

Nitrous oxide decomposition over $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ catalyst

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Abstract Nano-sized $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSFC3773) was prepared as a catalyst for nitrous oxide (N_2O) decomposition by a sonochemical method. The catalyst provided a complete conversion of N_2O at 450 °C, showing the best performance among most recent industrial catalysts, and offered 99.7–100% conversion at higher temperatures, e.g., 540–600 °C. A suitable operating temperature range for the reaction to avoid NO_x formation is from 400 to 600 °C. The activation energy and the pre-exponential factor were 42.96 kJ/mol and 161,135.35 mol/g_{cat} h bar. Oxygen inhibition was observed and was more obvious as the sample approached full surface coverage ($\theta = 1$) at 375 °C using a 100% N_2O feed. The reaction occurred via the Eley–Rideal mechanism. Two possible model mechanisms were suggested according to the experimental phenomenon and the rate coefficient order of each elementary steps.

Keywords Nitrous oxide decomposition · LSCF · Sonochemical synthesis · Eley–Rideal · Nanoparticles

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Introduction

N_2O is a powerful greenhouse gas (GHG) with 298–310 times greater global warming potential (GWP) than that of CO_2 , it can trap infrared energy from the sun and destroy the ozone layer in the stratosphere [1, 2]. The N_2O molecule is stable at room temperature and difficult to reduce under common thermodynamic conditions due to a very long lifetime in the atmosphere of approximately 150 years [3]. Under the Kyoto Protocol, industrialized countries agreed to reduce the emissions of six greenhouse gases (CO_2 , CH_4 , N_2O , HFCs, PFCs, SF_6) by 20% by 2020 [4, 5]. In industrial settings, nitrous oxide is an undesirable by-product from many chemical processes, such as nitric acid, adipic acid, caprolactam and acrylonitrile production plants [6, 7], which is used in an intermediate primarily to produce nylon and resins. There are numerous methods for industrial N_2O emissions abatement, such as thermal decomposition, selective adsorption, microwave plasma technology, and catalytic decomposition [8–10]. Direct thermal N_2O decomposition has an activation energy barrier of approximately 250–270 kJ/mol and is an exothermic reaction with an 82 kJ/mol heat of reaction [11]. However, this activation energy can be greatly reduced by using the proper catalyst; for instance, the activation energy was found to decrease from 250 to 270 kJ/mol in the non-catalytic process, to 87, 133.7 or 241 kJ/mol, when using CuO/CeO_2 , Fe-zeolite, or $\text{BaFeO}_{3-\delta}$ as a catalyst, respectively [12–14].

Catalysts are critical to reducing the activation energy, resulting in lower operating temperature and subsequently reduced operating costs. The catalysts used in the previous works are as follows: (i) noble metals such as metal oxide-supported Ru, Rh and Pd, (ii) transition metals over zeolite or other supported composites such as Cu-ZSM-5, Co, Fe-ZSM-5, Cu/Si-C, and (iii) mixed oxides with/without precious metals, such as Pd/LaFeO₃/Al₂O₃, RuO₂/Al₂O₃, LaMnO₃, LaCoO₃, LaFeO₃ and LaCoFeO₃ [15–27]. Among these types of materials, the mixed oxides have attracted the most attention recently due to its lower cost compared to noble metals and higher efficiency compared to transition metals over zeolite.

Perovskite (ABO_3) is a type of metal oxide that has drawn significant interest among other metal oxides in the past decade because they have a relatively high thermal stability, a high catalytic performance towards N_2O decomposition and are affordable compared to the other catalysts. In general, rare earth, alkaline earth, or alkali metals are normally chosen for the A site, while transition metals are chosen for the B site. The properties of the perovskites can be tailored based on purpose by (i) the selection/substitution of the A and B sites and (ii) the variation of the stoichiometry (x and y) of the A and B sites. Substitution of the A and B sites creates extrinsic point defects in the material (having A' and B' atoms added to the ABO_3 , causing a change in the oxidation state), which leads to intrinsic defects (oxygen atom is missing from its position in the crystal, creating an oxygen vacancy). This phenomenon establishes oxygen mobility, which leads to the ionic and electronic properties of the material and enhances its potential as a catalyst in the catalytic decomposition of N_2O [28–30].

The effect of the oxygen mobility and oxygen vacancy on the catalytic N_2O decomposition has been studied extensively [31–33]. Among these works, $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF3773) exhibited the highest value of oxygen non-stoichiometry ($\Delta\delta = 0.40$) compared to the other preferable stoichiometric ratios of the cations, i.e., LSCF4691 or LSCF4646, with cubic structure and a tolerance factor of approximately 0.9–1. LSCF3773, therefore, has a high redox capacity because of its high oxygen vacancies, oxygen storage capacity, and oxygen mobility. These properties are good for N_2O decomposition and other redox reaction processes.

In this work, LSCF3773 was selected because of it has the highest oxygen vacancies ($V_{\text{O}}^{\bullet}$), which are believed to be the active sites for N_2O decomposition. Nano-sized LSCF 3773 was prepared in-house by a sonochemical method. The N_2O feed composition was varied from 25 to 50, 75 and 100% to compare with other works [34–39] and to investigate the behavior of the reaction. The optimal operating temperature of LSCF3773 was found to be 450 °C with 100% complete conversion when the N_2O feed concentration was 50%. This is better than some of the most recent industrial processes, which provide 99.7–100% conversion at approximately 540–600 °C, respectively [34–39]. Kinetics parameters were achieved using an integral reactor model followed by differential analysis. The Eley–Rideal mechanism of the reaction was proposed according to the experimental phenomenon.

Experimental

Catalyst preparation

LSCF3773 was prepared using a sonication-assisted precipitation method [38]. A stoichiometric amount of the metal nitrate precursors; lanthanum (III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Fluka, 99.0%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, Himedia, 98.0%), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ajax, 98.0%), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Ajax, 98.0%), were mixed together according to the desired proportion. The precursors were dissolved in 70 V% ethanol ($\text{C}_2\text{H}_5\text{OH}$, Merck, 99.0%) under vigorous stirring in order to obtain a homogeneous solution. A 2 M sodium hydroxide solution (NaOH , Merck, 99.0%) was added dropwise to the precursor solution using a syringe pump until a pH value of 13–14 was reached, while the mixed solution was sonicated at 90 °C under high ultrasonic irradiation (Sonics Vibra Cell, titanium sonotrode) at 85% amplitude of 20 kHz, 750 W for 30 min. After the reaction was completed, the settling of the dark brown precipitate was formed in the solution. The resulting precipitate was then collected by centrifugation (MPW-223e, MED instrument) at 3500 rpm for 5 min, rinsed with distilled water repeatedly to remove the excess sodium compounds until the residue solution displayed a neutral pH value. The obtained material powder was dried overnight at 120 °C and calcined in air at 800 °C for 8 h to form a perovskite phase structure. The fine black LSCF powder was pelletized using 10 tons of hydraulic press (TMC HP 20) then crushed and sieved (Endecotts-7006354, Laboratory Test

Sieve). The size of the sieved catalyst ranged from 0.18 to 0.212 mm, giving a D to d_p ratio of 19–22 (> 10) to minimize any possible pressure drop and channeling [40].

Characterizations

The crystallinity of the prepared LSCF3773 was characterized by X-ray diffraction (XRD, Rigaku TTRAX III using Cu K_α radiation, $\lambda = 1.5418 \text{ \AA}$ in a range of $30^\circ < 2\theta < 80^\circ$ with a scanning step of 0.01°). The crystallite size was estimated using the Scherrer equation, $D = K\lambda/(\beta \cos \theta)$, where D is the mean size of the crystallites (nm), K is crystallite shape factor, λ is the X-ray wavelength, B is the full-width at half-maximum in radians of the X-ray diffraction peak, and θ is the Bragg angle. The morphology and particle size of the prepared material were investigated by field emission scanning electron microscopy (FE-SEM, JSM-7001F, JEOL at 20 kV). The specific surface area was determined using a nitrogen physisorption technique (BET, Quantachrome Autosorb-1).

Experimental set-up and procedures

All the catalytic N_2O decomposition experiments were operated at various temperatures under isothermal conditions in a tubular packed-bed quartz reactor (i.d. = 4 mm.) under atmospheric pressure. Before each run, the LSCF3773 was pretreated at 700°C in an Ar stream for 1 h to remove any possible adsorbed gases on the surface of the perovskite. The total volumetric flow rate of the reactant gas (F_T) was fixed at $100 \text{ mL}_N/\text{min}$ (which proved to ensure the rate controlling regime) using mass flow controllers (Brooks, model 4800). Ar was used for composition and as a carrier gas. The quartz tube reactor was placed vertically in an electric furnace with a 10 cm long heating zone. A type K thermocouple was put next to the reactor. The effluent gas stream was analyzed using an on-line gas chromatograph (Shimadzu GC-2014, TCD detector). A Molecular Sieve 13X and Porapak Q capillary column was used.

Results and discussion

Characterization

XRD pattern of the prepared LSCF3773 showed its high-purity perovskite crystalline phase indexed to cubic structure with no minor phase. A set of seven diffraction peaks was seen with 2θ peaks at $22.76, 32.44, 39.94, 46.54, 57.76, 67.82$, and 77.42 , as shown in Fig. 1. The pattern resembles the characteristic pattern of successfully synthesized LSCF3773 reported by other research [32]. The crystallite size of LSCF3773 was 20 nm, which was estimated from the highest peak of the XRD pattern using the Scherrer equation.

Fig. 2 indicates the morphological cylindrical-shaped polycrystalline structure of the synthesized LSCF3773 perovskite. From the result, agglomeration of the

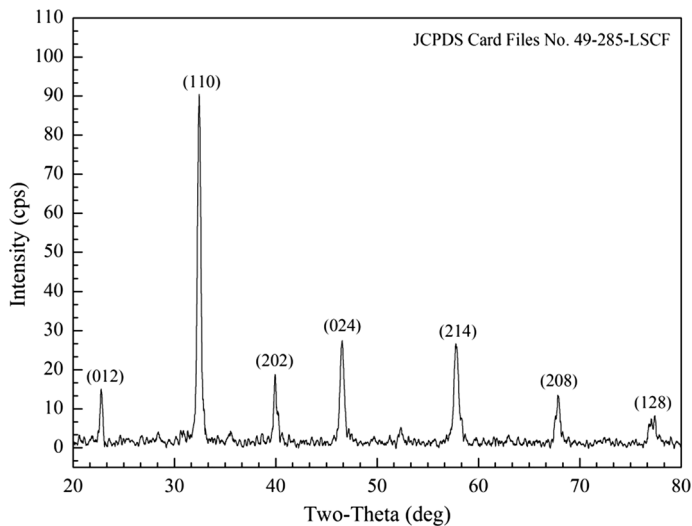


Fig. 1 X-ray diffraction patterns of LSCF3773 treated at 800 °C

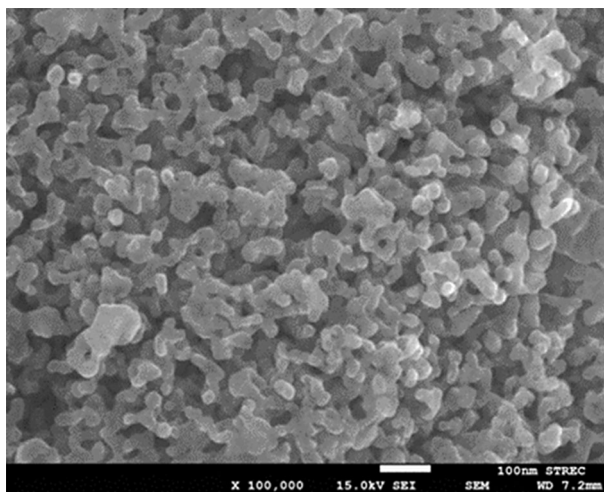


Fig. 2 SEM photographs of LSCF3773 perovskite (magnitude = 100,000)

particles was observed. The specific surface area of the material was measured by physical adsorption of gaseous N_2 on the material's surface where the volume of N_2 as a function of the relative pressure was determined. From the BET plot of the LSFC perovskite, the obtained results showed an estimated specific surface area of the material of $15 \text{ m}^2/\text{g}$.

Effect of temperature and effect of N₂O concentration in the feed stream

The influence of the N₂O concentration in the feed stream was studied, aiming to (1) understand the behavior of the reaction and (2) benchmark the process with the most recently available commercial processes of N₂O abatement technology for adipic acid manufacturing. The N₂O concentration in the tail gas of adipic acid manufacturing ranges from 23 to 57% [26, 34–41]. The low concentration of N₂O (0.1%) in the inlet gas stream was also studied, and this was designed for N₂O abatement for nitric acid plants rather than for adipic acid plants. Only DuPont used 100% N₂O in the inlet gas stream. In this research, 100 mg of the LSCF3773 was used as a catalyst in the decomposition of N₂O ($W_{\text{cat}}/F_{\text{N}_2\text{O},0}$ of 0.7467 g_{cat}.h/mol). The concentration of N₂O was varied from 25, 50 and 100% using Ar as a complementary gas, compared to commercial processes designed by BASF, Grande Paroisse and DuPont. The operating temperature was varied from 300 to 800 °C [26, 33–41].

The conversion of N₂O for all cases was initially detectable at 325 °C. LSCF3773 has a high sensitivity to change in the N₂O concentration in the temperature range from 300 to 500 °C. The primary observation was made for the effect of temperature on the conversion for all feed concentrations. The conversion was found to increase with increasing temperature because the reaction was more kinetically favored at higher temperatures, according to the Arrhenius temperature dependency equation. The conversion of N₂O was reported, as shown in Fig. 3, where generally a higher N₂O feed concentration caused greater conversion of N₂O. This was simply because a higher amount of the reactant was fed. However, the conversion order was 25% N₂O < 100% N₂O < 50% N₂O at temperatures of 375 °C and higher, which was likely influenced by oxygen inhibition in which the

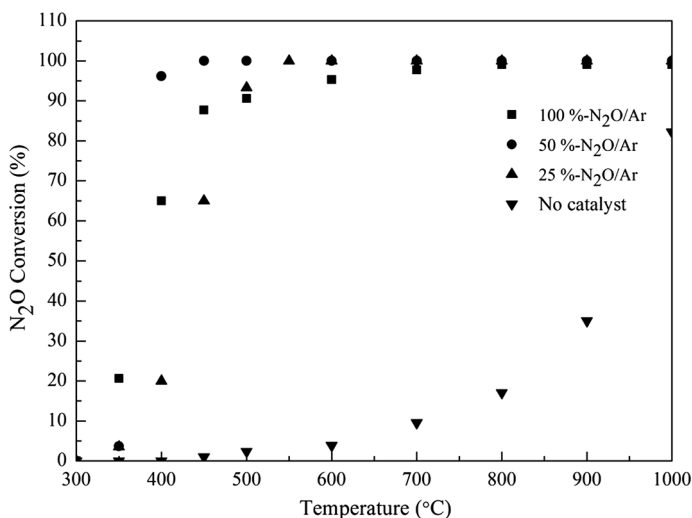
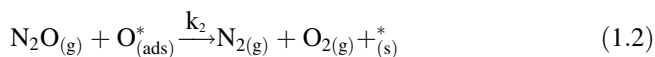
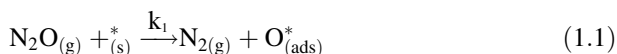


Fig. 3 N₂O conversion versus temperature curves at three different concentrations with 25, 50 and 100% N₂O/Ar (Total flow rate = 100 mL/min with WSHV = 0.7467 g_{cat} h/mol)

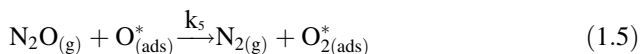
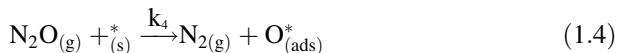
produced oxygen was being adsorbed back on the active sites and was competing with N_2O .

Oxygen inhibition occurred as the sample approached full surface coverage ($\theta = 1$). The increase in conversion started to slow down (for the 100% N_2O feed compared to 50% N_2O feed), which implied that O_2 competed with N_2O during the adsorption step, meaning that N_2O and O_2 are competitively adsorbed on the decomposition site (where N_2O adsorption and N_2O decomposition might occur on different active sites, e.g., adsorption-only sites and decomposition sites [25]). The N_2O adsorption then became the rate limiting step. The reaction occurred via the Eley–Rideal mechanism because the reaction was still going on after 375 °C despite the fact that the surface coverage was full. O_2 competed with N_2O during the adsorption step if the bonding dissociation energy of the gaseous O_2 molecule was weaker than that of the gaseous N_2O molecule. This was not always true because the bond dissociation energy of O_2 was 498 kJ/mol and that of N_2O was 222 and 590 kJ/mol for N–O and N=O, respectively [42–49]. Therefore, two model mechanisms were proposed here as follows:

Model 1



Model 2



From Fig. 3, the conversion was still increasing when the temperature increased but was less sensitive to the change in temperature. This means that the oxygen production step (reaction 2 in model 1 or reaction 6 in model 2) occurred at a higher rate than the oxygen re-adsorption step or oxygen inhibition step (reaction 3 in

model 1 and reaction 7 in model 2). Because the N_2O adsorption rate was inhibited by the O_2 adsorption rate (also evidenced by the drop in the N_2O conversion increase rate in the 100% N_2O feed), meaning that O_2 re-adsorption (reaction 3 in model 1 and reaction 7 in model 2) occurred faster than N_2O adsorption (reaction 1 for models 1 and reaction 4 for model 2). This leads to the following order of the rate coefficients for all the elementary steps: (i) for model 1, $k_2 > k_3 > k_1$ and (ii) for model 2, k_5 and $k_6 > k_7 > k_4$. Reaction 1 in model 1 and reaction 4 in model 2 was presumably suggested to be the rate limiting step for both models (reaction 1 is the same reaction as reaction 4, thus, $k_1 = k_4$).

In addition, complete conversion of N_2O could be achieved at as low as 450 °C when the feed concentration was 50%. This could be beneficial for adipic acid manufacturing, which has a high concentration of N_2O (~ 57%), and other manufacturing that has the same amount of the N_2O in the waste gas. From Fig. 3, this process using LSCF3773 showed better performance compared to the commercial process designed by Grande Paroisse, which offers the highest conversion of N_2O (99.7%) at 540 °C using Mordenite/ NH_4/Fe as a catalyst. For a 25% feed concentration, complete conversion was achieved at a higher temperature (550 °C) compared to that of the 50% N_2O feed. The 25% feed concentration can be useful for adipic acid plants who have a medium concentration of N_2O (~ 23%) in their tail gases and for other manufacturers that have the same amount of N_2O . This result is comparable to the result from BASF's N_2O abatement plants. Our process presumably offers 100% conversion, while BASF provides 99–99.9% conversion at temperatures ranging from 480 to 550 °C when using various types of mixed metal oxide catalysts. Fig. 3 shows the results from GC-2014 for the N_2O decomposition and the detectability at temperatures ranging from 300 to 500 °C. The results from temperatures from 600 to 800 °C were not included here as they were similar to the results at 500 °C. N_2O was not detectable at a reaction temperature from 400 °C and up, indicating that N_2O was 100% unless the N_2O level was less than the N_2O sensitivity of the GC. For the pure N_2O feed concentration (100%), DuPont technology reported achieving 98.5% conversion at 402 °C using CoO and NiO/ZrO_2 as a catalyst, while LSCF3773 gave the same conversion (98.5%) at a higher temperature, 700 °C. LSCF3773 is good for the 50% N_2O concentration feed and more suitable for treating the tail gas from adipic acid manufacturing which has a high concentration of N_2O in the tail gas.

Non-catalytic and catalytic N_2O decomposition using LSCF3773

The homogeneous non-catalytic (direct thermal decomposition) and heterogeneous catalytic N_2O decomposition using LSCF3773 was carried out for comparison purposes and is shown in Fig. 3. The conversion of both the catalytic and non-catalytic reaction were relatively very small at temperatures lower than 350 °C. At temperatures higher than 350 °C, LSCF3773 was found to significantly increase the activity of the reaction, compared to the non-catalytic reaction at the same temperature, which confirms that the activation energy of the reaction was reduced by the use of a catalyst. LSCF3773 was found to maximize the increase in the conversion from ~ 1 (non-catalytic) to 100% (catalytic) at 450 °C. A trace of

yellowish gaseous NO_x , as a by-product of N_2O decomposition, was found in the condenser at 800 °C and higher temperatures with or without catalyst use. The NO_x level was found to increase at higher temperatures. A lower operating temperature ranging from 400 to 600 °C is suggested for LSCF3773 to avoid NO_x production.

Kinetics

Rates

N_2O decomposition over perovskite is sensitive to the oxygen mobility at medium temperatures (300–600 °C) [41, 42]. The kinetics of the N_2O decomposition over LSCF3773 were examined at temperatures from 450 to 600 °C. Feed gas containing 50% N_2O in Ar was introduced to the top of the reactor. The catalyst weight was varied from 14.5 to 28.0, 42.5, and 56.0 mg to give different $W_{\text{cat}}/F_{\text{N}_2\text{O},0}$ values of 0.1083, 0.2091, 0.3173 and 0.4181 $\text{g}_{\text{cat}}/\text{mol}$. The rates of reaction, order of the reaction, activation energy and pre-exponential factor were achieved.

Apparent rate constant ($k_{\text{app}}(T)$) and order of the reaction (n)

Figure 4 represented rates of the reaction at each temperature. Both $k_{\text{app}}(T)$ and n were calculated and obtained by the graphical method shown in Fig. 5. The order of the reactions was slightly less than 1, varying from 0.7 to 0.8, for all temperatures. This indicates that oxygen inhibition was involved in the multi-step N_2O decomposition [26].

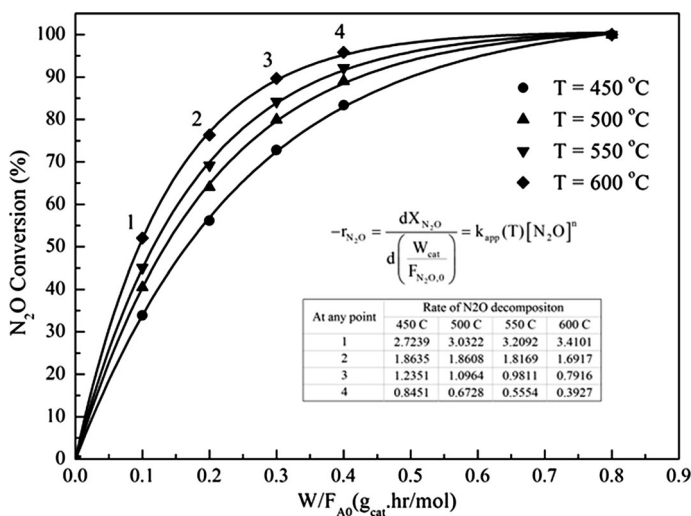


Fig. 4 N_2O conversion versus space time at various temperatures

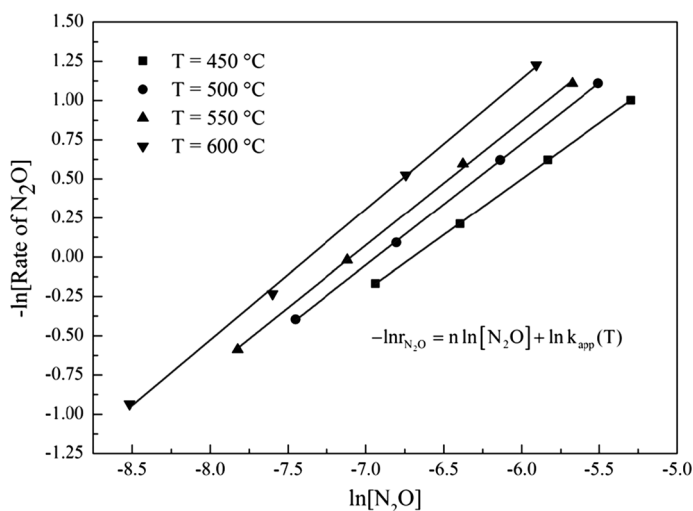


Fig. 5 The natural logarithm (ln) of the rate versus concentration of N₂O at different temperatures; **a** 450 °C, **b** 500 °C, **c** 550 °C and **d** 600 °C (total flow rate = 100 mL_N/min with 50% N₂O/Ar)

Activation energy (E_a) and frequency factor or pre-exponential factor (k_0)

E_a and k_0 were estimated. Fig. 6 shows the graph obtained by plotting $\ln k_{app}(T)$ against $1000/RT$.

From Fig. 6, the apparent activation energy and pre-exponential factors according to the Arrhenius plot for the temperature range of 450–600 °C were estimated to be 42.96 kJ/mol and 161,135.35 mol/g_{cat} h bar, respectively. E_a was

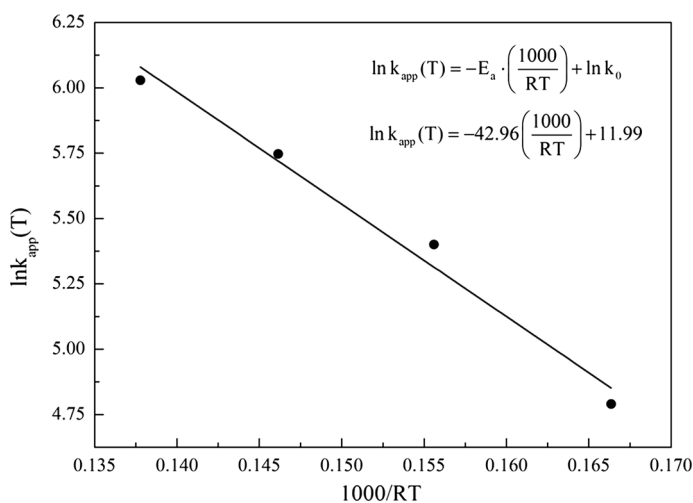


Fig. 6 Arrhenius plots of $\ln k_{app}(T)$ versus $1000/RT$ for the decomposition of N₂O in a temperature range of 450–600 °C

found to be lower than that of other catalysts invented by other works [12–14], indicating the good performance of LSCF3773 towards the N_2O decomposition.

Conclusion

Nano-sized LSCF3773 was successfully prepared using a sonication-assisted precipitation method and is a promising catalyst for N_2O decomposition. LSCF3773 showed better performance compared to other catalysts used in some of the most recent industrial processes, which provide 99.7–100% conversion at approximately 540–600 °C. LSCF3773 could be useful for adipic acid manufacturing, which often produces a high concentration of N_2O (40–57%). N_2O conversion values, rates and apparent rate constants increased with increasing operating temperatures according to the Arrhenius temperature dependency. Complete N_2O conversion (100%) was achieved at 450 °C when the N_2O composition in the feed was 50% and $W_{\text{cat}}/F_{\text{N}_2\text{O},0}$ was 0.7467 g_{cat}·h/mol. LSCF3773 maximizes the increase in conversion from a value of $\sim 1\%$ without the use of a catalyst use to 100% conversion in the presence of LSCF3773 at 450 °C. An operating temperature lower than 800 °C was recommended as NO_x was detected at higher temperatures. The activation energy and pre-exponential factor of the N_2O decomposition over LSCF3773 were 42.96 kJ/mol and 161,135.35 mol/g_{cat}·h bar, respectively. The activation energy was one of the lowest values compared to other previous works. This is possibly due to the large radius of La and Sr atoms, which are believed to cause an increase in the electron density of Co and Fe leading to a facilitated desorption of oxygen and an increase in oxygen mobility. Reaction order of the N_2O decomposition was slightly less than 1 due to the inhibition of the produced oxygen in the multi-step N_2O decomposition. Oxygen inhibition occurred when full surface coverage was presumably reached. This leads to the conclusion that the surface coverage approached 1 ($\theta = 1$) at 375 °C where the conversion of 100% N_2O started to be lower than that of the 50% N_2O feed, indicating that the disappearance of N_2O was limited by insufficient active sites. The conversions were still increasing during 375–400 °C despite the fact that the surface was fully covered. This confirms that the reaction occurs via the Eley–Rideal mechanism. In addition, the oxygen inhibition was believed to be the cause of Co use rather than La, Sr and Fe because of its oxygen binding energy, and therefore, substitution of the B site in LSCF3773 could be studied further to minimize the oxygen inhibition effect and enhance the catalytic activity of N_2O decomposition. Two model mechanisms were proposed according to the experimental phenomenon. The order of the rate coefficients was presumably $k_2 > k_3 > k_1$ for model 1 and k_5 and $k_6 > k_7 > k_4$ for model 2. The N_2O adsorption was suggested as the rate limiting step for both models. The detailed mechanism of N_2O decomposition could be achieved using a N_2O pulse injection decomposition technique. Temperature programmed desorption of oxygen could be carried out in order to prove that the Langmuir–Hinshelwood mechanism was not involved.

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References

- Li T, Rabuni MF, Kleiminger L, Wang B, Kelsall GH, Hartley UW, Li K (2016) *Energy Environ Sci* 9:3682–3686
- Seinfeld JH, Pandis SN (1998) *Atmospheric Chemistry and Physics from air pollution to climate change*. Wiley, New York
- Anderson B, Bartlett K, Froking S, Hayhoe K, Jenkins J, Salas W (2010) Methane and nitrous emissions from natural sources, EPA 430-R-10-001. EPA, Washington DC
- Breidenich C, Magraw D, Rowley A, Rubin JW (1998) *Am J Int Law* 92:315–331
- Eurostat Statistics Explained (2017) Greenhouse gas emission statistics—emission inventories. <http://ec.europa.eu>. Accessed 30 Mar 2017
- Perez-Ramirez J, Kapteijn F, Schoffele K, Moulijn JA (2003) *Appl Catal B* 44:117–151
- Shimizu A, Tanaka K, Fujimori M (2000) *Chemosphere-Global Change Sci* 2:425
- Centi G, Generali P, Dall'Olio L, Perathoner S, Rak Z (2000) *Ind Eng Chem Res* 39:131
- Wojtowicz MA, Miknis FP, Grimes RW, Smith WW, Serio MA (2000) *J Hazard Mater* 74:81
- Kapteijn F, Rodriguez-Mirasol J, Moulijn JA (1996) *Appl Catal B* 9:25
- Lide DR (1995) *Handbook of chemistry and physics*, 76th edn. CRC Press, Florida
- Zabilskiy M, Djinovic P, Tchernychova E, Tkachenko OP, Kustov LM, Pinta A (2015) *ACS Catal* 5:5357–5365
- Perbandt C, Bacher V, Groves M, Schwefer M, Siefert R, Turek T (2013) *Chem Ing Tech* 85:705–709
- Huang C, Zhu Y, Wang X, Liu X, Wang J, Zhang T (2017) *J Catal* 347:9–20
- Zeng HC, Pang XY (1997) *Appl Catal B* 13:113–122
- Yuzaki K, Yarimizu T, Aoyagi K, Ito S, Kunimori K (1998) *Catal Today* 45:129–134
- Yuichi O, Kazushi K, Ming B, Tatsuo M (1999) *J Chem Phys* 110:8221–8224
- Stoeva N, Atanasova G, Spassova I, Nickolov R, Khristova M (2016) *Reac Kinet Mech Cat* 118:199–214
- Ciambelli P, Benedetto AD, Garufi E, Pirone R, Russo G (1998) *J Catal* 175:161–169
- Cruz RS, Mascarenhas AJS, Andrade HMC (1998) *Appl Catal B* 18:223–231
- Scher M, Kesore K, Monnig R, Schwiager W, Tessler A, Turek T (1999) *Appl Catal A* 184:249–256
- Ivanova DV, Pinaeva LG, Sadovskaya EM, Isupova LA (2016) *J Mol Catal A* 412:34–38
- Dacquin JP, Lancelot C, Dujardin C, Costa PD, Djega-Mariadassou G, Beaunier P, Kaliaguine S, Vaudreuil S, Royer S, Granger P (2009) *Appl Catal B* 91:596–604
- Medkhalil AHA, Narasimharao K, Basahel SN, Mokhtar M (2014) *J Memb Separ Tech.* 3:206–212
- Wu Y, Cordier C, Berrier E, Nuns N, Dujardin C, Granger P (2013) *Appl Catal B* 140–141:151–163
- Li K, Wang XF, Zeng HC (1997) *Chem Eng Res Des* 75:807–812
- Akihiro T, Hisahiro E, Yasutake T (2015) *Reac Kinet Mech Cat* 114:409–420
- Kapteijn F, Rodriguez-Mirasol J, Moulijn JA (1996) *Appl Catal B* 9:25
- Swamy CS (1996) Christopher. *J Catal Rev Sci Eng* 34:409–425
- Arai H, Yamada T, Eguchi K (1986) Seiyama. *Appl Catal* 26:265–276
- Beaurain A, Dujardin C, Granger P (2012) *Appl Catal B* 125:149–157
- Ivanov DV, Sadovskaya EM, Pinaeva LG, Isupova LA (2009) *J Catal* 267:5–13
- Russo N, Mescia D, Fino D, Saracco G, Specchia V (2007) *Ind Eng Chem Res* 46:4226–4231
- Alini S, Basile F, Blasioli S, Vaccari A (2005) *Appl Catal B* 70:323–329
- Babiniec SM, Coker EN, Miller JE, Ambrosini A (2015) *Sol Energy* 118:451–459
- Franken T, Palkovits R (2015) *Appl Catal B* 176–177:298–305
- Technical Note (2012) BASF-The Chemical Company, New Jersey. www.catalysts.basf.com. Accessed Feb 2012
- Zhang R, Hua C, Wang B, Jiang Y (2016) *J Catal* 6:200
- Alini S, Basile F, Blasioli S, Rinaldi C, Vaccari A (2007) *Appl Catal B* 70:323–329
- Charoonsuk T, Vittayakorn W, Vittayakorn N, Seeharaj P, Maensiri S (2015) *Ceram Int* 41:S87–S94
- Russo N, Fino D, Saracco G, Specchia V (2007) *Ind Eng Chem Res* 119:228–232

42. Shimizu A, Tanaka K, Fujimori M (2000) *Chemosphere-Global Change Sci* 2:425–443
43. Berger RJ, Pérez-Ramírez J, Kapteijn F, Moulijn JA (2002) *J Chem Eng* 90:173–183
44. Kapteijn F, Rodríguez-Mirasol J, Moulijn JA (1996) *Appl Catal B* 9:25–64
45. Ivanov DV, Pinaeva LG, Sadovskaya EM, Isupova LA (2016) *J Mol Catal A* 412:34–38
46. Leglise J, Petunchi JO, Hall WK (1984) *J Catal* 86:392–399
47. Monshi A, Foroughi MR, Monshi MR (2012) *World J Nano Sci Eng* 2:154–160
48. Mieda H, Mineshige A, Saito A, Yazawa T, Yoshioka H, Mori R (2014) *J Power Sources* 272:422–426
49. Da Conceicao L, Silva A, Ribeiro NFP, Souza MMVM (2011) *Mater Res Bull* 46:308–314