Unconventional emission catalyst concepts and reactors

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Highlights

- Ammonia removal in the presence of oxygen required multicomponent catalyst reactors to prevent NO_x and N_2O formation
- Catalytic ammonia removal in gasification conditions is desired to prevent NO_x formation in following combustion
- Efficient nitrate reduction by H_2 in water solutions on Pd based catalysts, targeting to N_2 as a main product.
- Selective copper electrocatalysis of nitrates to NH_3 was reviewed as a comparison to the method using H_2 as a reductant.

1. Introduction

Emission catalysis is best known by three-way, oxidation, SCR and NO_x adsorbent catalysts in vehicle, machinery, marine and power plant applications. Commercial catalysts are based on ceramic and metallic honeycomb substrates, where porous support, active metals and promoters are added as a thin layer. Commercial emission catalysts are an excellent example of intensification and downsizing the chemical reactor by kinetics, mass transfer and expenses to the applications, where space, material costs (e.g. noble metals) and energy losses need to be minimal. Extruded catalysts with a low cell density match particularly fluids, which contain a higher number of particulates, pressure drop requirements are low or the high absolute catalyst amount (g/L) is essential. This study reviews a few unconventional catalytic removal methods related to the removal of nitrogen oxides (NO, NO_2, N_2O) and ammonia, which are harmful pollutants and greenhouse gases, emitted from combustion, processes or as side products in catalyst reactions.

2. Methods

Examples with emission catalyst concepts are based on laboratory experiments, thermodynamic calculations or published literature data. Reaction studies were conducted using synthetic gas bench reactors, where feed compositions were mixed by the mass flow controllers. In experiments, catalysts were coated catalysts on metallic or ceramic substrates. Reaction examples included ammonia removal on the combinatory oxidation, SCR and N_2O decomposition catalysts in series and nitrate removal in water solutions by H_2 reduction or electrocatalysis. Active metals in catalyst experiments included Pd, Pt, Ru, Cu, Fe and Pt on various porous supports. Thermodynamic calculations (HSC or Solgasmix programs) were applied to confirm reaction barriers. Simplified kinetic modelling was also introduced for nitrate reduction.

3. Results and discussion

Two concepts, utilizing catalytic units in parallel, sequential or layers structures were analyzed to remove ammonia in SCR or other flue gas applications. Ammonia slip catalyst catalysts (ASCs) have been in wide commercial use since Euro 6 emission regulations, requiring over 96% NO_x conversion even in transient test cycles. After intense development in past, utilized pore diffusion together with separated NH_3 adsorption (zeolite), oxidation (Pt) and SCR (Cu, Fe) reactions 2-layer structures result in a high selectivity from NH_3 to N_2 with minor nitrogen oxide formation (Fig. 1) [1]. It is also possible to oxidize NH_3 partially to NO_x, which is then converted downstream selectively to N_2 on a NH_3-SCR and N_2O decomposition catalyst [2].

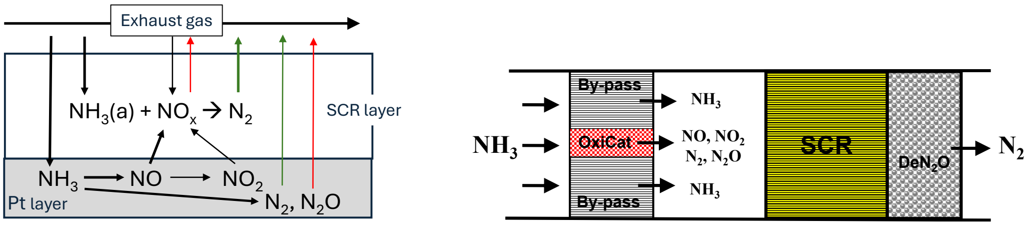

Figure 1. NH_3 removal with 2-layer ASC (left) and sequential catalyst (right) concepts.

In gasification of solid fuels, in addition to heavy hydrocarbons (tars) and sulfur species, ammonia is formed in harmful concentrations and should be removed before following combustion steps to prevent NO_x formation. Catalytic ammonia removal in gasification conditions at 800-900°C and higher pressures (up to 20 bar) is an application to convert NH_3 to N_2. However, the reducing conditions and high pressure set a limit to maximum NH_3 conversion (e.g. 80%), even if it was possible to reach over 90% conversions at 1 bar [3].

Nitrates are present in water as an impurity or as absorbed in purpose by NO_x scrubbing. Nitrate reduction by hydrogen was investigated in batch experiments, where nitrate solution was circulated through a catalytic honeycomb reactor [4]. The reduction selectivity to desired N_2 product was improved by the Pd catalyst development and optimization of conditions (Fig. 2). In addition to the complete 3-phase reaction model [4] with a storage tank and a circulating plug flow reactor, a simplified CSTR reactor model with analytical solutions was created by concentrations (NO_3, NO_2, NH_4; bal. N_2) in batch experiments.

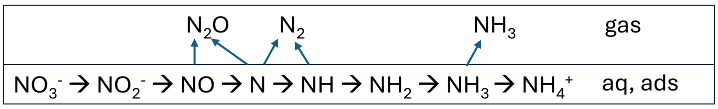

Figure 2. Catalytic nitrate removal by hydrogen in solid-liquid-gas reactions.

On the other hand, in the reviewed electrocatalysis of NO_3 and NO_2 on Cu nanomaterials, the target is to form NH_3 as the final useful chemical with a high selectivity at room temperature and normal pressure (Daiyan). The hydrogen to ammonia formation was received from H_2O with the assistance of the optimized electrocatalyst, electrolyzer structure and voltage. It was seen that selectivity can be designed using various conditions and electrolyzer properties, even if the alternative reaction paths are similar in these two methods.

4. Conclusions

Interesting emission catalyst reactions utilizing reaction engineering possibilities (mass transfer, multicomponent catalysts, electrolysis) were reviewed regarding ammonia and nitrate removal from fluid gases or liquids. Multifunctional 2-layer ASCs are a part of modern SCR systems. Ammonia removal methods are quite different in lean and rich conditions. Nitrates in water solutions can be converted as N_2 back to air or to ammonia, which is then utilized commercially as a chemical or fuel.

References

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Keywords
Nitrate, ammonia, catalyst, conversion