Catalysis Today 176 (2011) 365–368

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Laboratory and pilot scale synthesis, characterization and reactivity of multicomponent cobalt spinel catalyst for low temperature removal of N_2O from nitric acid plant tail gases

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ARTICLE INFO

Article history:
Received 21 September 2010
Received in revised form
15 November 2010
Accepted 16 November 2010
Available online 17 December 2010

Keywords:
Cobalt spinel catalyst
N_2O decomposition
Tail gases
Nitric acid pilot plant

ABSTRACT

Synthesis of a multicomponent (K, Zn-doped) cobalt spinel deN_2O catalyst developed in a laboratory was extended to a pilot scale. The optimal composition and morphology of the prototype catalyst elucidated in the laboratory conditions were successfully reproduced upon large scale synthesis and shaping. Tuning of the catalyst properties was guided by in situ work function measurements in conjunction with the TPRS tests of N_2O decomposition including the effect of water and oxygen inhibitors. In the pilot tests the engineered catalyst exhibited high performance (conversion >95% below 350 °C) in N_2O removal from the real tail gases of the nitric plant for at least 20 days.

1. Introduction

Nitrous oxide is formed as an undesirable by-product during catalytic oxidation of ammonia in nitric acid plants. Being poorly absorbed in water it has to be removed from tail gases discharged into the atmosphere. Global emission rate of N_2O from nitric industry is at the level of 0.4 million ton per year [1]. Due to its high global warming potential (310 times higher than CO_2), nitrous oxide has significant impact on the greenhouse effect and the ozone layer destruction [1].

A low-temperature catalytic decomposition of nitrous oxide is definitely more beneficial than selective catalytic reduction, because the additional reducing agents are not needed in this case. Furthermore, in contrast to high-temperature option (catalytic decomposition of N_2O directly in ammonia burner), the low-temperature one allows to minimize a possible depletion of the desired NO_x. However, the use of a catalyst in the low temperature zone is connected with the requirement of high activity, resistance to inhibitors always present in the tail gases such as oxygen and water, as well as other residual NO_x. Catalytic decomposition of nitrous oxide was a subject of numerous studies involving simple oxides [1–3], perovskites [4], spinels [5–8], zeolites [9], hydrotalcites [10,11], mesoporous silicas [12] and supported catalysts [13–15]. The active components of the catalysts usually contain transition metal ions such as cobalt, iron, nickel, copper, manganese or chromium [16]. The activity of the investigated catalysts was improved upon addition of various promoters, located in the bulk or at the surface [17–19].

Despite the large scientific activities in this field the ultimate practical solution has not been achieved yet. In this context the development of the economically appealing catalyst, scale-up procedures and large scale tests in real conditions are of particular importance. In this work we report on manufacturing, characterization of the shaped cobalt spinel based catalyst followed by activity and durability screening test in a pilot nitric acid plant.

2. Experimental

In the laboratory scale (grams) the (Zn, Co)-spinel catalysts were obtained via a precipitation method from the adequate nitrate precursors as described elsewhere in detail [20]. The potassium post-doping was achieved by incipient wetness impregnation using K_2CO_3 solution in the range of 0–15 at./nm^2. The samples were next dried at 100 °C for 1 h and finally calcined at 400 °C for 4 h. The cat-

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doi:10.1016/j.cattod.2010.11.044

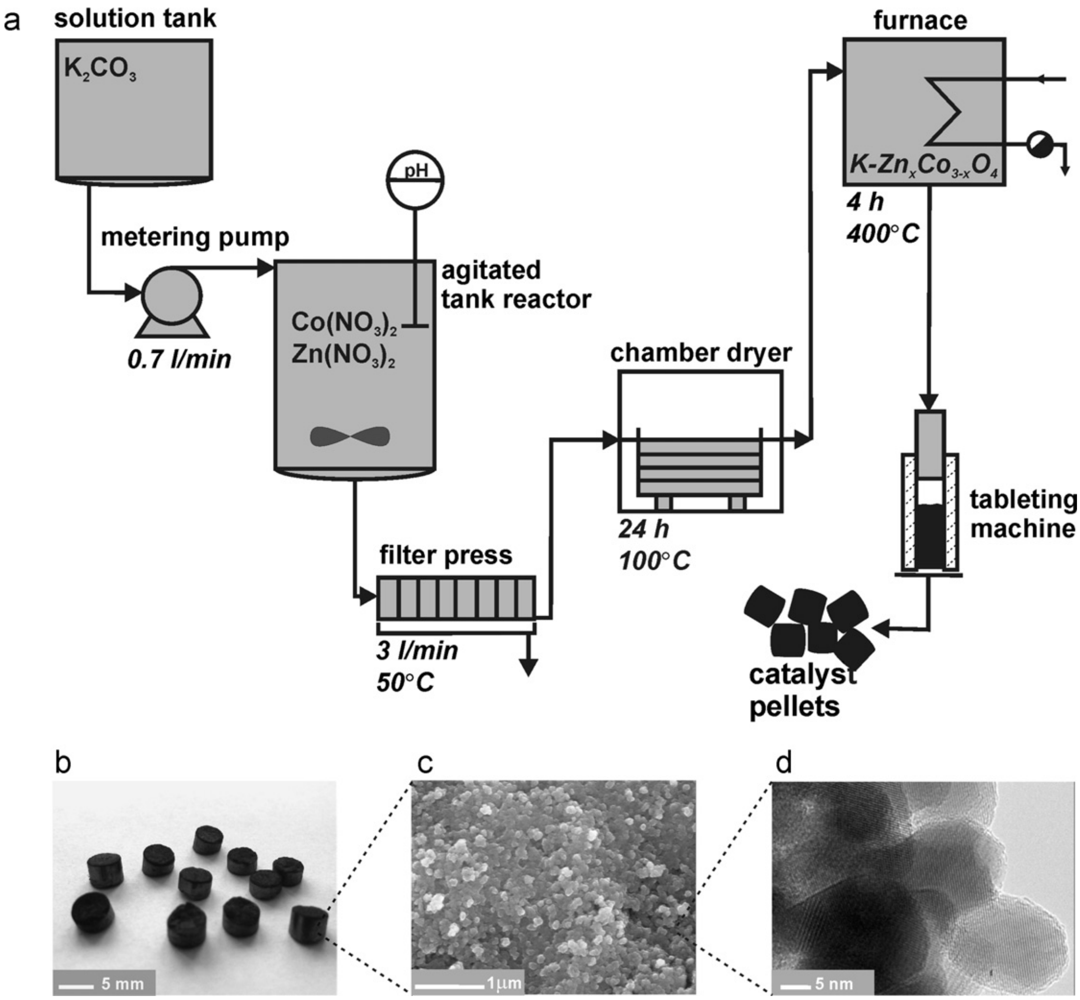

Fig. 1. The pilot installation for manufacturing of the deN_2O multicomponent cobalt spinel catalyst (a) and its shape and morphology at milimetric (b), SEM micrometric (c) and HRTEM nanometric (d) scales.

alysts were characterized by XRD, SEM, XPS, BET and Kelvin probe contact potential measurements as described elsewhere [8].

In the pilot scale (kilograms) synthesis the K_2CO_3 was dosed (with the rate of 0.7 l/min) to the reaction tank containing 15.5 kg $Co(NO_3)_2{\cdot}6H_2O$ and 2.4 kg $Zn(NO_3)_2{\cdot}6H_2O$ dissolved in 25 l of distilled water, until the pH 9 was achieved. The precipitate was digested for 2 h in the mother liquor under continuous stirring. It was next filtered under pressure, rinsed repeatedly with demineralized water at 50 °C with the rate of 3 l/min. During that process the aliquots were taken for periodic chemical analysis for potassium content. The resultant precursor of the catalyst was dried at 100 °C for 24 h and calcined at 400 °C for 4 h. The synthesis was repeated three times to obtain the total amount of the catalyst equal to about 50 kg. The scheme of the pilot installation used for manufacturing of the catalyst is presented in Fig. 1a. The final composition of the catalyst and its specific surface area were determined by AAS and BET methods, respectively. The analysis of the catalyst morphology was investigated at different magnification levels by a SEM (Hitachi S-4700) and TEM (Jeol JEM 2100HR) microscopes.

The laboratory TPSR studies of N_2O decomposition were performed in a quartz flow reactor in the range of 20–600 °C (10 °C/min) with the use of 300 mg of the catalyst (sieve fraction of 0.2–0.3 mm), flow rate of the feed (5% N_2O/He) with *GHSV* (*Gas Hourly Space Velocity* i.e. volume of gas feed per hour per volume of catalyst) of 7000 h^{-1}, as described elsewhere [8]. The reaction progress was monitored with a quadrupole mass spectrometer (RGA200, SRS). The measurements with the pilot scale prepared catalysts were performed in tubular reactor at *GHSV* of 10,000–30,000 h^{-1} in real tail gases from nitric acid installation (200–4000 ppm NO_x + 0.3–1.5% H_2O + 0.6–2.5% O_2 + 500–1200 ppm N_2O) with the use of the sieve fraction of 0.6–1.0 mm. The catalyst stability test was carried out at 350 °C for 20 days. The reaction progress was monitored with a FT-IR Gas Analyser (GASMET).

3. Results and discussion

The catalyst obtained in pilot scale successfully reproduced the optimal composition elucidated in the laboratory scale (Table 1). It was shaped in the form of 3 mm × 5 mm cylindrical extrudates shown in Fig. 1b. The BET surface area of the catalysts synthesized in laboratory and pilot scales were the same within the experimental limit and equal to $60 \pm 5\ m^2\ g^{-1}$. The morphology of the resultant material as revealed by SEM images (Fig. 1c) shows the aggregates of 50–150 nm. The aggregates consist of well-developed single nanocrystallites of average diameter of about 10 nm as shown by

Table 1
Comparison of the chemical composition of the catalysts prepared in laboratory and pilot scale determined by AAS method.

Element	Laboratory scale (wt.%)	Pilot scale (wt.%)
Co	62.97 ± 1.89	65.7 ± 1.50
Zn	10.7 ± 0.11	11.2 ± 0.12
K	0.7 ± 0.01	0.6 ± 0.39

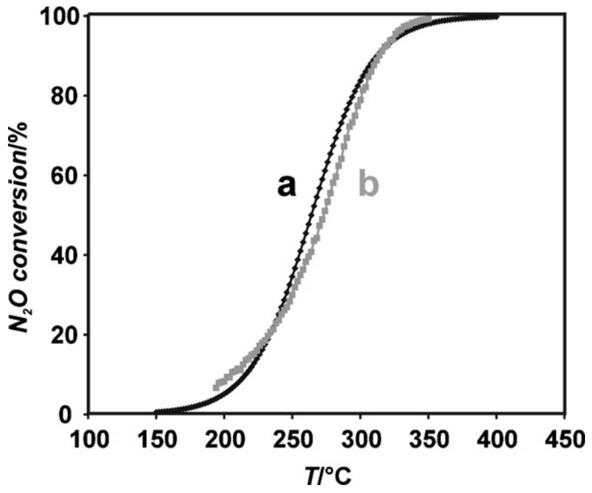

Fig. 2. Comparison of the deN_2O activity of the developed catalyst samples prepared in laboratory (a) and pilot (b) scales in model gas mixture (2000 ppm N_2O/N_2, GHSV = 20,000 h^{-1}) measured in the TPSR mode.

HR TEM images (Fig. 1d). The predominant rounded rhombicuboctahedral habit of the individual particles has been discussed in more detail elsewhere [21]. The distance between the clearly seen lattice fringes (d_{111} = 0.491 nm) correspond to those of the *Fd-3m* space group 227 of the cobalt spinel structure.

The comparison of the TPSR catalytic screening (conversion vs. temperature) of the laboratory and pilot scale prepared catalysts are shown in Fig. 2. Both curves remain in an excellent manual agreement indicating that the catalytic performance was well reproduced upon scaling up of the synthesis from gram to multikilogram level.

The catalyst stability test (T = 350 °C, GHSV = 10,000 h^{-1} and residual gas composition of 600–1200 ppm N_2O, 1400–1900 ppm NO_x, 0.5–1.0% H_2O, 1.1–1.9% O_2) showed that the investigated catalyst preserves its high initial activity for at least 20 days at the conversion level above 95% (Fig. 3). The observed undulation in the activity can be attributed to the changes in NO_x content. Indeed the catalytic data presented in Table 2 quantify the effect of variable NO_x content in the tail gases stream of the pilot plant on the spinel catalyst activity at GHSV of 20,000 h^{-1}. The increase of the NO_x concentration within the typical range of variation from 500 to 2700 ppm resulted in decrease of N_2O conversion by about 10%. To confirm this observation the laboratory experiments with the controlled inhibition of the reaction progress by NO_x were carried out on the crushed catalyst extrudates. As expected the addition of NO_x at the level of 1000 ppm to the feed (by stream switching) resulted in a gradual decline of the catalyst activity by 10% (Fig. 4a). This process, however, is reversible since upon cutting of the NO_x stream the initial N_2O conversion is gradually recovered (Fig. 4b). Complementary XPS measurements on the spent pilot-scale catalyst after the stability test revealed accumulation of the surface nitrogen in the form of nitrates as indicated by the characteristic N1s line at 407.1 eV. During the thermal treatment in the flow of helium at 250 °C in the attached preparation chamber the surface nitrogen species were completely depleted. The low stability of the surface nitrates is thus in line with the observed reversibility of the inhibition effect during the catalytic tests.

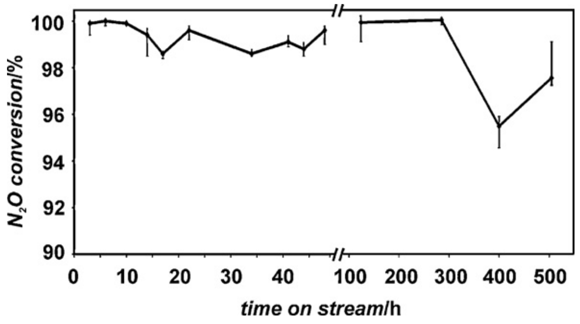

Fig. 3. The 20 days stability test of the final catalyst in pilot plant conditions (T = 350 °C, 200–4000 ppm NO_x + 0.3–1.5% H_2O + 0.6–2.5% O_2 + 500–1200 ppm N_2O, GHSV = 10,000 h^{-1}).

Table 2
Influence of the NO_x content on the N_2O conversion over spinel catalyst.

GHSV (h^{-1})	C_{NO_x} (ppm)	C_{N_2O} (ppm)	C_{H_2O} (vol.%)	C_{O_2} (vol.%)	N_2O conv. (%)
20,000	500	1170	0.50	1.10	96
20,000	1500	800	0.90	1.35	91
20,000	2700	420	0.50	2.40	87

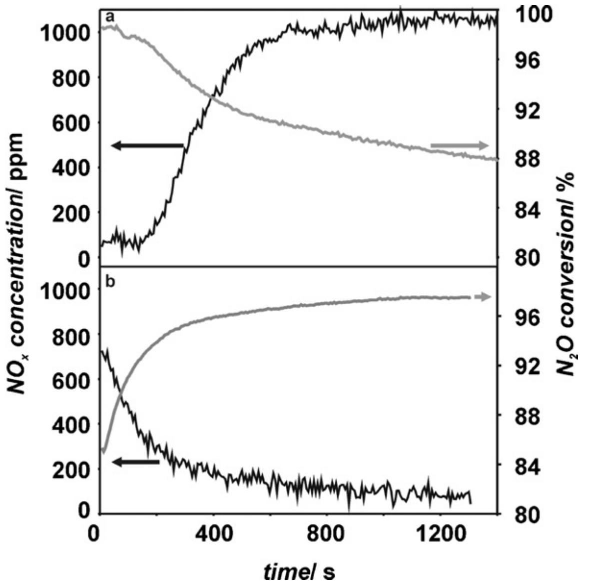

Fig. 4. The effect of NO_x on the N_2O conversion investigated at the laboratory scale on the crushed extrudates of the final catalyst upon addition (a) and removal (b) of 1000 ppm of the inhibitor (T = 350 °C, GHSV = 20,000 h^{-1}, residual gas composition: 1000 ppm NO, 1000 ppm N_2O in N_2).

4. Conclusions

The multicomponent spinel based catalyst was developed and manufactured at laboratory and pilot scale. The principal features of the final catalytic material were well reproduced upon the scale-up. The electron microscopic observations revealed that despite the large scale synthesis the uniform morphology at micro and nanoscale of the catalyst was preserved. The activity tests showed that the pilot scale prepared catalyst exhibits the same high activity (T = 350 °C, N_2O conversion >95%) as the laboratory samples. The composition and the preparation procedure of the spinel catalyst are subjects of several patent applications [20], and the further development of the industrial N_2O abatement technology based on the obtained catalyst is now in progress.

Acknowledgement

This work was supported by the project PZB-MEiN-3/2-2006.

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