Investigation of potassium doped mixed spinels $Cu_xCo_{3-x}O_4$ as catalysts for an efficient N_2O decomposition in real reaction conditions

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ABSTRACT

The influence of copper in the mixed spinel $Cu_xCo_{3-x}O_4$ on the catalytic activity in N_2O decomposition was investigated under ideal and real reaction conditions. A strong dependency of the catalytic activity on the amount of Cu in $Cu_xCo_{3-x}O_4$ catalysts was observed. Decreasing the amount of Cu increases the catalytic activity. Aiming for improved activity the influence of doping with alkaline (earth) metals was investigated. The use of potassium as dopant allowed a further increase of the catalysts activity. High activity was found for $K-Cu_{0.25}Co_{2.75}O_4$ and full conversion was already reached at 330 °C under ideal conditions. The effect of O_2, NO and H_2O in the gas mixtures on the decomposition of N_2O was evaluated. Overall, full N_2O decomposition could be reached at temperatures as low as 490 °C in realistic reaction conditions. Additionally, stability tests emphasise stable activity for at least 60 h. Furthermore, no irreversible deactivation even in the presence of NO, O_2 and H_2O was found. The catalysts were fully characterised by means of XRD, elemental analysis, TGA, TPR and N_2-physisorption. $TPD-O_2$ measurements were performed to investigate the influence of the catalyst composition on oxygen vacancies to elucidate the nature of active sites.

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1. Introduction

Nitrous oxide (N_2O) contributes to the depletion of the ozone layer [1], and contributes to the greenhouse effect due to its high ability to absorb and backscatter thermal radiation to the earth. Thus, it poses a huge global warming potential. N_2O has a 310 times larger global warming potential than CO_2 [2]. Major amounts of N_2O in the environment are of natural origin, while 35% of all emissions origin from anthropogenic sources. Especially chemical processes, such as the production of adipic acid and nitric acid or processes applying nitric acid as oxidising agent contribute to anthropogenic N_2O emissions. Considering a lifetime of nitrous oxide in the atmosphere of 150 years, a reduction of their emission from industrial sources is indispensable [3]. A promising way to decrease N_2O emissions from e.g. HNO_3 production is the catalytic decomposition of nitrous oxide into nitrogen and oxygen in a tertiary alignment [3]. Therefore, many types of catalysts such as supported noble metals [4–9], metal oxides [10–16] and ion-exchanged zeolites [17–19] were tested. Most of them suffer from deactivation in the

presence of O_2, NO and H_2O in the reactant stream or they require high temperatures for high conversions. So far only Fe-ZSM-5 shows sufficient activity and stability for industrial application [20]. Nevertheless, current operation temperatures of around 450 °C are still quite high compared to the temperatures of the exhaust gases.

Beside iron containing zeolites, cobalt based spinels ($A^{II}B^{III}_2O_4$) bear a high potential as feasible catalysts for N_2O decomposition. In these materials, oxygen atoms form a fcc lattice in the unit cell. In a regular spinel, the atom on the A site is typically a divalent metal ion which is tetrahedrally coordinated by oxygen atoms. The B atom is usually octahedrally coordinated with an oxidation state of +III. Also inversion and partial inversion of the occupation of sites is possible. The presence of a mixture of oxidation states the use of varying metal atoms, and changes in the metal environment make this material class highly suitable for a selected adjustment of the properties for an enhanced N_2O decomposition. Russo et al. investigated the activity of Co_3O_4 in N_2O decomposition and compared the activities with metal exchanged MCo_2O_4 (M = Cr, Mn, Fe, Co, Ni, Cu, Zn) [21]. They discovered that introducing Mg and Zn highly increases the activity and reduces the deactivation by oxygen. Therein, temperatures to reach 50% N_2O conversion ($T_{50\%}$) under ideal conditions were 440 and 475 °C for $MgCo_2O_4$ and $ZnCo_2O_4$, respectively [21]. Yan et al. confirmed that

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the degree of metal exchange in $M_xCo_{3-x}O_4$ (M = Mg, Ni, Zn) has a huge influence on the catalytic performance of the spinel materials [22,23]. Stelmachowski et al. claimed that the introduction of Zn into Co_3O_4 lowers the barrier for electron excitation from the Fermi level [24]. The effectiveness of double promotion was already shown with a K doped and Zn modified cobalt spinel which was prepared in a larger scale for testing in a pilot plant. The laboratory scale catalyst showed the same performance as the large scale catalyst with a $T_{50\%}$-value of 275 °C in ideal reaction conditions. On the pilot plant, the catalyst showed high and stable conversion rates in the presence of O_2, NO and H_2O at 350 °C [25,26].

From batch decomposition experiments Srinivasan and Sundararajan showed that the catalytic activity of $Cu_xCo_{3-x}O_4$ is dependent on the degree of exchange of Co by Cu [27]. This was later emphasised by Abu-Zied et al. for continuous operation conditions [28]. In their study, Abu-Zied et al. prepared catalysts by coprecipitation with K_2CO_3 whereby high amounts of K remained in the final catalysts [28]. Ohnishi et al. and Asano et al. described that doping with trace amount of alkaline metals, especially K, highly increases catalytic activity [29,30]. Consequently, the study of Abu-Zied et al. reflects the influence of Cu in combination with K [28]. Conclusions on the exclusive contribution of the Cu content on the catalytic activity are hardly possible. Overall, they observe maximum activity for high Cu amounts in the catalyst associated with an increasing K content. In the study of Asano et al., an optimal K/M ratio of 0.02 was identified for Co_3O_4 as catalyst [30]. Another study of Dou et al. focusses on the influence of the potassium precursor for $Cu_{0.8}Co_{2.2}O_4$ indicating an optimal molar ratio for K doping of 0.05 with K_2CO_3 as precursor [31]. The positive influence of the addition of K to Co_3O_4 was already described by Haneda et al. for the NO decomposition [32]. They explained the behaviour as follows: due to doping, a donation of electrons from the alkali metal to transition metals takes place and weakens the Co—O bond. Thus, it facilitates the reduction of Co^{3+} towards Co^{2+}. Therefore, more active Co^{2+} atoms appear on the surface of the catalyst [32]. Zasada et al. correlated the decrease in catalysts work functions due to potassium doping with the catalytic activity in N_2O decomposition. They described that a lower work function of the catalysts results in facilitated redox processes between the active species and adsorbed N_2O intermediates. Furthermore, they elucidated that the most preferred sites for K atoms on the surface are interstitials between two tetrahedral Co atoms [33].

Considering the nature of active sites in N_2O decomposition, either oxygen vacancies or metal centres are discussed as potential active sites for the catalytic decomposition of N_2O [4].

In general, it is proposed that N_2O adsorbs dissociative on the active centre (1) whereby N_2 is desorbed while an adsorbed oxygen species (adsorbed species marked with *) stays at the surface of the catalyst Desorption of adsorbed O species can either occur via a Langmuir–Hinshelwood (2) or a Eley–Rideal mechanism (3) (Scheme 1). In the Langmuir-Hinshelwood mechanism, the adsorbed oxygen species migrate on the surface until two oxygen atoms meet, combine to molecular oxygen, and desorb. This occurs under restoring of the active centre. In the Eley-Rideal mechanism, a N_2O molecule from the gas phase reacts with an adsorbed oxygen atom whereby N_2 and O_2 desorb by restoring of the active species.
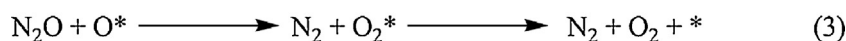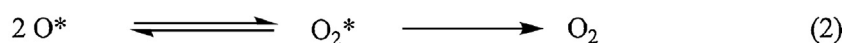
The literature about the kind of metal centre which forms the active species is controversial. Asano et al. proposed a cationic redox mechanism for Co_3O_4 where coordinatively unsaturated Co^{2+} atoms in tetrahedral sites form the active species [30]. It was suggested that due to potassium promotion of Co_3O_4 an increasing number of active sites is formed. Additionally, deactivation by oxygen was reduced via facilitated desorption of oxygen resulting in an overall enhanced activity of these materials in N_2O decomposition [30]. By exchanging Fe atoms into the Co_3O_4 structure, Maniak et al. found a correlation of the catalytic activity with the exchange of Co-atoms in tetrahedral and octahedral sites [34]. With $x < 1$ in $Fe_xCo_{3-x}O_4$ only Co atoms in tetrahedral sites are supposed to be exchanged by Fe. Introducing higher amounts of Fe with $x > 1$ also Co atoms in octahedral sites are exchanged. A drastic decrease in the $T_{50\%}$ values was found caused by the substitution of Co^{3+} in octahedral sites. Therefore, they concluded that Co^{3+} atoms in octahedral sites are responsible for high catalytic activities [34]. Recently, Stelmachowski et al. prepared a set of Mg, Co and Al containing spinels to create selectively catalysts with either Co^{2+} atoms in tetrahedral sites or Co^{3+} atoms in octahedral sites. They proposed that the primary active sites are Co^{3+} atoms in octahedral sites [35]. This explains on the one hand the decrease in catalytic activity due to exchange of the octahedral Co^{3+} atoms in Co_3O_4. But on the other hand, this does not explain why the exchange of Co^{2+} atoms by the proper amount of Mg^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} increases the catalytic activity compared to Co_3O_4 [21–23,27,28]. Furthermore, according to Krezhov et al. Mg^{2+} and Ni^{2+} show a preference for occupying octahedral sites, while Zn^{2+} prefers to occupy tetrahedral sites. In the case of Cu^{2+}, a statistical distribution among the tetrahedral and octahedral sites was described [36,37]. Furthermore, a comprehensive understanding of the influence of the crystalline bulk material composition on the exposed surface sites under reaction conditions appears indispensable to gain further insights concerning the nature and concentration of catalytically active sites.

Herein, we present a comprehensive investigation on the activity of $Cu_xCo_{3-x}O_4$ (x = 0, 0.25, 0.5, 0.75, 1) prepared by an alkaline free synthesis route in N_2O decomposition enabling a decoupled analysis of the contribution of copper content and dopant addition. Various alkaline (earth) metals were utilised as dopants and their influence on the catalytic activity of $Cu_xCo_{3-x}O_4$ for N_2O decomposition were investigated. The most active catalysts were investigated in the presence of NO, O_2 and H_2O examining the individual effect of these compounds and the stability of the optimum catalyst under real reaction conditions combining NO, O_2 and H_2O.

2. Experimental

2.1. Catalyst preparation

$Cu_xCo_{3-x}O_4$ (x = 0, 0.25, 0.5, 0.75, 1) catalysts were prepared by thermal decomposition at 600 °C of stoichiometric mixtures of metal nitrate precursors. The respective amounts of $Co(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich) and $Cu(NO_3)_2 \cdot 3H_2O$ (Sigma–Aldrich) were dissolved in distilled H_2O, the water was evaporated at 80 °C and the resulting solid was pestle in a mortar. The solid mixture of nitrates was decomposed at 600 °C

$$N_2O^* \longrightarrow O^* + N_2 \qquad\qquad (1)$$

$$2\,O^* \rightleftharpoons O_2^* \longrightarrow O_2 \qquad\qquad (2)$$

$$N_2O + O^* \longrightarrow N_2 + O_2^* \longrightarrow N_2 + O_2 + {}^* \qquad\qquad (3)$$

Scheme 1. Reactions during N_2O decomposition. (1) Dissociative adsorption of N_2O, (2) O_2 desorption via Langmuir–Hinshelwood mechanism, (3) O_2 desorption via Eley–Rideal mechanism.