Sr 取代 LaFeO₃ 钙钛矿的结构性质和催化性能

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摘要: Sr²⁺对 La³⁺的部分取代导致 LaFeO₃ 的结构性质和催化性能发生了显著变化。钙钛矿结构由 LaFeO₃ 的正交型变成了 La_{0.8}Sr_{0.2}FeO₃ 的近立方型。由于电荷补偿效应, Sr²⁺取代 La³⁺导致部分 Fe³⁺氧化为 Fe⁴⁺, 同时产生氧空穴, 因而提高了 La_{0.8}Sr_{0.2}FeO₃ 的还原性能。由于氧空穴的作用, La_{0.8}Sr_{0.2}FeO₃ 催化剂在 CO 氧化和 CH₄ 燃烧反应中均表现出较 LaFeO₃ 高的催化活性。在 CO 氧化反应中, 氧空穴有利于反应物分子的吸附并加速了气相氧分子在表面上的解离; 而在 CH₄ 燃烧反应中, 氧空穴则促进了晶格氧物种从体相到表面的扩散。

关键词: 钙钛矿; 铁酸镧; 取代; 还原性; 一氧化碳氧化; 甲烷燃烧

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Structural Properties and Catalytic Activity of Sr-Substituted LaFeO₃ Perovskite

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Abstract: Partial substitution of La³⁺ by Sr²⁺ in LaFeO₃ resulted in significant changes in its structure and catalytic activity. The perovskite structure was changed from orthorhombic in LaFeO₃ to nearly cubic in La_{0.8}Sr_{0.2}FeO₃. Replacement of La³⁺ by Sr²⁺ induced a positive charge deficiency that was compensated for by the oxidation of some Fe³⁺ to Fe⁴⁺ and the generation of oxygen vacancies, which greatly promoted the reducibility of the perovskite. La_{0.8}Sr_{0.2}FeO₃ gave considerably enhanced activity in CO oxidation and methane combustion because the oxygen vacancies accelerated the dissociation of gaseous oxygen on the surface in CO oxidation and facilitated the diffusion of lattice oxygen from the bulk to the surface during CH₄ combustion.

Key words: perovskite; lanthanum ferrite; substitution; reducibility; carbon monoxide oxidation; methane combustion

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Perovskite oxides with the general formula of ABO₃ have attracted increasing attention in environmental catalysis because of their superior activity for CO oxidation and methane combustion and high thermal stability [1]. In a typical perovskite structure, the large cation occupies the A site ($r_A > 0.090$ nm) and has 12 oxygen coordination atoms, while the cation with a smaller ionic radius occupies the B site ($r_B > 0.051$ nm) and coordinates with 6 oxygen atoms to ensure that the tolerance factor t is in the range 0.8–1.0 [2,3]. The A site cation is mostly either a rare earth, alkaline

earth, or alkali metal ion while the B site is usually a transition metal ion. LaMO₃ (M = Fe, Co, and Mn) are probably the most extensively studied perovskites. The B site cation in the LaMO₃ framework not only acts as the active sites but also accounts for structural stability under redox conditions [1,4,5]. LaCoO₃ and LaMnO₃ usually give higher activity [6,7] but are less stable at high temperatures [5]. LaFeO₃ has excellent thermal stability, especially under the fluctuating redox conditions of automobile exhaust gases [5].

Due to its structural flexibility, perovskites allow the par-

tial substitution of the A site or B site cation by other metal ions [8,9]. Partial replacement of the B site cation with precious metal ions has been extensively investigated. A typical example is $\text{LaFe}_{0.57}\text{Co}_{0.38}\text{Pd}_{0.05}\text{O}_3$, which even after long term aging at 1173 K still displayed good activity and stability in vehicle exhaust abatement [10]. The Pd species in this catalyst, in response to the redox condition fluctuations in automobile exhaust, could reversibly and rapidly be incorporated into and moved out of the perovskite lattice and thereby suppress the sintering of Pd crystallites [4,10–12]. Similarly, partial substitution of the trivalent A site cation (La^{3+}) with a bivalent metal ion also modifies the perovskite structure. Substitution of La^{3+} in LaMO_3 with Ca^{2+} or Sr^{2+} results in a positive charge deficiency, and to preserve electroneutrality there has to be an increase in the oxidation state of the transition metal at the B site and/or generation of structural defects such as oxygen vacancies [3,13–15]. These structural changes can give a much altered catalytic performance. For example, $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x = 0.4$ and 0.5) gave a higher activity in propane combustion than LaCoO_3 [14]. Sr^{2+} substitution of La^{3+} in LaMO_3 ($M = \text{Fe}, \text{Co},$ and Mn) significantly promoted the catalytic activity for toluene [16] and methane [17–19] combustion. However, it has also been reported that a substitution had no promotion or even a negative effect on catalytic performance. For example, compared with the parent LaFeO_3 , $\text{La}_{1-x}\text{Ca}_x\text{FeO}_3$ ($x = 0.1$ – 0.4) gave almost the same activity [3,15] while $\text{LaFe}_{1-x}\text{Mg}_x\text{O}_3$ ($x = 0.1$ – 0.5) gave much lower activity [20] in CH_4 combustion.

We have recently reported that Pd doping of the B site cation in LaFeO_3 perovskite enhanced the catalytic activity and structural stability at high temperatures and in a reducing atmosphere [21,22]. In this work, we extended this to examine the effect of Sr^{2+} substitution of the A site cation (La^{3+}) in LaFeO_3 on the structure and catalytic activity in CO oxidation and CH_4 combustion.

1 Experimental

1.1 Catalyst preparation

The $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskites ($x = 0$ or 0.2) were prepared by a sol-gel method described elsewhere [21]. Briefly, 75 ml aqueous solution containing La^{3+} , Sr^{2+} , and Fe^{3+} with a molar ratio of $(1-x):x:1$ was slowly added to 40 ml aqueous EDTA-citric acid-ammonia solution. The molar ratio of metal ions:EDTA: citric acid was fixed at 1:1:1.5. Then, 12 ml of 14.7 mol/L ammonia aqueous solution was added to the mixture to a final pH value of 4.0. The mixture was heated and refluxed at 353 K for 6 h under stirring and the excess water was slowly evaporated. The resulting gel was dried at 373 K overnight, calcined at 723 K for 3 h and at

1073 K for 5 h in air.

1.2 Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a D/MAX RB diffractometer (Rigaku) with a $\text{Cu } K_\alpha$ radiation source operated at 40 kV and 250 mA. The mean crystallite size was calculated from the most intense diffraction lines using the Scherrer equation [23]. Nitrogen adsorption-desorption isotherms were recorded at 77 K on a Nova 4200e instrument. Before the measurement, the sample was degassed at 573 K for 6 h. The specific surface areas were calculated by BET analysis of the nitrogen adsorption isotherms.

Transmission electron microscope (TEM) images were recorded on an FEI Tecnai G2 Spirit microscope operated at an acceleration voltage of 120 kV. The specimen was prepared by ultrasonically dispersing the powder sample in *n*-hexane and droplets of the suspension were deposited onto a copper grid and dried in air. Temperature-programmed reduction with hydrogen (H_2 -TPR) was performed in a microreactor equipped with a thermal conductivity detector (TCD). The sample (100 mg, 40–60 mesh) was pretreated with a 20% O_2 -80% He mixture (20 ml/min) at 973 K for 1 h to remove adsorbed carbonates and hydrates. After cooling to room temperature, the sample was fed with a 5% H_2 -95% N_2 mixture (30 ml/min) and heated to 1173 K at a rate of 10 K/min.

1.3 Catalytic tests

The catalytic reactions were tested with a fixed-bed quartz tubular reactor at atmospheric pressure. For CO oxidation, 100 mg catalyst (40–60 mesh) was loaded into the reactor and the feed gas (1% CO-20% O_2 -79% He, 30 ml/min) was introduced using a mass flow controller at a gas hourly space velocity (GHSV) of 18000 ml/(g·h). For methane combustion, 50 mg catalyst (40–60 mesh) was diluted with 250 mg of quartz sand (40–60 mesh) and the feed gas (0.5% CH_4 -10% O_2 -89.5% He, 60 ml/min) was introduced using a mass flow controller at a GHSV of 72000 ml/(g·h). The effluent from the reactor was analyzed by an online gas chromatograph equipped with a TCD and a flame ionization detector (FID). The concentration of CO_2 was determined quantitatively using a nickel catalyst for converting CO_2 to methane placed in front of the FID.

2 Results and discussion

2.1 Structural properties

Figure 1 shows the XRD patterns of the LaFeO_3 and

Fig. 1. XRD patterns of LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃. Standard XRD lines of LaFeO₃ (88-0641 and 75-0439) are given at the bottom.

La_{0.8}Sr_{0.2}FeO₃ samples. Both samples exhibited single crystalline perovskite structure. The diffraction lines of LaFeO₃ could be indexed to standard LaFeO₃ (88-0641) with an orthorhombic structure (Pnma (62) space group), while the Sr-substituted sample (La_{0.8}Sr_{0.2}FeO₃) exhibited an almost identical diffraction pattern to cubic LaFeO₃ (75-0439, Pm-3m (221) space group). This result showed that Sr substitution had induced a change in the crystalline symmetry and changed the orthorhombic structure to a nearly cubic structure. As shown in Table 1, the lattice parameters verified the structure change from orthorhombic to cubic. The lattice parameters were $a = 0.5540$ nm, $b = 0.7848$ nm, $c = 0.5520$ nm in LaFeO₃ but $a = b = c = 0.3885$ nm in La_{0.8}Sr_{0.2}FeO₃. This crystal lattice transformation from orthorhombic to nearly cubic was previously observed with La_{0.6}Ca_{0.4}FeO₃ [24,25].

Figure 1 also shows the magnified XRD patterns in 2θ range of 31.6° – 33.2° (inset). The most intense diffraction line was shifted toward a higher diffraction angle upon Sr substitution, from 32.21° in LaFeO₃ to 32.59° in La_{0.8}Sr_{0.2}FeO₃. This shrinkage of the unit cell was further confirmed by the decreased volume shown in Table 1. This was a consequence of the substitution of La³⁺ with the larger Sr²⁺ at the A site and the generation of smaller Fe⁴⁺ at the B site. Since Sr²⁺ has a lower oxidation state than La³⁺, the partial substitution of La³⁺ by Sr²⁺ caused a positive charge

deficiency. To restore the charge balance, an increase in the Fe oxidation state from Fe³⁺ to Fe⁴⁺ could occur and/or oxygen vacancies were generated. The ionic radius of Sr²⁺ (0.144 nm) was larger than that of La³⁺ (0.136 nm), but the ionic radius of Fe⁴⁺ (0.0585 nm) was smaller than that of Fe³⁺ (0.0645 nm) [26]. Therefore, the generation of smaller Fe⁴⁺ at the B site, even in small amounts, was the main reason for the unit cell shrinkage in La_{0.8}Sr_{0.2}FeO₃. Similar phenomena were observed with La_{1-x}Ca_xFeO₃ ($x = 0.1$ – 0.5 or $x = 0.2$ – 0.4) [3,24,25] and Sm_{1-x}Sr_xMnO₃ ($x = 0.1$ – 0.5) [27], where the typical diffraction lines were shifted to higher angles and the unit cell volumes were decreased compared to LaFeO₃ and SmMnO₃, respectively.

Moreover, as compared to LaFeO₃, the intensities of the diffraction lines in La_{0.8}Sr_{0.2}FeO₃ were weakened considerably and the FWHM (full width at half maximum) were broadened, indicating a decrease in crystallinity. The crystallite sizes of LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃, calculated from the most intense (121) or (110) lines, were 41.4 and 34.8 nm, respectively. The crystallite size decrease was probably caused by the change in crystal lattice symmetry and shrinkage of the unit cell, as had been demonstrated with La_{1-x}Ca_xFeO₃ [24,25]. The BET surface areas were 6.4 and 13.7 m²/g for LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃, respectively, indicating that Sr substitution at the A site of LaFeO₃ increased the surface area.

Figure 2 shows the TEM images of the LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃ samples. They were composed of agglomerated particles of irregular shapes. The sizes of the particles in both cases were 70–240 nm. These particle sizes were larger than the crystallite sizes calculated from the XRD patterns (35–41 nm), indicating that each particle was probably composed of several crystallites. However, Sr²⁺ substitution of La³⁺ in LaFeO₃ did not cause significant changes in the morphology.

Figure 3 shows the H₂-TPR profiles of the LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃ samples. LaFeO₃ gave a shoulder reduction peak at 680 K and two reduction peaks at 763 and 903 K. The shoulder peak was assigned to the reduction of Fe⁴⁺ to Fe³⁺ [3,28], which confirmed the presence of trace Fe⁴⁺ in LaFeO₃. The reduction peaks at 763 and 903 K were attributed to the reduction of Fe³⁺ to Fe²⁺ on the surface and in the bulk [28]. Quantitative analysis gave the amount of H₂ consumed at these two peaks as 0.09509 mol H₂ per mol perovskite, corresponding to 20% Fe³⁺ reduction to Fe²⁺ in

Table 1 Structural and textural parameters of LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃

Sample	Crystalline phase	$A_{\text{BET}}/(\text{m}^2/\text{g})$	D/nm	Lattice parameters (nm)			V^b/nm^3
				a	b	c	
LaFeO ₃	orthorhombic (32.21°, (121)) ^a	6.4	41.4	0.5540	0.7848	0.5520	0.2401
La _{0.8} Sr _{0.2} FeO ₃	cubic (32.59°, (110)) ^a	13.7	34.8	0.3885	0.3885	0.3885	0.0586

^a 2θ position of the most intense diffraction line and the corresponding plane. ^bUnit cell volume.

Fig. 2. TEM images of LaFeO₃ (a) and La_{0.8}Sr_{0.2}FeO₃ (b).

the perovskite structure. In another report, the H₂ consumption at 823–1023 K of LaFeO₃ was 0.22 mol H₂ per mol perovskite, corresponding to 44% Fe³⁺ reduction to Fe²⁺ [1].

Fig. 3. H₂-TPR profiles of the LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃ samples.

The La_{0.8}Sr_{0.2}FeO₃ sample, however, gave four reduction peaks at 635, 718, 826, and 923 K. Since La³⁺ and Sr²⁺ were not reducible under the current experiment conditions, all the peaks can be assigned to the reduction of Fe ions. As mentioned above, the partial replacement of La³⁺ by Sr²⁺ in LaFeO₃ resulted in a positive charge deficiency that was compensated by oxidizing Fe³⁺ to Fe⁴⁺ and/or the generation of oxygen vacancies. The peak at 635 K was due to the reduction of Fe⁴⁺ to Fe³⁺ [3,28] with a hydrogen consumption of 0.07880 mol H₂ per mol perovskite. For 20% substitution of trivalent La³⁺ by bivalent Sr²⁺ (La_{0.8}Sr_{0.2}FeO₃), 0.1 mol H₂ per mol perovskite would be required for reducing the Fe⁴⁺ species if the charge imbalance was entirely compensated for by increasing the oxidation state of Fe³⁺ to Fe⁴⁺. Here, the smaller hydrogen consumption in the H₂-TPR profile indicated that the generation of Fe⁴⁺ species was insufficient to compensate for the positive charge deficiency and oxygen vacancies were also simultaneously formed, resulting in oxygen non-stoichiometry in La_{0.8}Sr_{0.2}FeO₃. In the LaFe_{1-x}Mg_xO₃ and La_{1-x}Ca_xFeO₃ perovskites with substitution amounts $x > 0.2$, oxygen vacancies were also formed in

addition to the increase in oxidation state of Fe³⁺ to Fe⁴⁺ [20,24]. It appears that bivalent metal ion substitution of La³⁺ resulted in a similar behavior.

The reduction peaks from La_{0.8}Sr_{0.2}FeO₃ at 718, 826, and 923 K were ascribed to the reduction of Fe³⁺ to Fe²⁺ on the surface and in the bulk [28], respectively. The amount of hydrogen consumed by these peaks was 0.072 mol H₂ per mol perovskite, corresponding to 14% Fe³⁺ reduction to Fe²⁺. The reduction above 973 K in the two samples was ascribed to the reduction of Fe²⁺ to metallic Fe [28]. In summary, hydrogen reduction of La_{0.8}Sr_{0.2}FeO₃ was more and occurred at a lower temperature than LaFeO₃, demonstrating that Sr²⁺ substitution of La³⁺ significantly facilitated the reduction of the Fe ion and in turn promoted the reducibility of the perovskite.

2.2 CO oxidation and methane combustion

Figure 4 compares the activity of the LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃ catalysts for CO oxidation and CH₄ combustion. CO conversion increased with temperature (Fig. 4(a)). The La_{0.8}Sr_{0.2}FeO₃ catalyst showed a higher activity than the LaFeO₃ catalyst in the whole temperature range examined. The T_{50} (temperature at which the conversion of CO was 50%) was 559 K on La_{0.8}Sr_{0.2}FeO₃ and 585 K on LaFeO₃. CO oxidation at low temperature on perovskites is considered as a surface process [29], and the activity is closely linked with surface oxygen vacancies that facilitated the adsorption of the reactant molecule and accelerated the dissociation of oxygen molecules [14,24]. Therefore, the oxygen vacancies in La_{0.8}Sr_{0.2}FeO₃, observed in the H₂-TPR measurement, were mainly responsible for the better performance in CO oxidation.

Figure 4(b) shows the methane conversions over the LaFeO₃ and La_{0.8}Sr_{0.2}FeO₃ catalysts. Both samples exhibited S-type activity profiles and the conversion of methane increased with temperature. LaFeO₃ displayed a T_{50} of 901 K while with La_{0.8}Sr_{0.2}FeO₃, there was a decreased T_{50} to 827 K, showing its better activity. Unlike CO oxidation, CH₄

Fig. 4. CO oxidation (a) and CH₄ combustion (b) over the LaFeO₃, La_{0.9}Sr_{0.1}FeO₃, and La_{0.8}Sr_{0.2}FeO₃ catalysts.

combustion on oxides also includes a bulk process involving bulk oxygen species that are active at temperatures higher than 673 K [13,30]. Lattice oxygen species migrate from the bulk to the surface and participate in methane oxidation. Consumed lattice oxygen is replenished by gaseous oxygen through a Mars-Van Krevelen mechanism [13,29,30]. The higher activity of La_{0.8}Sr_{0.2}FeO₃ for methane combustion was probably related to the presence of oxygen vacancies, but the mechanism differed from that in CO oxidation. The oxygen vacancies increased lattice oxygen mobility and facilitated the diffusion of lattice oxygen from the bulk to the surface [14,24], and thus promoted the catalytic activity. La_{0.8}Sr_{0.2}CoO₃ and La_{0.9}Ce_{0.1}CoO₃ perovskites were also observed to show enhanced activity in CH₄ combustion due to the generation of oxygen vacancies by A site substitution [31].

Although the structure symmetry was changed from orthorhombic in LaFeO₃ to nearly cubic in La_{0.8}Sr_{0.2}FeO₃, the enhanced catalytic activity in CO oxidation and methane combustion cannot be simply associated with the crystalline symmetry. This is because the samples with less Sr substitution, for example, La_{0.9}Sr_{0.1}FeO₃, still had the orthorhombic perovskite structure but showed higher activity than the parent LaFeO₃. The T_{50} of La_{0.9}Sr_{0.1}FeO₃ in CO oxidation and CH₄ combustion were 566 and 840 K (Fig. 4), which were decreased by 19 and 61 K compared to LaFeO₃, respectively. On the other hand, although the surface area of La_{0.8}Sr_{0.2}FeO₃ (13.7 m²/g) was higher than that of LaFeO₃ (6.4 m²/g), the higher activity cannot be simply ascribed to the increased surface area. This is because La_{0.9}Sr_{0.1}FeO₃ had a smaller surface area (9.7 m²/g) than La_{0.8}Sr_{0.2}FeO₃ but still gave a similar catalytic performance. These results indicated that the superior activity of La_{0.8}Sr_{0.2}FeO₃ was mainly due to the oxygen vacancies in its perovskite structure.

3 Conclusions

Substitution of 20% La³⁺ by Sr²⁺ in LaFeO₃ changed the crystalline structure from orthorhombic to cubic. The resulting charge imbalance was compensated for by the oxidation state of some Fe³⁺ increase to Fe⁴⁺ and the generation of oxygen vacancies, which improved the reducibility of the perovskite. As a consequence, the La_{0.8}Sr_{0.2}FeO₃ catalyst showed enhanced activity in CO oxidation and methane combustion. The oxygen vacancies accelerated the dissociation of oxygen molecules in CO oxidation and facilitated the diffusion of lattice oxygen from the bulk to the surface in methane combustion.

References

- Ziaei-Azad H, Khodadadi A, Esmailnejad-Ahranjani P, Mortazavi Y. *Appl Catal B*, 2011, **102**: 62
- Tejucá L G, Fierro J L G. *Properties and Applications of Perovskite-Type Oxides*. New York: Marcel Dekker, 1993. 1
- Ciambelli P, Cimino S, Lisi L, Faticanti M, Minelli G, Pettiti I, Porta P. *Appl Catal B*, 2001, **33**: 193
- Tanaka H, Taniguchi M, Kajita N, Uenishi M, Tan I, Sato N, Narita K, Kimura M. *Top Catal*, 2004, **30/31**: 389
- Tan I, Tanaka H, Uenishi M, Kaneko K, Mitachi S. *J Ceram Soc Jpn*, 2005, **113**: 71
- Wang Y G, Ren J W, Wang Y Q, Zhang F Y, Liu X H, Guo Y, Lu G Zh. *J Phys Chem C*, 2008, **112**: 15293
- Najjar H, Lamonier J F, Mentre O, Giraudon J M, Batis H. *Appl Catal B*, 2011, **106**: 149
- Tanaka H, Misono M. *Curr Opin Solid State Mater Sci*, 2001, **5**: 381
- Tanaka H, Taniguchi M, Uenishi M, Kajita N, Tan I, Nishihata Y, Mizuki J, Narita K, Kimura M, Kaneko K. *Angew Chem, Int Ed*, 2006, **45**: 5998
- Nishihata Y, Mizuki J, Akao T, Tanaka H, Uenishi M, Kimura

- M, Okamoto T, Hamada N. *Nature*, 2002, **418**: 164
- 11 Uenishi M, Tanaka H, Taniguchi M, Tan I, Nishihata Y, Mizuki J, Kobayashi T. *Catal Commun*, 2008, **9**: 311
- 12 Matsumura D, Nishihata Y, Mizuki J, Taniguchi M, Uenishi M, Tanaka H. *J Appl Phys*, 2010, **107**: 124319
- 13 Leanza R, Rossetti I, Fabbrini L, Oliva C, Forni L. *Appl Catal B*, 2000, **28**: 55
- 14 Merino N A, Barbero B P, Grange P, Cadus L E. *J Catal*, 2005, **231**: 232
- 15 Pecchi G, Reyes P, Zamora R, Campos C, Cadus L E, Barbero B P. *Catal Today*, 2008, **133–135**: 420
- 16 Deng J G, Dai H X, Jiang H Y, Zhang L, Wang G Zh, He H, Au C T. *Environ Sci Technol*, 2010, **44**: 2618
- 17 Wang Ch H, Chen Ch L, Weng H Sh. *Chemosphere*, 2004, **57**: 1131
- 18 Ferri D, Forni L. *Appl Catal B*, 1998, **16**: 119
- 19 Ponce S, Pena M A, Fierro J L G. *Appl Catal B*, 2000, **24**: 193
- 20 Ciambelli P, Cimino S, De Rossi S, Lisi L, Minelli G, Porta P, Russo G. *Appl Catal B*, 2001, **29**: 239
- 21 Zhang X J, Li H J, Li Y, Shen W J. *Catal Lett*, 2012, **142**: 118
- 22 Zhang X J, Li Y, Li H J, Shen W J. *J Nat Gas Chem*, 2012, **21**: 113
- 23 Cullity B D. *Elements of X-Ray Diffraction*. 2nd Ed. Menlo Park: Addison-Wesley Press, 1978. 102
- 24 Barbero B P, Gamboa J A, Cadus L E. *Appl Catal B*, 2006, **65**: 21
- 25 Pecchi G, Jiliberto M G, Delgado E J, Cadús L E, Fierro J L G. *J Chem Technol Biotechnol*, 2011, **86**: 1067
- 26 Shannon R D. *Acta Crystallogr A*, 1976, **A32**: 751
- 27 Ciambelli P, Cimino S, De Rossi S, Faticanti M, Lisi L, Minelli G, Pettiti I, Porta P, Russo G, Turco M. *Appl Catal B*, 2000, **24**: 243
- 28 Zhang R D, Villanueva A, Alamdari H, Kaliaguine S. *J Catal*, 2006, **237**: 368
- 29 Voorhoeve R J H, Remeika J P, Trimble L E. *Ann N Y Acad Sci*, 1976, **272**: 3
- 30 Teng F, Han W, Liang S H, Gaugeu B, Zong R L, Zhu Y F. *J Catal*, 2007, **250**: 1
- 31 Chen Ch Q, Li W, Cao Ch Y, Song W G. *J Mater Chem*, 2010, **20**: 6968