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Ammonium formate decomposition over Au/TiO$_2$: A unique case of preferential selectivity against NH$_3$ oxidation†

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The unique selectivity of Au/TiO$_2$ for converting ammonium formate to CO$_2$ in the presence of excess O$_2$ and H$_2$O without oxidising NH$_3$ up to 300 °C 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.$^7$ 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 TiO$_2$ catalysts are found to show absolute selectivity for AmFo decomposition in the presence of excess O$_2$, yielding 100% NH$_3$ without any NH$_3$ oxidation up to temperatures as high as 300 °C. Anatase Au/TiO$_2$ catalysts synthesised via a facile modified incipient wetness impregnation method$^{12}$ were coated onto 400 cpsi cordierite monoliths$^7$ and tested in a laboratory reactor setup to study the decomposition of liquid NH$_3$ precursor compounds under spray conditions with precise temperature control.$^{3,14}$

Fig. 1 illustrates the CO$_2$, CO, NH$_3$, formic acid, methanamide and NO$_x$ (NO+NO$_2$) yields released upon the complete decomposition of 40% AmFo over 0.5 wt% Au/TiO$_2$.

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/TiO$_2$ reliably converted AmFo into NH$_3$, and CO$_2$ with 10% O$_2$ and 5% H$_2$O 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$_3$. Methanamide may dehydrate further to form HCN; however, under these reaction conditions, no HCN was formed over Au/TiO$_2$. To determine the stability of the catalysts at partial conversion, the washcoat loading was reduced by 99.5% and tested under identical conditions of
the fresh and aged catalysts across all temperatures. CO₂ 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, NH₃ yields always remained close to 100%, which further reiterates the discriminative oxidation behaviour of our catalyst, and contrasts the typical NH₃ 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/TiO₂ and fresh bare TiO₂ 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 TiO₂ 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/TiO₂ catalysts. Importantly, over bare TiO₂, the conversion of formic acid selectively produces CO₂ there is no CO₂ formation, under these conditions.

Because, formic acid undergoes secondary reactions to form CO and CO₂, 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 CO₂ formation and formic acid

<table>
<thead>
<tr>
<th>Catalyst sample</th>
<th>Temperature (K)</th>
<th>Rate constant $k_{\text{max}}$ (L·g⁻¹·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>300</td>
<td>12.5 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>6.1 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>4.4 ± 0.02</td>
</tr>
<tr>
<td>5 h Aged</td>
<td>300</td>
<td>4.4 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>2.7 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>2.0 ± 0.02</td>
</tr>
<tr>
<td>10 h Aged</td>
<td>300</td>
<td>3.7 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>2.4 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>2.0 ± 0.01</td>
</tr>
<tr>
<td>Bare TiO₂</td>
<td>300</td>
<td>3.2 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.8 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>0.3 ± 0.03</td>
</tr>
</tbody>
</table>

Table 1: Mass based rate constants at various reaction temperatures calculated using pseudo first order kinetics (refer to ESI†).
conversion remained essentially unchanged even after 10 h aging. A decrease in CO\textsubscript{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\textsubscript{2}O. The HAADF-STEM images of fresh and 10 h hydrothermally aged 0.5 wt% Au/TiO\textsubscript{2} are presented in Fig. S1. It appears that while the support (TiO\textsubscript{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\textsubscript{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\textsuperscript{2}/g to ~50 m\textsuperscript{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\textsubscript{2} from anatase to rutile was evident from the XRD patterns. Further mechanistic study is underway to determine the role of Au and TiO\textsubscript{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 ºC) was chosen to examine the low conversion stability. Both the fresh and aged catalysts exhibited stable activities, selectivities and nearly 100% NH\textsubscript{3} yields with no signs of deactivation with time-on-stream.

Conclusions

Au/TiO\textsubscript{2} demonstrating unique selectivity against NH\textsubscript{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\textsubscript{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\textsubscript{3} oxidation could entail new applications of monometallic gold in exhaust gas catalysts.

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Notes and references