A Comparative Mini-Review on Transition Metal Oxides Applied for the Selective Catalytic Ammonia Oxidation (NH₃-SCO)

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Abstract: The selective catalytic oxidation of NH₃ (NH₃-SCO) into N₂ and H₂O is an efficient technology for NH₃ abatement in diesel vehicles. However, the catalysts dedicated to NH₃-SCO are still under development. One of the groups of such catalysts constitutes transition metal-based catalysts, including hydrotalcite-derived mixed metal oxides. This class of materials is characterized by tailored composition, homogenously dispersed mixed metal oxides, exhibiting high specific surface area and thermal stability. Thus, firstly, we give a short introduction to the structure and composition of hydrotalcite-like materials and their applications in NH₃-SCO. Secondly, an overview of other transition metal-based catalysts reported in the literature is given, following a comparison of both groups. The challenges in NH₃-SCO applications are provided, while the reaction mechanisms are discussed for particular systems.

Keywords: selective ammonia oxidation; hydrotalcite-like compounds; mixed metal oxides; transition metals

1. Introduction

Ammonia (NH₃) is one of the most important chemicals in the world, e.g., used to produce fertilizers, synthetic fibers, dyes and synthetic foam, as well as to reduce NOₓ emissions, etc. (Figure 1). However, since 2001, the EU has listed NH₃ as one of the four main types of atmospheric pollutants (among NOₓ, SO₂, and non-methane volatile organic compounds (NMVOC)), and has released the EU National Pollutant Discharge Inventory (NECD) every year. Twelve Member States (including, e.g., Germany, France, Austria, etc.), and the United Kingdom need to reduce NH₃ emissions by up to 10% against 2018 levels to attain their 2020 and 2030 emission reduction commitments. Denmark and Lithuania need to reduce emissions by more than 10% [1]. Ammonia emitted from livestock, industrial processes or NH₃ emitted to the atmosphere through either the large-scale usage of fertilizers or gas slippage from the NH₃-SCR-DeNOₓ applications can cause serious damage to human health (i.e., to the eyes, throat, nose, etc., if its concentration exceeds 50–100 ppm) [2], and environment (e.g., acidification, formation of haze, Figure 1).

To control the ammonia slip, several different techniques used for the elimination of NH₃ (e.g., adsorption, absorption, catalytic decomposition, etc.) have been applied [3]. However, the selective catalytic oxidation of ammonia into nitrogen and water vapor is an ideal technology for removing NH₃ from O₂-containing waste gases, after the selective catalytic reduction of NOₓ by NH₃ (SCR-DeNOₓ), by the use of stoichiometric or even excess amount of NH₃ from stationary and mobile sources. Thus, ideally, the residual NH₃ (slip) could be selectively oxidized to N₂ and H₂O (i.e., inert, and non-toxic products, Equation (1)). However, the N₂ selectivity is affected by the undesired oxidation of ammonia to N₂O, NO, and NO₂ (Equations (2)–(4)): 
Thus, NH₃-SCO catalysts with enhanced activity, N₂ selectivity, stability (also in the presence of H₂O, SO₂, and CO₂, up to 600–700 °C in the cycle of diesel particulate filter regeneration) and low cost, at the same time are of both scientific and industrial importance. However, catalysts of sufficient activity, selectivity and stability under application-relevant reaction conditions are not yet available. To date, many catalysts have been proposed for NH₃-SCO and they can be classified into several groups, including noble metal-based catalysts, transition metal-based catalysts and noble/transition metal (bimetallic)-containing catalysts, etc. Particularly, the catalysts containing copper species are recognized as the most active and N₂ selective among other transition metal-containing materials. Copper oxide species and their redox properties were found to determine their catalytic properties [4]. Recently, we published on noble metal-based catalysts (including Pt-, Pd-, Ag-, and Au-, Ru-based catalysts) [5] and Cu-containing zeolite-based catalysts (e.g., Cu-SSZ-13 commercialized in NH₃-SCR-DeNOₓ) [6]. Thus, in the current mini-review, we focused on the application of transition metal oxides, excluding catalysts modified with noble metals or zeolite-based catalysts. However, the publications and results on the subject of transition metal-based catalysts increased recently, therefore, we found the mini-review timely. Particularly, we aim to compare hydrotalcite-based mixed metal oxides with other transition metal catalysts presented in the literature, and based on that propose an active, N₂ selective, and stable catalytic system (either single one or as a component for hybrid catalyst) for NH₃-SCO. The hybrid catalyst consists of an SCR catalyst for NOₓ control and catalyst with oxidation functionality for ammonia conversion. The different arrangements
of the hybrid catalysts, i.e., dual-layer, inverse dual-layer, hybrid dual layer, dual mixed layers, etc., were so far tested in the literature (e.g., [7]). The combination of the two active components for NH₃-SCR-DeNOₓ and NH₃ oxidation to yield NOₓ arise from the internal selective catalytic reduction mechanism (i-SCR) [3,4]. However, despite research in this direction, a debate remains on the elementary reaction steps and the active sites in NH₃-SCO. Moreover, for the i-SCR mechanism, the imide mechanism (with the formation of imide (-NH) and nitrosyl (-HNO) as intermediates), and the hydrazine mechanism (involving hydrazine (N₂H₄) as an intermediate) are reported as the main mechanisms for NH₃-SCO. Recently, the N₂⁻ mechanism (with adsorbed N₂ anion regarded as the intermediate), was also proposed to explain the high reactivity of nano-size Al₂O₃-supported Ag species [8]. Contrary to the micro-size Al₂O₃ supported Ag species, the i-SCR mechanism was proposed, evidencing that the reaction mechanism depends on the applied catalytic systems. Another example can constitute Cu species deposited on Al₂O₃. Depending on the applied treatment (calcination versus dynamic construction), NH₃-SCO over the catalysts can follow different routes. For example, the fast i-SCR mechanism characterized by the presence of consumable NOₓ adsorbed species was proposed on CuOₓ-OH interfacial sites [9]. Still, compared to NH₃-SCR-DeNOₓ, the reaction mechanisms of NH₃-SCO are not frequently discussed in the literature. Hence, it is vital to study the reaction mechanisms over more materials thoroughly and then rationally design high-performing NH₃-SCO catalyst with appropriate promotion strategies.

Although some review articles [3,4,10] have outlined the advances of transition-metal-based catalysts in NH₃-SCO, only examples of such materials have been given. Thus, in the current mini-review, we thoroughly discuss the hydrotalcite-derived mixed metal oxides and other transition metal oxides applied in NH₃-SCO, evidencing that for these materials their application as catalysts is quite relevant. Our objective was not to make a systematic review of the hydrotalcite-like compounds because several reviews have already been published, including preparation and physico-chemical characterization (e.g., [11–13]), catalytic applications (e.g., [14,15])—in particular nitrogen oxides removal [16,17]. Despite not being mentioned in the text, selective ammonia oxidation over (mixed) metal oxides into NO [18–22] or N₂O [23,24] was reported, in the present work we concentrate only on the ammonia oxidation into N₂ and H₂O. Throughout the mini-review, we highlight the structure-activity/selectivity correlations and try to narrow the gap between research and industrial applications. We hope that based on these correlations, a knowledge-driven industrial catalyst design and its optimization becomes possible, which will allow keeping the NH₃ emissions of diesel-powered vehicles at a very low level under various boundary conditions.

2. Hydrotalcite-Derived Mixed Metal Oxides

Hydrotalcite-like compounds (HT), otherwise referred to as anionic clays or layered double hydroxides (LDHs) are described by the general formula [M(II)₁₋ₓM(III)ₓ(OH)₂]ₓ⁺(Aⁿ⁻q/n)ₘH₂O, where M(II) and M(III) represent divalent and trivalent metal cations, respectively, Aⁿ⁻ represents interlayer anions of charge n⁻. Usually, the structure of the HT-like compounds is better visualized by analyzing the structure of brucite. Mg(OH)₂ octahedra of Mg²⁺ coordinated with six OH⁻ share edges to form successive sheets, with the hydroxide ions located perpendicularly to the plane of the layers. The resulting sheets are stacked on top of each other and held together by hydrogen bonds. When Mg²⁺ ions are substituted by Al³⁺, a positive charge is created in the hydroxyl part of the layer. The positive charge is neutralized by the negative CO₃²⁻ anions, which are located between the layers of brucite, along with H₂O that is also present in the interlayer space (Figure 2) [25,26]. To obtain a pure hydrotalcite-like phase, the x in the general formula of the material should be in the range of 0.15 and 0.34 [25]. Coprecipitation is the most common method for the synthesis of hydrotalcite-like compounds.

The structure and physico-chemical properties of the hydrotalcite-like compounds are dependent on the kind and amount of metal ions present in the brucite-like layers, the type and position of anions and water in the interlayer region, and the type of stacking between
the layers (i.e., rhombohedral (3R) versus hexagonal (2H)) [27]. It is possible to synthesize hydrotalcite-like compounds with more than two different metals (regarding different oxidation states, e.g., Li, Mg, Mn, Fe, Co, Al, Mn, Fe, Co, Ni, Cr, Ga) or anions (halides: Cl\(^-\), F\(^-\), I\(^-\), oxo-anions: CO\(_3^{2-}\), NO\(_3^-\), SO\(_4^{2-}\), BrO\(_3^-\), organic acids: adipic, oxalic, sebacic or malonic acid, oxo and polyoxo-metallates: (PW\(_{12}O_{40}\))\(^{3-}\), (PMo\(_{12}O_{40}\))\(^{3-}\), dichromate, anionic complexes: ferro and ferricyanide, PdCl\(_2\(^-\), etc.). Consequently, the size of the interlayer region varies depending on the introduced anions. e.g., Table 1 lists the products obtained from the preparation of CuM(II)M(III)CO\(_3\) hydrotalcite-like compounds.

**Figure 2.** In situ XRD diffraction patterns of the Cu-Mg-Al hydrotalcite-like material recorded in oxidizing conditions. HT—hydrotalcite-like compounds, P—MgO (periclase), C—CuO (cuprite), S—MgAl\(_2\)O\(_4\) (magnesium aluminate) and/or CuAl\(_2\)O\(_4\) (copper aluminate), B—CuAlO\(_2\): Reprinted from [28] with permission from Springer.

**Table 1.** Products obtained from the preparation of the CuM(II)M(III)CO\(_3\) hydrotalcite-like compounds. Reprinted from [25] with permission from Elsevier.

| Cations  | Cations' Ratio | Compounds Identified       |
|----------|----------------|----------------------------|
| CuAl     | 1.0/1.0        | Amorphous species          |
| CuZnAl   | 2.0/1.0/1.0    | HT + R                     |
| CuZnAl   | 3.3/1.6/1.0    | HT + R                     |
| CuZnAl   | 1.6/0.8/1.0    | HT + R                     |
| CuZnAl   | 1.5/1.5/1.0    | HT (HT + R)                |
| CuZnAl   | 1.2/1.2/1.0    | HT                         |
| CuZnAl   | 0.8/0.8/1.0    | HT                         |
| CuCr     | 1.0/1.0        | Amorphous species          |
| CuZnCr   | 1.5/1.5/1.0    | HT                         |
| CuCoCr   | 2.0/2.0/1.0    | HT + M                     |
| CuCoCr   | 1.5/1.5/1.0    | HT                         |
| CuZnCr   | 1.5/1.5/1.0    | HT                         |
| CuMgCr   | 1.5/1.5/1.0    | HT                         |
| CuMnCr   | 1.5/1.5/1.0    | MnCO\(_3\) + HT            |
| CuCoZnCr | 1.4/0.1/1.5/1.0| HT                         |
| CuZnAlCr | 3.0/3.0/1.0/1.0| HT                         |
| CuZnFe   | 1.5/1.5/1.0    | Au                         |

HT—hydrotalcite-like compounds; M—Cu\(_2\)CO\(_3\)(OH)\(_2\) (malachite); R—(Cu, Zn)\(_2\)CO\(_3\)(OH)\(_2\) (Rosasite); Au—aurichalcite.
The hydrotalcite-like compounds are used as the precursors for the catalysts more often than as layered materials themselves. During the thermal treatment, the HT-like compounds transform first to an amorphous oxide and then, at higher temperatures, to crystalline mixed metal oxides (Figure 2). The hydrotalcite-derived mixed metal oxides are characterized by key features such as relatively high specific surface area, homogenous dispersion of active metal ions, non-stoichiometry, and high thermal stability, etc. [15].

To the best of our knowledge, Trombetta et al. [29] reported for the first time the catalytic activity and N₂ selectivity over the CuMgAl hydrotalcite-derived mixed metal oxides in NH₃-SCO in 1997. They tested CuMgAl with n(Cu)/n(Mg)/n(Al) of 4.6–7.2/63.8–66.4/29 and found nearly full NH₃ conversion at ca. 400–500 °C and N₂ selectivity below 80%. Following such studies, Chmielarz et al. [30] studied the activity of hydrotalcite-derived mixed metal oxides (M(II, III)Mg(II)Al(III)) containing Ni, Fe, Cu or Co, and pointed out that both the kind and the number of metal ions introduced into hydrotalcite-like structure influenced the activity and selectivity in NH₃-SCO. Among the investigated compositions, Cu-containing catalysts (CuMgAl; n(Cu)/n(Mg)/n(Al) = 5/66/29, 10/61/29, 20/51/29) were the most active in NH₃-SCO, while the Fe-containing one (FeMgAl; n(Fe)/n(Mg)/n(Al) = 10/61/29) revealed enhanced N₂ selectivity. Based on these results, the catalytic properties were further optimized by the combination of both metals, i.e., the introduction of copper and iron ions into the brucite-like structure. The CuMgFe mixed metal oxides with different compositions, such as n(Cu)/n(Mg)/n(Fe) = 0–1/2/1, mol.% (with the optimum composition guaranteeing enhanced NH₃ conversion and N₂ selectivity being n(Cu)/n(Mg)/n(Fe) = 0.5/2/1 [31]) or n(Cu)/n(Mg)/n(Fe) = 5–15/52–62/33 (with the optimum composition of n(Cu)/n(Mg)/n(Fe) = 12/55/33 [32]) were reported. The temperature-programmed studies, i.e., sorption of NH₃ and desorption in He or O₂/He, as well as NH₃-SCR-DeNOₓ and NH₃-SCO with different spaces velocities, revealed that the reaction over the CuMgFe hydrotalcite-derived mixed metal oxides proceeds according to the i-SCR mechanism and NH₃ oxidation to NO is a rate-determining step (Figure 3) [31]. Thus, the modification of hydrotalcite-derived materials with noble metals (Pt, Pd, Rh) arose based on those studies [33].

Copper loading at about 5–8 mol.% in the CuMgAl mixed metal oxides allowed reaching full NH₃ conversion at 375–600 °C with N₂ selectivity above 60% [34]. The increase in copper loading led to the formation of bulk-like copper oxide species. The N₂ selectivity varied depending on the catalysts’ composition and the method used for the preparation of the hydrotalcite-like precursor. CuMgAl mixed metal oxides prepared via coprecipitation (cop.), and subsequent calcination of the hydrotalcite-like precursor revealed a significantly higher activity and N₂ selectivity compared to the material with similar composition obtained via rehydration (reh.) of calcined Mg-Al hydrotalcite-like compounds or thermal decomposition (decom.) of nitrate precursors (Figure 4a). This effect was ascribed to the presence of the highly dispersed copper oxide species in hydrotalcite-derived mixed metal oxides. Additionally, the catalysts containing the same copper content, but with variations in the n(Mg)/n(Al) ratio presented similar catalytic activity [34,35]. Beyond the optimization of the kind and loading of metal species, the optimization of the calcination temperature is also relevant. The thermal treatment of hydrotalcite-like materials influences the composition of mixed metal oxides and their physico-chemical properties and thus, the activity and N₂ selectivity in NH₃-SCO [28,35]. Hydrotalcite-derived CuMgAl, CuZnAl, CuMgFe mixed metal oxides calcined at 900 °C revealed significantly lower activity compared to the materials calcined at 600 °C (Table 2, pos. 5, Figure 4b), which was ascribed to the different copper oxide phases and their redox properties. Enhanced activity at low temperatures together with a drop of N₂ selectivity at higher temperatures were driven by the easily reduced copper oxides species. Otherwise, calcination temperature at ca. 800 °C led to the formation of the spinel phases, e.g., Cu₁₋ₓMgₓAl₂O₄ of lower reducibility, which caused higher N₂ selectivity [35].
Figure 3. Results of temperature-programmed desorption of NH3 in (a) pure He or (b) 5 vol.% O2/He, adsorption: 70 °C, 1 vol.% NH3/He, (c) comparison of conversion of NH3 and NO, and (d) comparison of the space velocities (SV) over the CuFeAl hydrotalcite-derived mixed metal oxides. Reprinted from [31] with permission of Springer.

Regarding the use of other metals as dopants in Cu-containing mixed metal oxides, Jabłońska et al. [36] introduced Ag, Ce and Ga (y = 0–1 mol.%) to the CuMgAl mixed metal oxides (n(M)/n(Cu)/n(Mg)/n(Al) = y/5/66-79/29). The redox properties determined the catalytic properties for materials with the loading of y ≤ 0.25, while for the higher metal loading (y ≥ 0.25) the catalytic properties were driven mainly by the metal oxide phases. Górecka et al. [37] investigated hydrotalcite-derived (5 mol.%) CuMgAl mixed metal oxides, also impregnated with cerium (4 wt.%) over different feed compositions, i.e., NH3 and O2 (2 vol.% versus 20 vol.%). Higher O2 concentration enhanced NH3 activity, while N2 selectivity dropped (the opposite effect was found for higher NH3 concentration in the feed). The effect of the enhanced NH3 activity over Cu-doped samples was ascribed to the synergetic effect of Ce–Cu redox pairs, which activated the lattice oxygen to react with NH3 species towards the formation of N2 (Equation (5)). The oxygen vacancies were filled again with the surface oxygen as the cerium and copper species were oxidized (Equation (6), where □ represents oxygen vacancies):

\[
\text{Ce}^{4+} - \text{O}^{2-} - \text{Cu}^{2+} + \text{NH}_3 \rightarrow \text{Ce}^{3+} - \square - \text{Cu}^+ + \text{N}_2 + \text{H}_2\text{O} \quad (5)
\]

\[
\text{Ce}^{3+} - \square - \text{Cu}^+ + \text{O}_2 \rightarrow \text{Ce}^{4+} - \text{O}_2 - \text{Cu}^{2+} \quad (6)
\]
were achieved over the Cu-containing hydrotalcite-derived mixed metal oxides. Thus, which makes them suitable for NH$_3$ oxidation.

However, from such studies, it was not clear why a rather high Ce loading was applied, since previous research showed that lower cerium loading (0.5 wt.% versus 3 wt.%) led to improved catalyst activity in NH$_3$-SCO [38]. Nevertheless, even higher Ce loading (8.14 wt.%) was applied in further studies over the hydrotalcite-derived CuZnAl mixed metal oxides [39]. Overall, such systems revealed significantly lower N$_2$ selectivity compared to the Ce/CuMgAl mixed metal oxides (Table 2, pos. 10). N$_2$O was a minor by-product. Nevertheless, it is also worth mentioning that the Co-Mn-containing materials were reported to selectively oxidize NH$_3$ to N$_2$O (ca. 100% below 250 °C) [40].

Concluding, the above-mentioned examples show that the hydrotalcite-derived mixed metal oxides offer a large variety of possible modifications and tuning of their properties, which makes them suitable for NH$_3$-SCO applications. Mainly Cu-containing hydrotalcite-derived mixed metal oxides were applied for NH$_3$ oxidation to N$_2$. Overall, the full NH$_3$ conversion between 375-650 °C and N$_2$ selectivity above 70% (based on the data gathered in Table 2, depending on the catalyst composition and preparation, reaction conditions, etc.), were achieved over the Cu-containing hydrotalcite-derived mixed metal oxides. Thus, further optimization of both chemical and phase compositions could lead to enhanced NH$_3$ conversion and N$_2$ selectivity below 350 °C. Still, intensive studies focused on the development of such catalytic systems in NH$_3$-SCO are required under application-relevant reaction conditions (i.e., minor NH$_3$ slip (O$_2$ excess), up to 600–700 °C (in the cycle of diesel particulate filter regeneration) in the presence of H$_2$O, CO$_2$ and/or SO$_2$), including an investigation of the reaction mechanisms.

3. Other Metal Oxides

In the literature, various types of other metal oxides (still excluding noble metal-doped catalysts and zeolite-based materials) have been reported for NH$_3$-SCO. The investigation of Co$_3$O$_4$, MnO$_2$, CuO, Fe$_2$O$_3$ and V$_2$O$_5$ in NH$_3$-SCO was reported in the early studies of I’chenko and Golodets in 1975 [41,42]. The specific catalytic activities at 230 °C ($p$(NH$_3$) = 0.1 atm, $p$(O$_2$) = 0.9 atm) of the selected metal oxides decreased in the following sequence: Co$_3$O$_4$, MnO$_2$ > CuO > NiO > Bi$_2$O$_3$ > Fe$_2$O$_3$ > V$_2$O$_5$ > TiO$_2$ > ZnO > WO$_3$. Among the transition metals, V$_2$O$_5$, MoO$_3$ and WO$_3$ exhibited nearly 100% N$_2$ selectivity at 230 °C [43]. A similar activity order (MnO$_2$ > Co$_3$O$_4$ > CuO > Fe$_2$O$_3$ ≈ V$_2$O$_5$ > NiO) was found by Hinokuma et al. [44] under 1 vol.% NH$_3$, 0.75 vol.% O$_2$. He balance. CuO reached higher N$_2$ selectivity than other oxides [43,45].

NH$_3$-SCO (as a side process) has been frequently studied with NH$_3$-SCR-DeNO$_x$, thus, the following studies focused on the supported V-containing catalysts, e.g., V$_2$O$_5$/TiO$_2$ [46,47]
V$_2$O$_5$/TiO$_2$-SiO$_2$ [48], V$_2$O$_5$-WO$_3$/TiO$_2$ [46,49], V$_2$O$_5$-WO$_3$/ZrO$_2$ [50], etc. E.g., Ueshima et al. [51] examined different supports for V$_2$O$_5$-WO$_3$ and found the decreasing order of catalytic activity in terms of support as follows: TiO$_2$-SiO$_2$ (binary oxide) > TiO$_2$ (anatase) > TiO$_2$ (rutile) > SiO$_2$. Contrary to such studies, V$_2$O$_5$ supported on the rutile form of TiO$_2$ led to a more active and N$_2$ selective (below 400 °C) catalyst [47]. In another study, V$_2$O$_5$/MgO was the least active among vanadium oxide supported on TiO$_2$, SiO$_2$ or MgO [52]. Furthermore, the commercial V$_2$O$_5$-WO$_3$-TiO$_2$ catalyst was modified with Cu (1 wt.%) and Ce (1–10 wt.%) Species. Overall, the catalyst with the composition of (1.02 wt.% Cu (4.79 wt.% Ce)/V$_2$O$_5$-WO$_3$-TiO$_2$ showed enhanced activity at 300 °C, while its modification with Ce enhanced H$_2$O and sulfur resistance [53]. The V$_2$O$_5$-WO$_3$-TiO$_2$ catalyst modified with Cu or Fe (1.0 wt.%) ions revealed the highest activity and N$_2$ selectivity above 350 °C (among other materials modified with Mn or Co species) [54]. Furthermore, K$_2$O was also suggested (but not experimentally tested) as an effective promoter for the V$_2$O$_5$/TiO$_2$ and V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts for N$_2$H$_5$SCO at 500 °C. Regarding, the reaction mechanisms in N$_2$H$_5$SCO, Yuan et al. [55] performed density functional theory (DFT) calculations in conjunction with cluster models on the V$_2$O$_5$ surfaces. According to such mechanisms (Figure 5a), N$_2$H$_7^+$ appears as the initial intermediate from the activated N$_2$H$_3$ which transfers an electron to the metal oxide surfaces. Further routes, depending on the availability of the O$_2$ species, can arise, i.e., the direct route appears in the case of limited O$_2$ or its absence. Consequently, formed N$_2$H$_4$ was oxidized to N$_2$ on V=O sites. In the presence of O$_2$, NH$_2$O$_2^+$ complex was formed, which further decomposes to NO (followed by NH$_3$-SCR-DeNO$_x$) with the N$_2$ formation. Such an indirect route (i.e., i-SCR mechanism) was reported also over the V-based catalysts [53,54] (e.g., Figure 5b). Recently, Liu et al. [56] identified based on the first-principle calculation method of DFT the adsorption sites of NH$_3$ on V$_2$O$_5$(001).

Carley et al. [57] revealed the structural characteristics of imide strings formed when a Cu(110) surface was exposed to the NH$_3$-O$_2$ mixture (30 vol.%–1 vol.%, 52 °C, 10$^{-8}$ mbar —UHV investigations). Contrary to that, no imide species were found on the surface of polycrystalline copper in NH$_3$-SCO at 1.2 mbar [58]. CuO was found to selectively oxidize NH$_3$ to N$_2$O, while Cu$_2$O to N$_2$, respectively [58,59]. Hirabayashi and Ichihashi [60] investigated reactions of copper oxide cluster cations, Cu$_{n}$O$_m^+$ ($n = 3–7$, $m \leq 5$) with NH$_3$ at near thermal energies using a guided ion beam tandem mass spectrometer. Depending on the applied clusters, H$_2$O, O$_2$ or -HNO were released, while the release of N$_2$ was observed in the multiple-collision reactions of Cu$_3$O$_7^+$ and Cu$_7$O$_4^+$ clusters. Never-

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**Figure 5.** (a) Two competitive routes for NH$_3$ oxidation over V$_2$O$_5$(010). Reprinted from [55] with permission from ACS Publications; (b) schematic representation of the mechanism of NH$_3$-SCO over Cu-Ce/V$_2$O$_5$-WO$_3$-TiO$_2$. Reprinted from [53] with permission from Elsevier.
theless, it is recognized that supported copper species (e.g., Cu/Al₂O₃ [61,62], CuO/carbon nanotubes [63]) or the combination of CuO and other transition or rare earth metal oxides, e.g., Fe₂O₃, CeO₂, La₂O₃, CuCr₂O₄ and CuCr₂O₄ or La₂Ce₂O₇ (nonporous pyrochlore structure—A₂B₂O₇) (e.g., [61,62,64–67]) result in catalysts with enhanced activity and N₂ selectivity in NH₃-SCO. E.g., Gang et al. [61,62] and afterward other authors [68–71] have proved the high catalytic activity of copper species deposited on γ-Al₂O₃. They claimed that copper species dispersion becomes poorer on Al₂O₃ at metal loading higher than ca. 10 wt.% (among 5–15 wt.%) [62]. Furthermore, many studies about similar catalytic systems concur on ca. 10 wt.% as an optimum loading of copper species [4]. The full NH₃ conversion of this group appears at 350–500 °C with N₂ selectivity above 75% (Table 2) depending on the preparation methods (e.g., copper precursors [70,72], treatment strategies [9]), and reaction conditions (e.g., fuel-lean/rich conditions [71,73,74]). Based on the studies of Lenihan and Curtin [69], the stability of Cu/Al₂O₃ through the dry, wet and subsequently dry conditions was proved. Moreover, the activity of CuO/Al₂O₃ catalyst was further enhanced by its doping with PbO, NiO, CoO or SnO (with (1–2 wt.%)Cu/Al₂O₃) [80]. Contrary to that, for the Cu-Mn species, deposition on Al₂O₃ resulted in a decrease of NH₃ conversion at 300–500 °C with N₂ selectivity > 70% compared to Ni/Al₂O₃ (500 °C) for NH₃ oxidation, possibly because of their enhanced redox properties. In addition, several groups have investigated Ni-based catalysts above 500 °C (e.g., prepared via microemulsion) [79,80].

He et al. [65] demonstrated that TiO₂ is a more suitable support (due to the higher oxygen mobility and lower oxygen bonding strength) than Al₂O₃ for copper-based catalysts, which was represented by the enhanced catalytic properties of Cu/TiO₂ compared to Cu/Al₂O₃. Contrary to that, for the Cu-Mn species, deposition on Al₂O₃ (compared to TiO₂) guaranteed enhanced activity [81]. In the case of Cu/TiO₂, NH₃ conversion was reported to depend on the Cu species loading, e.g., for (10 wt.%)Cu/TiO₂ full conversion occurs at about 250 °C with 95% N₂ selectivity [65], while for (1 wt.%)Cu/TiO₂—425–500 °C with < 60% N₂ selectivity was reported [82]. Duan et al. [83] investigated (10 wt.%) V, Cr, Zn and Mo supported on TiO₂. Comparatively tested Cu/TiO₂ and Cr/TiO₂ revealed lower NO and NO₂ selectivity over chromium-containing catalysts. The applied O₂ content in the feed gas ranging from 0.5 vol.% to 5 vol.% revealed similar NH₃ conversion (with an exception below 150 °C where NH₃ conversion was higher in the presence of 0.5 vol.% O₂). Moreover, NO selectivity was not affected by the different O₂ content during NH₃-SCO. TiO₂ anatase is the most common catalyst support, while the catalytic properties are affected by the properties of the support (i.e., anatase versus rutile) [84]. NH₃-SCO over Cu/TiSnO₂ and Cu/TiO₂ (10.5–11.8 wt.% of Cu) was reported to follow the i-SCR and imide (-NH) mechanisms, respectively [85]. For the i-SCR mechanism (Figure 6), NH₃ was first adsorbed on both Lewis and Brønsted acid sites. After that, it reacted with surface-active oxygen...
species to form nitrate species (intermediates in NH₃-SCO), which finally reacted with the remaining NH₃ with the formation of N₂ and H₂O. Gaseous NH₃ recombined with the released acid sites to participate in the next cycles.

\[
\begin{align}
\text{NH}_3 & \rightarrow \text{NH}_2 + \text{H} \\
\text{NH}_2 & \rightarrow \text{NH} + \text{H} \\
\text{NH} + \text{O} & \rightarrow \text{HNO} \\
\text{O}_2 & \rightarrow 2\text{O} \\
\text{HNO} + \text{O} & \rightarrow \text{NO} + \text{OH} \\
\text{NH} + \text{O}_2 & \rightarrow \text{NO} + \text{OH} \\
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} \\
\text{NH} + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H} \\
\text{H} + \text{OH} & \rightarrow \text{H}_2\text{O}
\end{align}
\]

(7) (8) (9) (10) (11) (12) (13) (14) (15)

The bands assigned to nitrate species were also found using in situ DRIFTS in the spectra of a series of CuO-Fe₂O₃ catalysts (with an optimum at n(Cu)/n(Fe) molar ratio of 5:5 with full NH₃ conversion > 250 °C) recorded at 250 and 350 °C [86]. The authors proposed the molecular steps of the i-SCR mechanism, in which the nitrosyl (-HNO) species were formed via a reaction between adsorbed NH₃₋ₓ species with atomic oxygen (Equations (7)–(10)). Then, the -HNO was oxidized by oxygen atoms from O₂ to form NO species (Equations (11) and (12)). Additionally, the -NH species interacted with O₂ to form NO. Meanwhile, the in situ-formed NO could react with -NH₂ to form N₂ or N₂O (Equations (13) and (14)).

**Figure 6.** Reaction mechanism of NH₃-SCO over Cu/TiSnO₂. Reprinted from [85] with permission of Elsevier.

To reveal the impact of calcination temperature on the catalytic properties of the CuO-Fe₂O₃ catalysts (at n(Cu)/n(Fe) molar ratio of 1/1), the materials were calcined between 400 and 700 °C [87]. Among them, CuO-Fe₂O₃ calcined at 500 °C revealed full NH₃ conversion at ca. 225 °C, i.e., at about 25 °C lower than for the material calcined at 400 °C. The increase in the calcination temperature (up to 600–700 °C) resulted in a decrease in the activity in NH₃-SCO, while selectivity was not affected. The simultaneous addition of H₂O and SO₂ to the feed gas led to a drop in activity and N₂ selectivity. Regarding the application of the Cu-Fe-containing spinel, Yue et al. [88] found that for
the mesoporous CuFe\textsubscript{2}O\textsubscript{4}—prepared with KIT-6 as the hard template, NH\textsubscript{3} was nearly completely consumed at 300 °C while the N\textsubscript{2} selectivity dropped below 90% up to 600 °C. CuMoO\textsubscript{4}, CoMoO\textsubscript{4} or FeMoO\textsubscript{4} were significantly less active in NH\textsubscript{3}-SCO [45]. For CuMoO\textsubscript{4}, activity and N\textsubscript{2} selectivity were completely inhibited by water vapor (10 vol.%). Beyond fully synthesized materials, natural vermiculite and phlogopite [89–91] or attapulgite [92] modified with Cu or Fe species are also active and N\textsubscript{2} selective catalysts for NH\textsubscript{3}-SCO (Table 2, pos. 42–46).

Similar to pure CuO and NiO, for CeO\textsubscript{2} the catalytic activity was also poor [93,94]. Despite this, the (10 wt.%)Ce/TiO\textsubscript{2} catalyst (calcined at 400–500 °C) revealed enhanced activity in NH\textsubscript{3}-SCO between 300–350 °C but did not reach full NH\textsubscript{3} conversion [94]. Furthermore, the catalytic activity increased from 50 to 90% at 300 °C for (10 wt.%)Ce/TiO\textsubscript{2} after its modification with vanadium (2 wt.% [95]. This effect was assigned to the dispersion of Ce\textsuperscript{4+} species on TiO\textsubscript{2}. The V/Co/TiO\textsubscript{2} catalyst showed resistance to SO\textsubscript{2} poisoning due to the reduced formation of the NH\textsubscript{4}HSO\textsubscript{4} species. The Ce-containing mixed metal oxides constitute a representative group of catalysts for NH\textsubscript{3}-SCO. E.g., Wang et al. [93] investigated a series of Ce\textsubscript{1−x}Zr\textsubscript{x}O\textsubscript{2} (0.2 ≤ x ≤ 0.8) mixed oxide catalysts, among which particularly Ce\textsubscript{0.4}Zr\textsubscript{0.6}O\textsubscript{2} reached the total NH\textsubscript{3} oxidation of about 360 °C (N\textsubscript{2} selectivity > 90%). Ce\textsubscript{0.4}Zr\textsubscript{0.6}O\textsubscript{2} was also subjected to further modifications with Ru species [96]. Cu-Ce-Zr catalyst prepared by a citric acid sol-gel method exhibited the highest activity among other materials (prepared via the homogenous precipitation and incipient wetness impregnation methods) achieving full NH\textsubscript{3} conversion at 230 °C with > 90% N\textsubscript{2} selectivity [97]. These results were attributed to the finely dispersed CuO, the Cu-Ce-Zr solid solution and the monomeric Cu\textsuperscript{2+} ions in octahedral sites (in contrast to monomeric Cu\textsuperscript{2+} in the square-planar pyramidal sites). Moreover, the adsorbed oxygen species were more active than the bulk lattice oxygen species in NH\textsubscript{3}-SCO. The co-presence of SO\textsubscript{2} and H\textsubscript{2}O or CO\textsubscript{2} in the feed resulted in the NH\textsubscript{3} conversion decreasing to 92 and 81%, respectively. NH\textsubscript{3}-SCO over the catalysts prepared via different techniques followed the i-SCR mechanism (with the -NH\textsubscript{2} and -HNO intermediates, Figure 7a) [98].

Lou et al. [99] have reported nearly complete NH\textsubscript{3} conversion at temperatures as high as 400 °C with an overall N\textsubscript{2} selectivity varying from 19 to 82% over Cu-Ce mixed oxides prepared by coprecipitation with an optimum at n(Cu)/n(Ce) = 6/4 (among 6–9/1–4). Afterward, the CuO-CeO\textsubscript{2} catalysts prepared by a surfactant-templated method exhibited full NH\textsubscript{3} conversion below 300 °C with more than 90% N\textsubscript{2} selectivity [100]. However, the thermal resistance of CuO-CeO\textsubscript{2} mixed oxides needs to be further enhanced. The finely dispersed CuO species as well as a strong synergetic interaction between the copper oxide species and cerium oxides significantly decreased the operation temperature. Thus, activated ammonia reacted with lattice oxygen in the Cu-O-Ce solid solution generating N\textsubscript{2} and H\textsubscript{2}O, while gaseous O\textsubscript{2} regenerated the oxygen vacancies in the Cu-O-Ce solid solution to maintain Ce\textsuperscript{4+}/Ce\textsuperscript{3+} redox couple (Figure 7b). NH\textsubscript{3} was oxidized over CeO\textsubscript{2} to NO\textsubscript{x}, which in the next step reacted with NH\textsubscript{3} forming N\textsubscript{2} over CuO (according to the i-SCR mechanism). CuO/La\textsubscript{2}O\textsubscript{3} (n(Cu)/n(La) = 6–9/1–4 with an optimum at 8/2) showed a significantly lower activity and N\textsubscript{2} selectivity of 93 and 53% at 400 °C, respectively [64], compared to CuO-CeO\textsubscript{2} (e.g., 98–99% NH\textsubscript{3} conversion with 85–86% N\textsubscript{2} selectivity at 400 °C for n(Cu)/n(Ce) = 6/4) [101,102].

Mn-based catalysts have been demonstrated to be active in NH\textsubscript{3}-SCO. E.g., natural manganese ore (NMO, consisting of manganese oxides and small amounts of Fe\textsubscript{2}O\textsubscript{3}, CaO, MgO, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}) was recognized as a low-cost catalyst possessing similar activity (ca. 50 % NH\textsubscript{3} conversion) to that of MnO\textsubscript{2} below 150 °C. Above 150 °C, Mn\textsubscript{2}O\textsubscript{3} was the most active one. Across the studied temperatures between 50–250 °C, N\textsubscript{2} selectivity decreased as follows: NMO > MnO\textsubscript{2} > Mn\textsubscript{2}O\textsubscript{3} [103]. Mn\textsubscript{2}O\textsubscript{3} supported on TiO\textsubscript{2} (anatase containing 1.15 wt.% sulfate) revealed significantly lower activity at 277–307 °C than the supported Cu-Mn mixed oxides (n(Cu)/n(Mn) = 20–80/20–80) [104]. It was found that the most active catalyst (with n(Cu)/n(Mn) = 20/80) contained a Cu\textsubscript{1+y}Mn\textsubscript{2−y}O\textsubscript{4} crystalline spinel phase and X-ray amorphous Mn\textsuperscript{2+}-containing species. Unfortunately, the selectivity...
was not reported. The activity of Cu-Mn/TiO₂ was further enhanced via its modification with Ce or La species [105]. Ce-Cu-Mn/TiO₂ prepared through the sol-gel method was the most active among the catalysts prepared via impregnation or coprecipitation and reached complete NH₃ conversion at ca. 200 °C, however with 96% NO selectivity. Song et al. [106] investigated a series of MnOₓ(z)-TiO₂ (z = 0.1–0.3) prepared by the sol-gel method. The optimum MnO₂(0.25)-TiO₂ showed nearly full NH₃ conversion around 200 °C with N₂ selectivity of more than 60% up to 350 °C. NO was formed only above 250 °C. Based on the in situ DRIFTS studies, they claimed that N₂ appeared as a product of the reaction between -HNO and -NH species. N₂O was formed from the combination of two -HNO species at low temperatures, as well as from the reaction between adsorbed NH₃ and nitrite/nitrate species at high temperatures. Additionally, the i-SCR mechanism was proposed over Fe₂O₃-Al₂O₃, Fe₂O₃-TiO₂, Fe₂O₃-ZrO₂ and Fe₂O₃-SiO₂ prepared by the sol-gel method [107]. The materials prepared from iron sulfate led to a higher N₂ selectivity than those prepared from nitrate. The higher N₂ selectivity was reported earlier for CuO/TiO₂ prepared from CuSO₄ compared to the corresponding catalyst prepared from Cu(NO₃)₂ [52], which is also valid for the pre-sulfated samples [68].

Figure 7. (a) Relationship of activity-adsorption-structure and reaction pathway over Cu-Ce-Zr prepared via different synthesis routes; SOL—citric acid sol-gel method; HP—homogeneous precipitation, IW—incipient wetness impregnation. Reprinted from [98] with permission from Elsevier; (b) NH₃-SCO oxidation over CuO-CeO₂. Reprinted from [100] with permission from Elsevier.
Chen et al. [108] developed a series of mullite-based $A$Mn$_2$O$_5$ ($A = $ Sm, Y, Gd) catalysts, among which SmMn$_2$O$_5$ achieved complete NH$_3$ conversion at 175–250 °C (albeit with a rather low N$_2$ selectivity of barely more than 45%). The imide mechanism was reported for NH$_3$-SCO over SmMn$_2$O$_5$. Furthermore, its modification with niobium oxide (5 wt.%$\text{Nb}_2\text{O}_5$/SmMn$_2$O$_5$ stood out with N$_2$ selectivity $>60\%$. The niobium oxide was supposed to enhance the catalyst surface attraction to the N atom lone-pair electron. Consequently, the reaction between the increased amount of -NH and -HNO species towards the formation of N$_2$ was favored (Figure 8a). In the other approach, SmMn$_2$O$_5$ was mixed with Cu-SAPO-34 [109]. Still, N$_2$ selectivity varied between 20–60% in the range of 150–400 °C.

For the mixed catalysts, the i-SCR mechanism was proposed (NH$_3$ oxidation to NO$_x$ over mullite catalyst), which stays contrary to the above-mentioned studies. The i-SCR mechanism was also proposed over the La$_{3}$Sr$_{1-x}$MnO$_3$ perovskite-based catalysts post-modified with a 3 M solution of HNO$_3$ (0.1–72 h, Figure 8b) [110]. As the treatment time increased, the perovskite phase changed from a mixture of perovskite and MnO$_2$ (10 h treatment) to pure MnO$_2$ (72 h treatment). Additionally, the materials subjected to a 72 h treatment were the most active, albeit selective to NO and N$_2$O, as well as poorly resistant to sulfur species.

Figure 8. Schematic representation of (a) Nb$_2$O$_5$ modification to enhance the N$_2$ selectivity of SmMn$_2$O$_5$. Reprinted from [108] with permission from Elsevier; (b) NH$_3$-SCO mechanism over modified La$_{3}$Sr$_{1-x}$MnO$_3$ perovskite. Reprinted from [110] with permission from ACS Publications.

Concluding, several transition metal-based catalysts were proposed for NH$_3$ oxidation to N$_2$. Among them, mainly Cu/Al$_2$O$_3$, Cu-Ce-Zr, CuO-Fe$_2$O$_3$ or CuO-CeO$_2$ were the most frequently studied materials (according to data gathered in Table 2). In the case of Cu/Al$_2$O$_3$, the optimal loading of 10 wt.% Cu guarantees an enhanced NH$_3$ conversion and N$_2$ selectivity (full NH$_3$ conversion at 350–500 °C with N$_2$ selectivity above 75%). For the other mentioned materials, i.e., Fe- or Ce-containing systems, the catalytic studies were carried out only in a narrow temperature range. The complete NH$_3$ conversion was achieved between 225/250–300 °C with N$_2$ selectivity above 80% (Table 2). Further attention should be given to the stability under conditions simulating real exhaust from diesel engines up to 600–700 °C of the mesoporous CuFe$_2$O$_4$ spinel.
Table 2. Comparison of complete NH₃ conversion and N₂ selectivity in the same temperature range over hydrotalcite-derived mixed metal oxides and other transition metal-based catalysts reported in the literature (related data are marked with asterisks).

| Pos. | Sample |
|------|--------|
|      | Preparation |
|      | Operation Temperature for Achieving 100% NH₃ Conversion/°C |
|      | N₂ Selectivity/% |
|      | Refs. |
|      | Hydrotalcite-derived mixed metal oxides |

1. CuMgAl<br>\(n(\text{Cu})/n(\text{Mg})/n(\text{Al}) = 4.6/66.4/29\), mol.%<br>Coprecipitation, calcination, 650 °C, air, 14 h<br>0.5 vol.% NH₃, 1.75 vol.% O₂, He balance, GHSV 10,000–12,000 h⁻¹<br>500 >80 [29]

2. CuMgAl<br>\(n(\text{Cu})/n(\text{Mg})/n(\text{Al}) = 5/66/29\), mol.%<br>Coprecipitation, calcination, 600 °C, air, 16 h<br>0.5 vol.% NH₃, 2.5 vol.% O₂, He balance, GHSV 30,000 h⁻¹<br>400–650 >80 [30]

3. CuMgFe<br>\(n(\text{Cu})/n(\text{Mg})/n(\text{Fe}) = 0.5/2/1\), mol.%<br>Coprecipitation, calcination, 600 °C, air, 12 h<br>0.5 vol.% NH₃, 2.5 vol.% O₂, He balance, GHSV 15,400 h⁻¹<br>400–450 >70 [31]

4. CuMgAl<br>\(n(\text{Cu})/n(\text{Mg})/n(\text{Al}) = 8/63/29\), mol.%<br>Coprecipitation, calcination, 600 °C, air, 6 h<br>0.5 vol.% NH₃, 2.5 vol.% O₂, Ar balance, WHSV 24,000 mL h⁻¹ g⁻¹<br>* 0.5 vol.% NH₃, 2.5 vol.% O₂, N₂ balance, WHSV 137,000–140,000 mL h⁻¹ g⁻¹<br>400–600 >60 * 450–600 * >60 [34] ** 600 ** >55 [111]

5. CuMgAl<br>\(n(\text{Cu})/n(\text{Mg})/n(\text{Al}) = 0.6/1.4/1.0\), mol.%<br>Coprecipitation, calcination, 600 °C, *900 °C, air, 12 h<br>0.5 vol.% NH₃, 2.5 vol.% O₂, He balance, WHSV 24,000 mL h⁻¹ g⁻¹<br>375–500 * 500 * >70 * >40 [28]

6. CuMgAl<br>\(n(\text{Cu})/n(\text{Mg})/n(\text{Al}) = 5/62/33\), mol.%<br>Coprecipitation, calcination, 600 °C, 800 °C *, air, 12 h<br>0.5 vol.% NH₃, 2.5 vol.% O₂, He balance, WHSV 24,000 mL h⁻¹ g⁻¹<br>475–500 * 475–500 * >85 [35]

7. GaCuMgAl<br>\(n(\text{Ga})/n(\text{Cu})/n(\text{Mg})/n(\text{Al}) = 0.25/5/65.75/29\)<br>Coprecipitation, calcination, 600 °C, air, 6 h<br>0.5 vol.% NH₃, 2.5 vol.% O₂, Ar balance, WHSV 24,000 mL h⁻¹ g⁻¹<br>375–500 * 375–500 * >80 * >50 [36]
Table 2. Cont.

| Pos. | Sample | Preparation | Reaction Conditions | Operation Temperature for Achieving 100% NH$_3$ Conversion/°C | N$_2$ Selectivity/% | Refs. |
|------|--------|-------------|---------------------|-------------------------------------------------------------|---------------------|-------|
| 8    | CuMgAl $n$(Cu)/$n$(Mg)/$n$(Al) = 10–15/52–57/33, mol.% | Coprecipitation, calcination, 800 °C, air, 9 h | 0.035 vol.% NH$_3$, 20 vol.% O$_2$, N$_2$ balance, WHSV 30,000 mL h$^{-1}$ g$^{-1}$ | 350 | <20 | [37] |
|      | * (4.1 wt.%)CeCuMgAl | * Impregnation, calcination, 800 °C, air, 9 h | * | 350 | * <70 |       |
| 9    | CuMgAl $n$(Cu)/$n$(Mg)/$n$(Al) = 5/62/33, mol.% | Coprecipitation, calcination, 600 °C, air, 12 h, * | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, He balance, WHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 500–600 | >60 | [38] |
|      | * (3 wt.%)CeCuMgAl | * Impregnation, calcination, air, 600 °C, 12 h | ** | 450–600 | * >75 |       |
|      | ** (0.5 wt.% Ce)CuMgAl | | | | ** >55 |       |
| 10   | CuZnAl $n$(Cu)/$n$(Zn)/$n$(Al) = 10–15/52/33, mol.% | Coprecipitation, calcination, 500 °C, air, 4 h; * | 0.035 vol.% NH$_3$, 20 vol.% O$_2$, N$_2$ balance, WHSV 30,000 mL h$^{-1}$ g$^{-1}$ | 350 | <30 | [39] |
|      | * (8.14 wt.%)CeCuMgAl | Mechnanochemical method, calcination, 500 °C, air, 4 h | * | 350 | * <40 |       |
| 11   | CoMnAl $n$(Co)/$n$(Mn)/$n$(Al) = 4/1/1 | Coprecipitation, calcination, 500 °C, air, 4 h; * | 0.5 vol.% NH$_3$, 2.5 vol.% O$_2$, He balance, WHSV 24,000 mL h$^{-1}$ g$^{-1}$ | 250–500 | >40 | [40] |
|      | Mechnanochemical method, calcination, 500 °C, air, 4 h | | * | 250–500 | * >45 |       |

Other metal oxides

| Pos. | Sample | Preparation | Reaction Conditions | Operation Temperature for Achieving 100% NH$_3$ Conversion/°C | N$_2$ Selectivity/% | Refs. |
|------|--------|-------------|---------------------|-------------------------------------------------------------|---------------------|-------|
| 12   | CuO/monolith | Precursors calcination on the monolith, 600 °C, air, 6 h | 0.05 vol.% NH$_3$, 3 vol.% O$_2$, N$_2$ balance, GHSV 40,000 h$^{-1}$ | 450–550 | 67–85 | [45] |
| 13   | (10 wt.%)V/TiO$_2$ | Impregnation, calcination, 550 °C, air, 6 h | 0.05 vol.% NH$_3$, 2.5 vol.% O$_2$, N$_2$ balance, GHSV 35,385 h$^{-1}$ | 225–300 | - | [83] |
| 14   | (10 wt.%)Cu/TiO$_2$ | Impregnation, calcination, 550 °C, air, 6 h | 0.05 vol.% NH$_3$, 2.5 vol.% O$_2$, N$_2$ balance, GHSV 35,385 h$^{-1}$ | 200–300 | - |       |
| 15   | (10 wt.%)Cu/TiO$_2$ | Impregnation, rotary evaporator, calcination, 450 °C, air, 3 h | 0.04 vol.% NH$_3$, 10 vol.% O$_2$, He balance, GHSV 50,000 h$^{-1}$ | 250–300 | >95 | [65] |
|      | * (10 wt.%)Cu/Al$_2$O$_3$ | He balance, GHSV 50,000 h$^{-1}$ | * | 350–375 | * >95 |       |
| 16   | (10 wt.%)Cu/Al$_2$O$_3$ | Impregnation, calcination, 450 °C, air, 3 h | 0.04 vol.% NH$_3$, 10 vol.% O$_2$, 3 vol.% H$_2$O, He balance, GHSV 50,000 h$^{-1}$ | 400 | >95 |       |
| 17   | (10–15 wt.%)Cu/Al$_2$O$_3$ | Impregnation, calcination, 600 °C, air, 24 h | 1.14 vol.% NH$_3$, 8.21 vol.% O$_2$, He balance, WHSV 2 240 mL h$^{-1}$ g$^{-1}$ | 350 | >90 | [61] |
| Pos. | Sample | Preparation | Reaction Conditions | Operation Temperature for Achieving 100% NH<sub>3</sub> Conversion/°C | N<sub>2</sub> Selectivity/% | Refs. |
|------|--------|-------------|---------------------|-------------------------------------------------|-----------------|------|
| 18   | (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> | Impregnation, calcination, 600 °C, air, 24 h | 1.14 vol.% NH<sub>3</sub>, 8.21 vol.% O<sub>2</sub>, He balance, WHSV 2240 mL h<sup>-1</sup> g<sup>-1</sup> | 350 | 94 * 95 | [62] |
| 19   | (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> | Impregnation, calcination, 600 °C, air, 3 h, *Cu(CH<sub>3</sub>COO)<sub>2</sub> as precursor, **Cu(NO<sub>3</sub>)<sub>2</sub> as precursor | 0.1 vol.% NH<sub>3</sub>, 10 vol.% O<sub>2</sub>, He balance, GHSV 50,000 h<sup>-1</sup> | * 350–400, ** 375–400 | * >85, ** >95 | [70] |
| 20   | (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> | Impregnation, calcination, 600 °C, air, 6 h | 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, N<sub>2</sub> balance, WHSV 137,000–140,000 mL h<sup>-1</sup> g<sup>-1</sup> | 450–600 | >60 * >50 | [111] |
| 21   | (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> | Impregnation, calcination, 600 °C, air, 12 h | 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, Ar balance, WHSV 24,000 mL h<sup>-1</sup> g<sup>-1</sup> | 425–500 | >75 | [112] |
| 22   | (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> * (10 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> | Impregnation, rotary evaporation, calcination, 500 °C, air, 2 h, *Impregnation, rotary evaporation, 500 °C, H<sub>2</sub>/N<sub>2</sub>, 2 h, 0.05 vol.% NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, N<sub>2</sub> balance | 0.05 vol.% NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, N<sub>2</sub> balance, GHSV 60,000 h<sup>-1</sup> | 330 | not shown * not shown | [9] |
| 23   | (1.3 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> * (1 wt.%)Cu/CeO<sub>x</sub>/Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> | Impregnation, calcination, 350 °C, air, time not given; homogenous deposition precipitation, H<sub>2</sub> reduction, 400 °C, 2 h | 2 vol.% NH<sub>3</sub>, 2 vol.% O<sub>2</sub>, Ar balance, GHSV 2500 h<sup>-1</sup> | 400 | 100 * 100 | [76] |
| 24   | (3.4 wt.%)Cu/Al<sub>2</sub>O<sub>3</sub> | Impregnation, calcination, 450 °C, air, 5 h | 0.54 vol.% NH<sub>3</sub>, 8 vol.% O<sub>2</sub>, He balance, WHSV 240 mL h<sup>-1</sup> g<sup>-1</sup> | 400–450 | not shown | [69] |
Table 2. Cont.

| Pos. | Sample | Preparation | Reaction Conditions | Operation Temperature for Achieving 100% NH₃ Conversion/°C | N₂ Selectivity/% | Refs. |
|------|--------|-------------|---------------------|-----------------------------------------------------------|-----------------|-------|
| 25   | (20 wt.%)Cu/Al₂O₃/monolith | Impregnation, calcination, 800 °C, air, 4 h | 0.04 vol.% NH₃, 8.2 vol.% O₂, 1.3 vol.% CH₄, 3.9 vol.% CO₂, 4.1 vol.% CO, 2.9 vol.% H₂, GHSV 100,000 h⁻¹ | 400–500 | 0 | [71] |
| 26   | (1 wt.%)PbO-(4.3 wt.%)Cu/Al₂O₃ | Impregnation, calcination, 450 °C, air, time not shown | 0.54 vol.% NH₃, 8 vol.% O₂, He balance, WHSV 800 mL h⁻¹ g⁻¹ | 325 | 95 | [68] |
| 27   | (1–2 wt.%)Cu/η-Al₂O₃ | Impregnation, Rotary evaporator, calcination, 500 °C, air, 10 h; pre-treatment conditions: 20 vol.% O₂/He, 550 °C, 1 h | 0.1 vol.% NH₃, 8 vol.% O₂, 3.5 vol.% H₂O, He balance, WHSV 250,000 mL h⁻¹ g⁻¹ | 550 | not shown | [75] |
| 28   | CuO/CNTs (carbon nanotubes, 9.85 wt.% Cu) | Impregnation, ultrasonic treatment, evaporation, 350 °C, He, 3 h | 0.1 vol.% NH₃, 2 vol.% O₂, He balance, WHSV 60,000 mL h⁻¹ g⁻¹ | 189–250 | >98 | [63] |
| 29   | Cu/graphene (2.57–3.42 wt.%) | Impregnation, ultrasonic treatment, 400 °C, N₂, 3 h, *Cu(CH₃COO)₂·H₂O as precursor **Cu(NO₃)₂·H₂O as precursor | 0.05 vol.% NH₃, 1 vol.% O₂, N₂ balance, GHSV 35,000 h⁻¹ | * 300 | ** >80 | [72] |
| 30   | (5 wt.%)Ni/Al₂O₃ | Impregnation, calcination, 800 °C, air, 8 h | 0.1 vol.% NH₃, 18 vol.% O₂, N₂ balance, GHSV 61,000 h⁻¹ | 550–800 | >55 | [78] |
| 31   | (5 wt.%)Mn/Al₂O₃ | Impregnation, calcination, 800 °C, air, 8 h | 0.1 vol.% NH₃, 18 vol.% O₂, N₂ balance, GHSV 61,000 h⁻¹ | 300–800 | >55 | [78] |
| 32   | (10.5 wt.%)CuO/TiSnO₂ | Impregnation, calcination, 450 °C, air, 4 h | 0.05 vol.% NH₃, 3 vol.% O₂, N₂ balance, GHSV 60,000 mL h⁻¹ g⁻¹ | 300–400 | >70 | [85] |
| 33   | (5 wt.%)CuO₂/La₂Ce₂O₇ | Impregnation, calcination, 600 °C, air, 1 h | 0.05 vol.% NH₃, 5 vol.% O₂, N₂ balance, GHSV 20,000 h⁻¹ | 275–425 | >80 | [67] |
| 34   | (10 wt.%)Ce/(2 wt.%)V/TiO₂ | Impregnation, calcination, 400 °C, air, 4 h; pre-treatment conditions: 8 vol.% O₂/N₂, 400 °C, 0.5 h | 0.02 vol.% NH₃, 8 vol.% O₂, 6 vol.% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 300–350 | >90 | [95] |
| 35   | Ce₀.₄Zr₀.₆O₂ | Surfactant-templated method, calcination, 550 °C, air, 3 h | 0.1 vol.% NH₃, 10 vol.% O₂, He balance, GHSV 40,000 h⁻¹ | 360–380 | >90 | [93] |
| Pos. | Sample | Preparation | Reaction Conditions | Operation Temperature for Achieving 100% NH<sub>3</sub> Conversion/°C | N<sub>2</sub> Selectivity/% | Refs. |
|------|--------|-------------|---------------------|-------------------------------------------------|--------------------------|------|
| 36   | (6 wt.%)<sub>6</sub>Cu-Ce-Zr (Si)/Al = 4 | Sol-gel method, calcination, 450 °C, air, 3 h | 0.1 vol.% NH<sub>3</sub>, 10 vol.% O<sub>2</sub>, He balance, GHSV 40,000 h<sup>-1</sup> | 230 | >90 | [97] |
| 37   | CuO-Fe<sub>2</sub>O<sub>3</sub> (Cu)/Fe = 1:1 | Sol-gel method, calcination, 500 °C, air, 4 h | 0.08 vol.% NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, Ar balance, GHSV 60,000 h<sup>-1</sup> | 225–300 | >80 | [87] |
| 38   | CuO-Fe<sub>2</sub>O<sub>3</sub> (Cu)/Fe = 5:5 | Sol-gel method, calcination, 400 °C, air, 4 h | 0.08 vol.% NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, Ar balance, GHSV 60,000 h<sup>-1</sup> | 250–300 | >80 | [86] |
| 39   | CuFe<sub>2</sub>O<sub>4</sub> (8.59 wt.% Cu, 7.45 wt.% Fe) | Hard-template method, 600 °C, air, 6 h | 0.1 vol.% NH<sub>3</sub>, 0.2 vol.% O<sub>2</sub>, He balance, GHSV 35,000 h<sup>-1</sup> | 350–600 | >75 | [88] |
| 40   | CuO-Fe<sub>2</sub>O<sub>3</sub> (Cu)/Fe = 6/4 | Coprecipitation, calcination, 500 °C, air, 4 h | 0.1 vol.% NH<sub>3</sub>, 4 vol.% O<sub>2</sub>, 12 vol.% H<sub>2</sub>O, He balance, WHSV 92,000 mL h<sup>-1</sup> g<sup>-1</sup> | 400 | 82 | [99] |
| 41   | CuO-Fe<sub>2</sub>O<sub>3</sub> (10 wt.% Cu) | Surfactant templated method, 500 °C, air, 3 h | 0.1 vol.% NH<sub>3</sub>, 10 vol.% O<sub>2</sub>, He balance, GHSV 40,000 h<sup>-1</sup> | 250–300 | >90 | [100] |
| 42   | (1 wt.%)<sub>1</sub>Cu-PILC-Verm (Alumina pillared vermiculites) | Ion-exchange, calcination, 450 °C, air, 3 h | 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, He balance, WHSV 24,000 mL h<sup>-1</sup> g<sup>-1</sup> | 500–550 | >95 | [89] |
| 43   | (5.7 wt.%)<sub>5.7</sub>Fe-PILC-Phlog (Alumina pillared phlogopite) | Ion-exchange, calcination, 450 °C, air, 3 h | 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, He balance, WHSV 24,000 mL h<sup>-1</sup> g<sup>-1</sup> | 500–550 | >70 | |
| 44   | (0.59 wt.%)<sub>0.59</sub>Cu-PCH (Porous clay heterostructures) | Ion-exchange, 450 °C, air, 3 h | 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, He balance, WHSV 24,000 mL h<sup>-1</sup> g<sup>-1</sup> | 500–550 | >90 | [53] |
| 45   | (1.43 wt.%)<sub>1.43</sub>Cu-PCH (Porous clay heterostructures) | Ion-exchange, 450 °C, air, 3 h | 0.5 vol.% NH<sub>3</sub>, 2.5 vol.% O<sub>2</sub>, He balance, WHSV 24,000 mL h<sup>-1</sup> g<sup>-1</sup> | 400–550 | >90 | [90] |
| 46   | Cu/attapulgite (5–10 wt.% Cu) | Impregnation, 400 °C, air, 4 h | 0.005 vol.% NH<sub>3</sub>, 4 vol.% O<sub>2</sub>, N<sub>2</sub> balance, GHSV 150,000 h<sup>-1</sup> | 450–500 | >75 | [92] |
| 47   | natural manganese ore | Fluidization, 12 h | 0.05 vol.% NH<sub>3</sub>, 3 vol.% O<sub>2</sub>, He balance, GHSV 15,000–80,000 h<sup>-1</sup> | 240 | >70 | [103] |
| 48   | MnO<sub>2</sub> | Calcination, 400 °C, air, 2 h | | 210 | >60 | |
| 49   | Cu-Mn/TiO<sub>2</sub> (Cu)/Mn = 20/80 | Impregnation, rotary evaporator, calcination, 550 °C, air, 2 h | 0.06 vol.% NH<sub>3</sub>, 6 vol.% O<sub>2</sub>, N<sub>2</sub> balance, WHSV 200,000 mL h<sup>-1</sup> g<sup>-1</sup> | 307 | not shown | [104] |
| Pos. | Sample | Preparation | Reaction Conditions | Operation Temperature for Achieving 100% NH₃ Conversion/°C | N₂ Selectivity/% | Refs. |
|------|--------|-------------|---------------------|----------------------------------------------------------|------------------|-------|
| 50   | MnOₓ-TiO₂ (27.8 wt.% Mn) | Sol-gel method, calcination, 500 °C, air, 4 h | 0.05 vol.% NH₃, 5 vol.% O₂, He balance, WHSV 240,000 mL h⁻¹ g⁻¹ | 200–350 | >60 | [106] |
| 51   | SmMn₂O₅ | Organic solution combustion methods, 700 °C, air, 8 h | 0.05 vol.% NH₃, 10 vol.% O₂, N₂ balance, WHSV 120,000 mL h⁻¹ g⁻¹ | 175–250 | >45 | [108] |
| 52   | (5.0 wt.%)Nb₂O₅/SmMn₂O₅ | Impregnation, 450 °C, air, 2 h | 0.05 vol.% NH₃, 21 vol.% O₂, N₂ balance, GHSV 100,000 h⁻¹ | 200–250 | >60 | |
| 53   | (30 wt.%)SmMn₂O₅/ Cu-SAPO | Grinding the mixture; * after hydrothermal aging treatment conditions: 21 vol.% O₂, 10 vol.% H₂O, N₂ balance, 800 °C, 5 h | 0.05 vol.% NH₃, 21 vol.% O₂, N₂ balance, GHSV 100,000 h⁻¹ | 225–400 | * >20 | * not shown | [109] |
| 54   | LaₓSr₁₋ₓMnO₃ | Hydrothermal method, 400 °C, air, 2 h, post-treatment in 3 M HNO₃ | 0.05 vol.% NH₃, 3 vol.% O₂, N₂ balance, WHSV 120,000 mL h⁻¹ g⁻¹ | 300–450 | not shown | [110] |
4. Conclusions and Future Perspectives

In this short mini-review, we have discussed recent trends, limits and opportunities offered by hydrotalcite-derived mixed metal oxides as opposed to the other transition metal-based catalysts applied in NH$_3$-SCO. Although there are relatively several catalytic systems proposed in the literature, at the same time, their systematic investigations and further improvement are scarce. Furthermore, there is a lack of systematic investigations of the reaction mechanisms. The mechanisms of NH$_3$-SCO have been explored mainly by the application of in situ DRIFTS and the indication of the characteristic intermediates of the imide, hydrazine or i-SCR mechanism.

Overall, based on our comparison, two transition metal-based catalytic systems can be selected for the preparation of the next-generation catalysts, i.e., the CuMgAl hydrotalcite-derived mixed metal oxides and Cu/Al$_2$O$_3$. The complete NH$_3$ conversion activity between 375–650 °C and N$_2$ selectivity above 70% were reached over hydrotalcite-derived mixed metal oxides. Similarly, Cu/Al$_2$O$_3$ being the most frequently studied catalyst reached full NH$_3$ conversion at 350–500 °C with N$_2$ selectivity above 75%. Our revision is further supported by our previous study [111], where the activity and N$_2$ selectivity in NH$_3$-SCO over hydrotalcite-derived CuMgAl (n(Cu)/n(Mg)/n(Al) = 8/63/29, mol.%) mixed metal oxides and (10 wt.%)Cu/Al$_2$O$_3$ were tested under NH$_3$/O$_2$/CO$_2$/H$_2$O/N$_2$ conditions by applying ca. 6.5–6.7 g of catalysts. The mixture of the highly dispersed easily reducible copper oxide and bulk copper oxide species allowed for enhanced activity, N$_2$ selectivity and stability. Still, further work is needed on the systematic catalysts’ chemical and phase optimization and catalyst tests, including investigations under more applied reaction conditions concerning either reaction mixture composition (NH$_3$ concentration of about 100 ppm with O$_2$ concentrations of about 10 vol.%; in the presence of CO$_x$, SO$_x$ and H$_2$O) or temperature (up to 600–700 °C), should follow. Furthermore, thermal stability should be tested, as well as catalyst poisoning via the typical components of the lubricating oil for diesel engines (e.g., Ca, Zn, P and S species). A comprehensive understanding of the involved active species, e.g., through operando technologies under realistic working conditions, could facilitate a knowledge-based catalyst optimization to obtain desired NH$_3$ slip catalysts.

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References
1. European Environment Agency. Available online: https://www.eea.europa.eu/publications/national-emission-reduction-commitments-directive (accessed on 30 May 2022).
2. Arasu, P.T.; Khalaf, A.L.; Aziz, S.H.A.; Yaacob, M.H.; Noor, A.S.M. Optical fiber based ammonia gas sensor with carbon nanotubes sensing enhancement. In Proceedings of the 2017 IEEE Region 10 Symposium (TENSYMP), Cochin, India, 14–16 July 2017; pp. 1–4.
3. Chmielarz, L.; Jabłońska, M. Advances in selective catalytic oxidation of ammonia to dinitrogen: A review. RSC Adv. 2015, 5, 43408–43431. [CrossRef]
4. Jabłońska, M.; Palkovits, R. Copper based catalysts for the selective ammonia oxidation into nitrogen and water vapour-Recent trends and open challenges. Appl. Catal. B Environ. 2016, 181, 332–351. [CrossRef]
5. Jablotńska, M. Progress on noble metal-based catalysts dedicated to the selective catalytic ammonia oxidation into nitrogen and water vapor (NH₃-SCO). *Molecules* **2021**, *26*, 6461. [CrossRef] [PubMed]

6. Jablotńska, M. Progress on selective catalytic ammonia oxidation (NH₃-SCO) over Cu-containing zeolite-based catalysts. *ChemCatChem* **2002**, *12*, 4490–4500. [CrossRef]

7. Torp, T.K.; Hansen, B.B.; Vennestrom, P.N.R.; Janssens, T.V.W.; Jensen, A.D. Modeling and optimization of multi-functional ammonia slip catalysts for diesel exhaust aftertreatment. *Emis. Control Sci. Technol.* **2021**, *7*, 7–25. [CrossRef]

8. Wang, F.; Ma, J.; He, G.; Chen, M.; Zhang, C.; He, H. Nanosize effect of Al₂O₃ in Ag/Al₂O₃ catalyst for the selective catalytic oxidation of ammonia. *ACS Catal.* **2018**, *8*, 2670–2682. [CrossRef]

9. Lan, T.; Jiang, Z.; Zhang, X.; Liu, X.; Cheng, D.; Zhang, D. Unraveling the promotion effects of dynamically constructed CuO₂-OH interfacial sites in the selective catalytic oxidation of ammonia. *ACS Catal.* **2022**, *12*, 3959–3964. [CrossRef]

10. Gao, F.; Liu, Y.; Sani, Z.; Tang, X.; Yi, H.; Zhao, S.; Yu, Q.; Zhou, Y. Advances in selective catalytic oxidation of ammonia (NH₃-SCO) to dinitrogen in excess oxygen: A review on typical catalysts, catalytic performances and reaction mechanisms. *J. Environ. Chem. Eng.* **2020**, *9*, 104575–104595. [CrossRef]

11. Rives, V.; Ulibarri, M.A. Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. *Coord. Chem. Rev.* **1999**, *181*, 61–120. [CrossRef]

12. Evans, D.G.; Slade, R.C.T. Structural aspects of layered double hydroxides. In *Layered Double Hydroxides*; Springer: Berlin/Heidelberg, Germany, 2006; pp. 1–87.

13. Basile, F.; Forsasari, G.; Gazzano, M.; Vaccari, A. Synthesis and thermal evolution of hydrotalcite-type compounds containing noble metals. *Appl. Clay Sci.* **2000**, *16*, 185–200. [CrossRef]

14. Centi, G.; Peraforther, S. Catalysis by layered materials: A review. *Microporous Mesoporous Mater.* **2008**, *107*, 3–15. [CrossRef]

15. Karran, N. Catalytic applications of hydrotalcite-like materials and their derived forms. *Catal. Surv. Asia* **2006**, *10*, 117–137. [CrossRef]

16. Jablotńska, M.; Palkovits, R. Nitrogen oxide removal over hydrotalcite-derived mixed metal oxides. *Catal. Sci. Technol.* **2016**, *6*, 49–72. [CrossRef]

17. Jablotńska, M.; Palkovits, R. It is no laughing matter: Nitrous oxide formation in diesel engines and advances in its abatement over rhodium-based catalysts. *Catal. Sci. Technol.* **2016**, *6*, 7671–7687. [CrossRef]

18. Schmidt-Szałowski, K.; Krawczyk, K.; Petryk, J. The properties of cobalt oxide catalyst for ammonia oxidation. *Appl. Catal. A Gen.* **1998**, *175*, 147–157. [CrossRef]

19. Petryk, J.; Kołakowska, E. Cobalt oxide catalysts for ammonia oxidation activated with cerium and lanthanum. *Appl. Catal. B Environ.* **2000**, *24*, 121–128. [CrossRef]

20. Escandón, L.S.; Ordóñez, S.; Díez, F.V.; Sastre, H. Ammonia oxidation over conventional combustion catalysts. *React. Kinet. Catal. Lett.* **2002**, *76*, 61–68. [CrossRef]

21. Zakharchenko, N.I. Catalytic Properties of the Fe₂O₃-MnO System for Ammonia Oxidation. *Kinet. Catal.* **2001**, *42*, 679–685. [CrossRef]

22. Sadykov, V.A.; Isupova, I.A.; Zolotarskii, I.A.; Bobrova, L.N.; Noskov, A.S.; Parmon, V.N.; Brushtein, E.A.; Telyatnikova, T.V.; Chernyshev, V.I.; Lunin, V.V. Oxidation catalysts for ammonia oxidation in nitric acid production: Properties and perspectives. *Appl. Catal. A Gen.* **2000**, *204*, 59–87. [CrossRef]

23. Noskov, A.S.; Zolotarskii, I.A.; Pokrovskaya, S.A.; Korotkikh, V.N.; Slavinskaya, E.M.; Mokrinskii, V.V.; Kashkin, V.N. Ammonia oxidation into nitrous oxide over Mn/Bi/Al catalyst: I. Single cooling tube experiments. *Chem. Eng. J.* **2003**, *91*, 235–242. [CrossRef]

24. Slavinskaya, E.M.; Veniaminov, S.A.; Notté, P.; Ivanova, A.S.; Boronin, A.I.; Chelalov, Y.A.; Polukhina, I.A.; Noskov, A.S. Studies of the mechanism of ammonia oxidation into nitrous oxide over MnBiO/α-Al₂O₃ catalyst. *J. Catal.* **2004**, *222*, 129–142. [CrossRef]

25. Cavani, F.; Trifiro, F.; Vaccari, A. Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catal. Today* **1991**, *11*, 173–301. [CrossRef]

26. Yan, K.; Wu, G.; Jin, W. Recent advances in the synthesis of layered, double-hydroxide-Based materials and their applications in hydrogen and oxygen evolution. *Energy Technol.* **2016**, *4*, 354–368. [CrossRef]

27. Newman, S.P.; Jones, W.; O’Connor, P.; Stamires, D.N. Synthesis of the 3R₂ polytype of a hydrotalcite-like mineral. *J. Mater. Chem.* **2002**, *12*, 153–155. [CrossRef]

28. Jablotńska, M.; Chmielarz, L.; Węgrzyn, A.; Güzik, K.; Piwowarska, Z.; Witkowski, S.; Walton, R.I.; Dunne, P.W.; Kovanda, F. Thermal transformations of Cu-Mg (Zn)-Al(Fe) hydrotalcite-like materials into metal oxide systems and their catalytic activity in selective oxidation of ammonia to dinitrogen. *J. Therm. Anal. Calorim.* **2013**, *114*, 731–747. [CrossRef]

29. Trombetta, M.; Ramis, G.; Busca, G.; Montanari, B.; Vaccari, A. Ammonia adsorption and oxidation on Cu/Mg/Al mixed oxide catalysts prepared via hydrotalcite-type precursors. *Langmuir* **1997**, *13*, 4628–4637. [CrossRef]

30. Chmielarz, L.; Kuśtrowski, P.; Rafalska-Lasocha, A.; Dziembaj, R. Selective oxidation of ammonia to nitrogen on transition metal containing mixed metal oxides. *Appl. Catal. B Environ.* **2005**, *58*, 235–244. [CrossRef]

31. Chmielarz, L.; Węgrzyn, A.; Wojciechowska, M.; Witkowski, S.; Michalik, M. Selective catalytic oxidation (SCO) of ammonia to nitrogen over hydrotalcite originated Mg-Cu-Me mixed metal oxides. *Catal. Lett.* **2011**, *141*, 1345–1354. [CrossRef]

32. Górecka, S.; Pacultová, K.; Górecki, K.; Šmýkalová, A.; Pamin, K.; Obalová, L. Cu-Mg-Fe-O(Ce) complex oxides as catalysts of selective catalytic oxidation of ammonia to dinitrogen (NH₃-SCO). *Catalysts* **2020**, *10*, 153. [CrossRef]
33. Chmielarz, L.; Jabłońska, M.; Strumiński, A.; Piwowarska, Z.; Węgryn, A.; Witkowski, S.; Michalik, M. Selective catalytic oxidation of ammonia to nitrogen over Mg-Al, Cu-Mg-Al and Fe-Mg-Al mixed metal oxides doped with noble metals. *Appl. Catal. B Environ.* 2013, *130*, 152–162. [CrossRef]

34. Jabłońska, M.; Nocuń, M.; Golabek, K.; Palkovits, R. Effect of preparation procedures on catalytic activity and selectivity of copper-based mixed oxides in selective catalytic oxidation of ammonia into nitrogen and water vapour. *Appl. Surf. Sci.* 2017, *423*, 498–508. [CrossRef]

35. Basag, S.; Piwowarska, Z.; Kowalczyk, A.; Węgryn, A.; Baran, R.; Gil, B.; Michalik, M.; Chmielarz, L. Cu-Mg-Al hydrotalcite-like materials as precursors of effective catalysts for selective oxidation of ammonia to dinitrogen—The influence of Mg/Al ratio and calcination temperature. *Appl. Clay Sci.* 2016, *129*, 122–130. [CrossRef]

36. Jabłońska, M.; Nothdurft, K.; Nocuń, M.; Girman, V.; Palkovits, R. Redox-performance correlations in Ag-Cu-Mg-Al, Ce-Cu-Mg-Al, and Ca-Cu-Mg-Al hydrotalcite derived mixed metal oxides. *Appl. Catal. B Environ.* 2017, *207*, 385–396. [CrossRef]

37. Górecka, S.; Paculová, T.; Smýkalová, A.; Frídrihová, D.; Górecki, K.; Rokicińska, A.; Kuśrowski, P.; Žebrák, R.; Obalová, L. Role of the Cu content and Ce activating effect on catalytic performance of Cu-based selective catalytic oxidation. *Appl. Surf. Sci.* 2022, 573, 151540–151555. [CrossRef]

38. Basag, S.; Kecoł, K.; Piwowarska, Z.; Rutkowska, M.; Baran, R.; Chmielarz, L. Activating effect of cerium in hydrotalcite derived Cu-Mg-Al catalysts for selective ammonia oxidation and the selective reduction of NO with ammonia. *React. Kinet. Mech. Catal.* 2017, *121*, 225–240. [CrossRef]

39. Górecka, S.; Paculová, T.; Frídrihová, D.; Górecki, K.; Bílková, T.; Žebrák, R.; Obalová, L. Catalytic oxidation of ammonia over cerium-modified copper aluminium zinc mixed oxides. *Materials* 2021, *14*, 6681. [CrossRef]

40. Ludvíková, J.; Jabłońska, M.; Jirítová, K.; Chmielarz, L.; Balabáňová, J.; Kovanda, F.; Obalová, L. Co-Mn-Al mixed oxides as catalysts for ammonia oxidation to N₂O. *Res. Chem. Intermed.* 2016, *42*, 2669–2690. [CrossRef]

41. Il’chenko, N.I.; Golodets, G.I. Catalytic oxidation of ammonia: I. Reaction kinetics and mechanism. *J. Catal.* 1975, *39*, 57–72. [CrossRef]

42. Il’chenko, N.I.; Golodets, G.I. Catalytic oxidation of ammonia: II. Relationship between catalytic properties of substances and surface oxygen bond energy. General regularities in catalytic oxidation of ammonia and organic substances. *J. Catal.* 1975, *39*, 73–86. [CrossRef]

43. Il’chenko, N.I. Catalytic oxidation of ammonia. *Russ. Chem. Rev.* 1976, *45*, 1119. [CrossRef]

44. Hinokuma, S.; Shimanoe, H.; Matsuki, S.; Kawano, M.; Kawabata, Y.; Machida, M. Catalytic activity and selectivities of metal oxides and surface oxygen bond energy. General regularities in catalytic oxidation of ammonia and organic substances. *J. Catal.* 1992, *135*, 135–148. [CrossRef]

45. Gandhi, H.S.; Shelef, M. Selectivity for nitrogen formation in NH₃ oxidation in wet and dry systems over mixed molybdenum oxides. *J. Catal.* 1975, *40*, 312–317. [CrossRef]

46. Chen, J.P.; Yang, R.T. Role of WO₃ in mixed V₂O₅-WO₃/TiO₂ catalysts for selective catalytic reduction of nitric oxide with ammonia. *Appl. Catal. A Gen.* 1992, *80*, 135–148. [CrossRef]

47. Cavani, F.; Trifiro, F. Oxidation of NH₃ on V/Ti oxide based catalysts prepared by precipitation. *Catal. Today* 1989, *4*, 253–265. [CrossRef]

48. Biermann, J.J.; Janssen, F.J. Low temperature isotopic exchange of molecular oxygen via the reaction of NO, NH₃ and O₂ over supported vanadia and molybdena catalysts. *Catal. Lett.* 1989, *2*, 385–393. [CrossRef]

49. Nova, I.; D’All’Acqua, L.; Lietti, L.; Giacomo, E.; Forzatti, P. Study of thermal deactivation of a de-NOₓ commercial catalyst. *Appl. Catal. B Environ.* 2001, *35*, 31–42. [CrossRef]

50. Due-Hansen, J.; Kustov, A.L.; Christensen, C.H.; Fehrman, R. Impact of support and potassium-poisoning on the V₂O₅-WO₃/Fe₂O₃ catalyst performance in ammonia oxidation. *Catal. Commun.* 2009, *10*, 803–806. [CrossRef]

51. Ueshima, M.; Sano, K.; Ikeda, M.; Yoshino, K.; Okamura, J. New technology for selective catalytic oxidation of ammonia to nitrogen. *Res. Chem. Intermed.* 1998, *24*, 133–141. [CrossRef]

52. Sazonova, N.N.; Simakov, A.V.; Nikoro, T.A.; Barannik, G.B.; Lyakhova, V.F.; Zheivot, V.I.; Ismagilov, Z.R.; Veringa, H. Selective catalytic oxidation of ammonia to nitrogen. *React. Kinet. Catal. Lett.* 1996, *57*, 71–79. [CrossRef]

53. Liu, W.; Long, Y.; Liu, S.; Zhou, Y.; Tong, X.; Yin, Y.; Li, X.; Hu, K.; Hu, J. Promotional effect of Ce in NH₃-SCO and NH₃-SCR reactions over Cu-Fe/SCR catalysts. *J. Ind. Eng. Chem.* 2021, *107*, 197–206. [CrossRef]

54. Liu, W.; Long, Y.; Tong, X.; Yin, Y.; Li, X.; Hu, J. Transition metals modified commercial SCR catalysts as efficient catalysts in NH₃-SCO and NH₃-SCR reactions. *Mol. Catal.* 2021, *515*, 111888–111897. [CrossRef]

55. Yuan, R.-M.; Fu, G.; Xu, X.; Wan, H.-L. Mechanisms for selective catalytic oxidation of ammonia over vanadium oxides. *J. Phys. Chem. C* 2011, *115*, 21218–21229. [CrossRef]

56. Liu, Y.; Hu, Q.; Ma, D.; Liu, X.; You, Z.; Qiu, G.; Lv, X. Periodic DFT study on the adsorption and deoxygenation process of NH₃ on V₂O₅ (001) surface. *JOM* 2022, *74*, 1870–1877. [CrossRef]

57. Carley, A.F.; Davies, P.R.; Roberts, M.W. An STM-XPS study of ammonia oxidation: The molecular architecture of chemisorbed imide ‘strings’ at Cu (110) surfaces. *Chem. Commun.* 1998, *17*, 1793–1794. [CrossRef]

58. Mayer, R.W.; Hävecker, M.; Knop-Gericke, A.; Schlögl, R. Investigation of ammonia oxidation over copper with in situ NEXAFS in the soft X-ray range: Influence of pressure on the catalyst performance. *Catal. Lett.* 2001, *74*, 115–119. [CrossRef]
85. Ge, S.; Liu, X.; Liu, J.; Liu, H.; Liu, H.; Chen, X.; Wang, G.; Chen, J.; Zhang, G.; Zhang, Y.; et al. Synthesis of Ti₃Sn₁₄O₃ mixed metal oxide for copper catalysts as high-efficiency NH₃ selective catalytic oxidation. *Fuel* 2022, 314, 123061–123071. [CrossRef]

86. Zhang, Q.; Wang, H.; Ning, P.; Song, Z.; Liu, X.; Duan, Y. In situ DRIFTS studies on CuO-FeOₓ catalysts for low temperature selective catalytic oxidation of ammonia to nitrogen. *Appl. Surf. Sci.* 2017, 419, 733–743. [CrossRef]

87. Wang, H.; Zhang, Q.; Zhang, T.; Wang, J.; Wei, G.; Liu, M.; Ning, P. Structural tuning and NH₃-SCO performance optimization of CuO-FeOₓ catalysts by impact of thermal treatment. *Appl. Surf. Sci.* 2019, 485, 81–91. [CrossRef]

88. Yue, W.; Zhang, R.; Liu, N.; Chen, B. Selective catalytic oxidation of ammonia to nitrogen over orderly mesoporous CuFeOₓO₄ with high specific surface area. *Chin. Sci. Bull.* 2014, 59, 3980–3986. [CrossRef]

89. Chmielarz, L.; Kuśtrowski, P.; Piwowarska, Z.; Michalik, M.; Dudek, B.; Dziembaj, R. Natural micas intercalated with AlₓOᵧ and modified with transition metals as catalysts of the selective oxidation of ammonia to nitrogen. *Top. Catal.* 2009, 52, 1017–1022. [CrossRef]

90. Chmielarz, L.; Kuśtrowski, P.; Drozdek, M.; Dziembaj, R.; Cool, P.; Vansant, E.F. Selective catalytic oxidation of ammonia into nitrogen over PCH modified with copper and iron species. *Catal. Today* 2006, 114, 319–325. [CrossRef]

91. Chmielarz, L.; Kuśtrowski, P.; Dziembaj, R.; Cool, P.; Vansant, E.F. Natural micas intercalated with AlₓOᵧ and modified with transition metals as catalysts of the selective oxidation of ammonia to nitrogen. *Appl. Catal. A Gen.* 2004, 58, 68–76. [CrossRef]

92. Lee, S.M.; Hong, S.C. Promotional effect of vanadium on the selective catalytic oxidation of NH₃ to N₂ over Ce/V/TiO₂ catalyst. *Appl. Catal. B Environ.* 2014, 148, 12199–12205. [CrossRef]

93. Wang, Z.; Qu, Z.; Quan, X.; Wang, H. Selective catalytic oxidation of ammonia to nitrogen over ceria-zirconia mixed oxides. *Appl. Catal. A Gen.* 2012, 411, 131–138. [CrossRef]

94. Lee, S.M.; Lee, H.H.; Hong, S.C. Influence of calcination temperature on Ce/TiO₂ catalysts of selective catalytic oxidation of NH₃ to N₂. *Appl. Catal. A Gen.* 2014, 470, 189–198. [CrossRef]

95. Lee, S.M.; Hong, S.C. Promotional effect of vanadium on the selective catalytic oxidation of NH₃ to N₂ over CuO-FeOₓ catalyst. *Appl. Catal. Environ.* 2002, 6, 158–165. [CrossRef]

96. Chen, W.; Ma, Y.; Qu, Z.; Liu, Q.; Huang, W.; Hu, X.; Yan, N. Mechanism of the selective catalytic oxidation of slip ammonia over Ru-modified Ce-Zr complexes determined by in situ diffuse reflectance infrared Fourier transform spectroscopy. *Environ. Sci. Technol.* 2014, 48, 12199–12205. [CrossRef]

97. Qu, Z.; Wang, Z.; Zhang, X.; Wang, H. Role of different coordinated Cu and reactive oxygen species on the highly active Cu-CE-Zr mixed oxides in NH₃-SCO: A combined in situ EPR and O₂-TPD approach. *Catal. Sci. Technol.* 2016, 6, 4491–4502. [CrossRef]

98. Quan, X.; Wang, H.; Wang, Z.; Qu, Z.; Adsorption and surface reaction pathway of NH₃ selective catalytic oxidation over different Cu-CE-Zr catalysts. *Appl. Surf. Sci.* 2018, 447, 40–48. [CrossRef]

99. Lou, J.-C.; Hung, C.-M.; Yang, S.-F. Selective catalytic oxidation of ammonia over copper-cerium composite catalyst. *J. Air Waste Manag. Assoc.* 2004, 54, 68–76. [CrossRef]

100. Wang, Z.; Qu, Z.; Quan, X.; Li, Z.; Wang, H.; Fan, R. Selective catalytic oxidation of ammonia to nitrogen over CuO-CeO₂ mixed oxides prepared by surfactant-templated method. *Appl. Catal. B Environ.* 2013, 134, 153–166. [CrossRef]

101. Hung, C.-M. Catalytic decomposition of ammonia over bimetallic CuO/CeO₂ nanoparticle catalyst. *Aerosol Air Qual. Res.* 2008, 8, 447–458. [CrossRef]

102. Hung, C.-M. Selective catalytic oxidation of ammonia to nitrogen on CuO-CeO₂ bimetallic oxide catalysts. *Aerosol Air Qual. Res.* 2006, 6, 150–169. [CrossRef]

103. Lee, J.Y.; Kim, S.B.; Hong, S.C. Characterization and reactivity of natural manganese ore catalysts in the selective catalytic oxidation of ammonia to nitrogen. *Chemosphere* 2003, 50, 1115–1122. [CrossRef]

104. Wöllner, A.; Lange, F.; Schmelz, H.; Knözinger, H. Characterization of mixed copper-manganese oxides supported on titania catalysts for selective oxidation of ammonia. *Appl. Catal. A Gen.* 1993, 94, 181–203. [CrossRef]

105. Kayijao, D.; Xiaolong, T.; Honhongh, Y.; Ping, N.; Lida, W. Rare earth oxide modified Cu-Mn compounds supported on TiO₂ catalysts for low temperature selective catalytic oxidation of ammonia and in lean oxygen. *J. Rare Earths* 2018, 28, 338–342. [CrossRef]

106. Song, D.; Shao, X.; Yuan, M.; Wang, L.; Zhan, W.; Guo, Y.; Guo, Y.; Lu, G. Selective catalytic oxidation of ammonia over MnOₓ-CuO mixed oxides. *RSC Adv.* 2016, 6, 88117–88125. [CrossRef]

107. Song, D.; Peng, Y.; Yang, Q.; Xiong, S.; Li, J.; C. J. Performance of modified LaₓSrₓOₓ as NH₃ selective catalytic oxidation. *Appl. Catal. B Environ.* 2022, 7, 8633–8639. [CrossRef]

108. Dong, A.; Yang, Z.; Wang, W. Mixed catalyst SmMnO₃/Cu-SAPO-34 for NH₃-selective catalytic oxidation. *ACS Omega* 2020, 5, 4491–4502. [CrossRef]

109. Wang, D.; Peng, Y.; Yang, Q.; Xiong, S.; Li, J.; C. J. Performance of modified LaₓSrₓOₓ as NH₃ selective catalytic oxidation. *Appl. Catal. B Environ.* 2020, 28, 338–342. [CrossRef]

110. Chmielarz, L.; Kuśtrowski, P.; Piwowarska, Z.; Michalik, M.; Dudek, B.; Dziembaj, R. Natural micas intercalated with AlₓOᵧ and modified with transition metals as catalysts of the selective oxidation of ammonia to nitrogen. *Top. Catal.* 2009, 52, 1017–1022. [CrossRef]

111. Chmielarz, L.; Kuśtrowski, P.; Drozdek, M.; Dziembaj, R.; Cool, P.; Vansant, E.F. Selective catalytic oxidation of ammonia into nitrogen over PCH modified with copper and iron species. *Catal. Today* 2006, 114, 319–325. [CrossRef]

112. Lee, S.M.; Hong, S.C. Promotional effect of vanadium on the selective catalytic oxidation of NH₃ to N₂ over Ce/V/TiO₂ catalyst. *Appl. Catal. B Environ.* 2014, 148, 12199–12205. [CrossRef]