Korean J. Chem. Eng., **24**(3), 503-507 (2007)

Influences of A- or B-site substitution on the activity of $LaMnO_3$ perovskite-type catalyst in oxidation of diesel particle

Bailei He, Qiang Song†, Qiang Yao, Zhongwei Meng and Changhe Chen

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education,
Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

(*Received 25 August 2006 • accepted 11 November 2006*)

Abstract−$LaMnO_3$ was partially substituted at A- or B-site by Sol-Gel method and characterized by XRD, SEM and BET. Perovskite oxides were formed in all substitutions. The catalytic activities of substituted catalysts on carbon black oxidation were measured by Temperature Programming Oxidation (TPO). Experimental results showed that all substitutions increased the catalytic activity of $LaMnO_3$, and $La_{0.8}Cs_{0.2}MnO_3$ showed the highest catalytic activity. Under tight contact, the activity enhancement of different substitutions decreased in the order Cs>K>V>Ce>Co>Cu>Fe. Dynamic analysis showed that partial substitutions increased the pre-exponential factor and the catalytic activity by increasing the oxygen vacancy on the catalyst surface. The active components on the surfaces of $La_{0.8}Ce_{0.2}MnO_3$ and $LaMn_{0.8}V_{0.2}O_3$ included CeO_2 and $LaVO_4$, which changed the apparent activities and dynamic parameters of these two catalysts.

Key words: Substitution, $LaMnO_3$, Diesel Particle, Oxidation

INTRODUCTION

Diesel engines are widely used for their high efficiency and economics, while particle and NO_x emissions cause serious environmental and health problems. Many countries enact strict limitations to pollutant emissions. This requires fast development of efficient after-treatment devices, and the catalytic trap is regarded as the most promising one to limit diesel particle emission. The temperature of exhaust gas from diesel engine usually ranges in 473-673 K, while the automatic oxidation temperature of diesel particles is usually above 873 K [1], so the diesel particles cannot be burnt off even though they are combustible. Once the diesel particles are caught by the catalytic trap, they are easy to burn with the aid of catalyst [2]. Catalyst activity is very important in this technology.

Several kinds of catalysts have been tested for diesel particle oxidation, such as expensive metal [3] and molten salts [4], and the perovskite-type catalysts, such as $LaMnO_3$ [5,6], have exhibited great advantages in diesel particle oxidation for the high catalytic activity, high thermal stability, low cost and simultaneous removal of diesel particle and NO_x. When $LaMnO_3$ was partially substituted at A- or B-site, its activity was much improved. $La_{1-x}K_xMnO_3$ showed good activity on simultaneous removal of diesel particles and NO_x [7,8]. When 20-30% of La in $LaMnO_3$ was substituted by K, the catalyst showed the best activity. Hong and Lee found A-site substitution of $LaCoO_3$ by Cs was very effective in improving activity for producing more oxygen vacancy [9]. Zhang et al. [10] found that $La_{0.6}Ce_{0.4}MnO_3$ had some sulfate-poison resistance and retained high activity towards CH_4 oxidation.

Partial substitutions of $LaMnO_3$ have been tried by different researchers and all the results show an improvement in catalyst activity, but it is difficult to screen substituted catalysts just based on published data, since the results given by different researchers are closely related to the experimental conditions. Usually, the activity of catalyst is tested by TPO test and assessed by characteristic temperatures (ignition temperature, peak temperature and burn-off temperature). The experimental conditions, such as oxygen concentration, NO_x concentration, heating rate, contact way, mass ratio of catalyst versus diesel particle and so on, affect characteristic temperatures greatly, which makes the comparison of catalysts under different conditions difficult. Thus, it's necessary to assess all the promising substitutions under uniform operation conditions.

In this work, more substitutions were tried and the activities of these substituted catalysts were tested under same conditions. The influence of A- or B-site substitution on catalyst's property was investigated and the reaction mechanism of catalytic oxidation of diesel particle was discussed.

EXPERIMENTAL

1. Catalyst Preparation

A series of A- or B-site substituted $LaMnO_3$ catalysts were prepared by Sol-Gel method. For A-site substitutions, the nitrates of La, Mn and M (M=Cs, K, Ce) were co-dissolved with a molar ratio of La : Mn : M=0.8 : 1 : 0.2. For B-site substitution, the nitrates of La, Mn and M (M=Cu, V, Fe, Co) were co-dissolved with a molar ratio of La : Mn : M=1 : 0.8 : 0.2. Then, a solution of citric acid 100% in excess was injected. A proper mass of γ-Al_2O_3 was added to occupy the 50% mass of the final catalyst. The precursor solution was strongly stirred at 363 K, dried at 393 K for 2 h, and calcined at 973 K for 6 h to get the final catalyst.

2. Catalyst Characterization

Surface analysis of the catalysts was developed by powder X-ray diffraction (BRUKER D8 Advance), using Cu K_α radiation, op-

---

†To whom correspondence should be addressed.
E-mail: qsong@mail.tsinghua.edu.cn

‡This work was presented at the 6th Korea-China Workshop on Clean Energy Technology held at Busan, Korea, July 4-7, 2006.

Table 1. Ultimate analysis of simulation diesel particles

Mass fraction of carbon (%)	Mass fraction of hydrogen (%)	Mass fraction of nitrogen (%)	Mass fraction of remains (%)
95.89	0.67	0.34	3.10

erating power 3 kW. BET specific surface area was measured by N_2 adsorption with a Micromeritics ASAP2010 analyzer. The ultimate analysis of diesel particles was performed on a CE440 elemental analyzer of EAI Company.

3. Activity Measurement

Printex-U carbon black supplied by Degussa was reported to have similar properties as diesel particle [11]. It was used as simulated diesel particle in this work. Its primary particle size was 25 nm, and its ultimate analysis is given in Table 1.

Diesel particle and catalyst mixture was ground carefully for 40 min to get tight contact between diesel particle and catalyst. The TPO tests were carried out on the thermogravimetric apparatus TA 2100 to evaluate the catalyst activity. 30 mg sample of diesel particle and catalyst mixture (mass ratio 1 : 10) was loaded onto the reactor pan and was heated from room temperature to 1,073 K with a rate of 5 K/min. The flow rate of reactant gas (10% O_2, N_2 as balance) was 200 mL/min.

Three characteristic temperatures were used for catalyst evaluation: the ignition temperature T_{10}, which was the temperature point where 10% of the diesel particle weight was lost; the peak temperature T_p, which was corresponding to the temperature point where the peak of diesel particle reaction rate appeared; and the burn-off temperature T_{90}, which represented the temperature point where 90% of the diesel particle weight was lost. Besides, the activation energy and the pre-exponential factor were also calculated by Coats-Redfern method for activity assessment.

RESULTS AND DISCUSSIONS

1. Catalyst Characterization

Different substituted catalysts' BET specific surface areas are listed in Table 2. It can be seen from the results that catalyst loading decreased the specific surface area of γ-Al_2O_3, and $LaMnO_3$ had the smallest specific surface area, 62.14 m^2/g. All substitutions increased the specific surface area of $LaMnO_3$, and A-site substitutions had a more obvious effect. $La_{0.8}K_{0.2}MnO_3$ has the largest specific surface area, 83.36 m^2/g.

The XRD patterns of the A-site substituted catalysts are shown in Fig. 1. All these substitutions obtained typical perovskite structure $LaMnO_{3.26}$, but A-site substitutions decreased the value of diffraction peaks, which meant that substitutions produced more lattice vacancy and decreased the concentration of $LaMnO_{3.26}$ crystal.

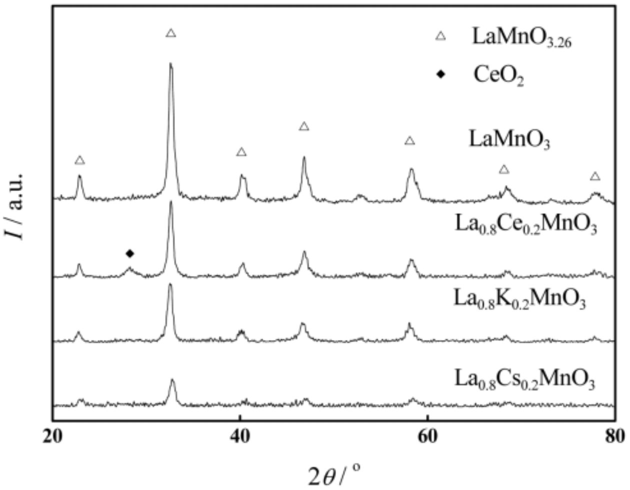

Fig. 1. XRD patterns of A-site substituted $LaMnO_3$.

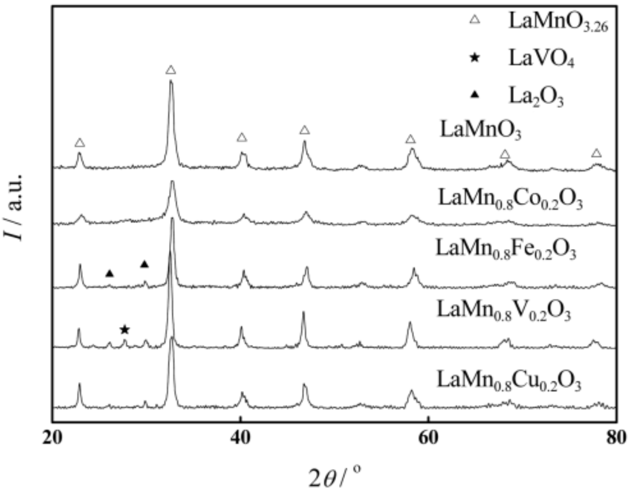

Fig. 2. XRD patterns of B-site substituted $LaMnO_3$.

When A-site (La^{3+}) was substituted by a lower valency cation, according to the principle of electron neutrality, the reduced positive charge could be balanced either by the formation of ions in higher oxidation state at B-site (Mn^{4+}) or by the formation of oxygen vacancy in $LaMnO_3$ [7]. As the valency of Cs^+ and K^+ was +1, they produced more oxygen vacancy than Ce. Furthermore, the diameters of Cs^+ and K^+ were 0.167 nm and 0.145 nm, respectively, and from Eq. (1), the calculated tolerant factors were 1.0678 (>1) and 0.9464, which meant Cs might produce more oxygen vacancy than K.

$$t=(r_A+r_O)/\sqrt{2}(r_B+r_O)=1 \tag{1}$$

Table 2. BET specific surface area of different catalysts

Catalysts	$LaMnO_3$	$La_{0.8}Cs_{0.2}MnO_3$	$La_{0.8}K_{0.2}MnO_3$	$La_{0.8}Ce_{0.2}MnO_3$	γ-Al_2O_3
$BET/m^2\cdot g^{-1}$	62.14	73.54	83.36	75.28	159.82
Catalysts	$LaMn_{0.8}Cu_{0.2}O_3$	$LaMn_{0.8}V_{0.2}O_3$	$LaMn_{0.8}Fe_{0.2}O_3$	$LaMn_{0.8}Co_{0.2}O_3$	-
$BET/m^2\cdot g^{-1}$	69.96	69.75	72.31	73.00	-

where, t is tolerant factor, r_A is the A-site cation diameter (m), r_B is the B-site cation diameter (m), r_O is the diameter of oxygen ion (m). For $La_{0.8}Ce_{0.2}MnO_3$ catalyst, an additional peak besides perovskite was observed at 28.25°. According to Zhang's paper [10], such a peak could be assigned to CeO_2, which suggested there contained some cation vacancy after Ce^{4+} was added into catalysts and extra Ce appeared on the catalyst surface as CeO_2.

The XRD patterns of the B-site substituted catalysts are shown in Fig. 2. The results indicate that the B-site substitution kept the perovskite structure. Compared with A-site substitutions, B-site substitutions had higher peak of perovskite structure. The peak values decreased by turn of V>Cu>Fe>Co, which meant the lattice vacancy increased by the turn of V<Cu<Fe<Co.

For $LaMn_{0.8}Cu_{0.2}O_3$ and $LaMn_{0.8}Fe_{0.2}O_3$ catalysts, additional peaks were found at 26.1° and 29.8° which represented the formation of La_2O_3. It suggests that the addition of Cu^{2+} and Fe^{3+} induced loss of A-site cation and produced cation vacancy. For $LaMn_{0.8}V_{0.2}O_3$, additional peaks were found at 26.1°, 27.7°, and 30° and they could be assigned to La_2O_3 and $LaVO_4$. The highest peak value indicated that little of V was present in the perovskite phase. No additional peak was found in $LaMn_{0.8}Co_{0.2}O_3$, but its lower peak value showed more lattice vacancy existing in the perovskite phase.

2. Catalytic Activity

The TPO curves of A-site substituted catalysts under condition of tight contact are shown in Fig. 3. The characteristic temperatures and the kinetic parameters are listed in Table 3. Compared with non-catalytic oxidation of diesel particle, the ignition temperature of diesel particle was reduced over 200 K by $LaMnO_3$ catalyst. A-site substitution enhanced the activity of $LaMnO_3$, and the enhancement decreased by turn of Cs>K>Ce. $La_{0.8}Cs_{0.2}MnO_3$ had the best activity, which could decrease the characteristic temperature of diesel particle oxidation to 606, 663 and 679 K, respectively, 16, 38 and 54 K lower than those of $LaMnO_3$.

Kinetic analysis found that A-site substitution increased the activation energy and the pre-exponential factor of diesel particle oxidation. Cs and K substituted catalysts had relatively high activation energies (1.395×10^5 and 1.377×10^5 J·mol^{-1}) and highest pre-exponential factor (5.367 and 3.580 s·m^{-1}). Since surface area was not included in the pre-exponential factor in this work, the pre-exponential factor was proportional to the surface active site concentration. It suggests that A-site substitution increased the surface active site concentration, then increased the reaction rate and decreased the characteristic temperatures. Non-catalytic oxidation of diesel particles had the highest pre-exponential factor because the non-catalytic oxidation of diesel particle was a gas-solid reaction while the catalytic oxidation of diesel particle was gas-solid-solid reaction.

The TPO curves of B-site substituted catalysts under condition of tight contact are shown in Fig. 4. The characteristic temperatures and the kinetic parameters are listed in Table 4. Compared with La

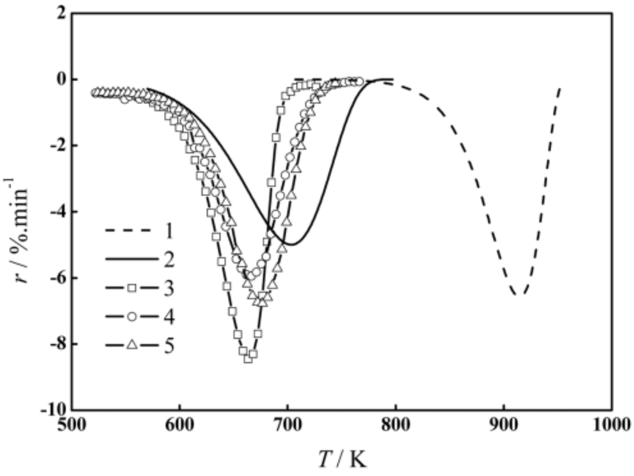

Fig. 3. TPO curves of A-site substituted catalysts under tight contact.
1. No catalyst
2. $LaMnO_3$
3. $La_{0.8}Cs_{0.2}MnO_3$
4. $La_{0.8}K_{0.2}MnO_3$
5. $La_{0.8}Ce_{0.2}MnO_3$

Table 3. The influence of A-site substitution on $LaMnO_3$ under tight contact

	T_{10}/K	T_p/K	T_{90}/K	E/J·mol^{-1}	A/s·m^{-1}
$La_{0.8}Cs_{0.2}MnO_3$	606	663	679	1.377×10^5	5.367
$La_{0.8}K_{0.2}MnO_3$	608	666	697	1.395×10^5	3.580
$La_{0.8}Ce_{0.2}MnO_3$	610	676	703	1.289×10^5	0.749
$LaMnO_3$	622	701	733	1.022×10^5	5.60×10^{-3}
No catalyst	857	928	956	1.988×10^5	5.956

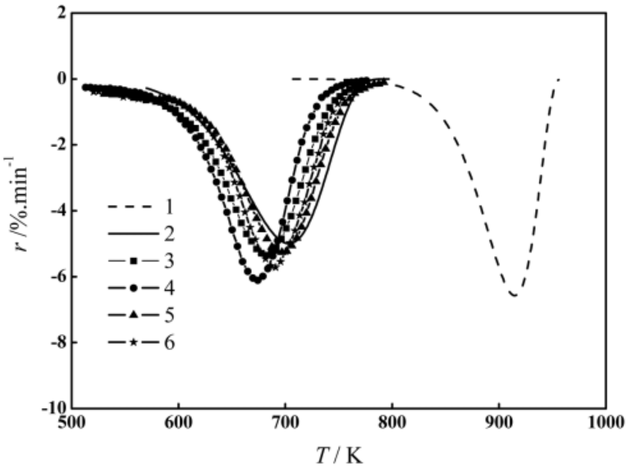

Fig. 4. TPO curves of B-site substituted catalysts under tight contact.
1. No catalyst
2. $LaMnO_3$
3. $La_{0.8}Cu_{0.2}MnO_3$
4. $La_{0.8}V_{0.2}MnO_3$
5. $La_{0.8}Fe_{0.2}MnO_3$
6. $La_{0.8}Co_{0.2}MnO_3$

Table 4. The influence of B-site substitution on $LaMnO_3$ under tight contact

	T_{10}/K	T_p/K	T_{90}/K	E/J·mol^{-1}	A/s·m^{-1}
$LaMn_{0.8}Cu_{0.2}O_3$	609	691	722	1.040×10^5	6.30×10^{-3}
$LaMn_{0.8}V_{0.2}O_3$	601	675	707	1.140×10^5	0.315
$LaMn_{0.8}Fe_{0.2}O_3$	610	696	733	1.120×10^5	1.62×10^{-2}
$LaMn_{0.8}Co_{0.2}O_3$	609	682	718	1.203×10^5	8.27×10^{-2}
$LaMnO_3$	622	701	733	1.022×10^5	5.60×10^{-3}
No catalyst	857	928	956	1.988×10^5	5.956

MnO_3 catalyst, B-site substitution enhanced the catalytic activity and decreased the characteristic temperatures. The enhancement decreased by turn of V>Co>Cu>Fe. Among them, $LaMn_{0.8}V_{0.2}O_3$ had the highest activity, which decreased the characteristic temperature of diesel particle oxidation to 601, 675 and 707 K, respectively, 21, 26 and 26 K lower than those of $LaMnO_3$. Its ignition temperature was lower, and peak temperature and burn-off temperature were higher than $La_{0.8}Cs_{0.2}MnO_3$.

From kinetic analysis, it was found that B-site substitution increased the activation energy and the pre-exponential factor of La MnO_3 catalyst. $LaMn_{0.8}Co_{0.2}O_3$ had the highest activation energy 1.203×10^5 J·mol^{-1}, and $LaMn_{0.8}Cu_{0.2}O_3$ had the lowest activation energy 1.040×10^5 J·mol^{-1}. $LaMn_{0.8}V_{0.2}O_3$ had the largest pre-exponential factor (0.315 s·m^{-1}) and the medium activation energy (1.140 $\times10^5$ J·mol^{-1}), which made it the most active one in B-site substitution. Compared with A-site substitutions, B-site substitutions had less effect on increasing the pre-exponential factor (the surface concentration of free sites) of $LaMnO_3$ catalyst.

Comparison of characteristic temperatures in Table 3 with Table 4 showed that the catalytic activity decreased by turn of Cs>K> V≈Ce>Co>Cu>Fe. All substitutions increased the activation energy a little and increased the pre-exponential factor greatly. The small increase in activation energy would decrease the catalytic activity, but a significant increase in pre-exponential factor could offset it. All substitutions increased the catalytic activity, which meant that the increase in the pre-exponential factor was dominant. The pre-exponential factors decreased by Cs>K>Ce>V>Co>Fe>Cu, which was similar to the order of catalytic activity except V and Cu.

3. Reaction Mechanism

3-1. Reaction Mechanism of Catalyzed C/O_2 Reaction

The catalytic oxidation of diesel particles occurred on the points where diesel particles contacted catalyst and oxygen. The adsorbed oxygen on the catalyst oxidized diesel particles into CO_x through the reactions below [12]:

$$\frac{1}{2}O_2(g)+[\ ]\leftrightarrow[O] \tag{1}$$

$$[O]+C_f\rightarrow C[O] \tag{2}$$

$$C[O]+[O]\rightarrow CO_2(g)(+C_f) \tag{3}$$

$$C[O]+\frac{1}{2}O_2\rightarrow CO_2(g)(+C_f) \tag{4}$$

$$C[O]\rightarrow CO+C_f \tag{5}$$

Gaseous oxygen is adsorbed dissociatively on the catalyst surface active site [ ] (reaction 1) and then the resulting adsorbed oxygen [O] species attack the reactive free carbon C_f to give the oxygen-containing active intermediate C[O] over carbon surface (reaction 2). Then, this active intermediate produces CO_2 by reaction with either [O] (reaction 3) or molecular oxygen (reaction 4), thereby leaving other reactive free carbon species C_f available for the reaction process. Finally, CO production from the reaction intermediate has to be hypothesized (reaction 5) to account for the fact that CO_2 selectivity is close to but not equal to 100%.

3-2. Increase in Pre-exponential Factor

Various catalysts could affect diesel particle oxidation through reactions 1, 2 and 3. The catalysts' surface concentration of active site [ ] and absorbed oxygen [O] were the key factors which decided the reaction rate and thus the catalytic activity. The bigger the surface concentration of active sites [ ] was, the bigger was the surface concentration of absorbed oxygen [O], thus the faster was the reaction rate. The catalysts' characterization gave the surface concentration of free sites [ ] and absorbed oxygen [O].

According to the mechanism before, diesel particle oxidation only occurs on the point where free carbon species, catalyst active site and oxygen contact each other. Thus the pre-exponential factor was not only affected by the catalysts' surface concentration of active sites, but also by the contact between diesel particles and catalysts. For perovskite-type catalysts, the oxygen vacancies, which can strongly absorb oxygen molecules, are the surface active site. Therefore, the catalysts' surface concentration of active sites is that of oxygen vacancy. When Cs and K were applied as A-site substitutions, they produced relatively more oxygen vacancy because of their lowest valency. According to Fig. 2, Cu, Fe and V substituted catalysts had higher value of XRD peaks, which meant their weaker destruction to the crystal lattice. According to the XRD analysis, their substitutions mainly produced cation vacancy while not oxygen vacancy, and there existed some $LaVO_4$ on the surface of $LaMn_{0.8}V_{0.2}O_3$. Ce and Co substituted catalysts gave medium value of XRD peaks, which suggests that their lattice vacancy was more than Cu, Fe and V but less than Cs and K. Ce substitution also produced cation vacancy mainly, but CeO_2 remaining on the surface increased the catalytic activity.

From the analysis before, under tight contact, the surface concentrations of oxygen vacancy were decreased by Cs>K>Co>Cu> Fe>Ce>V, which was not very coherent with the turn of the pre-exponential factor Cs>K>Ce>V>Co>Fe>Cu or the turn of the catalytic activity Cs>K>V≈Ce>Co>Cu>Fe. V and Ce showed obvious difference. $LaVO_4$ on the surface of $LaMn_{0.8}V_{0.2}O_3$ was molten salt (melting point 733 K), which could increase the pre-exponential factor by enhancing the contact between catalyst and diesel particles. CeO_2 on the surface of $La_{0.8}Ce_{0.2}MnO_3$ was active and could produce more active sites [10], which increased the pre-exponential factor of $La_{0.8}Ce_{0.2}MnO_3$.

CONCLUSIONS

$LaMnO_3$ catalysts substituted by different cations were prepared by Sol-Gel method. XRD patterns showed the formation of perovskite catalysts in all substitutions. Among them, Cs^+ and K^+ substitutions produced the most oxygen vacancies; Cu, Fe and V substitutions produced relatively fewer oxygen vacancies, and the concentration of lattice vacancy decreased by the turn of Cs>K>Co> Cu>Fe>Ce>V. Furthermore, some $LaVO_4$ and CeO_2 were observed on the surfaces of $LaMn_{0.8}V_{0.2}O_3$ and $La_{0.8}Ce_{0.2}MnO_3$, respectively.

Under tight contact, all substitutions improved catalytic activity of $LaMnO_3$. $La_{0.8}Cs_{0.2}MnO_3$ was the most active one, which could decrease the characteristic temperature of diesel particle oxidation to 606, 663 and 679 K, respectively. Catalyst activity decreased by Cs>K>V≈Ce>Co>Cu>Fe. The kinetic parameters of diesel particle oxidation were increased by substitutions. The pre-exponential factors decreased by Cs>K>Ce>V>Co>Fe>Cu. Large increase in pre-exponential factor compensated for the small increase in activation energy, the catalytic activities were increased. Mechanism analysis showed that all substitutions increased the catalyst surface concentrations of active sites (oxygen vacancy), thus the pre-exponential factors and the catalytic activities. As molten salt $LaVO_4$ enhanced the contact between catalyst and diesel particles, and CeO_2 produced many oxygen vacancies, each of them increased the pre-exponential factors and catalytic activities of $LaMn_{0.8}V_{0.2}O_3$ and $La_{0.8}Ce_{0.2}MnO_3$.

ACKNOWLEDGMENT

The research assitance received from National Key Basic Research and Development Program of China (2002CB211606) for this study is gratefully acknowledged.

REFERENCES

1. Q. Y. Su, W. G. Liu, J. X. Chen and J. H. Chen, *Trans. Csice*, **19**, 443 (2001).
2. D. Fino, P. Fino, G. Saracco and V. Specchia, *Korean J. Chem. Eng.*, **20**, 445 (2003).
3. J. Oi-Uchisawa, A. Obuchi and R. Enomoto, *Appl. Catal. B: Environ.*, **26**, 17 (2000).
4. B. A. A. L. van Setten, C. van Gulijk, M. Makkee and J. A. Moulijn, *Top. Catal.*, **16**, 275 (2001).
5. Y. Teraoka, K. Nakano, W. Shangguan and S. Kagawa, *Catal. Today*, **27**, 107 (1996).
6. H. Wang, Z. Zhao, C. M. Xu, J. Liu and Z. X. Lu, *Chine. Sci. Bullet.*, **50**, 1 (2005).
7. Y. Teraoka, K. Kanada and S. Kagawa, *Appl. Catal. B: Environ.*, **34**, 73 (2001).
8. H. Wang, Z. Zhao, C. M. Xu, J. Liu and Z. X. Lu, *Catal. Lett.*, **50**, 1440 (2005).
9. S. S. Hong and G. D. Lee, *Catal. Today*, **63**, 397 (2000).
10. Y. Zhang-Steenwinkel, H. L. Castricum, J. Beckers, E. Eiser and A. Bliek, *J. Catal.*, **221**, 523 (2004).
11. C. Kilroy and P. J. McGinn, *Catal. Today*, **98**, 423 (2004).
12. D. Fino, P. Fino, G. Saracco and V. Specchia, *Appl. Catal. B: Environ.*, **43**, 243 (2003).