_2, 85% N_2 and 0.05 mL·min^{-1} liquid spray of 40 wt% AmFo), showing nearly 100% NH_3 yields between 200 °C and 300 °C.

GHSV and feed composition. Additionally, the fresh catalyst was subjected to two incremental hydrothermal aging steps each lasting for 5 h at 800 °C in air containing 10% H_2O, and the activity tests were repeated.

Fig. 2 (a), (b) and (c) depict the yield of all products formed from the decomposition of 40 wt% AmFo over fresh, 5 h and 10 h hydrothermally aged 0.5 wt% Au/TiO_2, respectively. 100% conversion for AmFo decomposition was achieved with all catalysts. NH_3, formic acid and CO_2 were the major products, while CO and methanamide formed in low yields. The CO yield decreased from ~10% over fresh catalyst to ~3% over aged catalysts. Methanamide, which was not observed in the case of 100 g·L^{-1} catalyst, started to appear when using 0.5 g·L^{-1} catalyst and accounted for ~3% yield or lesser over both

Table 1 Mass based rate constants at various reaction temperatures calculated using pseudo first order kinetics (refer to ESI†).

Catalyst sample	Temperature (K)	Rate constant k_{mass} (L·$g^{-1}s^{-1}$)
Fresh	300	12.5 ± 0.03
	250	6.1 ± 0.01
	190	4.4 ±0.02
5 h Aged	300	4.4 ± 0.02
	250	2.7 ± 0.01
	190	2.0 ± 0.02
10 h Aged	300	3.7 ± 0.03
	250	2.4 ± 0.02
	190	2.0 ± 0.01
Bare TiO_2	300	3.2 ± 0.04
	250	0.8 ± 0.04
	190	0.3 ± 0.03

the fresh and aged catalysts across all temperatures. CO_2 yields were decreased due to aging from ~43% over the fresh catalyst to ~20% and ~17% over 5 h and 10 h aged catalysts, respectively, at 300 °C. The product yield patterns over the 5 h and 10 h aged catalysts suggest a kind of stabilisation of the catalytic activity after the first aging step. Moreover, NH_3 yields always remained close to 100%, which further reiterates the discriminative oxidation behaviour of our catalyst, and contrasts the typical NH_3 oxidation behaviour of precious metal containing catalysts.[17,18]

Pseudo-first-order kinetic constants were calculated to assess the relative activities of catalysts tested under identical operating conditions.[19–21] Table 1 lists the mass based rate constants calculated for the fresh, 5 h aged, 10 h aged 0.5 wt% Au/TiO_2 and fresh bare TiO_2 catalysts. The rate constants progressively decreased for all catalysts with decreasing temperature, indicative of generic Arrhenius behaviour. Hydrothermal aging at 800 °C for 5 h decreased the rate constants by over 60%, while, 5 h further treatment resulted in a marginal drop of ~15% when comparing the activities at 300 °C. At lower temperatures, the rate constants tend to nearly identical values for 5 h and 10 h aged catalysts. To elucidate the influence of Au, a control experiment using similar washcoat loading of bare TiO_2 was performed under identical conditions. The resultant rate constants were found to be a magnitude of at least 4 lower than that of the fresh Au/TiO_2 catalysts. Importantly, over bare TiO_2, the conversion of formic acid selectively produces CO; there is no CO_2 formation, under these conditions.

Because, formic acid undergoes secondary reactions to form CO and CO_2, the evolution of their selectivities as a function of temperature over the fresh and aged catalysts is interesting. Fig. 3 (a) and (b) show that the temperature dependence of the selectivities for CO and CO_2 formation and formic acid
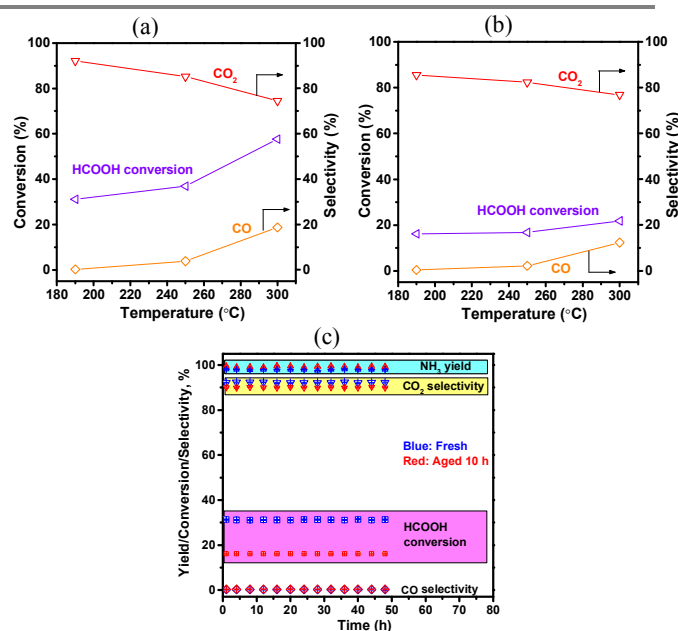
Fig. 3 Relationship between selectivity and conversion with temperature for fresh (a) and 10 h aged (b) 0.5% Au/TiO_2 catalysts and (c) Time on stream plot portraying long term stability of fresh (blue) and 10 h hydrothermally aged (red) catalysts at 190 °C (0.5 g·L^{-1} washcoat loading on the monolith, GHSV = 19,490 h^{-1}; feed gas: 5% H_2O, 10% O_2, 85% N_2 and 0.05 mL·min^{-1} liquid spray of 40 wt% AmFo).

conversion remained essentially unchanged even after 10 h aging. A decrease in CO_2 selectivity was accompanied by an increase in the CO selectivity with increasing temperature for all catalysts. Formic acid conversion was significantly affected by the hydrothermal aging translating to a drop in conversion from ~57% to ~17% after 10 h treatment in 10% H_2O. The HAADF-STEM images of fresh and 10 h hydrothermally aged 0.5 wt% Au/TiO_2 are presented in Fig. S1. It appears that while the support (TiO_2) morphology exhibited signs of sintering upon 10 h hydrothermal aging at 800 ºC, the particle sizes of the visible Au particles were only subtly affected. TiO_2 support particles of the aged catalyst are in an aggregated state upon sintering which is in consensus with the lowering of BET surface area from ~80 m^2/g to ~50 m^2/g (Table S1). An increase in average crystallite size from ~25 nm to ~32 nm was obtained from XRD measurements (Fig. S2). However, no phase transformation of TiO_2 from anatase to rutile was evident from the XRD patterns. Further mechanistic study is underway to determine the role of Au and TiO_2 in our reaction.

The time on stream activities of the fresh and 10 h hydrothermally aged catalysts were evaluated over 48 h (Fig. 3 (c)). A low temperature (190 °C) was chosen to examine the low conversion stability. Both the fresh and aged catalysts exhibited stable activities, selectivities and nearly 100% NH_3 yields with no signs of deactivation with time-on-stream.

Conclusions

Au/TiO_2 demonstrating unique selectivity against NH_3 oxidation in a highly oxidizing environment during AmFo decomposition is reported here for the first time. The catalysts display excellent stability giving close to 100% NH_3 yields for 48 h of time on stream showing no signs of deactivation. The observations evidenced in this work, reflecting the exceptional selectivity against NH_3 oxidation could entail new applications of monometallic gold in exhaust gas catalysts.

Notes and references

[a] Paul Scherrer Institut, 5232 Villigen, Switzerland
E-mail:oliver.kroecher@psi.ch
[b] ETH Zurich, Institute for Chemical and Bioengineering, 8093 Zurich, Switzerland
[c] École Polytechnique Fédérale de Lausanne (EPFL), Institute of Chemical Sciences and Engineering, 1015 Lausanne, Switzerland
†Electronic Supplementary Information (ESI) available: Experimental details and calculation of pseudo-first order rate constants
‡These authors contributed equally to this work.

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