

Kinetics and mechanism of NO decomposition over $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ perovskite-type oxides

Junjiang Zhu^{a,b}, Dehai Xiao^a, Jing Li^a, Xiangguang Yang^{a,*}, Yue Wu^a

^a Environment Catalysis Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b Graduate Schools of Chinese Academy of Sciences, Beijing 100039, PR China

Received 28 February 2005; received in revised form 23 April 2005; accepted 24 April 2005

Available online 25 May 2005

Abstract

Perovskite-type oxide $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ showed high activity for NO decomposition and thus was taken as the catalyst for investigation. Based on the ‘recycle’ mechanism of NO decomposition (NO_2 acts as an intermediate of O_2 formation) we reported recently, the kinetics of NO decomposition over $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ was investigated. The NO decomposition rate was practically first-order for NO in the range 0.5–2.0 vol.% NO/He, while the reaction order varied from -0.24 to -0.08 for O_2 (0–6 vol.% O_2 /He), depending on the temperature. The kinetics deduced from the ‘recycle’ mechanism accords well with that observed in practice by introducing the item $K_{-6} (K_{-7})^{1/2} P_{\text{NO}} (P_{\text{O}_2})^{1/2}$, which reflects the reciprocity of O_2 and NO in the reaction and is introduced in the kinetics for the first time. The rates and NO_2 dissociation equilibrium constants calculated from the practical reaction certified that NO_2 dissociation is indeed an important step of NO decomposition, and hence suggested that the ‘recycle’ mechanism is believable.

© 2005 Elsevier B.V. All rights reserved.

Keywords: NO; Direct decomposition; Perovskite-type oxide; $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$; Kinetics

1. Introduction

NO_x removal from various combustion sources is one of the urgent tasks in environmental catalysis, because of the harm NO_x caused [1]. Although several NO reduction technologies have been proposed and have obtained great success over the years [2–5], they became more challenging as lean-burn strategies were used to increase energy efficiency. On the other hand, direct decomposition of NO into N_2 and O_2 ($2\text{NO} = \text{N}_2 + \text{O}_2$) is considered to be the most ideal reaction for NO_x removal, because NO is thermodynamically unstable related to N_2 and O_2 at temperatures below 1000°C and the reaction itself is quite simple so that no reducing agents are required [6].

Perovskite-type oxides have attracted much attention as one kind of interesting catalysts for NO removal, since

the earlier studies of Libby [7] and Voorhoeve et al. [8]. Many mechanisms and kinetics have been established [9–12] to interpret the process of NO decomposition over perovskite-type catalysts. In all the mechanisms and kinetics proposed previously, it was considered that the way of NO_2 and O_2 formation was occurred through the reactions of $\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons \text{NO}_{2(\text{g})}$ and $\text{O}_{(\text{a})} + \text{O}_{(\text{a})} \rightleftharpoons \text{O}_{2(\text{g})}$, respectively. However, according to our recent work [13] NO decomposition might occur in a recycle way, i.e., the way of O_2 and NO_2 formation was occurred through the reactions of $\text{NO}_{(\text{a})} + \text{O}_{(\text{a})} \rightleftharpoons \text{NO}_{2(\text{a})}$ and $2\text{NO}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})}$, we also have the trend to deduce the kinetics of NO decomposition over the perovskite-type catalysts and illuminate the validity of the ‘recycle’ mechanism.

The kinetics was deduced based on the assumption that the NO decomposition rate obeyed the equation: $r = k [\text{NO}]^m [\text{O}_2]^n$, where r is the NO decomposition rate; k the rate constant; m and n the apparent reaction order of NO and O_2 , respectively. The deduced kinetics indicated that NO

* Corresponding author. Tel.: +86 431 5262228; fax: +86 431 5685653.
E-mail address: xgyang@ciac.jl.cn (X. Yang).

decomposition rate was practically first-order for NO in the range 0.5–2.0 vol.% NO/He, while the reaction order varied from -0.24 to -0.08 for O₂ (0–6 vol.% O₂/He), depending on the temperature. Besides, it is worthwhile to point out that the item $K_{-6} (K_{-7})^{1/2} P_{\text{NO}} (P_{\text{O}_2})^{1/2}$, which reflects the reciprocity of O₂ and NO in the reaction, was introduced in the kinetics based on the ‘recycle’ mechanism. This is interesting since the reciprocity of NO and O₂ in the reaction is unavoidable. Most of all, the deduced kinetics was in well accordance with that observed in practice, which suggested that the ‘recycle’ mechanism is believable and thus a new way of NO decomposition might occur.

2. Experimental

La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ was prepared by citrate method as described elsewhere [14]. Briefly, to an aqueous solution of La³⁺, Sr²⁺, Mn²⁺, and Ni²⁺ nitrates (all obtained from Beijing Chemical Co.) with appropriate stoichiometry, a solution of citric acid 50% in excess of stoichiometry was added. The resulting solution was evaporated to dryness, and then the precursors obtained were decomposed in air at 300 °C, calcined at 600 °C for 1 h and finally palletized and calcined at 900 °C in air for 6 h. The product was identified as having the perovskite structure by powder X-ray diffraction analysis (see Fig. 1).

Steady-state activities of the catalyst were evaluated using a single-pass flow micro-reactor made of quartz, with an internal diameter of 6 mm. The reactant gas was passed over 0.5 g catalyst (0.5–2.0 vol.% NO/He) at a rate of 25 mL/min or 0.8 g catalysts (1% NO + 1–6% O₂/He) at a rate of 40 mL/min (to keep W/F = 1.2 g s mL⁻¹). The gas composition was analyzed before and after the reaction by an online gas chromatography, using molecular sieve 5A column for separating NO, N₂, and O₂. N₂O was not analyzed because

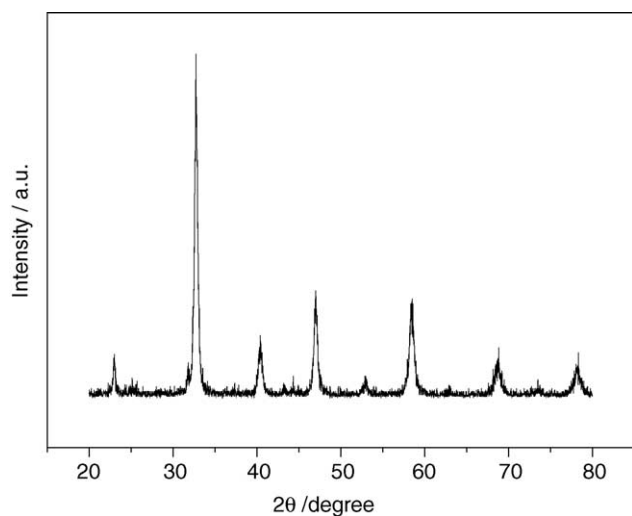


Fig. 1. X-ray diffraction patterns of La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ perovskite oxides.

it was difficult to form between 500 and 850 °C as reported by Teraoka et al. [15]. Before the data were obtained, reactions were maintained for a period of ~ 2 h at each temperature to ensure the steady-state conditions. The activity was calculated as follows: $\text{N}_2 \text{ yield} = \frac{2[\text{N}_2]_{\text{out}}}{[\text{NO}]_{\text{in}}}$, where $[\text{NO}]_{\text{in}}$ and $[\text{N}_2]_{\text{out}}$ are the inlet and outlet concentration of NO and N₂, respectively.

3. Results and discussion

3.1. Catalytic activity for NO decomposition

Table 1 lists the activity of La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃, La_{0.8}Sr_{0.2}CoO₃, and La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ for NO decomposition, the former two catalysts were considered to be active for NO decomposition as reported by Ishihara et al. [12] and Teraoka et al. [10], respectively. La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ showed far higher activity for NO decomposition when they were carried out in the same conditions, indicating that La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ is a more promising candidate for NO decomposition at elevated temperatures. Therefore, La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ was chosen to be the catalyst for investigating the NO decomposition reaction in this study.

3.2. Effects of reaction condition on NO decomposition

For the determination of the reaction orders, a power rate law was assumed; this was written as: $r = k [\text{NO}]^m [\text{O}_2]^n$, where $[\text{NO}]$ and $[\text{O}_2]$ were the concentrations of NO and O₂ (when O₂ was added) in the feed gas, respectively; m and n the apparent reaction order of NO and O₂, respectively. Thus, to determine the reaction order for NO, values of $\ln(r)$ were plotted versus $\ln[\text{NO}]$. The concentration was varied in the feed while keeping the total flow rate constant. Similarly, to determine the reaction order for O₂, streams of NO/He and O₂/He were mixed inside the furnace and near the catalyst bed. The values of $\ln(r)$ were plotted against $\ln[\text{O}_2]$ while keeping the total flow and the partial pressure of NO in the mixed NO/O₂/He stream constant.

Fig. 2 shows the N₂ formation rate as a function of NO partial pressure at different temperatures. It is obvious that the N₂ formation rate increased monotonically with the increase of

Table 1
Comparative activities of NO decomposition (in the absence of oxygen) over the catalysts

Catalyst	BET surface area (m ² /g)	Space velocity (W/F: g s mL ⁻¹)	N ₂ yield (%) (T = 800 °C)
La _{0.4} Sr _{0.6} Mn _{0.8} Ni _{0.2} O ₃ ^a	6.4	1.2	54
La _{0.7} Ba _{0.3} Mn _{0.8} In _{0.2} O ₃ ^b	8.0	1.2	27
La _{0.8} Sr _{0.2} CoO ₃ ^c	4.6	1.2	25

^a In this study.

^b Data obtained from Ref. [12].

^c Data obtained from Ref. [10].

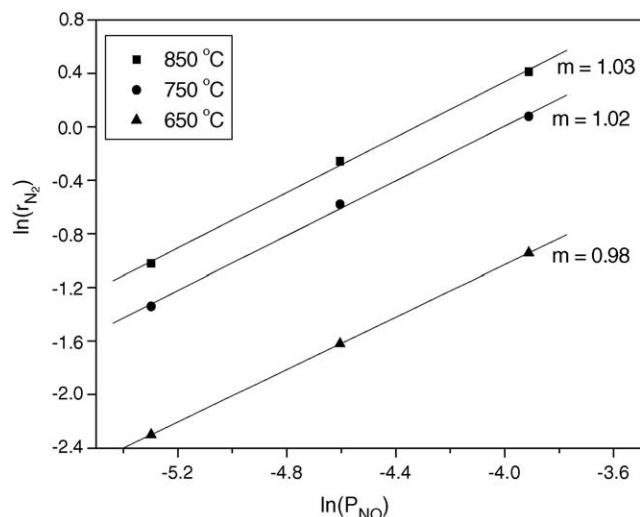


Fig. 2. N₂ formation rate on La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ as a function of NO partial pressure at different temperatures.

NO partial pressure and the reaction order of NO at different temperature ranges is similar ($m \sim 1$), indicating that NO partial pressure facilitates NO decomposition to occur with the reaction order of 1 at temperature range of 650–850 °C (NO concentrations varied from 0.5 to 2%). This is in accordance with the results reported by Teraoka et al. [10]. Fig. 3 shows the N₂ formation rate as a function of oxygen partial pressure at different temperatures. In contrast to the effects of NO partial pressure, the N₂ formation rate decreased monotonically with the increase of oxygen partial pressure, indicating that the oxygen has negative effect on NO decomposition. The reaction order of O₂ is various at different temperatures and increased with the increase of temperature (from $n = -0.24$ at 650 °C to $n = -0.08$ at 850 °C), indicating that mitigation of the inhibitory action of O₂, which is one of the great demands for NO decomposition reaction, would be

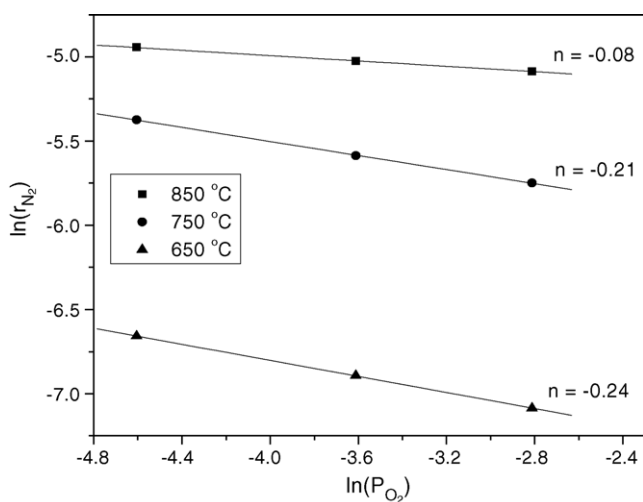


Fig. 3. N₂ formation rate on La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ as a function of O₂ partial pressure at different temperatures.

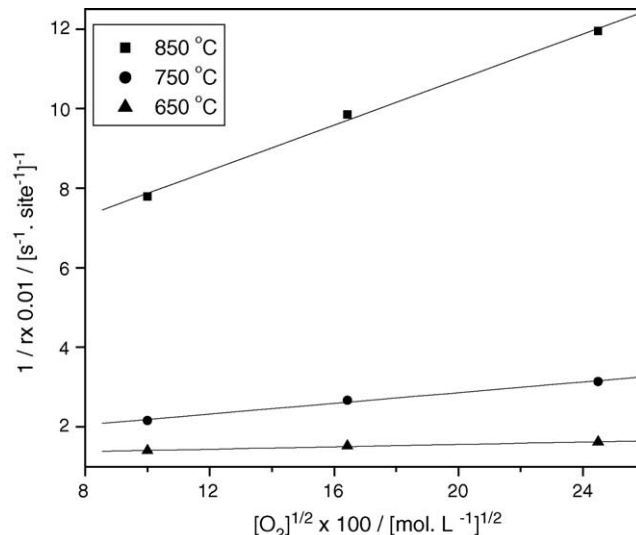


Fig. 4. Relationships between the reciprocal rate ($1/r$) and the square root of O₂ concentration ($[O_2]^{1/2}$) on La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃. Data were taken from Fig. 3.

attained by the high temperature operation. This is also in agreement with the results reported by Teraoka et al. [10]. The reason might be that the high temperature facilitates the NO₂ dissociation reaction to occur.

Interestingly, by plotting the function of $1/r$ and $[O]^{1/2}$, as shown in Fig. 4, it is seen that the reciprocal of the rates increased linearly with the square root of the oxygen partial pressure, suggesting that the apparent reaction order of O₂ could be taken as -0.5 . Based on these results, the rate equation of NO decomposition reaction on La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ can be written as:

$$r = \frac{k[\text{NO}]}{1 + K[\text{O}_2]^{1/2}} \quad (\text{R0})$$

Where conventionally, r is the turnover rate in units of $[\text{s}^{-1} \text{site}^{-1}]$, k the rate constant in units of $[\text{s}^{-1} \text{site}^{-1} (\text{mol L}^{-1})]$, and K is the equilibrium constant of NO₂ dissociation on the catalytic sites in units of $[\text{mol L}^{-1}]^{-1/2}$. The concentrations of NO and O₂ are in units of $[\text{mol L}^{-1}]$. The rate constants and the NO₂ dissociation equilibrium constants listed in Table 2 are the results of our experimental determinations over La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃. It is seen that the NO₂ dissociation equilibrium constant is an important term in the rate equation, indicating that NO₂

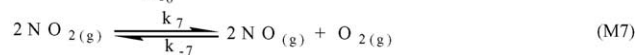
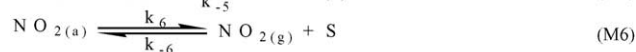
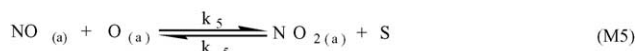
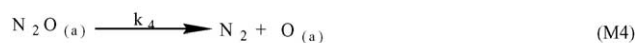
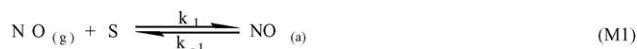
Table 2
The rates and NO dissociation equilibrium constants

T/K	k ^a	K ^b
923	0.2	5.72
1023	0.66	4.44
1123	0.8	1.21

Data were obtained on La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃, [O₂] and [NO] were in units of mol mL⁻¹.

^a k in units of $[\text{s}^{-1} \text{site}^{-1} (\text{mol mL}^{-1})^{-1}]$.

^b K in units of $(\text{mol mL}^{-1})^{-1/2}$.



Scheme 1. The elementary steps of NO decomposition over the perovskite-type oxides.

dissociation is indeed an important step in the process of NO decomposition.

3.3. Reaction mechanism

To explain consistently the obtained kinetic results, a reaction mechanism for NO decomposition over perovskite(-like) oxides was proposed (see Scheme 1), which was derived based on the recycle route occurred in the process of NO decomposition as we reported previously [13].

Here, the attack of the second gaseous NO molecule on the adsorbed NO molecule is assumed to be occurred stepwise since the simultaneous attack of two gaseous NO molecules, as suggested by Shin et al. [9], would give second-order kinetics in NO concentration, which is not the present case. This step is considered to be the reaction-determined step (RDS) as proposed by Teraoka et al [10]. However, it should be noted that the oxygen desorption reaction ($\text{O}_{(a)} + \text{O}_{(a)} \rightleftharpoons \text{O}_{2(g)}$) was not involved in the kinetics, because it is not the main route of O_2 formation [13], while the NO_2 formation route ($\text{NO}_{(a)} + \text{O}_{(a)} \rightleftharpoons \text{NO}_{2(a)}$) was considered to be one of the elementary steps.

Using the pseudo-steady-state approximation for all adsorbed species and quasiequilibrium assumptions for some of the reaction steps, the sequence of elementary steps showed above can be used to obtain a rate expression. In what follows, equilibrium constants are denoted as K_i and rate constants as k_i . The quasiequilibrium step M1 related $\text{NO}_{(a)}$ and $\text{NO}_{(g)}$ could be written as:

$$[\text{NO}_{(a)}] = K_1 P_{\text{NO}} [S] \quad (\text{R1})$$

If step M2 is quasiequilibrated, after using Eq. (R1) to eliminate $[\text{NO}_{(a)}]$, we obtain:

$$[\text{N}_2\text{O}_2] = K_2 P_{\text{NO}} [\text{NO}_{(a)}] = K_1 K_2 P_{\text{NO}}^2 [S] \quad (\text{R2})$$

Then, the reaction rate is determined by the rate of the decomposition of $\text{N}_2\text{O}_{2(a)}$ in step M3 (RDS):

$$r = r_3 = k_3 [\text{N}_2\text{O}_2] = k_3 K_1 K_2 P_{\text{NO}}^2 [S] \quad (\text{R3})$$

A site balance for all active sites $[L]$ contains $[S]$, $[\text{NO}_{(a)}]$, $[\text{O}_{(a)}]$ and $[\text{NO}_{2(a)}]$ could be expressed as:

$$[L] = [S] + [\text{NO}_{(a)}] + [\text{O}_{(a)}] + [\text{NO}_{2(a)}] \quad (\text{R4})$$

Because $\text{N}_2\text{O}_{2(a)}$ and $\text{N}_2\text{O}_{(a)}$ were not detectable as a denominator term in any of the acceptable rate equations or as adsorbed species in infrared studies during the reaction [16], they were not involved in the Eq. (R4).

From the quasiequilibrium steps M5–M7, the following equations could be obtained:

$$[\text{O}_{(a)}] = K_{-5} [\text{NO}_{2(a)}] [S] / [\text{NO}_{(a)}] \quad (\text{R5})$$

$$[\text{NO}_{2(a)}] = K_{-6} P_{\text{NO}_2} [S] \quad (\text{R6})$$

$$P_{\text{NO}_2} = (K_{-7})^{1/2} P_{\text{NO}} P_{\text{O}_2}^{1/2} \quad (\text{R7})$$

After combination of Eqs. (R1), (R5)–(R7) and integration, the following equations could be further obtained:

$$[\text{O}_{(a)}] = (K_{-5} K_{-6} (K_{-7})^{1/2} P_{\text{O}_2}^{1/2} [S]) / K_1 \quad (\text{R8})$$

$$[\text{NO}_{2(a)}] = K_{-6} (K_{-7})^{1/2} P_{\text{NO}} P_{\text{O}_2}^{1/2} [S] \quad (\text{R9})$$

Eqs. (R1), (R8) and (R9) contain the concentrations of all abundant species in terms of the concentration of reduced dimers $[S]$, which can be substituted into Eq. (R4) to obtain an expression for $[S]$ in terms of $[L]$:

$$[L] = [S] (1 + K_1 P_{\text{NO}} + (K_{-5} K_{-6} (K_{-7})^{1/2} P_{\text{O}_2}^{1/2}) / K_1 + K_{-6} (K_{-7})^{1/2} P_{\text{NO}} P_{\text{O}_2}^{1/2}) \quad (\text{R10})$$

Or

$$[S] = [L] / (1 + K_1 P_{\text{NO}} + (K_{-5} K_{-6} (K_{-7})^{1/2} P_{\text{O}_2}^{1/2}) / K_1 + K_{-6} (K_{-7})^{1/2} P_{\text{NO}} P_{\text{O}_2}^{1/2}) \quad (\text{R10}')$$

By introducing the Eq. (R10') into Eq. (R3), the following equation could be obtained:

$$r = \frac{k_3 K_1 K_2 P_{\text{NO}}^2 [L]}{1 + K_1 P_{\text{NO}} + (K_{-5} K_{-6} K_{-7}^{1/2} / K_1) P_{\text{O}_2}^{1/2} + K_{-6} K_{-7}^{1/2} P_{\text{NO}} P_{\text{O}_2}^{1/2}} \quad (\text{R11})$$

Where $K_1 = k_1/k_{-1}$, $K_{-5} = k_{-5}/k_5$, $K_{-6} = k_{-6}/k_6$, and $K_{-7} = k_{-7}/k_7$.

This rate Eq. (R11) suggests that the apparent reaction order for NO to be between 1 and 2, while for O_2 , it varies from -0.5 to 0 . This equation reflects the reciprocity of O_2 and NO by introducing the item of $K_{-6} (K_{-7})^{1/2} P_{\text{NO}} (P_{\text{O}_2})^{1/2}$, which is introduced to the kinetic equation for the first time to our knowledge. This is interesting since the reciprocity of NO and O_2 in the reaction is unavoidable.

Because of the instability of $\text{NO}_{2(a)}$ and/or $\text{NO}_{3(a)}$ at higher temperatures ($650^\circ\text{C} \leq T \leq 850^\circ\text{C}$), the converse reaction of M5 is difficult to occur and the value of K_{-5} is far lower than that of K_1 . Hence, the term of $\{K_{-5} K_{-6}$

$(K_{-7})^{1/2}/K_1\}(P_{O_2})^{1/2}$ could be neglected in the denominator in Eq. (R11). Besides, “1” could also be neglected at this time. Based on these two assumptions, the Eq. (R11) could be simplified as follows:

$$r = \frac{k_3 K_1 K_2 P_{NO}^2 [L]}{K_1 P_{NO} + K_{-6} K_{-7}^{1/2} P_{NO} P_{O_2}^{1/2}} \quad (R12)$$

Or

$$r = \frac{k P_{NO}}{1 + K P_{O_2}^{1/2}} \quad (R12')$$

Where $k = [L] k_3 K_2$, $K = K_{-6} (K_{-7})^{1/2}/K_1$. By comparing the Eqs. (R0) and (R12'), it is seen that these two equations consist well with each other, and hence suggests that the new mechanism is believable. Here, because of the involvement of k_3 (rate constant of RDS), the value of k is certainly lower as listed in Table 2. The increase of k value at high temperatures (see Table 2) indicates that high temperatures facilitate $N_2O_{2(a)}$ dissociation to occur. While for ‘ K ’, the decreasing value at high temperatures is ascribed to the reason that both the adsorption and formation of NO_2 (see M6 and M7) are difficult to occur at high temperatures.

At low temperatures (650 °C), because of the high value of K (comparing with 1), the contribution of $K (P_{O_2})^{1/2}$ in Eq. (R12') is larger than that of 1, as a result, the reaction order of O_2 became more negative (−0.24, trends to −0.5). While at high temperatures, the value of K became smaller and the contribution of $K (P_{O_2})^{1/2}$ decreased (comparing with 1), as a result, the influence of O_2 became weak and the reaction order increased (−0.08, trends to zero). These might be the reason why the reaction order of O_2 varies with changing the temperature. But for NO, because there is only one item ($k P_{NO}$) appears in the numerator in Eq. (R12'), the reaction order of NO keeps constant ($m \sim 1$) in the whole temperature range.

4. Conclusions

Based on the ‘recycle’ mechanism of NO decomposition and the power rate law: $r = k [NO]^m [O_2]^n$, the kinetics of

NO decomposition over $La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O_3$ perovskite-type oxide, which showed high activity for NO decomposition, was deduced. The NO decomposition rate was practically first-order for NO in the range 0.5–2.0 vol.% NO/He, while the reaction order varied from −0.08 and −0.24 for O_2 (0–6 vol.% O_2), depending on the temperature. The kinetics deduced from the ‘recycle’ mechanism accords well with that observed in practice by introducing the item $K_{-6} (K_{-7})^{1/2} P_{NO} (P_{O_2})^{1/2}$, and hence suggested that the ‘recycle’ mechanism of NO decomposition is believable.

Acknowledgements

This work was supported by the Ministry of Science and Technology of China (2001AA 324060) and the Natural Science Foundation of China (20177022).

References

- [1] Y. Li, J.N. Armor, Appl. Catal. B 1 (1992) L21.
- [2] N.Y. Topsoe, Catech 1 (1997) 125.
- [3] M. Iwamoto, H. Yahiro, N. Mizuno, Y. Mine, S. Kagawa, J. Phys. Chem. 95 (1991) 3727.
- [4] R. Burch, D. Ottery, Appl. Catal. B 13 (1997) 105.
- [5] V.I. Pârvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
- [6] J.W. Hightower, D.A. Van Leirsberg, in: R.L. Klimish, J.G. Larson (Eds.), The catalytic chemistry of nitrogen oxides, Plenum Press, New York, 1975, p. 63.
- [7] W.F. Libby, Science 171 (1971) 499.
- [8] R.J.H. Voorhoeve, J.P. Remeika, P.E. Freeland, B.T. Matthias, Science 177 (1972) 353.
- [9] S. Shin, H. Arakawa, Y. Hatakeyama, K. Ogawa, K. Shimomura, Mater. Res. Bull. 14 (1979) 633.
- [10] Y. Teraoka, T. Harada, S. Kagawa, J. Chem. Soc., Faraday Trans. 94 (1998) 1887.
- [11] C. Tofan, D. Klvana, J. Kirchnerova, Appl. Catal. A 223 (2002) 275.
- [12] T. Ishihara, M. Ando, K. Sada, et al., J. Catal. 220 (2003) 104.
- [13] J. Zhu, D. Xiao, J. Li, X. Xie, X. Yang, Y. Wu, J. Mol. Catal. A 233 (2005) 29.
- [14] Z. Yu, L. Gao, S. Yuan, Y. Wu, J. Chem. Soc., Faraday Trans. 88 (1992) 3245.
- [15] Y. Teraoka, H. Fukada, S. Kagawa, Chem. Lett. (1990) 1.
- [16] M.V. Konduru, S.S.C. Chuang, J. Phys. Chem. B 103 (1999) 5802.