Recycle—new possible mechanism of NO decomposition over perovskite(-like) oxides

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Abstract

Mechanism of NO decomposition over perovskite(-like) oxides was explored through investigating the experiments of O_2-TPD and the activity of NO decomposition. It was found that the mechanism of NO decomposition over perovskite(-like) oxides was performed in a 'recycle' way, in which the recycle of NO_2 (its formation and dissociation) plays an important role in the reaction and relates greatly with the activity. Because NO_2 dissociation reaction ($2NO_2 = 2NO + O_2$) is an important step in the process of NO decomposition, catalytic activity of NO decomposition over perovskite(-like) mixed oxides achieved only at high temperatures, at which the NO_2 dissociation reaction occurs.
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1. Introduction

For NO decomposition reaction ($2NO = N_2 + O_2$) over the non-noble catalysts (i.e., M-ZSM5, mixed or compound oxides, etc.), it is traditionally accepted that the formation of N_2 and O_2 occurred through reactions of $2NO_{(g)} \rightarrow N_2O_{(a)} \rightarrow N_{2(g)}$ and $O_{(a)} + O_{(a)} = O_{2(g)}$, respectively [1–9]. Accordingly, the under-stoichiometric oxygen (compared with nitrogen) observed in the experiments was ascribed to the reason of NO_2 formation in the cool region downstream from the reactor, by the reaction: $NO_{(g)} + \frac{1}{2}O_{2(g)} = NO_{2(g)}$ [5–9]. However, this widely accepted interpretation (especially for the way of O_2 and NO_2 formation) was neither approved by theoretical deduction nor confirmed by experimental data in literatures to our knowledge. Hence, its authenticity is uncertain although it seemed reasonable.

Recently, based on the technique of spectroscopy (i.e., IR and DRIFTS), it was found that $NO_{2(a)}/NO_{3(a)}$ species were strongly adsorbed on catalyst surface after passing of NO, [8–14] indicating that $NO_{2(a)}/NO_{3(a)}$ species might be an intermediate in NO decomposition. According to this fact, Iglesia and co-workers [11] suggested a new mechanism for NO decomposition (over Cu-ZSM5), in which N_2 and O_2 were formed through the dissociation of $N_2O_{(a)}$ and $NO_{3(a)}$ species, respectively. However, the results of their work were obtained from Cu-ZSM-5 catalyst system and at low temperatures, which might not be applied to the case (for example, perovskite(-like) oxides) occurred at high temperatures.

In this work, based on our previous work, [15] we explored the mechanism of NO decomposition occurred on perovskite(-like) catalyst through investigating the formation way of NO_2 and O_2, both of which were products of NO decomposition reaction. It was found that both NO_2 and O_2 were mainly formed on the catalyst surface by the way of $NO + O_{(a)} \Leftrightarrow NO_{2(a)}$ and $2NO_{2(g)} \Leftrightarrow 2NO_{(g)} + O_{2(g)}$, respectively. The mechanism of NO decomposition, then, was supposed to occur in a recycle way, in which the recycle of NO_2 (its formation and dissociation) plays an important role in the reaction and relates greatly with the activity.

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2. Experimental

The samples, $LaSrNiO_4$ and $La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O_3$, were prepared by citric combustion method as described elsewhere. [16] Briefly, to an aqueous solution of La^{3+}, Sr^{2+}, Mn^{2+} and/or Ni^{2+} nitrates (all obtained from Beijing Chemical Co., China) with appropriate stoichiometry, a solution of citric acid 50% in excess (molar ratio) was added. The resulting solution was evaporated to dryness, and then the precursors obtained were decomposed in air at 573 K, calcined at 873 K for 1 h and finally pelletized and calcined at 1173 K in air for 6 h, the synthesized pellets were pulverized to 40–80 mesh size to be used.

O_2-TPD experiment was carried out on a conventional apparatus equipped with a thermal conductivity detector (TCD). The samples (0.2 g) were first treated in O_2 at 1073 K for 1 h and cooled to room temperature in the same atmosphere, then swept with pure He (or 0.5% O_2/He) at a rate of 11.8 mL min^{-1} until the base line on the recorder remained unchanged. Finally, the sample was heated at a rate of 20 K min^{-1} in He (or 0.5% O_2/He) to record the TPD profile.

Steady-state activities of catalysts were evaluated using a single-pass flow micro-reactor made of quartz, with an internal diameter of 6 mm. In the blank experiment, the reactor was filled with quartz instead of catalyst; the flow rate of the reactant gas (0.5% NO + 0.25% O_2/He) was 25 mL min^{-1}; the reaction temperature was kept at 1073 K. The O_2 concentration in the downstream was measured by an on-line gas chromatography (in this experiment, because the reaction (10) in Scheme 1 is the only way of O_2 consumption, the amount of O_2 consumed can represent the amount of NO_2 produced, in the relation of $[O_2]_{consumed} = 2[NO_2]_{produced}$).

In measuring the activity of NO decomposition, the reactant gas was passed over 0.5 g catalyst (1% NO/He) at a rate of 25 mL min^{-1} or 0.8 g (1% NO + 1–6% O_2/He) catalysts at a rate of 40 mL min^{-1} (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, N_2 and O_2. N_2O was not analyzed here because it was difficult to form between 773 and 1123 K as reported by Teraoka et al. [2] Before the data were obtained, reactions were maintained for a period of ~2 h at each temperature to ensure the steady-state conditions.

3. Results and discussion
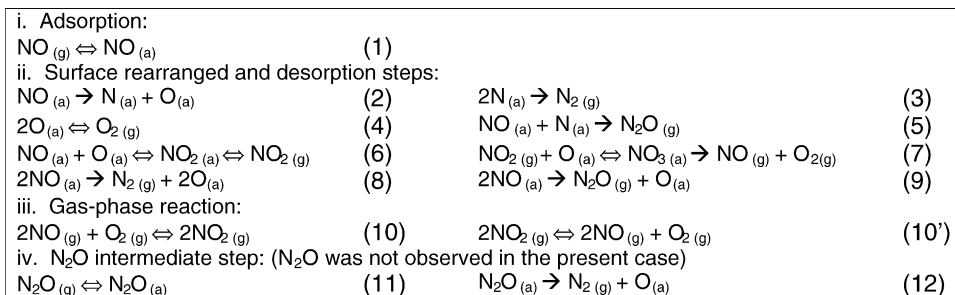
3.1. Way of NO_2 formation

According to literatures reported previously, the possible reaction steps occurred in the process of NO decomposition could be summarized as given further (Scheme 1).

In Scheme 1, there are two possible reaction routes, reactions (6) and (10), corresponding to NO_2 formation. The reaction (10) occurred mainly in the cool region downstream from the reactor, [9] while the reaction (6) occurred mainly on catalyst surface due to the participation of adsorbed oxygen ($O_{(a)}$). In order to investigate which one is the main route of NO_2 formation, a blank experiment (without catalyst) was carried out. In this experiment, the O_2 conversion (which can represent the twice amount of NO_2 yield in the reaction, as noted above) measured was 25%. However, when catalyst was loaded in the reactor, the O_2 conversion measured reached 80% (also see elsewhere [8]), which was far higher than 25% that measured in the blank experiment. These two results implied that NO_2 formation was mainly occurred on the catalyst surface by the way of reaction (6).

3.2. Way of O_2 formation

There are three possible reaction routes, reactions (4), (7) and (10') in Scheme 1, corresponding to O_2 formation. In reaction (4), O_2 was formed through the simple desorption of two vicinal oxygen; [4] in reaction (7), O_2 was formed through the decomposition of $NO_{3(a)}$ species, which was derived from NO_2; [11] while in reaction (10'), O_2 was formed through the direct dissociation of NO_2 species. It should be noted that the only difference between reactions (7) and (10') was whether the oxygen was formed through the direct or indirect dissociation of NO_2. This is mainly decided by the experimental condition, as discussed below.

Two experiments were performed to clarify the main route of O_2 formation. One is the activity of NO decomposition, which was performed with and without gaseous oxygen in the feed gas. The results in Fig. 1 showed that the activity decreased largely with the increase of oxygen partial pressure, namely, the gaseous oxygen has large impact on the activity. The other is O_2-TPD experiment, which was per-

i. Adsorption:

$NO_{(g)} \Leftrightarrow NO_{(a)}$ (1)

ii. Surface rearranged and desorption steps:

$NO_{(a)} \rightarrow N_{(a)} + O_{(a)}$	(2)	$2N_{(a)} \rightarrow N_{2(g)}$	(3)
$2O_{(a)} \Leftrightarrow O_{2(g)}$	(4)	$NO_{(a)} + N_{(a)} \rightarrow N_2O_{(g)}$	(5)
$NO_{(a)} + O_{(a)} \Leftrightarrow NO_{2(a)} \Leftrightarrow NO_{2(g)}$	(6)	$NO_{2(g)} + O_{(a)} \Leftrightarrow NO_{3(a)} \rightarrow NO_{(g)} + O_{2(g)}$	(7)
$2NO_{(a)} \rightarrow N_{2(g)} + 2O_{(a)}$	(8)	$2NO_{(a)} \rightarrow N_2O_{(g)} + O_{(a)}$	(9)

iii. Gas-phase reaction:

$2NO_{(g)} + O_{2(g)} \Leftrightarrow 2NO_{2(g)}$	(10)	$2NO_{2(g)} \Leftrightarrow 2NO_{(g)} + O_{2(g)}$	(10')

iv. N_2O intermediate step: (N_2O was not observed in the present case)

$N_2O_{(g)} \Leftrightarrow N_2O_{(a)}$	(11)	$N_2O_{(a)} \rightarrow N_{2(g)} + O_{(a)}$	(12)

Scheme 1. Possible reaction routes occurred in the process of NO decomposition.
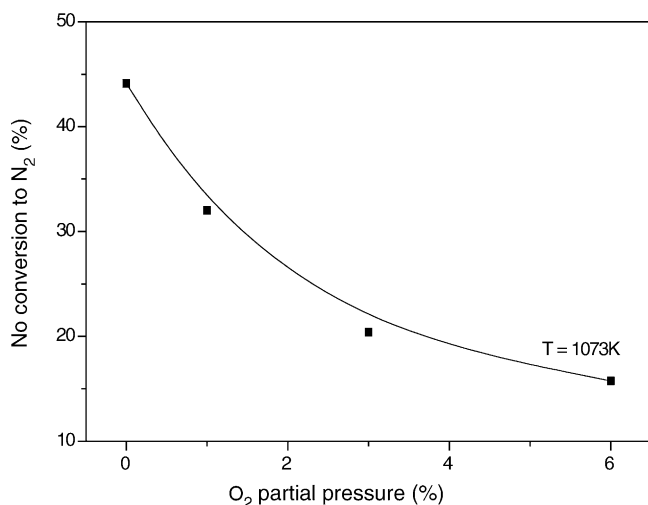
Fig. 1. Activity of NO decomposition over LaSrNiO$_4$ as a function of O$_2$ partial pressure.

formed with and without oxygen in helium and the result was shown in Fig. 2. It is seen that only a minor difference both in the two desorption temperatures ($\Delta T_{max} \leq 10$ K) and in the two desorption peak areas ($A_b/A_a = 1.04$) was observed when oxygen was added. Namely, the impact of gaseous oxygen on oxygen desorption ($O_{(a)} + O_{(a)} = O_{2(g)}$) can be neglected. These two experiments suggested that the oxygen in NO decomposition reaction was not formed through the reaction (4), otherwise, the gaseous oxygen should have no or minor impact on the activity, since the gaseous oxygen has minor impact on the oxygen desorption as observed in O$_2$-TPD experiment.

While for the two other ways (reactions (7) and (10')), it is difficult to distinguish which one is the main route of O$_2$ formation on the above basis, since both of them involved the NO$_2$ species. Therefore, other criteria must be considered. From the stability of NO$_{3(a)}$ species and the
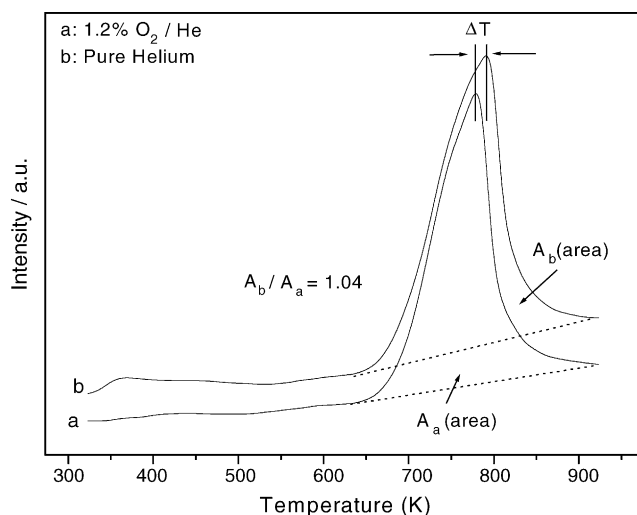
thermodynamic equilibrium of NO$_2$ dissociation reaction ($\Delta G^{\circ}_{767\,K} = 0$), it might be deduced that at low temperatures ($T < 767$ K), reaction (7) is the main route of O$_2$ formation, since NO$_2$ dissociation reaction cannot occur spontaneously at low temperatures. This route was mainly performed on the catalysts having activity for NO decomposition below 767 K, for example, M-ZSM5 (M: Cu, Fe, Co, etc.) [11–13,17]. While at high temperatures ($T > 873$ K), because NO$_{3(a)}$ species is unstable and difficult to form [8,18] and NO$_2$ direct dissociation reaction can occur, [19] it is unnecessary for NO$_2$ converting into NO$_{3(a)}$ species before dissociation into NO and O$_2$. Thus, reaction (10') becomes the main route of O$_2$ formation at high temperature range. This route was mainly performed on these catalysts, of which the activity was exhibited only at high temperatures ($T > 873$ K), for example, the perovskite(-like) mixed oxides [5,8].

According to the route of O$_2$ formation discussed above, the decrease of activity in the presence of gaseous oxygen, then, was ascribed to the suppression of gaseous oxygen on NO$_2$ dissociation reaction, by the way of $2NO_{2(g)} = 2NO_{(g)} + O_{2(g)}$. Furthermore, from the apparent NO$_2$ dissociation equilibrium, it is seen that the rate of NO dissociation is inversely proportional to the square root of oxygen (i.e., $r_{NO_2} = K \frac{P_{NO_2}}{P_{NO} P_{O_2}^{1/2}}$, or $r_{NO_2} = K' \frac{1}{P_{O_2}^{1/2}}$, $K' = K \frac{P_{NO_2}}{P_{NO}}$). This relation will also be exhibited in NO decomposition reaction, since the NO$_2$ dissociation reaction is the main route of O$_2$ formation as discussed above. Namely, the NO decomposition rate (or NO decomposition activity) was inversely proportional to the square root of oxygen. This is basically true (within the uncertainty of 1% in linear regression analysis) as confirmed by the data shown in Fig. 3, in which the activity of NO decomposition was plotted as a function of square root of oxygen. In all, the above results supported that the oxygen was formed through NO$_2$ dissociation, reaction (10').

Fig. 2. O$_2$-TPD profiles of LaSrNiO$_4$ examined with and without oxygen in helium.
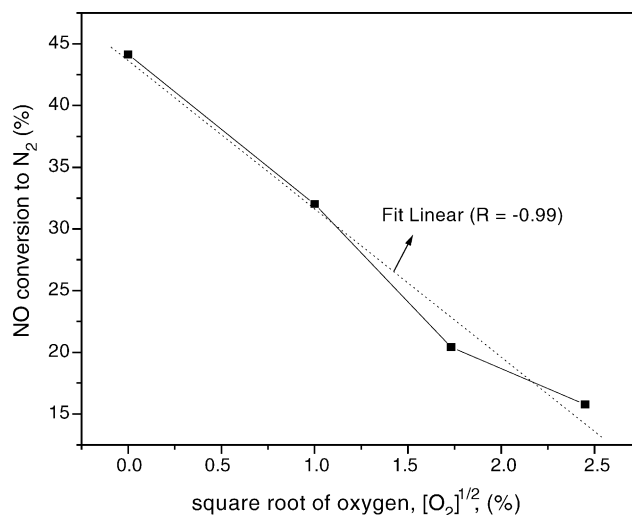

Fig. 3. Activity of NO decomposition as a function of square root of oxygen. Data obtained from Fig. 1.
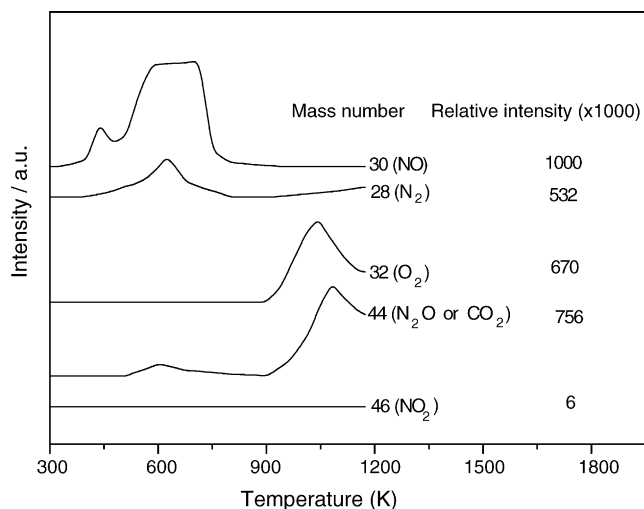
Fig. 4. Mass spectrum of $LaSrNiO_4$ in NO-TPD experiment.

3.3. NO-TPD experiment

NO-TPD was also performed to investigate the process of NO decomposition. The result in Fig. 4 showed that NO was the major desorption species in the experiment. N_2 desorption peak appeared at the range of $673\,K < T < 773\,K$ suggested that the dissociation of NO and the formation of N−N bond were easy to occur. Hence, a transitory activity for N_2 at $T < 767\,K$ was observed in the experiment. [5] However, the difficulty of oxygen desorption ($T > 1023\,K$) suppressed the NO dissociation reaction to be carried out further by occupying the active site. Generally, the O_2 formed in NO-TPD is ascribed to the following two steps [8]: $3NO + S = N_2 + NO_{3(a)}$ and $NO_{3(a)} = NO + O_2 + S$ (S: surface). However, the over-stoichiometric oxygen (compared with nitrogen) suggested that this is not the only way of O_2 formation; otherwise the amount of O_2 should be lower than that of N_2. Hence, some of oxygen must be originated from the desorption of two vicinal oxygen as that in O_2-TPD experiment, namely, $O_{(a)} + O_{(a)} \Leftrightarrow O_{2(g)}$. The species with M.N. = 44 (M.N.: mass number) were detected, which might means the appearance of N_2O and/or CO_2. However, according to [2], it is known that N_2O is unstable and difficult to form at $T > 900\,K$. Thus, this species is mainly attributed to CO_2 formed from the decomposition of carbonates (i.e., $SrCO_3$) [20]. The low quantity of NO_2 suggested that the formation of NO_2 was difficult to occur or the formed NO_2 ($NO_{(a)} + O_{(a)} = NO_{2(a)}$) was dissociated into NO and O_2 before elution. According to the facts that $NO_{2(a)}/NO_{3(a)}$ species is easy to form after passing of NO [8,12,14] and lots amount of NO_2 will be formed when catalyst was loaded in the reactor (see Section 3.1), it might be concluded that the low quantity of NO_2 was mainly ascribe to the reason that the formed NO_2 was dissociated into NO and O_2 before elution. In all, the above results indicated that N_2 formation is easy to occur, while O_2 formation is difficult and the O_2 was formed through the way of NO_2 dissociation. The data obtained
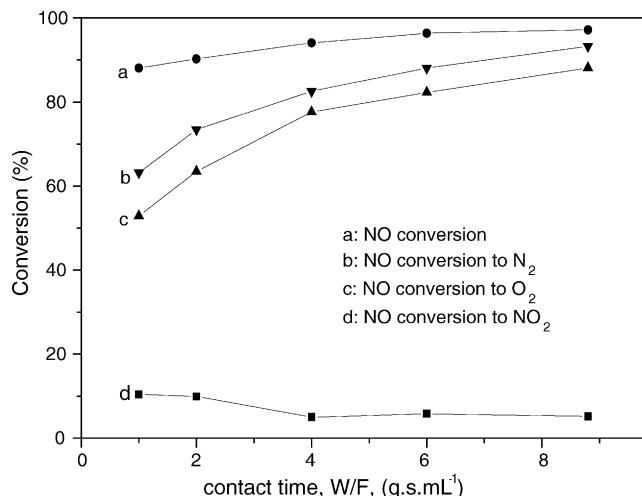

Fig. 5. Activity of NO decomposition over $La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O_3$ as the function of contact time (W/F).

in this work were in well accordance with those reported elsewhere, [5] in which the data were obtained from the gas-chromatogram.

3.4. Influence of contact time (W/F)

Fig. 5 showed the activity of NO decomposition measured at different contact time (W/F) [21]. The amount of O_2 was always lower than that of N_2 and the difference between them kept constant at high NO conversion (W/F > 4 g s mL^{-1}). One may imagine that the under-stoichiometric oxygen was ascribed to the formation of NO_2 occurred in the cool region downstream through the reaction (10), but it was expatiated above that reaction (10) was difficult to occur under this condition. Thus, the under-stoichiometric oxygen must be ascribed to the existence of the equilibrium among NO_2, NO and O_2 (see reaction (10')), since NO_2 cannot be dissociated
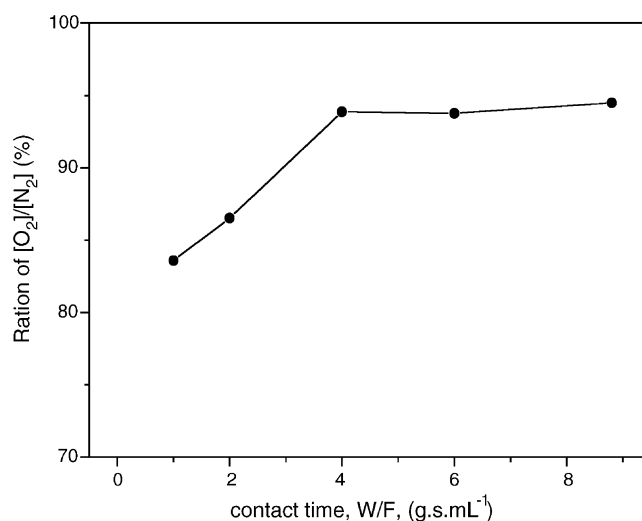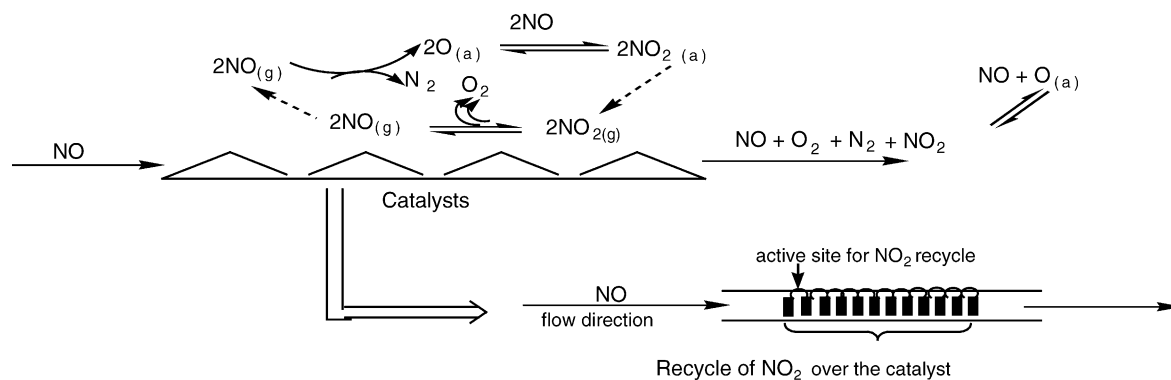

Fig. 6. Ratio of $[O_2]/[N_2]$ as a function of contact time (W/F). Data obtained from Fig. 5.

Scheme 2. The 'recycle' mechanism of NO decomposition over perovskite(-like) oxides.

into NO and O_2 completely due to the restriction of thermodynamics.

Besides, from the correlation between $[O_2]/[N_2]$ and W/F shown in Fig. 6, it is seen that the ratio of $[O_2]/[N_2]$ increased with W/F at first, then kept constant at W/F > 4 g s mL^{-1}. The increasing ratio of $[O_2]/[N_2]$ at W/F ≤ 4 g s mL^{-1} might be that, with the increase of contact time, the time for NO_2 staying on the catalyst surface is longer and there were more opportunities for NO_2 formation and dissociation reaction to occur over the catalyst. As a result, more amount of O_2 was produced and the $[O_2]/[N_2]$ ratio increased. When NO_2 dissociation reaction reached thermodynamic equilibrium (W/F > 4 g s mL^{-1}), it cannot be carried out further, the ratio of $[O_2]/[N_2]$, then, kept constant. The constant of $[O_2]/[N_2]$ ratio measured in our experiment is ~95% (1073 K), which is in compliance with the percent of NO_2 being dissociated in thermodynamics (96% at 1100 K in reaction: $NO_2 = NO + \frac{1}{2}O_2$). This result supported that O_2 was indeed produced from the dissociation of NO_2 as the experimental value was in well accordance with that calculated from thermodynamics. Hence, it is confident that in NO decomposition reaction, the oxygen was mainly formed through NO_2 dissociation, as shown in Scheme 2.

In Scheme 2, the gaseous NO was first adsorbed and dissociated into N_2 and atomic oxygen, which then reacted with another NO to form the adsorbed NO_2, after that, the adsorbed NO_2 desorbed and dissociated into NO and O_2. In this process, NO_2 acted as an intermediate of O_2 formation. Besides, it should be noted that in the cool region downstream of the reactor, the detected NO_2 species was mainly ascribed to the NO_2 formed in the catalyst surface but were not dissociated before emitting, i.e., reaction (6) in Scheme 1, $NO_{(a)} + O_{(a)} \Leftrightarrow NO_{2(a)} \Leftrightarrow NO_{2(g)}$.

4. Conclusions

By investigating the formation way of NO_2 and O_2, both of which were main products of NO decomposition reaction, we found that they are formed through the way of $NO_{(a)} + O_{(a)} = NO_{2(a)}$ and $2NO_{2(g)} = 2NO_{(g)} + O_{2(g)}$, respectively, and thus suggested that the mechanism of NO decomposition over perovskite(-like) oxides was performed in a 'recycle' way, in which NO_2 plays an important role in the reaction. This is confirmed by the results of NO decomposition activity and $[O_2]/[N_2]$ ratio measured at different contact time. Because NO_2 dissociation reaction ($2NO_2 = 2NO + O_2$) is an important step in the process of NO decomposition, catalytic activity of NO decomposition over perovskite(-like) mixed oxides achieved only at high temperatures, at which the NO_2 dissociation reaction occurs.

Acknowledgements

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[21] Here, $La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O_3$ was chosen to be the catalyst because of the highest activity it exhibited in our experiment.