Catalysis Communications 106 (2018) 40–43

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Apparent activation energies and reaction rates of N_2O decomposition via different routes over Co_3O_4

Haibiao Yu, Xinping Wang*

State Key Laboratory of Fine Chemical, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Keywords:
Apparent activation energy
L-H reaction route
E-R mechanism
N_2O decomposition
Co_3O_4

ABSTRACT

Apparent activation energies and reaction rates of N_2O decomposition via L-H and E-R routes over Co_3O_4 were experimentally estimated after considering the increase of active sites with reaction temperature. It was found that the apparent activation energy is 32.9 kJ/mol for the L-H route and 44.8 kJ/mol for the E-R route, while the order of reaction with respect to O_2 is − 0.367 at 350 °C and − 0.338 at 450 °C. The contribution of the E-R route to the total reaction rate was found to be considerably increased with the reaction temperature and which was well interpreted by the apparent activation energies of the two reaction routes.

1. Introduction

Nitrous oxide (N_2O) is not only responsible for the greenhouse effect but also contributes to the destruction of the stratospheric ozone layer [1,2]. Thus, effectively eliminating N_2O release in the atmosphere, in particular N_2O emissions in the tail gas of nitric and adipic acid plants by catalytic decomposition at low-temperatures becomes one of the important topics in the field of environmental catalysis. For the N_2O catalytic decomposition over alkaline-earth metal oxides, transition metal oxides as well as their composite oxides, the reaction mechanism involving the following three basic elementary steps is widely accepted [1,3–7]:

$$N_2O + * \rightarrow O* + N_2 \quad (1)$$

$$2O* \leftrightarrow O_2 + 2* \quad \text{(L-H)} \quad (2)$$

$$N_2O + O* \rightarrow O_2 + N_2 + * \quad \text{(E-R)} \quad (3)$$

Herein, symbol "*" denotes an active site of the catalyst, i.e. some type of oxygen vacancies over the catalyst capable of taking away the oxygen atom from the N_2O molecule at reaction temperature. When the reaction temperature is increased over a large range, the oxygen vacancies acting as active sites might be changed in their entity. For instance, as reported by Zasada and coworkers [8,9], when the reaction temperature is lower than 450 °C, surface oxygen vacancies play the role of abstracting the oxygen from the N_2O and when the temperature is increased up to 500 °C, lattice oxygen vacancies become the active sites. Accordingly, the active site recovery is changed from the suprafacial oxygen recombination to interfacial cross oxygen recombination. Thus, steps (I) and (II) constitute a complete N_2O catalytic decomposition cycle A, as described in Fig. 1. Apparently, step (III) also provides the active sites for step (I), thus these two elementary steps describe cycle B (Fig. 1).

As the reaction could occur via the two different reaction routes, knowing the corresponding individual apparent activation energy and the reaction rate at given reaction conditions becomes quite important for the design and development of more active catalysts. Recently, the activation energies for the N_2O decomposition via the two routes mentioned above over alkaline-earth metal oxides have been studied by theoretical calculations [10,11]. Pettersson et al. [10] found that the activation energy for route A ($E_{a,\,A}$) is generally dependent on the O—O distance of the alkaline earth metal oxide, while the activation energy for route B ($E_{a,\,B}$) is a function of the atomic oxygen surface coverage over the oxide surface. In the case of MgO, the $E_{a,\,A}$ and $E_{a,\,B}$ were found to be 19.6 and 34.8 kcal/mol, respectively, whereas those over CaO were 39.3 and 31 kcal/mol, respectively. It was also suggested that the reaction over SrO and BaO can only be carried out through route B, due to the long O—O distance. Most recently, Piskorz et al. [11] reported that the $E_{a,\,A}$ and $E_{a,\,B}$ over SrO were 56.1 and 26.9 kcal/mol, respectively, which is in agreement with the work of Pettersson et al. [10] that the $E_{a,\,A}$ depends on the O—O distance.

Due to the outstanding catalytic performance of the cobalt-based catalysts in the present reaction, the apparent E_a over Co_3O_4 has been determined experimentally by many researchers [12–19]. However, no individual apparent activation energies related to the different reaction routes were reported yet, likely due to the following reasons. First, the reaction rate via a given route among other routes is hard to be estimated, and secondly the M-O bond strength follows a distribution for the transition metal oxides (M_xO_y), which depends on the type of M_xO_y

---

* Corresponding author.
E-mail address: dllgwxp@dlut.edu.cn (X. Wang).

https://doi.org/10.1016/j.catcom.2017.12.004
Received 7 September 2017; Received in revised form 3 December 2017; Accepted 7 December 2017

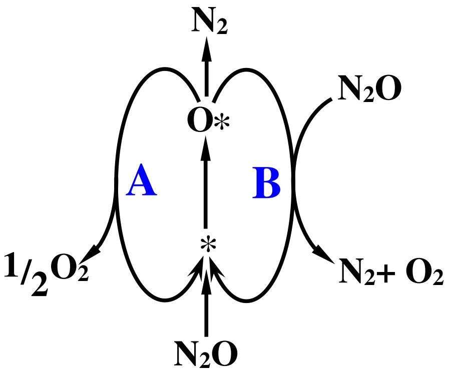

Fig. 1. Reaction cycles in the catalytic N_2O decomposition.

and the preparation conditions [20,21]. The latter makes the concentration of *active sites* participating in the reaction path to increase with reaction temperature, and, therefore, use of the Arrhenius equation is hard to be applied for determining the correct E_a.

The present work is focused on the determination of the reaction rates of N_2O decomposition via the two routes over a Co_3O_4 catalyst at different reaction conditions, as well as the corresponding apparent activation energies, where the increase in the concentration of active sites with reaction temperature was taken into account for the first time.

2. Experimental

The Co_3O_4 sample was prepared by the precipitation method as previously reported [19]. O_2-TPD and N_2O-TPSR experiments were performed in a quartz flow-reactor using 0.2 g of catalyst. The sample was pretreated in situ at 500 °C in Ar flow for 20 min, and then cooled down to 50 °C in 15 vol% O_2/Ar flow. The gas was then switched to Ar (O_2-TPD) or 2000 ppmv N_2O/Ar (N_2O-TPSR) at the flow rate of 100 mL/min. When the baseline became stable, the transient gas concentration profiles were recorded with temperature at the ramp rate of 10 °C/min using a quadruple mass spectrometer (Pfeiffer Vacuum GSD 301) as detector, monitoring the m/z = 44 (N_2O), 32 (O_2), and 28 (N_2) mass numbers. Kinetic rate measurements of the reaction over the Co_3O_4 catalyst were conducted as reported in our previous studies [19]. To ensure that the conversion of N_2O in the gas mixture 2000 ppmv N_2O, 0–30 vol% O_2/Ar fall in the range of 8–15%, an appropriate amount of catalyst (0.007–0.450 g; 60–80 mesh) was used.

3. Results and discussion

3.1. The effect of O_2 in the feed gas stream on reaction rate

For the reaction route A, since it is controlled by step (II) [22,23], step (I) would easily take place on the catalyst surface, as long as the oxygen vacancies can be regenerated by step (II) or step (III). This means that the temperature at which an active site participates in the reaction via route A must be associated with the temperature at which the active site, occupied by oxygen, could be regenerated by releasing the oxygen atom. As shown in Fig. 2, two overlapped oxygen desorption peaks, which are centered at 220 and 420 °C appear in the O_2-TPD over the Co_3O_4. Clearly, the former (T_M = 220 °C) is due to oxygen desorption from weakly bonded O species and the latter (T_M = 420 °C) is due to the oxygen recombination from suprafacial O species over the catalyst, according to the literature [8,24]. On the other hand, the TPSR of N_2O decomposition over the Co_3O_4 shows that the reaction begins at about 270 °C and the reaction rate is significantly increased with the temperature. These results are in agreement with the literature [8,24] that the sites accommodating weakly bonded O species do not participate in the reaction. Octahedral cobalt cations (Co*) were reported to be the active sites, in the form of Co^{4+} or Co^{3+}, when N_2O decomposition or suprafacial atomic oxygen species recombination occurs in the 300–500 °C range [9,25]. This means that the amount of O_2 desorption in the 270–500 °C range of the O_2-TPD has a direct relation with the population of active sites.

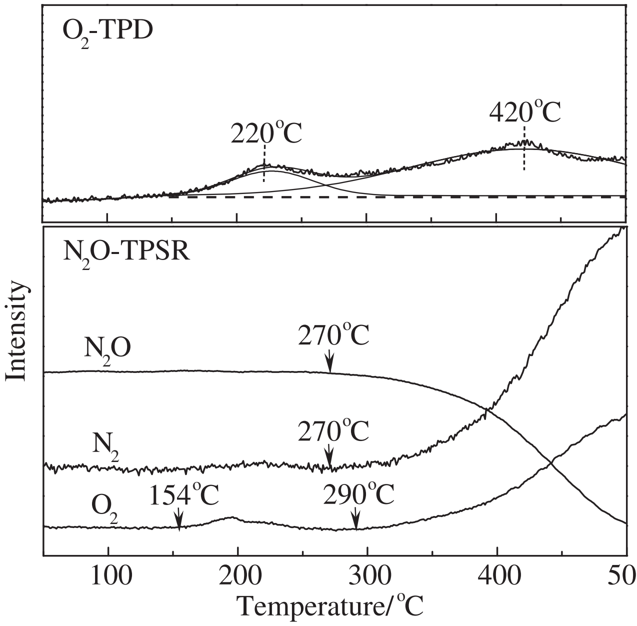

Fig. 2. O_2-TPD and N_2O-TPSR on the Co_3O_4 catalyst.

Fig. 3 presents the specific reaction rate, r_s (μmol s^{-1} $g_{cat.}^{-1}$), at 350, 400 and 450 °C over Co_3O_4 as a function of the O_2 partial pressure (p_{O2}) in the feed stream. With the p_{O2} increasing in the range of 0–0.3 atm, the r_s at each temperature steeply declines and finally takes a definite constant value. For instance, at 350 °C, the r_s is 0.14 μmol s^{-1} $g_{cat.}^{-1}$ for the feed stream of 2000 ppmv N_2O/Ar, while it decreases to 0.06 μmol s^{-1} $g_{cat.}^{-1}$ when the p_{O2} exceeds 0.2 atm. Herein, it can be considered that the inhibition effect of O_2 on the N_2O decomposition must arise from the O_2 adsorption on the surface Co* vacancies (Co^{3+}), as shown by the backward step of the reversible step (II) [26]. Accordingly, the constant values of r_s obtained at extreme large p_{O2} at each temperature should be resulted from the fact that nearly all surface Co^{3+} are occupied by oxygen atoms on the catalyst surface and thereby, route A is entirely blocked.

On the other hand, with the O_2 concentration increasing in the range of 0–0.3 atm, the concentration of Co^{4+}–O suprafacial species over the catalyst surface must be increased, which in turn leads to an increasing rate of step (III), r_{III}, in principle. Nevertheless, as the reaction rate associated with route A is controlled by the oxygen atoms recombination, step (II) [22,23], it can be considered that almost all the active sites on the catalyst surface are occupied by oxygen, even for the case of O_2-free conditions at the lower temperature. This means that the increase of r_{III} with increasing O_2 concentration is negligible. Therefore, it can be further deduced that the r_{III} for the reaction at 350 °C under the O_2-free conditions is approximately 0.06 μmol s^{-1} $g_{cat.}^{-1}$, and the approximate reaction rate via step (I), r_I at this temperature is 0.08 μmol s^{-1} $g_{cat.}^{-1}$, according to the formula: $r_I = r_s - r_{III}$. In the same way, the approximate reaction rates r_I and r_{III} at 400 and 450 °C were also obtained, as shown in Table 1.

3.2. The apparent activation energies for the specific reaction routes A and B

In general, for a given catalytic reaction over a stable solid catalyst