Review

Progress on Noble Metal-Based Catalysts Dedicated to the Selective Catalytic Ammonia Oxidation into Nitrogen and Water Vapor (NH₃-SCO)

Magdalena Jabłońska

Institute of Chemical Technology, Universität Leipzig, Linnéstr. 3, 04103 Leipzig, Germany; magdalena.jablonska@uni-leipzig.de

Abstract: A recent development for selective ammonia oxidation into nitrogen and water vapor (NH₃-SCO) over noble metal-based catalysts is covered in the mini-review. As ammonia (NH₃) can harm human health and the environment, it led to stringent regulations by environmental agencies around the world. With the enforcement of the Euro VI emission standards, in which a limitation for NH₃ emissions is proposed, NH₃ emissions are becoming more and more of a concern. Noble metal-based catalysts (i.e., in the metallic form, noble metals supported on metal oxides or ion-exchanged zeolites, etc.) were rapidly found to possess high catalytic activity for NH₃ oxidation at low temperatures. Thus, a comprehensive discussion of property-activity correlations of the noble-based catalysts, including Pt-, Pd-, Ag- and Au-, Ru-based catalysts is given. Furthermore, due to the relatively narrow operating temperature window of full NH₃ conversion, high selectivity to N₂O and NOₓ as well as high costs of noble metal-based catalysts, recent developments are aimed at combining the advantages of noble metals and transition metals. Thus, also a brief overview is provided about the design of the bifunctional catalysts (i.e., as dual-layer catalysts, mixed form (mechanical mixture), hybrid catalysts having dual-layer and mixed catalysts, core-shell structure, etc.). Finally, the general conclusions together with a discussion of promising research directions are provided.

Keywords: noble metals; supported oxides; bifunctional catalysts; NH₃-SCO

1. Introduction

Ammonia (NH₃) is a corrosive, highly toxic, and reactive inorganic gas with a pungent odor under ambient conditions. It is an atmospheric pollutant that is dangerous to health and life because it could corrode skin, eyes, and lungs, and cause permanent injury or even death when the concentration is higher than 300 ppm [1,2]. Ammonia is also reported to be the most common pollutant found in water streams, further affecting human health as the consequence of eating toxic fish and drinking water [3]. The toxic action of ammonia on aquatic animals can lead to the extinction of the entire population, threatening many important ecosystems and fisheries worldwide [4,5]. NH₃ is referred to as one of four major atmospheric pollutants together with NOₓ, SOₓ, and nonmethane volatile organic compounds (NMVOC). Approximately 5600 kt y⁻¹ of ammonia are emitted into the atmosphere each year, i.e., up to 4-times higher emission levels than in the previous century, and it continues to increase [6]. NH₃ is emitted by several various processes, including nitric acid production, urea manufacturing, nitrogen fertilizer production, biomass, and coal gasification, petroleum refining and refrigeration, livestock waste, and animal agriculture, transport (as a gas slip from the process of selective catalytic reduction of NOₓ using NH₃ or urea (SCR) in DeNOₓ applications), etc. More attention was given to the removal of NH₃ from gaseous and waste streams, e.g., through its oxidation.
The selective catalytic oxidation of ammonia (NH$_3$-SCO) into nitrogen and water vapor is considered as the most promising method for the elimination of NH$_3$ from oxygen-containing exhaust gases (Equation (1)) [7]:

\[
4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O}
\]  

(1)

NH$_3$ is generated by an onboard aqueous urea dosing system. The obtained ammonia acts as a NO$_x$ reductant in the DeNO$_x$ process. There is a serious risk that unreacted ammonia is released into the atmosphere. Thus, the active SCO catalysts (so-called guard catalyst, ammonia slip catalyst—ASC, ammonia oxidation catalyst—AMOX) should operate in a broad temperature range (up to 600–700 °C—in the cycle of diesel particulate filter regeneration) in the presence of typical components of the exhausts (H$_2$O, CO$_x$, and SO$_x$), and additionally should selectively direct the reaction to the formation of N$_2$ and H$_2$O. Euro VI emission standards for heavy-duty vehicles (HDVs) introduced for the first time limits for NH$_3$ emissions up to 10 ppm [8]. Currently, there are no limits for NH$_3$ emitted from light-duty vehicles (LDVs, i.e., passenger cars), despite their high levels of emissions (e.g., [9,10]). Thus, potentially NH$_3$ will be considered next to ultra-fine particles smaller than 23 nanometers (PN$_{10}$) and nitrous oxide (N$_2$O) in the upcoming regulations, e.g., upcoming Euro emission standards.

Various kinds of catalysts were studied for NH$_3$-SCO, including noble metals (e.g., Ru [11]), supported noble metals (e.g., Au/Nb$_2$O$_5$, Au/ZrO$_2$ [12]), (mixed) metal oxides, supported metal oxides, modified zeolites (e.g., Pt-CuMgAlO$_x$ [13], Ag-USY [13]), etc. These groups of catalysts investigated in NH$_3$-SCO were summarized by Jabłońska et al. [7,14], Gao et al. [15] and Lan et al. [16]. In general, noble metal-based catalysts tend to possess high activity at low temperatures (< 300 °C), while their high cost and relatively low N$_2$ selectivity have restrained their widespread application. Transition metal-containing oxides and zeolites show improved selectivity toward N$_2$ than noble metal-based catalysts; however, they need higher operating temperatures (300–600 °C). Consequently, the proper combination of these two metals (in the form of bifunctional catalysts) could produce the catalysts with enhanced activity and N$_2$ selectivity. In general, the concept of bifunctional catalysts is based on the internal selective catalytic reduction (i-SCR) mechanism. This mechanism consists of two main steps. In the first step, part of ammonia is oxidized to NO and NO$_2$—minor by-product, while in the second step, NO and NO$_2$ are reduced by ammonia (unreacted in the first step) with the formation of N$_2$ and H$_2$O (DeNO$_x$, NH$_3$-SCR). In this step, also the formation of N$_2$O is possible. Besides the i-SCR mechanism, other major reaction pathways, i.e., the imide (NH, in which NH$_3$ transforms to N$_2$ and N$_2$O as final products, with nitrosyl (HNO) as an intermediate) mechanism and the hydrazine (with the formation of a hydrazine-type (N$_2$H$_4$) intermediate) mechanism were proposed for NH$_3$-SCO over different types of catalysts. The details of the abovementioned reaction mechanisms can be found in previous review articles (e.g., [7,14]). Additionally, due to lack of identification of the characteristic intermediates of the aforementioned three mechanisms, recently Wang et al. [17] proposed a N$_2$O$^-$ mechanism of NH$_3$-SCO on a Ag/nano-Al$_2$O$_3$. Li et al. [18] postulated an Eley–Ridel mechanism over perovskite-based catalysts, where gaseous NH$_3$ reacts with adsorbed -ONH$_2$ species to form the surface diazo species (−N=−N) with the rate-determining step depending on the catalysts composition.

Recent interest focuses on bifunctional catalysts consisting of noble metal-based catalyst and transition metal-based catalyst. Previous review articles, including ammonia oxidation, give a clear statement about high activity, N$_2$ selectivity, and stability over Cu-containing materials [Jabłońska et al., 2016, Jabłońska, 2020] [7,19]. From the noble metal-based catalysts the most frequently applied—Pt/Al$_2$O$_3$, provides high activity but also significant selectivity to byproducts (N$_2$O and NO$_x$). Besides Pt/Al$_2$O$_3$, also the Ag/Al$_2$O$_3$ catalyst has received extensive concerns on the low-temperature NH$_3$-SCO. Other systems were less investigated for NH$_3$-SCO than Pt/Al$_2$O$_3$ or Ag/Al$_2$O$_3$. Thus, the present mini-review aims to provide a broad picture of the property-activity correlations of no-
ble metal-based catalysts investigated for NH$_3$-SCO up to now (including Pt-, Pd-, Ag- and Au-, Ru-based catalysts). The NH$_3$-SCO catalysts are classified considering their full NH$_3$ conversion and N$_2$ selectivity in the same temperature range. If not provided in the references, the catalytic activity and N$_2$ selectivity were roughly estimated based on NH$_3$ conversion-temperature profiles. This overview will shed light on future research directions regarding catalyst composition and architecture that maximizes the oxidation of NH$_3$ into N$_2$ over a broad temperature range and in the presence of the typical components of exhaust, such as H$_2$O, SO$_x$, and CO$_x$.

2. Pt- and Pd-Based Catalysts

Early work on NH$_3$ oxidation was given by Il’chenko et al. [20]. Among metal-based catalysts, Pt and Pd are the most active for the ammonia oxidation ($p$(NH$_3$) = 0.1 atm, $p$(O$_2$) = 0.9 atm) but also the most selective to N$_2$O—according to the following order: Pt, Pd > Ni > Fe > W > Ti (note that Rh was not mentioned in Il’chenko review). The catalytic ammonia oxidation over platinum is a key step in the industrial manufacturing of nitric acid. The ammonia oxidation exhibits a moderate structure sensitivity, while the activity decreased in the order of: Pt foil > Pt(865) > Pt(533) > Pt(443) > Pt(100) due to different oxygen sticking coefficient [21]. Novell–Leruth et al. [22] used periodic slab density functional theory (DFT) calculations and found that NH$_3$ adsorbs preferentially on the top sites, NH$_2$ (dehydrogenation intermediates) on the bridge sites, while NH and N species on the hollow sites on both the (111) and (100) surfaces. The ammonia oxidation with atomic or molecular oxygen over Pt(100), Pt(111), stepped Pt(111)/Pt(211) or terrace Pt(111) orientations, etc., yields N$_2$, NO, N$_2$O, and H$_2$O, in varying amounts depending on reactant conditions. Steady-state reaction studies [23] under ultra-high vacuum (UHV) conditions with a stepped Pt(111) surface revealed that excess NH$_3$ lead to N$_2$ formation, while under excess O$_2$, NO formation was preferred. No other nitrogen-containing products, i.e., N$_2$O were detected in the gas phase (note that N$_2$O was never observed under UHV conditions [24]). Similar conclusions were given by Pérez–Ramírez et al. [25], who studied the sequence of steps in NH$_3$ oxidation (applying the isotope $^{15}$NH$_3$) over Pt, Pd, and Rh wires in the temporal analysis of products (TAP) reactor at relevant temperatures in industrial ammonia burners. High NO selectivity is favored at a high ratio of adsorbed $n$(O)/$n$(NH$_3$) species, e.g., at $c$(O$_2$)/$c$(15NH$_3$) = 0.1, the $^{15}$NO selectivity over Pt reached 45%, while at $c$(O$_2$)/$c$(15NH$_3$) = 10—ca. 100% selectivity. NO was found to be a primary reaction product in NH$_3$ oxidation, while N$_2$ and N$_2$O originate from consecutive NO transformations. Pd and Rh were more active for the reduction of nitric oxide by ammonia than Pt (Figure 1). Additionally, DFT calculations showed that the N$_2$O formation over Rh(100) plane needs higher activation energy than over Pt(100) or Pd(100). Furthermore, Rh(100) was more active in NH$_3$ decomposition (possessed a lower activation barrier for the NH$_3$ $\rightarrow$ NH$_2$ step) than Pt and Pd surfaces, and strongly stabilized the dehydrogenated NH and N species [22].

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Conversion of NO over the PGMs on pulsing of $c$(15NH$_3$):$c$(NO):$c$(Ne) = 1:0.2:1 (solid bars) and $c$(15NH$_3$):$c$(NO):$c$(Ne) = 1:2:1 (open bars) at 800 °C. Reprinted from [25] with permission from Elsevier.
\( \gamma\text{-Al}_2\text{O}_3 \) and ZSM-5 are often used as the supports for noble metal-based catalysts for the selective catalytic oxidation of NH\(_3\). A summary of Pt-, Pd-based catalysts is presented in Table 1. Pt/Al\(_2\text{O}_3\) is usually applied to provide high low-temperature activity. The main drawback of such catalyst is low N\(_2\) selectivity due to the formation of N\(_2\)O (below 250 °C) and NO\(_3\) (above 250 °C). The metallic Pt is significantly more active for NH\(_3\)-SCO than oxidized platinum [26,27], which provide limited sites for O\(_2\) dissociation [28]. The operando XANES/EXAFS studies revealed the highest N\(_2\) selectivity (ca. 80%) over H\(_2\)-reduced (2 wt.%)Pt/Al\(_2\text{O}_3\). Nevertheless, under reaction conditions, at least 40% of Pt surface remains oxidized resulting in the formation of N\(_2\)O [29]. Otherwise, the metal-support interactions of Pt/TiO\(_2\) were reported to stabilize Pt in the metallic state (also under reaction conditions) [30]. The Pt\(^0\) content can also be manipulated by preparation procedure of Pt/SiO\(_2\)-Al\(_2\text{O}_3\), i.e., by adding ascorbic acid (vitamin C, vC; \( n(\text{vC})/n(\text{Pt}) = 0.25\)–1.5) [31]. Ostermaier et al. [26] reported that small Pt particles (2.0 and 2.7 nm) of (1–2.93 wt.%)Pt/Al\(_2\text{O}_3\) demonstrate lower activity in comparison to larger crystallites (15.5 nm). The catalysts with a small size of Pt\(^0\) crystallites were characterized by the strongest deactivation during NH\(_3\) oxidation due to their oxidation to PtO\(_x\), where \( x \) depends on the particle size [32]. Later, Sobczyk et al. [33,34] demonstrated with positron emission profiling (PEP) that the catalysts deactivate due to poisoning of the surface mainly by nitrogen species (NH and NH\(_2\)).

The dispersion of Pt species was increased after the introduction of ethylenediamine (from 2.8 to 2.0 nm) during the preparation of (1 wt.%)Pt/SiO\(_2\)-Al\(_2\text{O}_3\) [35], and thus lead to higher activity in NH\(_3\)-SCO in the presence of CO\(_2\) and H\(_2\)O, compared to that of unmodified samples. The N\(_2\) selectivity remained nearly unaffected by the Pt particle size. Contrary to these studies, Slavinska et al. [36] found that a larger Pt particle size (ca. ~23 nm compared to ~1 nm) of (2 wt.%)Pt/Al\(_2\text{O}_3\) enhanced activity. Additional measurements in the presence of CO\(_2\) and H\(_2\)O did not change the trends of activity and selectivity of Pt/Al\(_2\text{O}_3\) on the Pt dispersion and Pt state. Similar to the above discussed studies over Pt/SiO\(_2\)-Al\(_2\text{O}_3\), N\(_2\) selectivity did not depend on the Pt particle size, while in all cases, N\(_2\) selectivity was below 70% (>300 °C). Furthermore, authors [27] showed no deactivation of the catalysts, i.e., the oxidation state of platinum in Pt/Al\(_2\text{O}_3\) did not increase after the catalytic experiments. Also, the hydrothermal aging (in a feed containing O\(_2\), H\(_2\)O, CO\(_2\), at 550 °C over 250 h) of a Pt/Al\(_2\text{O}_3\) wascoated monolith did not influence its activity below 250 °C [37]. Above 300 °C the activity significantly decreased with aging time (0, 122, 253 h) but the product selectivity remains the same. Recently, Machida et al. [38] found that a thin-film catalyst, which was prepared by depositing a nanoscale-thickness Pt(111) overlayer on a 50 μm-thick Fe-Cr-Al metal foil (Pt/SUS) achieved more than 180-fold higher TOF compared with the conventional (0.13 wt.%)Pt/Al\(_2\text{O}_3\). The thermal stability of Pt/SUS was enhanced by the insertion of the Zr layer between the Pt and SUS foil. For the Pt surfaces, the NH mechanism was mostly proposed by experimental and DFT simulation studies; e.g., over Pt(100) or Pt(111) [39–41]. Also, the so-called NH mechanism (i.e., NH as the intermediates in the imide mechanism) occurred on Pt/Al\(_2\text{O}_3\), while the HNO and N\(_2\)H\(_4\) mechanism (i.e., HNO and N\(_2\)H\(_4\) as the intermediates in the imide and hydrazine mechanism, respectively) coexisted on Pt/CeZrO\(_2\) (Figure 2) [42].

Li and Armor [43] studied a series of zeolite ZSM-5 ion-exchanged with (4.07 wt.%)Pd, (2.66 wt.%)Rh, and (2.55 wt.%)Pt as catalysts for NH\(_3\)-SCO. Among them, relatively high activity and N\(_2\) selectivity in the low-temperature range (≤300 °C) were found for the Pd-containing catalysts (i.e., full ammonia conversion with 91% N\(_2\) selectivity at 300 °C in the presence of 5 vol.% H\(_2\)O), 58–61% of N\(_2\)O selectivity on (2.55 wt.%)Pt-ZSM-5 and 16–25% on (4.01 wt.%)Pd-ZSM-5 was obtained at 250–300 °C. The noble metal-exchanged ZSM-5 materials were less affected by water vapor than the corresponding Al\(_2\text{O}_3\) supported catalysts. Similar results, i.e., 92% NH\(_3\) conversion and 73% N\(_2\) selectivity at 350 °C over (5.51 wt.%)Pd-ZSM-5 in NH\(_3\)-SCO (feed without H\(_2\)O), were also reported by Long and Yang [44]. Furthermore, Jabłońska et al. [45] investigated zeolites HY modified with palladium (0.05–2.5 wt.%). An increase in Pd loading leads to higher catalysts activity.
together with the drop in N₂ selectivity. The palladium oxide species (PdOₓ) were found to be active sites for ammonia oxidation (based on FT-IR studies). A part of ammonia was stabilized against oxidation over the zeolite framework acid sites (in the form of NH₄⁺), and lead to enhanced N₂ selectivity in the higher temperature range. The analysis of the results of temperature-programmed (NH₃-SCO with various spaces velocity) and spectroscopic studies lead to the conclusion that the ammonia oxidation over Pd-Y followed the i-SCR mechanism. On the other hand, an appearance of hydrazine species (intermediates in the hydrazine mechanism) on the ammonia pre-adsorbed Pd-Y catalyst at 250 °C during FT-IR studies, suggested that the ammonia oxidation is more complicated and followed different parallel routes. Otherwise, Wells et al. [46,47] identified PdNₓ under reaction conditions over H₂-reduced (1.5 wt.%Pd/Al₂O₃ and Pd/Y (n(Si)/n(Al) = 2.6) as the dominant species during N₂ formation (based on combined operando spectroscopy and DFT calculations). As stated above, palladium-containing materials appear as promising NH₃-SCO catalysts, although, their stability (also in the presence of H₂O, SOₓ, and COₓ) needs confirmation.

The state-of-the-art NH₃-SCO systems include a combination of a noble metal-based catalyst—usually Pt/Al₂O₃, and an SCR catalyst, e.g., Cu- or Fe-containing zeolite. Thus, a part of ammonia is oxidized over the noble metal-based catalyst to N₂ and NOₓ which is further transformed to N₂ over the SCR catalyst. Different arrangements of both metals were reported in the literature, i.e., noble/transition metal deposited on one support in systems such as (0.05 wt.%)Pt/(1 wt.%Cu/Al₂O₃ [48], (0.5–4 wt.%)Pt/(20 wt.%Cu/Al₂O₃ [49], (1 wt.%)Pt/(20 wt.%Cu/Al₂O₃ [50–52], (1.5 wt.%Pt-(5.5 wt.%Cu/ZSM-5 [53], (0.5 wt.%)Pt-(1.5 wt.%Fe-ZSM-5 [54], (1.5 wt.%Pt-(0.5 wt.%Fe/ZSM-5 [55], (0.21 wt.%Pt/CuMgAlOₓ hydrotalcite-derived mixed metal oxides [13], (2 wt.%PdO/5 wt.%CuO/Al₂O₃ [56], etc. Besides such form, the active components may be present in different configurations—dual-layer configuration, mixed and hybrid layer sample types, that are presented in Figure 3. The dual-layer catalytic systems consist of noble metal-based catalyst as a bottom layer, and transition metal-based catalysts as an upper layer, i.e., Pt/Al₂O₃ and Cu-ZSM-5, Pt/Al₂O₃ and Cu-SSZ-13, Pt/Al₂O₃, and Fe-ZSM-5 investigated by Shrestha et al. [57–59], Pt/Al₂O₃ and Fe-zeolite investigated by Scheuer et al. [60] and Colombo et al. [61]. E.g., Shrestha et al. [57] pointed out the increase of N₂ selectivity (with a corresponding decrease in NO selectivity) with increasing copper loading of Cu/ZSM-5 (NH₃-SCR layer), e.g., from 58% to 82% at 250 °C for 0.8 and 2.5 wt.% of Cu, respectively. Still, N₂O selectivity reached a maximum of about 40% at 260 °C in all
cases. Similar N$_2$O selectivity was reported over Pt/Al$_2$O$_3$ and Fe-ZSM-5 arranged as both dual-layer and mixed catalysts [58]. Also, the NH$_3$ oxidation depended on the applied conditions, i.e., space velocity (66,000 \textit{versus} 265,000 h$^{-1}$). At higher space velocity mixed catalyst revealed (ca. 7\%) higher NH$_3$ conversion, while dual-layer catalyst provided higher N$_2$ selectivity (especially above 350 $^\circ$C). The hybrid catalyst (bottom layer of mixed Cu-SSZ-13 + Pt/Al$_2$O$_3$, top layer of Cu-SSZ-13) allowed to achieve (ca. 5\%) higher NH$_3$ conversion than that of the dual-layer catalyst [59]. Furthermore, Dhillon et al. [62] applied sacrificial agents (yeast or polymer) to generate macropores on a (2.90 wt.%)Cu-SSZ-13 top-layer washcoat supported on (1.47 wt.%)Pt/Al$_2$O$_3$, and thus to enhance NH$_3$ conversion (still below 90\% up to 500 $^\circ$C) without impact on N$_2$ selectivity. Recently, Gosh et al. [63] reported a Pt/Al$_2$O$_3$@Cu-ZSM-5 (0.05 wt.\% Pt, 2.93 wt.\% Cu) core-shell catalyst that allowed full NH$_3$ conversion at ca. 300 $^\circ$C and 100\% N$_2$ selectivity (up to 275 $^\circ$C). The NH$_3$ conversion was negligibly affected by the variation in the shell thickness (0.5 $\mu$m \textit{versus} 1.2 $\mu$m), while the thicker shell was beneficial in improving N$_2$ selectivity at higher temperatures. The addition of H$_2$O (5 vol.\%) to the feed had a minor impact on the catalyst activity, while more tests in the presence of CO$_x$ and SO$_x$ are still required.

Concluding this part, as can be seen from the above presented data, a great variety of Pt- and Pd-based catalytic systems were developed and tested for NH$_3$-SCO. In particular, (1–2 wt.\%)Pt/Al$_2$O$_3$ was reported as one of the most active catalyst that allowed to obtain full NH$_3$ conversion around 200–450 $^\circ$C with N$_2$ selectivity of 15–87\% (according to data gathered in Table 1), depending on the applied catalyst preparation procedure as well as pretreatment and reaction conditions. Pt$^0$ serves as the active species responsible for high catalytic activity, and thus most of the catalytic systems were prepared by an impregnation method and subsequently reduced in H$_2$. Great research efforts aimed at determining the role of Pt dispersion in NH$_3$-SCO, but there is no clear consensus about it yet. Platinum (0.05–1.5 wt.\%) was also applied as the most active noble metal component in the bifunctional catalysts. Such systems fully oxidized NH$_3$ in a broad temperature range of 195–500 $^\circ$C with 44–100\% N$_2$ selectivity (according to data gathered in Table 1) depending on their architecture, i.e., Pt deposited on one support with transition metal component, as dual-layer catalysts, mixed form, hybrid catalysts or incorporated in the core-shell structure, etc. Among them the (0.46 wt.\%)Pt/Al$_2$O$_3$-(2.5 wt.\%)Cu-ZSM-5 dual-layer catalyst (full NH$_3$ conversion at 250–500 $^\circ$C, 82–100\% N$_2$ selectivity) and (0.05 wt.\%)Pt/Al$_2$O$_3$@(2.93 wt.\%)Cu/ZSM-5 core-shell catalyst (full NH$_3$ conversion at 310–500 $^\circ$C, 91–94\% N$_2$ selectivity) appear as the most interesting systems for further catalysts optimization. However, the stability of these catalysts and the influence of the potential catalyst pollutants usually present in the exhausts, i.e., H$_2$O, SO$_x$ and CO$_x$, were not fully provided within the scope of the studies. A similar conclusion can be given for other Pt- or Pd-containing catalysts (only a few materials were tested in the presence of H$_2$O and CO$_2$). Hence, further studies are required to understand structure-activity relationships and reaction mechanisms under application-relevant reaction conditions.

![Figure 3](image-url). Schematic diagram representing bifunctional ammonia slip catalyst in three different washcoated structured methodologies. Reprinted from [64] with permission from Science Direct.
Table 1. Comparison of full NH\textsubscript{3} conversion and N\textsubscript{2} selectivity in same temperature range over Pt-based catalysts reported in literature.

| Catalyst            | Catalyst Preparation | Reaction Conditions | NH\textsubscript{3} Conversion, N\textsubscript{2} Selectivity | Ref. |
|---------------------|----------------------|---------------------|---------------------------------------------------------------|------|
| (3 wt.%)Pt-Rh       | wash-coated on Al\textsubscript{2}O\textsubscript{3}, calcination, 400 °C, air | 0.08 vol.% NH\textsubscript{3}, 4 vol.% O\textsubscript{2}, He balance, GHSV 92,000 h\textsuperscript{-1} | 100/62% (400 °C) | [65] |
| (4.4 wt.%)Pt-Rh     | wash-coated on Al\textsubscript{2}O\textsubscript{3}, calcination, 500 °C, air | 0.1 vol.% NH\textsubscript{3}, 4 vol.% O\textsubscript{2}, He balance, GHSV 92,000 h\textsuperscript{-1} | 100/80% (400 °C) | [66] |
| (1.2 wt.%)Pt/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 600 °C, air; reduction conditions not shown | 0.1 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, He balance, 50 mL min\textsuperscript{-1}, mass of the catalyst: 0.1 g, WHSV 30,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/75% (200 °C) | [67] |
| (1.73 wt.%)Pt/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 400 °C, air; reduction, 250 °C, H\textsubscript{2} | 0.1 vol.% NH\textsubscript{3}, 4 vol.% O\textsubscript{2}, He balance, GHSV 120,000 h\textsuperscript{-1} | 100/40–60% (200–400 °C) | [27] |
| (2 wt.%)Pt/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 400 °C, air; oxidation, 400 °C, O\textsubscript{2}/He | 0.1 vol.% NH\textsubscript{3}, 4 vol.% O\textsubscript{2}, He balance, 50 mL min\textsuperscript{-1}, mass of the catalyst: 0.145 g, GHSV 120,000 h\textsuperscript{-1} | 100/40–50% (325–400 °C) | [36] |
| (1 wt.%)Pt/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 550 °C, air | 0.02 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 407,000 mL g\textsuperscript{-1} h\textsuperscript{-1} | 100/25–49% (250–450 °C) | [68] |
| (1 wt.%)Pt/CeO\textsubscript{2}-SiO\textsubscript{2} | impregnation, calcination, 550 °C, air | 0.02 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, 8 vol.% CO\textsubscript{2}, 5 vol.% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/10–40% (300–450 °C) | [35] |
| (1 wt.%)Pt/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} | impregnation; treatment strategies—conditions not shown; monolithic catalyst; Vc—ascorbic acid | 0.02 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, 8 vol.% CO\textsubscript{2}, 5 vol.% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/28–60% (240–300 °C) | [31] |
| (1 wt.%)Pt/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} | impregnation; treatment strategies—conditions not shown; monolithic catalyst; Vc—ascorbic acid | 0.02 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, 8 vol.% CO\textsubscript{2}, 5 vol.% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/22–50% (240–300 °C) | [31] |
| (1 wt.%)Pt/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 550 °C, air | 0.02 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/15–30% (300–400 °C) | [42] |
| (1 wt.%)Pt/CeZrO\textsubscript{2} | impregnation, calcination, 550 °C, air; monolithic catalyst | 0.02 vol.% NH\textsubscript{3}, 8 vol.% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/15–30% (300–400 °C) | [42] |
| (1.5 wt.%)Pt/ZrO\textsubscript{2} | impregnation, calcination, 550 °C, air | 0.018 vol.% NH\textsubscript{3}, 8 vol.% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/25–60% (350–500 °C) | [53] |
| (1.5 wt.%)Pt/5 wt.% W/ZrO\textsubscript{2} | impregnation, calcination, 550 °C, air | 0.018 vol.% NH\textsubscript{3}, 8 vol.% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/28–50% (300–500 °C) | [53] |
| Catalyst | Catalyst Preparation | Reaction Conditions | NH\textsubscript{3} Conversion N\textsubscript{2} Selectivity/% (Temperature/°C) | Ref. |
|----------|----------------------|---------------------|-------------------------------------------------|-----|
| (2.0 wt.%Pt/TiO\textsubscript{2} | impregnation, calcination, 400 °C, air; oxidation, 400 °C, O\textsubscript{2}/He | 0.1 vol.% NH\textsubscript{3}, 4.0 vol.% O\textsubscript{2}, He balance, 500 mL min\textsuperscript{-1}, mass of the catalyst: 0.145 g, WHSV 206,897 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/38–55% (200–400 °C) | [30] |
| (0.1 wt.%Pt/ (2 wt.%)V/TiO\textsubscript{2} | impregnation, reduction, 600 °C, H\textsubscript{2}/N\textsubscript{2} | 0.02 vol.% NH\textsubscript{3}, 8.0 vol.% O\textsubscript{2}, 6.0 vol.% H\textsubscript{2}O, He balance, 500 mL min\textsuperscript{-1}, mass of the catalyst: 0.25 g, GHSV 60,000 h\textsuperscript{-1} | 100/63–81% (250–350 °C) | [69] |
| (1.2 wt.%Pd/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 600 °C, air; reduction—conditions not shown | 1.14 vol.% NH\textsubscript{3}, 8.21 vol.% O\textsubscript{2}, He balance, 74.7 mL min\textsuperscript{-1}, mass of the catalyst: 0.2 g, WHSV 22,410 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/98% (300 °C) | [67] |
| (4.2 wt.%PdO/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 500 °C, air**reduction, 400 °C, H\textsubscript{2}/He | 0.1 vol.% NH\textsubscript{3}, 4.0 vol.% O\textsubscript{2}, He balance, *0.1 vol.% NH\textsubscript{3}, 4.0 vol.% O\textsubscript{2}, 5 vol.% H\textsubscript{2}O, He balance, 100 mL min\textsuperscript{-1}, mass of the catalyst: 0.1 g, WHSV 60,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/67% (350 °C) ** 100/86% (300 °C) | [43] |
| (4.07 wt.%Pd-ZSM-5 | ion-exchange, calcination—conditions not shown | 0.5 vol.% NH\textsubscript{3}, 2.5 vol.% O\textsubscript{2}, He balance, 40 mL min\textsuperscript{-1}, mass of the catalyst: 0.05 g, GHSV 15,400 h\textsuperscript{-1} | 100/80–90% (250–500 °C) | [45] |
| (1.5 wt.%Pd/Y | impregnation, calcination—conditions not shown) | 0.5 vol.% NH\textsubscript{3}, 2.5 vol.% O\textsubscript{2}, He balance, 40 mL min\textsuperscript{-1}, mass of the catalyst: 0.05 g, GHSV 15,400 h\textsuperscript{-1} | 100/44–73% (325–500 °C) | [48] |
| (0.05 wt.%Pt/ (1 wt.%)CuO/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 600 °C; impregnation, calcination, 500 °C | 0.5 vol.% NH\textsubscript{3}, 2.5 vol.% O\textsubscript{2}, He balance, 40 mL min\textsuperscript{-1}, mass of the catalyst: 0.05 g, GHSV 15,400 h\textsuperscript{-1} | 100/88 (210–230 °C) * 100/95 (230 °C) | [49] |
| (1 wt.%Pt/ (20 wt.%CuO/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 500 °C; impregnation, calcination, 450 °C | 0.07 vol.% NH\textsubscript{3}, 0.5 vol.% O\textsubscript{2}, He balance*0.07 vol.% NH\textsubscript{3}, 8 vol.% O\textsubscript{2}, He balance100 mL min\textsuperscript{-1}, WHSV 180,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/83 (195–230 °C) * 100/90 (220–230 °C) | [49] |
| (1.5 wt.%Pt- (0.5 wt.%Fe)/ZSM-5 | ion-exchange, calcination, air, 500 °C, impregnation calcination, air, 500 °C | 0.1 vol.% NH\textsubscript{3}, 2 vol.% O\textsubscript{2}, He balance, 500 mL min\textsuperscript{-1}, WHSV 500,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/61–88% (200–300 °C) | [55] |
| (0.5 wt.%Pt- (1.54 wt.%Fe)/ZSM-5 | ion-exchange, calcination, air, 500 °C, impregnation calcination, air, 500 °C | 0.1 vol.% NH\textsubscript{3}, 2 vol.% O\textsubscript{2}, He balance, 500 mL min\textsuperscript{-1}, GHSV 230,000 h\textsuperscript{-1} | 100/77–89% (250–400 °C) | [54] |
| (1.5 wt.%Pt- (5.5 wt.%Cu)/ZSM-5 | impregnation calcination, air, 550 °C | 0.018 vol.% NH\textsubscript{3}, 8 vol.% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 100,000 h\textsuperscript{-1} | 100/56–73% (275–450 °C) | [53] |
Table 1. Cont.

| Catalyst                        | Catalyst Preparation | Reaction Conditions                                                                 | NH$_3$ Conversion, N$_2$ Selectivity /% (Temperature/°C) | Ref.       |
|--------------------------------|----------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------|-----------|
| (0.21 wt.%)Pt/CuMgAlO$_x$     | impregnation, calcination, air, 500 °C | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, He balance, 40 mL min$^{-1}$, mass of the catalyst: 0.05 g, GHSV 15,400 h$^{-1}$ | 100/67–89% / (350–500 °C) | [13]      |
| (0.21 wt.%)Pd/CuMgAlO$_x$     | impregnation, calcination, air, 500 °C | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, He balance, 40 mL min$^{-1}$, mass of the catalyst: 0.05 g, GHSV 15,400 h$^{-1}$ | 100/71–76% / (425–500 °C) | [13]      |
| (0.46 wt.%)Pt/Al$_2$O$_3$-(0.8 wt.%)Cu-ZSM-5 | impregnation, calcination, 500 °C, air; reduction, 500 °C, H$_2$/Ar; Cu-ZSM-5: preparation not provided; oxidation, 650 °C, O$_2$/Ar; monolithic catalyst | 0.05 vol.% NH$_3$, 5 vol.% O$_2$, Ar balance, GHSV 66,000 h$^{-1}$ | * 100/58–74% / (250–500 °C) | [57]      |
| (0.46 wt.%)Pt/Al$_2$O$_3$-(2.5 wt.%)Cu-ZSM-5 | impregnation, calcination, 500 °C, air; reduction, 500 °C, H$_2$/Ar; oxidation, 650 °C, O$_2$/Ar; monolithic catalyst | 0.05 vol.% NH$_3$, 5 vol.% O$_2$, Ar balance, GHSV 66,000 h$^{-1}$ | * 100/82–100% / (250–500 °C) | [57]      |
| (0.46 wt.%)Pt/Al$_2$O$_3$-Fe-ZSM-5 | impregnation, calcination, 500 °C, air; reduction, 500 °C, H$_2$/Ar; oxidation, 650 °C, O$_2$/Ar; Fe-ZSM-5: commercial; oxidation, 650 °C, O$_2$/Ar; monolithic catalyst | 0.05 vol.% NH$_3$, 5 vol.% O$_2$, Ar balance, GHSV 66,000 h$^{-1}$ | * 100/48–93% / (250–500 °C) | [58]      |
|                                | *dual layer catalyst  |                                                                                   | ** 100/57–82% / (250–500 °C)                           | [58]      |
| (0.05 wt.%)Pt/Al$_2$O$_3$(2.93 wt.%)Cu/ZSM-5 | core-shell catalyst, impregnation, calcination, 500 °C, air; Cu-ZSM-5: ion-exchange, calcination, 500 °C, air | 0.05 vol.% NH$_3$, 5 vol.% O$_2$, Ar balance, 100 mL min$^{-1}$, mass of the catalyst: 0.18 g, GHSV 280,000 h$^{-1}$ | 100/91–94% / (310–500 °C) | [63]      |

3. Ag-Based Catalysts

Il'chenko et al. [20,70] reported that the specific activity of metal Ag at 300 °C was lower than that of Pt and Pd. Among silver-based catalysts, γ-Al$_2$O$_3$ impregnated with Ag species (mainly 10 wt.%) was widely investigated. Depending on the applied conditions, i.e., catalyst (its preparation, pre-treatment strategies, etc.) and reaction conditions, the full NH$_3$ conversion can be reached in the range of 150–400 °C with 45–95% N$_2$ selectivity over 10 wt.% Ag/Al$_2$O$_3$ (according to data gathered in Table 2). However, at temperatures above 300 °C N$_2$ selectivity dropped due to the large NO production. For NH$_3$-SCO, the Ag/Al$_2$O$_3$ catalysts are mainly applied after H$_2$ pretreatment. E.g., gang et al. [71,72] reported extremely high activity of Ag/Al$_2$O$_3$ at 160 °C (full NH$_3$ conversion with N$_2$ selectivity of about 82%), which was even superior to H$_2$-reduced Ir/Al$_2$O$_3$ or Pt/Al$_2$O$_3$. The activity of Ag/Al$_2$O$_3$ was also higher than over silver powder and Ag/SiO$_2$ [72], indicating that the applied support influenced the Ag particle dispersion. However, the difference in the Ag particle size of the Ag/Al$_2$O$_3$ (8.2 nm) and Ag/SiO$_2$ (24 nm) catalysts was not discussed in these studies. The authors correlated the NH$_3$ oxidation activity at low temperatures to the catalysts’ ability to promote dissociative or nondissociative adsorption of O$_2$. However, again the role of different oxygen species (i.e., adsorbed molecular...
oxygen, adsorbed atomic oxygen, subsurface oxygen, and bulk dissolved oxygen) in the activity and the reaction mechanisms was not fully explored. Zhang and He [73] reported that the dissociation of O\(_2\) is a rate-determining step for NH\(_3\)-SCO. They concluded that molecular O\(_2\) can be dissociatively chemisorbed on the surface of H\(_2\)-reduced Ag/Al\(_2\)O\(_3\), i.e., metallic species (in contrast to fresh material) to form O species, and thus enhance NH\(_3\)-SCO activity [74]. Furthermore, the modification of Ag/Al\(_2\)O\(_3\) with CeO\(_2\) improved catalysts' ability in the adsorption and activation of O\(_2\) to form O species [75]. However, Wang et al. [76] claimed that the recovery of Brønsted acid sites via H\(_2\) reduction (i.e., break of Ag-O bonds on the Ag/Al\(_2\)O\(_3\) surface and formation of Ag clusters in the metallic state—Ag\(_n^0\), based on EXAFS analysis) is also responsible for the improved activity of H\(_2\)-reduced Ag/Al\(_2\)O\(_3\). Highly dispersed particles of Ag\(_0^0\) (3.5–25 nm) were found to enhance the catalytic activity below 140 °C, whereas large particles (12–50 nm) of Ag\(_0^0\) were responsible for improved N\(_2\) selectivity [74].

Furthermore, N\(_2\) selectivity of about 85% above 300 °C over (2.2 wt.%Ag/Al\(_2\)O\(_3\) (c(NH\(_3\)),c(O\(_2\)) = 1:1–1:25), was assigned to the small Ag particle size (<5 nm, based on XRD analysis) [77]. Ag\(^+\) cations are the main active species in NH\(_3\)-SCO at temperatures above 140 °C. The adsorbed NH\(_3\) mainly reacts with the gaseous O\(_2\) over fresh Ag/Al\(_2\)O\(_3\). Although besides Ag\(_0^0\) and Ag\(^+\), also Ag\(_n^\delta^+\) species were evidenced by DR UV-Vis analysis, the authors did not specify their role in ammonia oxidation. Also, Qu et al. [78] obtained highly dispersed Ag\(_0^0\) particles with a size of 5–6 nm (based on XRD and DR UV-Vis analyses) on the H\(_2\)-reduced (10 wt.%) Ag/Al\(_2\)O\(_3\) catalyst, which reached full conversion and 89% of N\(_2\) selectivity at 180 °C. Yang et al. [79] and Jabłoński et al. [80] studied (1–10 wt.%)/Al\(_2\)O\(_3\) and claimed that the low N\(_2\) selectivity above 200–300 °C over Ag/Al\(_2\)O\(_3\) was ascribed to the formation of Ag\(_2\)O crystals.

Besides the influence of the Ag particle size, Wang et al. [17] investigated the effect of the different support particle size (micro-Al\(_2\)O\(_3\) versus nano-Al\(_2\)O\(_3\)) on the activity of the final Ag/Al\(_2\)O\(_3\) catalysts in NH\(_3\)-SCO. The catalyst characterization indicated that nano-Al\(_2\)O\(_3\) was beneficial for Ag dispersion (the average Ag particle size of 3.7 nm, based on HRTEM analysis). The catalyst abundant acid sites (based on NH\(_3\)-TPD analysis) facilitated the adsorption and dissociation of NH\(_3\), therefore resulting in an enhanced activity. Furthermore, the same research group [81] studied Ag supported on TiO\(_2\), SiO\(_2\) as well as their mixture—Ag/SiO\(_2\)–TiO\(_2\). Although the (10 wt.%)/Ag/SiO\(_2\)-TiO\(_2\) catalyst reached full NH\(_3\) conversion at 140 °C, N\(_2\) selectivity in the whole studied range of 100–240 °C was below 70%. Significantly higher N\(_2\) selectivity was obtained over Ag/TiO\(_2\) (91–99% at 180–240 °C). Jabłońska et al. [82] compared commercial TiO\(_2\) with mesoporous TiO\(_2\) (prepared by evaporation induced self-assembly (EISA)) as support in NH\(_3\)-SCO. The activity and N\(_2\) selectivity were favored over (1.5 wt.%)/Ag-doped mesoporous TiO\(_2\) (calcined at 600 °C, with predominant anatase phase). The easily reducible highly dispersed oxidized silver species were converted into Ag\(_0^0\) and possibly Ag\(_n^\delta^+\) clusters through in situ H\(_2\)-pretreatment of catalyst. The metallic silver decomposed N\(_2\)O into N\(_2\) and surface oxygen species, leading to higher N\(_2\) selectivity. Further studies, concerning the stability tests, revealed that these materials are unstable, especially in the higher temperature range (>600 °C). However, temperature of the full conversion of NH\(_3\) over (9.8 wt.%)/Ag/Al\(_2\)O\(_3\) also gradually increased after ca. 4 reaction cycles (from 150 to 250 °C). A higher stability in subsequent catalytic runs revealed (9.9 wt.%)/Ag/ZSM-5 with the postsynthetic modified support. The micro-/mesoporous structure could prevent sintering and/or leaching of Ag particles during NH\(_3\)-SCO [83].

As stated above, while a broad number of studies examined NH\(_3\)-SCO over Ag-based catalysts, the mechanism of NH\(_3\) oxidation and N\(_2\) formation is still uncertain, and the studies are mainly based on temperature-programmed (TPD) or in situ DRIFTS studies. E.g., gang et al. [84] investigated NH\(_3\)-SCO over powder silver by TPD and in situ FT-Raman spectroscopy. They found NO as the main reaction intermediate yielding N\(_2\)O and/or N\(_2\) (Figure 4a). The dissociation of oxygen was believed to be the rate-controlling step for ammonia oxidation, while low surface coverage favors N\(_2\) formation. Similar
conclusions were given by Karatok et al. [85] The exposure of ozone on Ag(111) surfaces at −133 °C led to a disordered surface atomic oxygen overlayer (confirmed by LEED). Such oxygen species selectively catalyzed N-H bond cleavage, yielding mostly N₂ and minor amounts of by-products (NO and N₂O). Higher coverage O/Ag(111) surfaces at −133 °C led to bulk-like amorphous silver oxide species, forming NO and N₂O (Figure 4b). The ordered oxide surfaces—obtained through annealing of atomic oxygen-covered Ag(111) surface at 200 °C in UHV, showed only limited reactivity toward ammonia. Suppression of the N₂ formation at high oxygen coverages was also reported over Ir(510) and Ir(110) surfaces [86].

Zhang and He [73] investigated the reaction mechanisms over Ag/Al₂O₃ based on in situ DRIFTS studies and found that at low temperatures (<140 °C), NH₃ oxidation follows the -NH (imide) mechanism (Ag⁰ as the main active species), while above 140 °C, NH₃ oxidation follows an in situ selective catalytic reduction (i-SCR) mechanism (Ag⁺ as the main active species). Furthermore, they claimed that NH₃-SCO over Ag/nano-Al₂O₃ follows a reaction pathway called the N₂⁻ mechanism (based on in situ DRIFTS, kinetic measurements, and DFT calculation results) [17]. The intermediate N₂⁻ species appear from the combination of two -NH₂/NH species (considered to be the rate-determining step). In the next step, the N₂⁻ species are converted into N₂ and/or N₂O in the presence of O₂.

The activity and N₂ selectivity strongly depend on the loading of noble metal and can be steered into the desired direction by the introduction of transition metal. E.g., Yang et al. [79] studied Ag-Cu/Al₂O₃ with 5-5 or 10-10 wt.% of metal and indicated the material with the first composition as a highly efficient catalyst (full NH₃ conversion below 320 °C with N₂ selectivity of more than 95%). Unfortunately, the authors did not present results of catalytic tests above 350 °C. gang et al. [71] investigated (7.5 wt.%)Ag-(2.5 wt.%)Cu/Al₂O₃ and found the full conversion of ammonia at 200–300 °C with 95% N₂.
selectivity. Above 300 °C appeared significant amounts of by-products—NO and N₂O. A mechanical mixture of (10 wt.% Ag/Al₂O₃ and (10 wt.% Cu/Al₂O₃)—applied for comparative purposes, showed comparable activity and N₂ selectivity to a silver-based catalyst. The same oxidation state for bimetallic (Ag-Cu/Al₂O₃ (5–5 wt.%, 7.5–2.5 wt.%) and monometallic (10 wt.% Ag/Al₂O₃ or 10 wt.% Cu/Al₂O₃) catalysts were approved (based on XPS analysis). Additionally, LEIS analysis over (10–2.5 wt.%, 2.5–7.5 wt.%, 5–5 wt.%, 9–1 wt.% Ag-Cu/Al₂O₃ excluded formation of any Ag-Cu phases. Jabłońska et al. [80] found among all tested combinations—1–1, 1–10, 1.5–10, 5–5 wt.% of silver and copper, respectively, the (1.5 wt.%Ag-(10 wt.%Cu/Al₂O₃ catalyst with an optimum activity, N₂ selectivity (full ammonia conversion and 94% N₂ selectivity at 375 °C) and stability in NH₃-SCO under wet conditions and time-on-stream tests. (0.59–2.34 wt.%Ag-promoted CuMgAlOₓ hydrotalcite derived mixed metal oxides [87] with noble metal deposited inside the structure revealed relatively low NH₃ conversion below 350 °C. Silver loading of 2.34 wt.% (n(Ag)/n(Cu)/n(Mg)/n(Al) = 1/5/65/29) led to the formation of CuOₓ and Ag₂O—that caused higher catalytic activity and the observed drop in N₂ selectivity. Significantly higher catalytic activity was reported for the Ag-Cu alloy nanoparticles (Figure 5a–d) synthesized by a solventless mix-bake-wash method. Ag-Cu (n(Ag)/n(Cu) = 2/1, 77.25 wt.% of Ag) revealed full NH₃ conversion at 200 °C. The AgCu alloy structure maintains the metallic state of Ag and Cu as well as structure stability, which enhanced activity and thermal stability in NH₃ oxidation. The calcination of precursors of noble metal and transition metal did not form the alloy structure (Figure 5e–h). Besides, above-mentioned catalyst architectures, the (7.2 wt.%Ag-(12.2 wt.%Cu species were deposited onto wire-mesh honeycomb (WMH; characterized by open frontal area: 74.1%; geometric surface area: 16.2 cm² cm⁻³; pressure drop: 2.58 × 10⁻² Pa) [88]. Such catalyst revealed enhanced N₂ selectivity (above 89% at 180–320 °C) compared to Ag/WHM as well as stability in the presence of H₂ and CH₄.

Concluding this part, Ag-based catalysts (especially Ag/Al₂O₃) received extensive concerns in NH₃-SCO. As can be seen from the above examples, the research focuses mainly on the influence of the valance state of Ag species and particle size on the catalytic properties. As mentioned above, (10 wt.%Ag/Al₂O₃ was suited for full NH₃ conversion at about 150–400 °C with 45–95% N₂ selectivity. Based on the presented above studies, the dispersed Ag⁰ with an average particle size in the range between 3.5–6.0 nm was found as the active species for NH₃-SCO below 200 °C. On the other hand, there are limited studies that discuss the stability (especially concerning oxidation state) of the Ag-based catalysts, i.e., in the consecutive reaction cycles or the presence of H₂O, SOₓ, and CO₂. Furthermore, despite their high potential, only a few studies addressed Ag-containing bifunctional catalysts for NH₃-SCO. A rather high content of Ag species (compared to Pt-based bifunctional catalysts, e.g., (7.5 wt.%Ag-(2.5 wt.%Cu/Al₂O₃ or (7.2 wt.%Ag-(12.2 wt.%Cu/WHM) was necessary to reach high activity and N₂ selectivity (i.e., full NH₃ conversion with 81–95% N₂ selectivity at 200–320 °C, according to data gathered in Table 2). The catalysts containing lower content of Ag species, i.e., 0.59–1.5 wt.% required a higher temperature of 375–500 °C to fully oxidize NH₃. Another important aspect of NH₃-SCO over Ag-based catalysts is the investigation of the reaction mechanisms, which were explored mainly by the application of in situ DRIFTS and the indication of the characteristic intermediates of the imide, hydrazine, or i-SCR (internal) mechanism. Overall, FT-IR investigations suggest that NH₃-SCO may follow different parallel pathways. Thus, the combination of the advantages of in situ DRIFTS with the advantages of other (e.g., temperature-programmed and/or transient) techniques will be strategic to clarify the pathways of NH₃-SCO. Furthermore, the exploration of the reaction mechanisms should be ongoing in the realistic catalytic mixture containing besides NH₃ and O₂ in the inert gas also H₂O, SOₓ, and CO₂.
Figure 5. Energy-dispersive X-ray mapping for corresponding elemental distribution of Ag, Cu, and O on Ag$_2$Cu$_1$ (a–d) and AgCuO$_x$ NPs (e–h). Reprinted from [89] with permission from ACS Publications.

Table 2. Comparison of full NH$_3$ conversion and N$_2$ selectivity in same temperature range over Ag-based catalysts reported.

| Catalyst     | Catalyst Preparation | Reaction Conditions                                                                 | NH$_3$ Conversion, N$_2$ Selectivity/% (Temperature/°C) | Ref. |
|--------------|----------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------|------|
| Ag powder    | Ag$_2$O, triple reduction, 400 °C, H$_2$/He; oxidation, 400 °C, O$_2$/He | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, 50 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 30,000 mL g$^{-1}$ h$^{-1}$ | 100/33–77% (185–400 °C) [72] |
| (10 wt.%Ag/Al$_2$O$_3$) | impregnation, calcination, 500 °C, air; reduction, 400 °C, H$_2$/He | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, 50 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 30,000 mL h$^{-1}$ g$^{-1}$ | 100/70–88% (160–400 °C) [72] |
| (10 wt.%Ag/Al$_2$O$_3$) | impregnation, calcination, 500 °C, air; *reduction, 400 °C, H$_2$/N$_2$ | 0.05 vol.% NH$_3$, 10 vol.% O$_2$, N$_2$ balance, 100 mL min$^{-1}$, GHSV 28,000 h$^{-1}$ | 100/93–95% (180 °C) *100/80–82% (160–180 °C) [76] |
| (10 wt.%Ag/Al$_2$O$_3$) | calcination, 600 °C, air; reduction, 400 °C, H$_2$/N$_2$ impregnation | 0.05 vol.% NH$_3$, 10 vol.% O$_2$, N$_2$ balance, 200 mL min$^{-1}$, mass of the catalyst: 0.2 g, GHSV 1000 mL h$^{-1}$ g$^{-1}$ | 100/45–55% (150–200 °C) [74] |
| (10 wt.%Ag/Al$_2$O$_3$) | incipient wetness impregnation sol-gel |                                                                                       | 100/55–60% (150–200 °C) | |
| (10 wt.%Ag/Al$_2$O$_3$) | impregnation, calcination, 600 °C, air; reduction, 300 °C, H$_2$/N$_2$ | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, N$_2$ balance, 400 mL min$^{-1}$, mass of the catalyst: 0.4 g, GHSV 50,000 h$^{-1}$ | 100/89 (180–260 °C) [78] |
| (5 wt.%Ag/Al$_2$O$_3$) | impregnation, calcination, 600 °C, air | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, Ar balance, 40 mL min$^{-1}$, mass of the catalyst: 0.1 g, GHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 100/58–83% (275–500 °C) [80] |
Table 2. Cont.

| Catalyst        | Catalyst Preparation | Reaction Conditions                                                                 | NH\textsubscript{3} Conversion\textsubscript{N\textsubscript{2}} Selectivity/% (Temperature/°C) | Ref. |
|-----------------|----------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|------|
| (10 wt.%)Ag/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 600 °C, air | 1 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, He balance, 400 mL min\textsuperscript{-1}, mass of the catalyst: 0.8 g, WHSV 30,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/70–83% (200–250 °C) | [79] |
| (10 wt.%)Ag/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 500 °C, air | 1.14 vol.% NH\textsubscript{3}, 8.21 vol.% O\textsubscript{2}, 74.7 mL min\textsuperscript{-1}, mass of the catalyst: 0.2 g, WHSV 22,410 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/83% (300 °C) | [71] |
| (1.5 wt.%)Ag/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 600 °C, air | 0.5 vol.% NH\textsubscript{3}, 2.5 vol.% O\textsubscript{2}, Ar balance, 40 mL min\textsuperscript{-1}, mass of the catalyst: 0.1 g, WHSV 24,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/78% (325 °C) | [82] |
| (10 wt.%)Ag/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 600 °C, air | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, Ar balance, 100 mL min\textsuperscript{-1}, GHSV 28,000–115,000 h\textsuperscript{-1} 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, GHSV 28,000–115,000 h\textsuperscript{-1} 5 vol.% H\textsubscript{2}O, He balance, 100 mL min\textsuperscript{-1}, GHSV 136,000 h\textsuperscript{-1} | 100/94–96% (160–180 °C) | [17] |
| (2.2 wt.%)Ag/Al\textsubscript{2}O\textsubscript{3} | homogenous deposition, precipitation, reduction, 400 °C, H\textsubscript{2} | 2 vol.% NH\textsubscript{3}, 2 vol.% O\textsubscript{2}, Ar balance, 40 mL min\textsuperscript{-1}, GHSV 2,500 h\textsuperscript{-1} 0.15 vol.% NH\textsubscript{3}, 3.85 vol.% O\textsubscript{2}, Ar balance, 40 mL min\textsuperscript{-1}, GHSV 2,500 h\textsuperscript{-1} | 100/100% (368–400 °C) *100/85–100% (342–400 °C) | [77] |
| (1.6 wt.%)Ag/CeO\textsubscript{2}/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 500 °C, air | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, He balance, 100 mL min\textsuperscript{-1}, GHSV 28,000–115,000 h\textsuperscript{-1} | 100/66–76% (120–180 °C) *100/74–90% (250–400 °C) | [77] |
| (9.8 wt.%)Ag/Al\textsubscript{2}O\textsubscript{3} | impregnation, calcination, 500 °C, air; reduction, 400 °C, H\textsubscript{2}/Ar | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, He balance, 100 mL min\textsuperscript{-1}, GHSV 35,000 h\textsuperscript{-1} | 100/70–74% (140–190 °C) | [83] |
| (9.9 wt.%)Ag/ZSM-5 | impregnation, calcination, 500 °C, air; reduction, 400 °C, H\textsubscript{2}/He | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, 50 mL min\textsuperscript{-1}, mass of the catalyst: 0.2 g, WHSV 30,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/40–73% (200–400 °C) | [72] |
| (10 wt.%)Ag/Si\textsubscript{2}O\textsubscript{2} | impregnation, calcination, 600 °C, air; reduction, 300 °C, H\textsubscript{2}/N\textsubscript{2} | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, N\textsubscript{2} balance, 0.4 g, GHSV 30,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/50–63% (220–260 °C) | [78] |
| (10 wt.%)Ag/TiO\textsubscript{2} | impregnation, calcination, 600 °C, air; reduction, 300 °C, H\textsubscript{2}/N\textsubscript{2} | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, N\textsubscript{2} balance, 0.4 g, GHSV 50,000 h\textsuperscript{-1} | 100/64% (260 °C) | [81] |
| (10 wt.%)Ag/Si\textsubscript{2}O\textsubscript{2} | impregnation, calcination, 600 °C, air; reduction, 300 °C, H\textsubscript{2}/He | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, N\textsubscript{2} balance, 0.4 g, GHSV 28,000 h\textsuperscript{-1} | 100/60–62% (180–240 °C) | [81] |
| (10 wt.%)Ag/TiO\textsubscript{2} | impregnation, calcination, 600 °C, air; reduction, 300 °C, H\textsubscript{2}/Ar | 0.05 vol.% NH\textsubscript{3}, 10 vol.% O\textsubscript{2}, N\textsubscript{2} balance, 0.4 g, GHSV 50,000 h\textsuperscript{-1} | 100/60–70% (140–240 °C) | [81] |
| (1.5 wt.%)Ag/mesoTiO\textsubscript{2} | impregnation, calcination, 600 °C, air; reduction, 600 °C, H\textsubscript{2}/Ar | 0.05 vol.% NH\textsubscript{3}, 2.5 vol.% O\textsubscript{2}, Ar balance, 40 mL min\textsuperscript{-1}, mass of the catalyst: 0.1 g, WHSV 24,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/74–76% (375–400 °C) *100/81–87% (350 °C) | [82] |
| (10 wt.%)Ag/mesoTiO\textsubscript{2} | impregnation, calcination, 600 °C, air; reduction, 600 °C, H\textsubscript{2}/Ar | 0.05 vol.% NH\textsubscript{3}, 2.5 vol.% O\textsubscript{2}, Ar balance, 40 mL min\textsuperscript{-1}, mass of the catalyst: 0.1 g, WHSV 24,000 mL h\textsuperscript{-1} g\textsuperscript{-1} | 100/60–90% (180–240 °C) *100/72–78 (275–400 °C) | [82] |
| Catalyst                  | Catalyst Preparation                      | Reaction Conditions                                                                 | NH$_3$ Conversion$_{N_2}$ Selectivity/% (Temperature/°C) | Ref.  |
|--------------------------|-------------------------------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------------|-------|
| (7.3 wt.%)Ag/MnO$_2$     | multi-step process, calcination, 400 °C, air | 0.005 vol.% NH$_3$, 20 vol.% O$_2$, Ar balance *0.005 vol.% NH$_3$, 20 vol.% O$_2$, 0.057 vol.% H$_2$O, Ar balance 100 mL min$^{-1}$, mass of the catalyst: 0.15 g, WHSV 40,000 mL h$^{-1}$ g$^{-1}$ | 100/98–99% (90–120 °C) *100/95–96% (115–130 °C) | [90]  |
| (10 wt.%)Ag-Y            | impregnation, calcination, 600 °C, air; reduction, 300 °C, H$_2$/N$_2$ | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, N$_2$ balance, 400 mL min$^{-1}$, mass of the catalyst: 0.4 g, GHSV 50,000 h$^{-1}$ | 100/32–50% (220–260 °C) | [78]  |
| (21 wt.%)Ag-Y            | ion-exchange, calcination, 400–500 °C, air | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, He balance *0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, 3.2 vol.% H$_2$O, He balance **0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, 4.8 vol.% CO$_2$, He balance 40 mL min$^{-1}$, mass of the catalyst: 0.05 g, WHSV 48,000 mL h$^{-1}$ g$^{-1}$ | 100/92–95% (200–300 °C) *100/98% (200–300 °C) **100/90–95% (200–300 °C) | [91]  |
| (21 wt.%)Ag-USY           | ion-exchange, calcination, 600 °C, air | 0.05 vol.% NH$_3$, 7 vol.% O$_2$, N$_2$ balance, 800 mL min$^{-1}$, mass of the catalyst: 0.25 g, WHSV 192,000 mL h$^{-1}$ g$^{-1}$ | 100/70–80% (300–400 °C) | [92]  |
| (33 wt.%)Ag-Y            | impregnation, calcination, 600 °C, air | 1 vol.% NH$_3$, 10 vol.% O$_2$, He balance 400 mL min$^{-1}$, mass of the catalyst: 0.8 g, WHSV 30,000 mL h$^{-1}$ g$^{-1}$ | 100/95% (320 °C) | [79]  |
| (5 wt.%)Ag-(5 wt.)Cu/Al$_2$O$_3$ | impregnation, calcination, 600 °C, air | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, He balance, 50 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 30,000 mL h$^{-1}$ g$^{-1}$ | 100/95% (200–300 °C) | [71]  |
| (7.5 wt.%)Ag-(2.5 wt.)Cu/Al$_2$O$_3$ | impregnation, calcination, 500 °C, air | 1.14 vol.% NH$_3$, 8.21 vol.% O$_2$, 74.7 mL min$^{-1}$, mass of the catalyst: 0.2 g, WHSV 22,410 mL h$^{-1}$ g$^{-1}$ | 100/82% (300 °C) | [71]  |
| (10 wt.%)Ag/Al$_2$O$_3$+(10 wt.)Cu/Al$_2$O$_3$ (mixture 3:1) | impregnation, calcination, 500 °C, air | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, Ar balance *0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, 3.2 vol.% H$_2$O, Ar balance 40 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 100/83–94% (375–500 °C) *100/83–94% (375–500 °C) | [80]  |
| (1.5 wt.%)Ag-(10 wt.)Cu/Al$_2$O$_3$ | impregnation, calcination, 600 °C, air | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, Ar balance 40 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 100/83–94% (375–500 °C) | [80]  |
| (0.59 wt.%)AgCuMgAlO$_x$ | coprecipitation, calcination, 600 °C, air | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, Ar balance 40 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 100/88% (425–500 °C) | [87]  |
| (2.34 wt.%)AgCuMgAlO$_x$ | solvothermal mix-bake-wash method, 300 °C, air | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, Ar balance 40 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 100/78–92% (400–500 °C) | [87]  |
| (77.25 wt.%)Ag-Cu nanoalloy | calcination, 500 °C, air | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, N$_2$ balance, 100 mL min$^{-1}$, GHSV 12,000 h$^{-1}$ | 100/72–85% (210–240 °C) | [89]  |
| (67.57 wt.%)AgCuO$_x$ | calcination, 500 °C, air | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, He balance, 300 mL min$^{-1}$, GHSV 2,250 h$^{-1}$ | 100/64–72% (300–340 °C) | [88]  |
| (7.4 wt.%)Ag/WMH | WMH—wire-mesh honeycomb | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, He balance, 300 mL min$^{-1}$, GHSV 2,250 h$^{-1}$ | 100/63–73% (210–320 °C) | [88]  |
| (7.2 wt.%)Ag-(12.2 wt.)Cu/WMH | impregnation, calcination, 500 °C, air | 0.1 vol.% NH$_3$, 10 vol.% O$_2$, He balance, 300 mL min$^{-1}$, GHSV 2,250 h$^{-1}$ | 100/81–89% (220–320 °C) | [88]  |
4. Au- and Ru-Based Catalysts

Gold-based catalysts are well-known for their high catalytic activity at low temperatures, e.g., in the oxidation of CO \[93,94\]. However, such catalysts were rarely investigated in NH\(_3\)-SCO (Table 3). Interestingly, Lin et al. \[95\] investigated NH\(_3\) oxidation over the in situ H\(_2\)-reduced (5 wt.%) Au/MO\(_x\)/Al\(_2\)O\(_3\) (M = Cu, Fe, Ce, Li, and Ti) catalysts in the temperature range from 200 to 400 °C. Among all investigated catalysts, Au/Cu-Al\(_2\)O\(_3\) was the most active and N\(_2\) selective (full NH\(_3\) conversion at 300 °C with 95% N\(_2\) selectivity). The H\(_2\)-reduced Au/Al\(_2\)O\(_3\) catalyst revealed significantly lower NH\(_3\) conversion (ca. 30% above 400 °C). However, the NH\(_3\) conversion increases with an increasing O\(_2\) in the feed (\(c(\text{NH}_3):c(\text{O}_2) = 1:10\); NH\(_3\) conversion of 45% at 400 °C) \[77\]. Gong et al. \[96\] and Liu et al. \[97\] reported from experimental and theoretical studies that NH\(_3\) did not dissociate on the Au(111) surface until it was precovered with oxygen atoms or hydroxyl groups. Thus, Lippits et al. \[77\] observed the enhanced NH\(_3\) conversion (full NH\(_3\) conversion at 338 °C with N\(_2\) selectivity below 50%) over Au/Al\(_2\)O\(_3\) after its doping with CeO\(_x\) (able to provide and store oxygen) and Li\(_2\)O (responsible for decreasing the catalyst acidity and thus improved oxygen adsorption). Recently, Lin et al. \[12\] reported the acidic metal-oxide-supported gold catalyst (Au/Nb\(_2\)O\(_5\)) with improved N\(_2\) selectivity compared to other metal-oxide-supported gold catalysts (e.g., Au/SiO\(_2\), Au/Al\(_2\)O\(_3\), Au/Fe\(_2\)O\(_3\), etc., Figure 6a). Specifically, Au/Nb\(_2\)O\(_5\) contains both Brønsted and Lewis acid sites that allowed NH\(_3\) oxidation according to hydrazine mechanism (N\(_2\)H\(_4\) as the intermediate) and imide mechanism (HNO as the intermediate), respectively (Figure 6b). Overall, further detailed property-activity studies over Au-containing materials could path the way for further catalysts design and their optimization.

Some studies were carried out on RuO\(_2\)(110) surface characterized by two types of atoms with unsaturated bonds along [1] direction: a) the twofold coordinated oxygen atoms (O-bridge; O-br) and b) the fivefold coordinated Ru atoms (Ru-cus; the adsorption site for ammonia) \[98\]. NH\(_3\) decomposes to NH\(_2\) at \(-183^\circ\text{C}\), while successive annealing to \(-23–27^\circ\text{C}\) produces N \[98,99\]. N\(_2\) is predominantly formed over polycrystalline RuO\(_2\) in a direct combination of Ru-coordinated N atoms (at ambient pressure, 6% of NO at \(c(\text{O}_2):c(\text{NH}_3) = 2:1\); 65% of NO at \(c(\text{O}_2):c(\text{NH}_3) = 140:1\) \[100\]. The selectivity to NO increases with increasing temperature (100% around 257 °C, in UHV, \(p(\text{NH}_3) = 10^{-7}\) mbar,
and c(O2):c(NH3) = 20:1) because of the high desorption temperature for NO (227 °C). At lower temperatures, NO-formation is hindered by surface water molecules [98,99]. Seitsonen et al. [99] estimated energy barriers to the elementary H-abstraction steps and the recombination of N and O atoms on RuO2(110) surface by using DFT calculations and high-resolution core-level shift spectroscopy (Figure 7). The high activity of RuO2(110) arose from low activation energies from the successive H-abstraction.

Figure 7. Microscopic reaction steps in NH3 oxidation over RuO2(110). Activation energies (red) and total adsorption energies (black) are determined by DFT calculations and are given in kJ mol−1. -Hdiff means that abstracted H from NHx is removed from its direct neighborhood by diffusion along with various O species on the surface. Reprinted from [99] with permission from Elsevier.

Also, RuO2-supported catalysts are active for ammonia oxidation (Table 3). E.g., Cui et al. investigated the RuO2-CuO/Al-ZrO2 [101] and CuO/RuO2 [102] catalysts with 5–30 wt.% and 70–95 wt.% of Ru loading, respectively. The catalysts possessed excellent activity and N2 selectivity at low temperatures, i.e., for (20 wt.%RuO2-CuO/Al-ZrO2 full NH3 conversion at 195 °C with 100% N2 selectivity [101], or for (10 wt.%CuO/RuO2 full NH3 conversion at 180 °C and N2 selectivity above 95% [102] were achieved. However, these catalysts are relatively expensive and therefore their commercialization is hindered. Thus, Chakrobaty et al. [103] investigated the Cu/Ru catalysts with varying overlaying thickness of Cu film (with the optimum of 0.8 monolayers) deposited by physical vapor deposition on (5 nm)Ru/TiO2 (111). The synergistic interaction between Cu and Ru species led to a threefold higher ammonia conversion rate than was achieved over Ru-based catalyst. Concerning the powder materials, Wang et al. [104] studied a series of WO3-modified RuO2-Fe2O3 catalysts with a lower cost, i.e., with 1 wt.% of ruthenium. The introduction of 5 wt.% of WO3 (among 1–9 wt.% of WO3) tuned the surface acidity, and thus, enhanced activity and N2 selectivity of RuO2-Fe2O3 (full NH3 conversion at 250–400 °C and 93–97% N2 selectivity). In situ DRIFTS results indicated that NH2-SCO over (1 wt.%RuO2-(5 wt.%)WO3-Fe2O3 proceeds according to the i-SCR mechanism. The -NH2 intermediate reacted with the in situ-generated NOx ad-species with the formation of N2. Furthermore, Chen et al. [105,106] studied (0.2 wt.%Ru/Ce0.6Zr0.4O2(PVP) or (0.2 wt.%IrO2/Ce0.6Zr0.4O2(PVP) (PVP, polyvinylpyrrolidone) and claimed that -HNO appeared as an intermediate in the i-SCR mechanism of NH3-SCO (Figure 8). The formed -HNO interacted with atomic oxygen with the formation of NO, which furthermore reacts with -NH2 (-NH2 and -NH) species with the formation of N2 and N2O (minor by-product).
The presence of SO$_2$ in the feed gas effectively inhibits the production of N$_2$O, i.e., the reactions between gaseous NO and -NH$_2$ will be enhanced (more adsorbed ammonia on the sulfated (acidic) surface). SO$_2$ can also inhibit NH$_3$ oxidation resulting in higher N$_2$ selectivity (up to 100%) in the absence of NO$_x$. Similar conclusions were given for RuO$_x$/TiO$_2$-SO$_4^{2-}$, however, the time of the sulfated treatment (0.5–6 h) of the support varied activity and N$_2$ selectivity of the final catalysts (with an optimum at 2 h) [107].

Figure 8. Mechanism of NH$_3$-SCO and effect of SO$_2$. Reprinted from [105] with permission of ACS Publications.

Concluding this part, both Au- and Ru-based catalysts were significantly less investigated in NH$_3$-SCO. A highly loaded Ru-containing materials (10–20 wt.% Ru; (10 wt.%)CuO-RuO$_2$ or (20 wt.%)RuO$_2$-CuO/Al-ZrO$_2$) present a class of highly active and N$_2$ selective catalysts at relatively low temperatures (i.e., full NH$_3$ conversion at 180–350 °C with 95–100% N$_2$ selectivity; according to data gathered in Table 3). Otherwise, the materials with significantly lower content of Ru species (0.5–3 wt.%) were less active (full NH$_3$ conversion at 175–400 °C) and N$_2$ selective (43–99%). However, again, concerning the influence of the preparation variables (e.g., the different total amount of ruthenium, variety of applied metal promoters and supports) as well as pretreatment and reaction conditions, the comparison of activity and N$_2$ selectivity over Ru-based catalysts each other or even with other noble metal-based catalysts is limited. Furthermore, for both Au- and Ru-based catalysts, oxidized metal species (i.e., Au$^+/Au^{3+}$, Ru$^{4+}$) ensure enhanced activity and N$_2$ selectivity (in contrast to the Pt- or Ag-based catalysts). Nevertheless, an in-depth understanding of the role of active species in NH$_3$-SCO is still lacking and needs to be demonstrated clearly in further studies (especially over Au-based catalysts). Furthermore, the presented catalytic systems were mainly investigated under ideal conditions (only NH$_3$ and O$_2$ diluted in inert gas) also concerning the investigation of the reaction mechanisms, i.e., through in situ DRIFTS experiments (NH$_3$ adsorption/desorption in inert gas or oxygen). Otherwise, surface reactions are fast (residence time in a range of seconds) and the reaction mechanism involves a series of parallel and consecutive reactions. Thus, the reaction intermediates and conversion of the substrate molecules on the catalyst surface should be followed with more detailed ex situ, in situ, and operando spectroscopic studies as well as transient kinetic investigations under-applied reaction conditions.
Table 3. Comparison of full NH$_3$ conversion and N$_2$ selectivity in same temperature range over Au- and Ru-based catalysts reported in literature.

| Catalyst | Catalyst Preparation | Reaction Conditions | NH$_3$ Conversion, N$_2$ Selectivity/°C | Ref. |
|----------|----------------------|---------------------|----------------------------------------|------|
| (5 wt.%)Au/CuO/Al$_2$O$_3$ | impregnation, calcination, 300 °C, air; reduction, 300 °C, H$_2$ | 2 vol.% NH$_3$, 2 vol.% O$_2$, He balance, 30 mL min$^{-1}$, mass of the catalyst: 0.15 g, WHSV 12,000 mL h$^{-1}$ g$^{-1}$ | 100/95% (300 °C) | [95] |
| (4 wt.%)Au/CoO$_2$/Li$_2$O/Al$_2$O$_3$ | homogenous deposition precipitation, reduction, 400 °C, H$_2$ | 2 vol.% NH$_3$, 2 vol.% O$_2$, Ar balance, 40 mL min$^{-1}$, GHSV 2500 h$^{-1}$ | 100/34–49% (338–400 °C) | [77] |
| (10 wt.%)CuO-RuO$_2$ | conacasting-replication method, calcination, 500 °C, air | 0.1 vol.% NH$_3$, 2 vol.% O$_2$, Ar balance, 100 mL min$^{-1}$, mass of the catalyst: 0.08 g, WHSV 75,000 mL h$^{-1}$ g$^{-1}$ | 100/95–97% (180–350 °C) | [102] |
| (20 wt.%)RuO$_2$/CuO/ZrO$_2$ | impregnation, calcination, 500 °C, air | 0.04 vol.% NH$_3$, 5 vol.% O$_2$, 6 vol.% H$_2$O, Ar balance, 200 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 120,000 mL h$^{-1}$ g$^{-1}$ | 100/68–98% (250–275 °C) | [101] |
| (20 wt.%)RuO$_2$/Al-ZrO$_2$ | impregnation, calcination, 500 °C, air | 0.08 vol.% NH$_3$, 5 vol.% O$_2$, Ar balance, 400 mL min$^{-1}$, GHSV 60,000 h$^{-1}$ | 100/67–90% (250–400 °C) | [104] |
| (1 wt.%)RuO$_2$-Fe$_2$O$_3$ | sol-gel route, calcination, 500 °C, air | 0.05 vol.% NH$_3$, 0.5 vol.% O$_2$, 5 vol.% N$_2$, 0.5 vol.% CO, 5 vol.% O$_2$, N$_2$ balance, GHSV 300,000 h$^{-1}$ | 100/94–96% (220–300 °C) | [108] |
| (1.13 wt.%)Ru/Cu-ZS3-13 | impregnation, 500 °C, air; pretreatment, 300 °C, O$_2$/N$_2$ | 0.1 vol.% NH$_3$, 5 vol.% O$_2$, 3 vol.% H$_2$O, N$_2$ balance, 150 mL min$^{-1}$, mass of the catalyst: 0.1 g, WHSV 90,000 mL h$^{-1}$ g$^{-1}$ | 100/47–72% (350–400 °C) | [109] |
| (3 wt.%)RuO$_2$/TiO$_2$ | impregnation, calcination, 400 °C, air | 0.02 vol.% NH$_3$, 10 vol.% O$_2$, 6 vol.% H$_2$O, N$_2$ balance, 500 mL min$^{-1}$, mass of the catalyst: 0.3 g, GHSV 60,000 h$^{-1}$ | 100/54–63% (275–300 °C) | [110] |
| (1 wt.%)Ru/TiO$_2$ | impregnation, calcination, 400 °C, air; pretreatment, 400 °C, O$_2$/N$_2$ | 0.08 vol.% NH$_3$, 5 vol.% O$_2$, N$_2$ balance, 400 mL min$^{-1}$, GHSV 60,000 h$^{-1}$ | 100/43–85% (200–400 °C) | [107] |
| (0.5 wt.%)Ru/TiO$_2$ | impregnation, calcination, 400 °C, air; pretreatment, 400 °C, O$_2$/N$_2$ | 0.02 vol.% NH$_3$, 10 vol.% O$_2$, 6 vol.% H$_2$O, N$_2$ balance, 500 mL min$^{-1}$, mass of the catalyst: 0.3 g, GHSV 60,000 h$^{-1}$ | 100/54–63% (275–300 °C) | [110] |

5. Conclusions and Outlook

NH$_3$-SCO is the most efficient method for ammonia removal from oxygen-containing exhausts. The number of publications related to this process successively increases with the main researchers’ interest in the development of the catalyst with high activity, N$_2$ selectivity, and stability in the broad temperature range. The present mini-review provides a broad picture of the property-activity correlations of noble metal-based catalysts investigated for NH$_3$-SCO. Among presented Pt-, Pd-, Ag- and Au-, Ru-based catalytic systems, mainly H$_2$-reduced (1–2 wt.%)Pt/Al$_2$O$_3$ and (10 wt.%)Ag/Al$_2$O$_3$ were recognized as the most active NH$_3$-SCO systems in the low temperatures (<300 °C). Unfortunately,
they caused significant formation of N₂O and NOₓ. Moreover, as can be seen from the above examples, although Pt- and Ag-based catalysts were more intensively investigated regarding their property-activity correlations—compared to that of the Pd-, Au-, and Ru-containing catalysts—there is still a lack of systematic studies concerning the nature and role of active species as well as the influence of (a) the particle size of active components and their aggregation state; (b) the catalyst supports (i.e., inorganic oxides versus zeolites); (c) the preparation methods (i.e., catalysts in the structured forms, e.g., monolith), and (d) feed composition (i.e., various c(NH₃):c(O₂) ratios (1:1–25)—an excess of oxygen together with minor NH₃ slip, presence of H₂O, SOₓ, COₓ, etc.) on activity, N₂ selectivity, and stability in catalysis. Contrary to the transition metal-based catalysts only a few examples concern catalytic studies over noble metal-based zeolites. Otherwise, concerning the discussed material requirements (i.e., enhanced ammonia conversion, N₂ selectivity and stability in the presence of typical components of exhaust gases and the broad temperature range up to 600–700 °C (in the cycle of diesel particulate filter regeneration)), the zeolite-based catalysts present a class of highly promising materials. For instance, ion-exchanged zeolites showed higher activity also in the presence of H₂O, compared to that of alumina-supported oxides with the same metal loading due to high dispersion of metal species and acid sites of high strength. Furthermore, the studies on the reaction mechanisms are rather scarce. The reaction mechanisms must be clarified to rationally develop a process for NH₃ oxidation to N₂ over applied catalysts. These problems highlight the importance of more detailed ex situ and in situ methods (i.e., temperature-programmed, spectroscopic, and/or transient methods) in studying the catalysts under real working environments.

Furthermore, a relatively narrow operating temperature window of full NH₃ conversion (Tables 1–3), high selectivity to N₂O and NOₓ, and high costs of noble metals motivated researchers to develop suitable bifunctional systems. Cu-ZSM-5 or even Cu-chabazite (SSZ-13, SAPO-34) are already recognized (also discussed in the previous review articles concerning NH₃-SCO, Jabłońska et al., 2016, Jabłońska et al., 2020) as the active and N₂ selective catalysts for NH₃-SCR. Despite presented here developments in bifunctional catalysts (mainly Pt-Cu or Ag-Cu catalysts systems), challenges remain in achieving enhanced NH₃ conversion, N₂ selectivity, and stability (in the presence of real flue gases, such as H₂O, SOₓ, and COₓ). Further investigations concerning bifunctional catalysts with a low number of noble metals, e.g., Au, Pt-Au, Pt-Rh, etc., constitute a promising research direction. Nevertheless, the present findings, indications, and thoughts given in the mini-review form a solid basis for further developments of structured catalysts (i.e., in the form of dual-layer or core-shell structure) and their optimization.

Funding: This research received no external funding.

Acknowledgments: The author acknowledges support from the german Research Foundation (DFG) and Leipzig University within the program of Open Access Publishing.

Conflicts of Interest: The authors declare no conflict of interest.

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