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Abatement of nitrous oxide by ruthenium catalysts: Influence of the support

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ABSTRACT

As a reaction of high environmental relevance, the catalytic abatement of N_2O by ruthenium supported on different oxide and carbon or carbide supports was studied. Activities of Ru catalysts were determined in the presence and absence of oxygen. They were found to be significantly affected by the support material used. Ru particles on oxide supports ($MgO, SiO_2, CeO_2, Al_2O_3, TiO_2$) were very active, with Ru/TiO_2 exhibiting the best performance. The presence of oxygen in the gas feed significantly lowered reaction rates by blocking Ru surface sites. Ru catalysts supported on carbon-based carriers (activated carbon, silicon carbide) were clearly less active than their oxide counterparts. In fact, carbon and silicon carbide support materials do not act as inert structural carriers only but also as reducing agents. The oxidation of the carbon support was found to be strongly enhanced by the presence of Ru particles. Temperature programmed oxidation and reduction experiments revealed that the redox properties of the ruthenium catalysts correlate with catalytic activity and represent a key parameter for deeper understanding of the reaction mechanism.

1. Introduction

N_2O is a greenhouse gas which has a 310 times higher Global Warming Potential (GWP) than CO_2 [1]. It was reported that the global N_2O concentration increased by approximately 19% from 1750 to 2007 [2,3]. N_2O is known to be naturally emitted by soil bacteria, which break down nitrogen via nitrification and denitrification. Anthropogenic N_2O sources are responsible for significant increase of N_2O in the atmosphere in the past centuries. These anthropogenic activities involve the agricultural sector, where synthetic fertilizers are added to soil, the automotive emissions, when fuels are burnt, and the industrial production of nitric acid and adipic acid [2]. Compared to other technologies, the direct catalytic decomposition of N_2O is the preferable method for its removal. It does not require reducing agents and forms only harmless products (N_2 and O_2). Supported noble metal catalysts, e.g. Rh, Ru, Pd and Pt, have been shown to be highly active for N_2O decomposition [4–6]. Ru is highly interesting among these metals because of the lower price compared to Rh, Pd and Pt. Most publications dealing with Ru catalysts for the N_2O decomposition agree on two possible mechanisms, listed in Eqs. (I)–(IV) [7–9]. Starting with dissociative adsorption of N_2O, molecular nitrogen (N_2) and adsorbed oxygen atoms (*–O) can be formed. The latter recombine and desorb as oxygen molecules (O_2). Besides, adsorbed oxygen atoms can react with gaseous N_2O to form O_2 and N_2. The desorbed O_2 can adsorb on the active site to form surface oxygen atoms as well (Equations III and IV are reversible) [10]. According to several literature reports, desorption of O_2 is assumed to be the rate-limiting step herein [11–14].

$$N_2O + * \rightarrow *{-}N_2O \tag{I}$$

$$*{-}N_2O \rightarrow N_2 + *{-}O \tag{II}$$

$$2*{-}O \leftrightharpoons O_2 + 2* \tag{III}$$

$$N_2O + *{-}O \leftrightharpoons N_2 + O_2 + * \tag{IV}$$

where a $*$ shall represent an active site.

The catalytic activity of supported Ru catalysts is among other factors influenced by the support material used. It is generally accepted that the size of active metal particles can change with the support material even for identical preparation procedures [15–18]. In case of rhodium catalysts, Rh/MgO and Rh/SiO_2 with mean Rh particle diameters of 2.1–2.4 nm are highly active for the decomposition of N_2O. On the contrary, Rh/CeO_2, Rh/Al_2O_3 and Rh/TiO_2 exhibit significantly lower activities with smaller rhodium particles observed (d_m = 1.0–1.4 nm) [18]. Besides, the reducibility of the supported metal particles was found to be a crucial factor, which influences the activity of catalytic reactions. For instance, the

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activity in the N_2O decomposition of ceria-based noble metal catalysts (Rh, Pd and Pt) could be correlated with their reducibility by H_2 [19]. It was found that lower reduction temperature resulted in higher catalytic activity. The reducibility in turn is closely related to the nature of oxidic support materials [18,20]. Metal–support interactions were considered as an important influence on the activity of supported metal catalysts [21–23]. It was shown that $Pd/LaCoO_3$ has a higher activity in the N_2O decomposition than Pd/Al_2O_3. The difference was ascribed to the interaction between Pd species and the support [23].

Besides the oxidic supports, carbon materials have been intensively used as supports for the catalytic reduction and decomposition of NO_x due to their interesting characteristics [24,25]. However, carbon may not only act as inert support, but can be a reducing agent due to its limited thermodynamic stability in oxidizing atmosphere at elevated temperature. It was suggested that carbon acts as reactant in the N_2O decomposition with Pt and Cu catalysts loaded on carbon films [26]. By measuring complete N and C balances during the NO_x abatement with carbon-based catalysts, it was found that the stoichiometric oxidation of the carbon support by adsorbed oxygen from NO_x is crucial to achieve steady-states reaction rates. The lifetime of carbon based catalysts is hence limited by the stoichiometric oxidation of the support material [27,28].

The role of the support for the catalytic performance of the active components is a very complex question in heterogeneous catalysis and not well understood for many reactions. For the N_2O decomposition by supported Ru catalysts, only few publications investigated this influence of the support material on catalytic activity and reaction mechanism. In the present study, we compare for the first time a variety of different oxides (MgO, SiO_2, CeO_2, Al_2O_3, TiO_2) and also carbon-based Ru catalysts (activated carbon and SiC). The investigations should provide directly comparable data for a variety of supports and allow conclusions on the impact of the supports and the electronic and structural properties of immobilized Ru particles on their activity in the N_2O decomposition.

2. Experimental

2.1. Catalyst preparation

Ru catalysts supported on different materials were synthesized by incipient wetness impregnation with an aqueous solution of $Ru(NO)(NO_3)$. Al_2O_3 (Aluminiumoxid C), SiO_2 (Aerosil 200) and TiO_2 (Aeroxide P25) were obtained from Evonik. MgO (MgO nanopowder) was purchased from Aldrich. CeO_2 (SNAC-10000) was received from Priem, SiC was obtained from SiCAT and active carbon was purchased from Fluka. Prior to impregnation, all of the supports were agglomerated, sieved to grain sizes of 300–500 μm and dried at 200 °C for 8 h. The support materials were impregnated with the $Ru(NO)(NO_3)$ solution according to Table 1, wherby the ratio n_{Ru}/V_{bulk} of the resulting catalyst bed was kept constant. After impregnation, the catalysts were dried at 100 °C overnight and calcined in air (oxide-supported catalysts) or He (active carbon or SiC-supported catalysts) at 450 °C for 6 h.

2.2. Catalyst characterization

BET surface area analysis and temperature programmed reduction (TPR) experiments were performed on a Micromeritics Autochem 2910. For reducibility measurements by H_2-TPR, the catalysts ($V_{bulk} = 0.25\ cm^3$, $n_{Ru} = 8\ \mu mol$) were subjected to a flow of 33 mL/min of 2.5% H_2 in Ar after pretreatment in He at 300 °C for 1 h. The water evolved was removed by a cold trap with a mixture of liquid nitrogen and isopropanol in front of the thermal conductivity detector. All samples were heated to 800 °C with a heating rate of 5 K/min. The oxidation stability of active carbon was studied by O_2-TPO. After pretreatment of the catalyst in pure He at 300 °C for 1 h, the sample was heated to 800 °C (heating rate 5 K/min) in a flow of 50 mL/min of 5% O_2 in He. The gas evolution was detected with a Pfeiffer ThermoStar GSD 320 mass spectrometer.

Structure and morphology of the samples were analyzed by transmission electron microscopy (TEM) on a JEOL 100 CX microscope. Ru mean particle sizes were calculated from the measured diameters of more than 500 particles. X-ray powder diffractions (XRD) were conducted using a Philips X'Pert diffractometer operating with Cu/K_{a1} radiation in the range of 5–70° 2θ.

2.3. Catalytic measurements

The activity of the catalysts in the N_2O decomposition reaction was measured in the temperature range of 150–550 °C using a U-shaped quartz reactor of 4 mm inner diameter. The bulk volume of the catalyst bed ($V_{bulk} = 0.25\ cm^3$) and the molar amount of Ru ($n_{Ru} = 8\ \mu mol$) were kept constant for all measurements. The catalysts, with grain sizes of 300 and 500 μm, were reduced in H_2 at 500 °C for 1 h prior to catalytic testing. The feed gas mixture contained 1000 ppm N_2O in He at a flow rate of 100 mL/min (GHSV = 24,000 h^{-1}). After the system has reached a steady state, the conversion of N_2O was analyzed by FTIR using an Agilent 660 spectrometer equipped with a gas cell (Axiom Analytical Inc). N_2 and O_2 were analyzed with a Pfeiffer ThermoStar GSD 320 mass spectrometer.

3. Results and discussion

3.1. Ru catalysts supported on oxides

3.1.1. Characterization of oxide-supported Ru catalysts

The particle size distribution of oxide-supported Ru catalysts was measured by TEM. As shown in Fig. 1, the average particle sizes of Ru species differ for the different catalysts. Since all of them were prepared by the same procedure and with the same Ru precursor, the size variations of Ru particles is expected to be caused by the support material used. The following order of decreasing mean particle sizes was found: Ru/Al_2O_3 (2.3 nm) > Ru/SiO_2 (2.1 nm) > Ru/CeO_2 (1.7 nm) > Ru/TiO_2 (<1.5 nm). In contrast to Rh/MO_x catalysts, a correlation of these values with the catalytic performance of Ru/MO_x catalysts cannot be deduced [18]. This is ascribed to the very small range of particle sizes in case of the Ru catalysts (1.5–2.3 nm). It implies that the catalytic activity is controlled by different factors, whereby the reducibility of RuO_x species represents one of the most important ones (see below).

In order to obtain information on structure and oxidation states of the supported Ru species, the oxide-supported catalysts were studied by XRD. As depicted in Fig. 2, reflections at $2\theta = 28.1°$, $35.1°$ and $54.4°$ are observed for MgO, SiO_2 and Al_2O_3 catalysts. The peaks correspond to the (110), (101) and (211) planes of crystalline RuO_2. The weak peak intensities (and the absence of peaks in case of Ru/CeO_2 and Ru/TiO_2) can be expected from the TEM measurements, which show very small RuO_2 particles causing significant line broadening. Since no peaks corresponding to metallic $Ru^{(0)}$ phases are present, it is concluded that the majority of the Ru species exists in form of RuO_2 particles on the oxide supports after calcination in air. Other peaks of the XRD pattern shown in Fig. 2 belong to the crystalline supports.

The catalysts were investigated by temperature-programmed reduction with H_2 (H_2-TPR) to study the influence of the support material on the reducibility of RuO_x species. As shown in Fig. 3, H_2 consumption occurs at different temperatures for the different