Metal-substituted hexaaluminates for high-temperature N_2O abatement†

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Metal-substituted hexaaluminates are highly active, selective, stable, and inexpensive catalytic materials for high-temperature N_2O abatement in the chemical industry, such as in nitric acid and caprolactam plants, and in combustion processes.

N_2O mitigation is a topic of environmental relevance due to the adverse contribution of this harmful gas to global warming and ozone depletion. Policies and regulations are being enforced to develop and implement technology to reduce anthropogenic N_2O emissions. These mostly derive from the Kyoto Protocol which came into force on 16 February 2005, where targets for the reduction of greenhouse gas emissions to signatory nations were assigned.[1] Nitric acid plants currently represent the largest single source of N_2O in the chemical industry (125 Mton CO_2-equiv. per year). In the process, nitrous oxide is formed as a by-product of catalytic ammonia oxidation over Pt–Rh alloy gauzes.[2] Abatement options at different locations in the nitric acid plant have been extensively investigated in the last decade.[3] Direct N_2O decomposition below the noble metal gauzes in the ammonia burner (process-gas option) and in the tail-gas train (tail-gas option) were concluded to be cost-effective abatement measures for existing plants. A major advantage of the process-gas decomposition is the universal application in all nitric acid facilities. In contrast, N_2O abatement using Fe-zeolites is prohibitive in plants with low-temperature tail gases (<673 K), since addition of reducing agents and gas preheating is required.[4]

Successful process-gas catalysts should, of course, be active in order to achieve high N_2O conversions, but establishing a high chemical stability and selectivity at the extreme conditions of temperature and gas composition in the ammonia burner (1073–1173 K, wet oxidizing atmosphere) is critical to ensure a long lifetime and safe operation. Because of this, component volatilization and solid-state reactions between active phase and support, leading to catalyst deterioration, must be minimized. Volatilization may have fatal consequences, as leached transition metal ions efficiently catalyze the highly exothermic decomposition of the end fertilizer product (NH_4NO_3), with the subsequent explosion risk. No study has been published in the open literature on design strategies and performance of high-temperature de-N_2O catalysts under simulated process conditions. Available information on catalytic systems generally arises from patents and mainly relates to supported spinels and bulk perovskite recently developed by industry: CuO/Al_2O_3 (BASF),[5] $La_{0.8}Ce_{0.2}CoO_3$ (Johnson Matthey),[6] and Co_2AlO_4/CeO_2 (Yara International).[7]

Metal-substituted hexaaluminates can be considered as promising candidates for high-temperature N_2O abatement. These materials have been mainly applied in the catalytic combustion of methane in gas-turbine applications involving temperatures up to 1773 K,[8] due to their stable phase composition and resistance to sintering and thermal shock. This is associated with their layered structure, consisting of alternate stacking along the *c*-axis of γ-Al_2O_3 spinel blocks and mirror planes in which large alkaline (K^+), alkaline-earth (Ba^{2+}, Ca^{2+}, Sr^{2+}), or rare-earth (La^{3+}) cations are located.[9] Substitution of noble metal or transition metal ions in Al^{3+} positions of the spinel blocks enables the introduction of redox active sites in the structure with little effect on the sintering resistance of the material.[8]

Herein we show that various Me-hexaaluminates fulfil the stringent performance requirements (activity, selectivity, and chemical stability) for process-gas N_2O abatement. This makes them competitive catalysts with respect to commercial systems for mitigation of this harmful gas in the chemical industry, primarily in nitric acid and caprolactam plants.

The preparation of Me-hexaaluminates with general formula $ABAl_{11}O_{19-\alpha}$ (A = La, Ba, and B = Mn, Fe, Ni) started with the co-precipitation of dawsonite-type precursors using the recently developed ILDP (in-line dispersion precipitation) method.[10] An aqueous solution of the cations (1.1 M Al-nitrate, 0.1 M A-nitrate, and 0.1 M B-nitrate) acidified with concentrated nitric acid to pH = 1, and an aqueous solution of $(NH_4)_2CO_3$ (2 M) were continuously pumped at 333 K to a precipitation micro-reactor. Syntheses were carried out at constant pH = 7.5–8, using a fixed residence time of 18 s and a stirring speed of 13 500 rpm. The resulting slurry was aged at 333 K for 3 h, followed by filtration, washing, and drying. Finally, the dried solids were calcined in static air at 1473 K for 10 h. The catalytic performance was measured at ambient pressure in a quartz fixed-bed micro-reactor (10 mm id) using *ca.* 200 mg of sample (sieve fraction 200–300 μm) and a space velocity (WHSV) of 30 000 ml g^{-1} h^{-1}. Two protocols were applied for catalytic evaluation. Temperature-programmed reaction (TPR) was carried out by ramping the temperature from 673 to 1273 K at 10 K min^{-1} using a mixture of 5000 ppm N_2O in He. Steady-state tests were conducted isothermally in the range 623–1123 K. Feed mixtures containing 1500 ppm N_2O in He and additionally individual or combined components such as O_2 (10 vol%), NO (1.5 vol%), and H_2O (10 vol%) were used so as to realistically simulate the gas composition at the outlet of the Pt–Rh

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† Electronic supplementary information (ESI) available: N_2O conversion *versus* time on stream over Ba–Fe–Al hexaaluminate. See DOI: 10.1039/b613602h

Table 1 Characterization data of the samples

Catalyst	Metal ratio in solid/mol mol^{-1}		Cell parameter/Å		S_{BET}/m^2 g^{-1}
	Al/A	Al/B	a_0	c_0	
La–Al	11.2	—	5.565	21.91	35
La–Mn–Al	11.1	10.6	5.615	22.21	13
La–Fe–Al	10.8	10.8	5.598	22.15	16
La–Ni–Al	10.7	12.1	5.604	22.11	27
Ba–Al	11.0	—	5.591	22.76	25
Ba–Mn–Al	10.6	11.1	5.645	22.74	9
Ba–Fe–Al	10.7	10.6	5.615	22.79	12
Ba–Ni–Al	10.6	14.6	5.610	22.70	18

gauzes in ammonia burners. Reactant and product gases were analyzed by means of a quadrupole mass spectrometer (Pfeiffer OmniStar GSD 301O) and a gas chromatograph (SRA Instruments Micro-GC 3000).

The chemical composition of the calcined samples is shown in Table 1. The molar ratios between Al, the A (Ba, La) and/or B (Mn, Fe, Ni) metals in the solids, as determined by ICP-OES, were very close to the nominal values, indicating that the co-precipitation step was carried out effectively. The content of A and B metals was in the range of 16–19 wt% and 5.5–7.5 wt%, respectively. XRD of the samples (Fig. 1) exhibited hexaaluminate as the only crystalline phase. The calculated cell parameters of the non-substituted La–Al and Ba–Al samples (see Table 1) are in very good agreement with those in the corresponding JCPDS cards (given in the legend to Fig. 1). The value of a_0 in the transition metal-containing materials is always higher than that of the non-substituted ones. This indicates that the larger Mn, Fe, and Ni ions are located in the hexaaluminate structure, replacing smaller Al^{3+} ions. Since Ba^{2+} has a larger ionic radius than La^{3+} (0.149 *versus* 0.117 nm), the c_0 parameter was higher in the Ba-containing samples, but was not significantly affected upon substitution by the different transition metals. As shown in Table 1, the BET surface area for the La–Al and Ba–Al hexaaluminates (25–35 m^2 g^{-1}) is reduced upon substitution by transition metals, decreasing in the order Ni > Fe > Mn. The La-samples have somewhat higher surface area than the Ba-samples for all metals substituted.

Temperature-programmed reaction experiments (Fig. 2) were suitable for screening the N_2O decomposition activity of the hexaaluminate catalysts. Blank experiments with the empty tube revealed the inertness of the quartz reactor walls below 1050 K. The iron and manganese-substituted hexaaluminates were the most active catalysts, yielding very similar conversion profiles. Over these systems, N_2O conversion starts at 800 K and reaches 100% above 1050 K. The temperature required for achieving 50% conversion is *ca.* 900 K. The catalytic performance was practically not influenced by the A cation in the structure, *i.e.*, La or Ba. The Ni-substituted catalysts were considerably less active, exhibiting similar conversion curves as the non-substituted hexaaluminates. The latter group displays measurable N_2O conversions above 900 K, *i.e.*, 100 K higher temperature than the Fe- and Mn-containing catalysts. The fact that the iron-substituted hexaaluminates were the most active catalysts was *a priori* not expected considering the established activity order of transition metals in different supports and oxide matrices for direct N_2O decomposition. As reviewed by Kapteijn *et al.*,[11] Fe is a considerably less active transition metal as compared with Mn, Ni, or Co in pure oxides, solid solutions of transition metals in inert matrices, mixed oxides such as perovskites and spinels, and zeolites. Accordingly, our results show the high relative activity of iron-based systems when the transition metal is located in a hexaaluminate matrix.

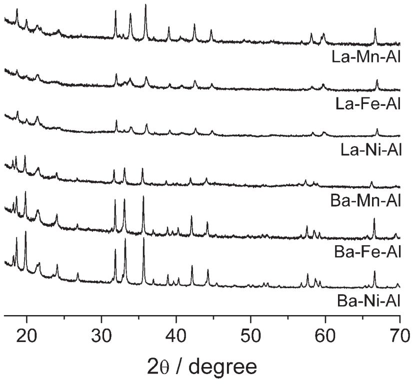

Fig. 1 XRD patterns of the Me-hexaaluminates. Diffraction lines in all samples exclusively belong to single hexaaluminate phases: $LaAl_{11}O_{18}$ (JCPDS 33–699) and $BaAl_{12}O_{19}$ (JCPDS 26–135).

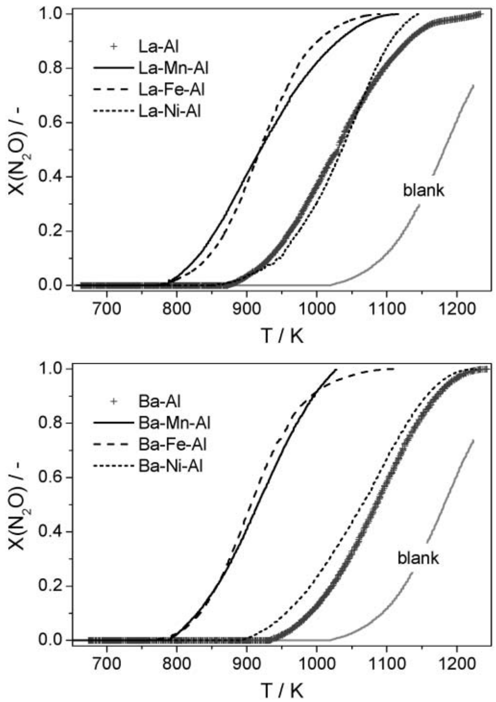

Fig. 2 N_2O conversion *versus* *T* in TPR experiments over the hexaaluminate catalysts. Conditions as described in text.

In order to realistically establish the potential of hexaaluminates for high-temperature N_2O abatement in industrial sources, the steady-state catalytic performance under realistic process conditions of temperature, feed composition, and space velocity was assessed. In this respect, the influence of additional gases accompanying N_2O on the catalytic performance is of particular relevance. In ammonia burners, ammonia–air mixtures (typically 10 vol.% NH_3, ratio $NH_3 : O_2 = 1 : 2$) react on Pt–Rh gauzes at 1173 K, leading to NO selectivities of 95–97%. The outlet gas contains small N_2O amounts (1500 ppm) and large amounts of

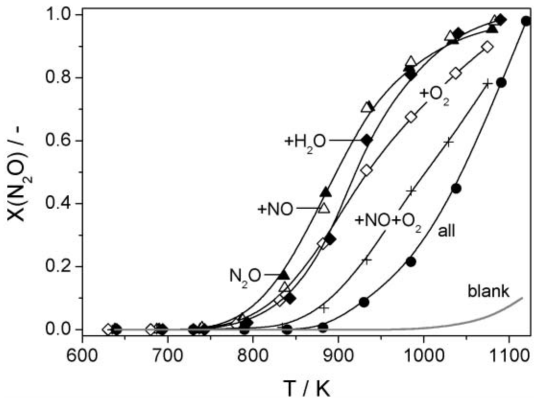

Fig. 3 N_2O conversion *versus* T over Ba–Fe–Al hexaaluminate in feed mixtures with N_2O and additional components at the outlet of the Pt–Rh gauzes in ammonia burners. Conditions as described in text.

unreacted O_2 (*ca.* 6.5 vol%) and the main reaction products NO (*ca.* 10 vol%) and H_2O (*ca.* 15 vol%). Fig. 3 illustrates the N_2O conversion *versus* temperature in different feed mixtures over the Ba–Fe–Al hexaaluminate. As expected, the conversion profile in N_2O + He for all the catalysts in isothermal experiments were shifted *ca.* 25–50 K to lower temperature with respect to the transient TPR experiments in Fig. 2. However, the activity order coming from both testing approaches was the same. Ba–Fe–Al hexaaluminate displays significant N_2O conversion in N_2O + He feed above 750 K, being >90% above 1025 K. NO has no effect on the N_2O decomposition performance. The presence of O_2 inhibits the N_2O decomposition, shifting the conversion profile by *ca.* 25–50 K to higher temperatures. H_2O also inhibits the reaction, presenting a very similar behaviour to that of O_2 below 900 K and approaching the conversion with the N_2O + He mixture around 973 K. The negative influence of O_2 and H_2O in the reaction can be attributed to competitive adsorption over active N_2O decomposition sites in the catalyst.[11] Severe inhibition of the catalytic activity was experienced in N_2O + NO + O_2 mixtures as compared with the individual components. This result suggests the formation of stable nitrate-type species on the catalyst surface, probably initiated by NO_2. The N_2O conversion profile in N_2O + NO + O_2 + H_2O (referred to as 'all' in Fig. 3) is further shifted to a higher temperature. In this mixture, total N_2O conversion was attained around 1100 K, *i.e.*, somewhat lower than the gas temperature at the outlet of the Pt–Rh gauzes in the ammonia burner (in the range of 1123–1173 K).[3] Very similar results to those shown for Ba–Fe–Al hexaaluminate in Fig. 3 were obtained over the Mn-substituted hexaaluminates. In order to assess the short-term stability of the catalysts, the N_2O conversion was monitored with time in the mixture containing all the gases. The temperature was set so as to operate at intermediate degrees of N_2O conversion and visualize any sign of deactivation more clearly. As illustrated in the Electronic Supplementary Information†, the N_2O conversion at 1073 K (*ca.* 50%) was practically constant during 60 h on-stream over Ba–Fe–Al hexaaluminate. This result is promising, since average high-temperature catalysts (>973 K) show rapid deactivation in the first few hours of operation.

In the activity tests with simulated mixtures, attention was also paid to analyzing any possible conversion of NO over the catalyst. This is highly detrimental, since the ability of a catalyst to assist NO decomposition (the desired product of ammonia oxidation) would annihilate any prospect of this family of materials assisting process-gas N_2O abatement. Our results enable us to conclude that the degree of the NO conversion to N_2 was below the detection limit of the analytical method (<1%), evidence of the selective nature of the metal-substituted hexaaluminates for N_2O decomposition.

In summary, we have shown that La and Ba-hexaaluminates substituted by transition metals such as Fe and Mn fulfil the rigorous requirements of activity, selectivity, and stability and can be effectively applied in high-temperature (process-gas) catalytic N_2O decomposition. The tests reported in this manuscript were primarily conducted by simulating conditions at the outlet of the noble metal gauzes in ammonia burners of nitric acid and caprolactam production plants. These are currently the most important sources of N_2O in the chemical industry. The hexaaluminate catalysts can be considered as a promising alternative to the recently commercialized Co_2AlO_4/CeO_2 and $La_{0.8}Ce_{0.2}CoO_3$ systems. Firstly, the chemical stability of hexaaluminates is superior to that of spinel and perovskite-based mixed oxides. Besides, the cost of the hexaaluminate systems can be anticipated to be highly competitive because inexpensive active phases are used (*e.g.*, Fe as compared with Co) within a stabilized alumina matrix, and the applied coprecipitation method for catalyst preparation is relatively simple.

Finally, it should be mentioned that the application of this family of materials in N_2O abatement is not limited to sources in the chemical industry. The reduction of N_2O emissions in stationary combustion processes, particularly in fluidized bed combustors, can be practised at high temperature (up to 1200 K)[11,12] and the unique combination of stability and de-N_2O activity of the hexaaluminates presents great prospects.

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