



Cite this: *RSC Adv.*, 2019, 9, 31035

Comparative study of mesoporous Ni_xMn_{6-x}Ce₄ composite oxides for NO catalytic oxidation

Li Weiman,^{id}abcd Liu Haidi,^a Zhang Min^{ab} and Chen Yunfa^{id}*ad

In this work, a series of mesoporous Ni_xMn_{6-x}Ce ternary oxides were prepared to investigate their NO catalytic oxidation ability. The sample Ni₂Mn₄Ce₄ showed a 95% NO conversion at 210 °C (GHSV, ~80 000 h⁻¹). Characterization results showed the good catalytic performance of Ni₂Mn₄Ce₄ was due to its high specific surface area, more surface oxygen and high valance manganese species, which can be ascribed to the incorporation of three elements. Based on the results of XRD, H₂-TPR, O₂-TPD and XPS, we confirmed the existence of Ni³⁺ + Mn³⁺ → Ni²⁺ + Mn⁴⁺, Ce⁴⁺ + Ni²⁺ → Ce³⁺ + Ni³⁺ in Ni₂Mn₄Ce₄, and the oxidation–reduction cycles were proved to be helpful for NO oxidation. The results from an *in situ* DRIFTS study indicated the presence of bidentate nitrate and monodentate nitrate species on the catalyst's surface. The nitrate species were proved to be intermediates for NO oxidation to NO₂. A nitrogen circle mechanism was proposed to explain the possible route for NO oxidation. Nickel introduction was also helpful to improve the SO₂ resistance of the NO oxidation reaction. The activity drop of Ni₂Mn₄Ce₄ was 13.15% in the presence of SO₂, better than Mn₆Ce₄ (25.29%).

Received 5th July 2019
Accepted 23rd September 2019

DOI: 10.1039/c9ra05098a

rsc.li/rsc-advances

1 Introduction

Nitrogen monoxide, nitrogen dioxide and nitrous oxide, known as nitrogen oxides (NO_x) are important pollutants in causing a series of environmental problems, such as acid rain, photochemical smog, and ozone depletion.¹ Many technologies have been developed to deal with NO_x, such as NH₃-selective catalytic reduction, ozone assisted NO oxidation, and NO_x storage reduction.² The oxidation of NO to NO₂ is an important step for almost all the NO abatement technologies; for example, NO oxidation can enhance NH₃-SCR to follow a fast SCR mechanism,³ and in the wet scrubbing method, the conversion of NO to NO₂ is helpful to increase NO_x removal efficiency.^{4,5} Therefore, much effort has been made to develop catalysts with good NO oxidation ability.

Several types of catalysts, including noble metal catalysts,⁶ supported catalysts,⁷ and multi-metal oxide catalysts^{8,9} were reported to have good catalytic activities under different reaction conditions. Multi-metal composites have good catalytic activities in the low and middle temperature range (100–320 °C), which are suitable to be applied in flue gas. Among them, manganese and ceria composite oxides have been reported

several times for their excellent redox properties, oxygen storage capacity, and excellent performance in NO oxidation.¹⁰ However, the NO oxidation ability of Mn–Ce composites is severely affected by SO₂ in real application condition. Researches confirmed that SO₂ can react with manganese species to form sulfate salts, leading to irreversible activity decrease.¹¹ It is commonly accepted that in the process of NO catalytic oxidation, NO were firstly adsorbed on the surface of catalysts to form nitrates; and then nitrates were reacted with O₂ to form NO₂.^{9,12} On one hand, the introduction of SO₂ in the flue gas may influence the formation of different types of nitrates. On the other hand, the type of nitrates formed on the catalysts surface are related to surface oxygen species and manganese valence, which were influenced by morphology, element dopant *et al.* To get catalysts with excellent catalytic performance and good SO₂ resistance, a second/third element dopant is a facile way. Several studies have reported a third dopant to Mn–Ce composites to improve their NO oxidation performance, because the regulated manganese and oxygen species.^{11b,13} However, few were focused on both catalytic performance and SO₂ tolerance. The goal of this study is to improve both NO oxidation ability and SO₂ tolerance of classical Mn–Ce composites. Nickel was selected as the third dopant, because introduction of nickel lead to more surface oxygen and regulate metal valence. Moreover, SO₂-TPD confirmed that introduction of nickel to Mn–Ce composites was helpful to reduce SO₂ adsorption.¹⁴ In this study, we fabricated a series of Ni_xMn_{6-x}Ce₄ ternary oxides to further discuss interaction among three elements. The Ni₂Mn₄Ce₄ catalysts showed best low temperature activity and good SO₂ resistance.

^aState Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China. E-mail: chenyl@ipe.ac.cn

^bUniversity of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, China

^cZhongke Langfang Institute of Process Engineering, Langfang Economic & Technical Development Zone, Fenghua Road No 1, Hebei, China

^dCAS Center for Excellence in Urban Atmospheric Environment, Xiamen 361021, China



2 Experimental sections

2.1 Catalysts preparation

Previous studies^{15,16} had shown that Mn/Ce composites with a molar ratio equal or slightly more than 1 showed a most active catalytic activity; similar with our previous work, in which the catalyst with a molar ratio of Mn/Ce = 6/4 had the best catalytic performance, because strong interaction between manganese and ceria. As a result, nickel substituted Mn₆Ce₄ catalysts were prepared, denoted as Ni_xMn_{6-x}Ce₄, where *x* represented the relative molar ratio of Ni and Mn. All chemicals used in this study, such as Mn(NO₃)₂ (50 wt%), Ce(NO₃)₃·6H₂O, Ni(NO₃)₂·6H₂O and NaOH were purchased from Xilong Cop. (China) and used without further purification. The mesoporous composites were prepared through a nano-casting method by employing KIT-6 as templates. KIT-6 silica was prepared as previously reported studies.¹⁷ In a typical procedure, 1.0 g KIT-6 was suspended in 80 mL *n*-hexane and stirred at room temperature for 2 h. Then a mixed solution of Mn(NO₃)₂, Ni(NO₃)₂ and Ce(NO₃)₃ was added slowly with vigorous stirring. After stirred overnight, the mixture was filtered and dried at 80 °C for 24 h. The obtained powder was calcined at 550 °C for 4 h, with a heating rate of 2 °C min⁻¹ in air. Finally, the sample was treated three times with a 2 M NaOH solution, washed to pH ~ 7 and dried at 80 °C.

2.2 Catalytic activity evaluation

The NO catalytic oxidation activity tests of prepared samples were performed in a fix-bed quartz tubular reactor. 100 mg catalysts (40–60 mesh) were placed in the reactor, with a weight hourly space velocity (WHSV) of 60 000 mL g⁻¹ h⁻¹ (GHSV ~ 85 000 h⁻¹). The feed gas consisted of 200 ppm NO, 5% O₂, 200 ppm SO₂ (when used) and balance N₂, with a flow rate of 0.1 L min⁻¹. The concentration of NO and NO₂ were monitored by a two channel CLD60 (Eco physics) instrument. NO conversion rate was calculated by:

$$\text{NO conversion} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}}) / \text{NO}_{\text{in}} \times 100\%$$

2.3 Characterization

XRD patterns were recorded on a PANalytical X'Per PRO X-ray diffraction in 2θ from 5° to 90° with a scanning step of 0.0334°. The specific surface area and pore size distributions of all catalysts were obtained according to the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively, using N₂ adsorption–desorption method on an automatic surface analyzer (SSA-7300, BJ-Builder, China) at 77 K. Each sample was pre-degassed at 150 °C for 3 h. H₂ temperature-programmed reduction (H₂-TPR) was conducted on a Micromeritics Chemisorb 2720 analyzer (Micromeritics, USA) at a heating rate of 10 °C min⁻¹ with 5% H₂/Ar gas. The H₂ consumption was recorded continuously to investigate reduction abilities. O₂-TPD was performed on a BJ-Builder 1200 apparatus; 100 mg 40–60 mesh sample was firstly heated to 500 °C and kept for 30 min in He flow to remove surface

adsorptive species. After cooling down to 50 °C, the sample was treated in O₂ for 1 h, and then blew with He for 30 min. Finally, the TCD signal was collected to 900 °C at 10 °C min⁻¹ in 30 mL min⁻¹ He flow. Surface species of as-prepared catalysts were determined by X-ray photoelectron spectroscopy (XPS) using a XLESCALAB 250 Xi electron spectrometer (Thermo Scientific, USA) with monochromatic Al Kα radiation (1486.6 eV). A Bruker Vertex 70 spectrometer (Bruker, USA) equipped with diffuse reflectance accessory (PIKE, and MCT/A detector cooled by liquid nitrogen) was used for recording the *in situ* DRIFT spectra of the samples. The sample was pretreated at 300 °C for 2 h in N₂ (50 mL min⁻¹). The reaction system was cooled to 200 °C in N₂, and the spectra were collected as background. The feed gas was 250 ppm NO, 5% O₂ (when used), and balance N₂, with a flow rate of 0.1 L min⁻¹. When the spectra was pre-adsorbed by NO or NO + O₂, then purged by N₂ for 30 min to remove weakly adsorbed species, and finally recorded by accumulating 32 scans at a resolution of 4 cm⁻¹.

3 Results and discussions

3.1 Catalytic performances

The NO–NO₂ catalytic activities of as-prepared catalysts were tested and compared from 120 °C to 360 °C, and the results were shown in Fig. 1. NO conversion rate over all catalysts firstly raised to a peak with the temperature increasing; then NO conversion rate decreased as the reaction temperature continuous increasing. Ni₁Mn₅Ce₄ and Ni₂Mn₄Ce₄ reached its highest NO conversion of 90% and 95% at 210 °C, respectively. Mn₆Ce₄ and Ni₃Mn₃Ce₄ reached their maximum NO conversion of 85% and 81% at 240 °C, respectively. Ni₄Mn₂Ce₄ and Ni₁Mn₅Ce₄ had a similar NO conversion of 77% at 270 °C. Ni₆Ce₄ performed the worst NO conversion, with its maximum conversion of 60% at 300 °C. The catalytic activity of different samples varied at low temperature, and mainly followed the sequence of Ni₂Mn₄Ce₄ > Ni₁Mn₅Ce₄ > Mn₆Ce₄ > Ni₃Mn₃Ce₄ > Ni₄Mn₂Ce₄ > Ni₅Mn₁Ce₄ > Ni₆Ce₄. The sample Ni₂Mn₄Ce₄ can reach its maximum NO conversion of 95% at 210 °C, better than previous studies shown in Table 1.

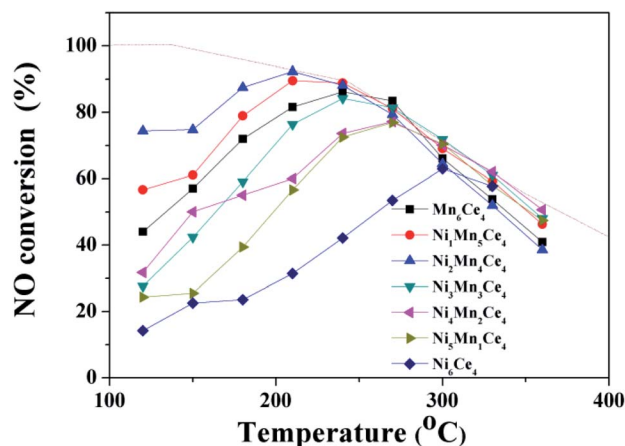


Fig. 1 NO catalytic oxidation performance of Ni_xMn_{6-x}Ce₄ composites.

Table 1 Summary of the properties of catalysts in literature

Catalyst	Preparation method	Reaction conditions	NO conversion	References
γ -MnO ₂	Hydro-thermal synthesis, powder	500 ppm NO, 5% O ₂ , 24 000 h ⁻¹	250 °C, 86.4%	19
MnO ₂	Precipitation method, powder	500 ppm NO, 5% O ₂ , 48 000 mL g ⁻¹ h ⁻¹	210 °C, 91%	12a
Ce-Co composite oxides	Sol-gel method, powder	300 ppm NO, 10% O ₂ , 20 000 h ⁻¹	230 °C, 93%	18
Urchin-like γ -MnO ₂	Hydro-thermal synthesis, powder	500 ppm NO, 10% O ₂ , 75 000 h ⁻¹	280 °C, 88%	20
Ni ₂ Mn ₄ Ce ₄	Nano-casting method, powder	200 ppm NO, 5% O ₂ , 60 000 mL g ⁻¹ h ⁻¹	210 °C, 95%	This work

As the conversion of NO to NO₂ is an exothermal reaction, and the reaction is thermodynamic limited at higher temperature.^{12,18} The thermodynamic equilibrium of NO to NO₂ under the same condition was shown in dashed line. At high temperature, the catalytic activity was closely related to the equilibrium, which indicated the reaction was thermodynamic control. However, it can be seen that the low temperature catalytic activity was related to the relative ratios of manganese and nickel. To investigate the effect, further characterizations were applied and discussed in the following parts.

3.2 Physicochemical properties

3.2.1 Structural characterization. The structural properties of all oxides were examined by XRD, and the results were shown in Fig. 2. All the catalysts exhibited peaks associated with CeO₂ (JCPDS 00-001-0800). The peaks located at 28.6°, 33.2°, 47.8°, 59.6°, corresponding to the (111), (200), (220), and (222) planes of CeO₂, respectively. No peaks related to MnO_x were observed,

indicating in all samples manganese incorporated into ceria lattice, similar with previous study.²¹ When $x > 4$, the peaks (Ni₅Mn₁Ce₄ and Ni₆Ce₄) located at 37.4°, 43.4°, 62.7°, 75.6°, 78.6°, can be assigned to (111), (200), (220), (311), (222) planes of NiO (JCPDS 00-001-1239). At a high Ni level, separate phase NiO were formed in the composites. But when $x \leq 4$, there were no peaks of NiO. At a low Ni level, as there is no NiO related peaks, nickel may exist in two forms: (i) NiO clusters in ceria lattice, and (ii) Ni²⁺ in ceria lattice. C. Lamonier²² reported in Ni-Ce composites, when Ni/Ce \leq 0.5, Ni²⁺ can entrance ceria lattice to substitute Ce⁴⁺, which can be proved by XRD peak shift of ceria. As there were peak shifts in all samples shown in Fig. 2(B), manganese and part of nickel may both can enter ceria lattice. The ceria lattice constants obtained from XRD reflections of all samples were shown in Fig. 2(C), and it may be influenced both by manganese and nickel in this study. With x increased from 0 to 6, the calculated lattice constants gradually increased, and then was stable at \sim 0.5411 nm, which was close

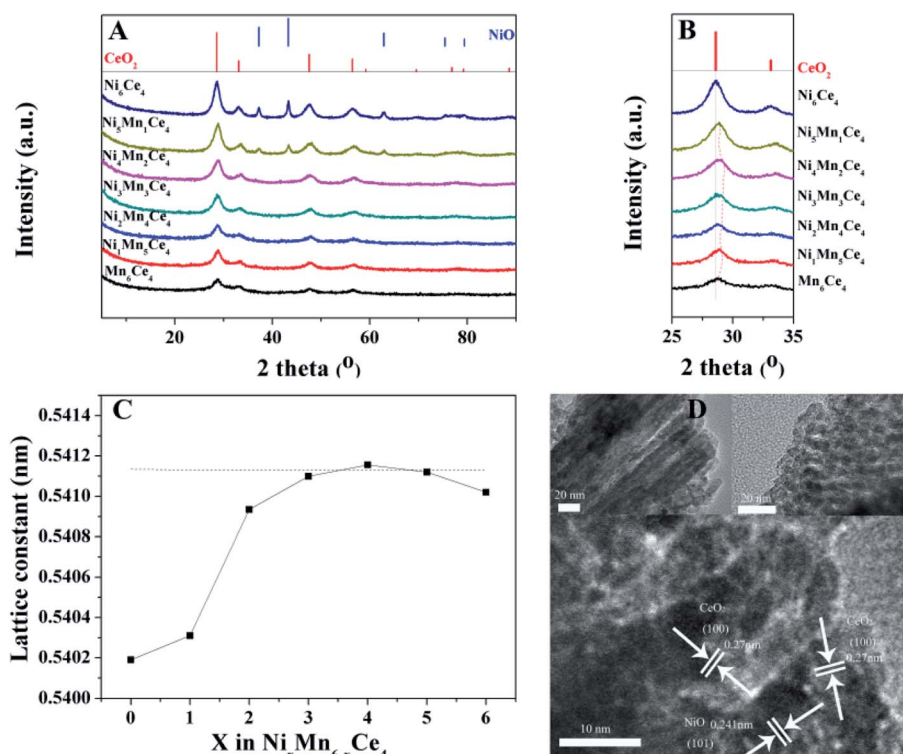


Fig. 2 (A) X-ray diffraction patterns of Ni_xMn_{6-x}Ce₄ composites; (B) magnification of a peak assigned to CeO₂ (111); (C) CeO₂ lattice constants of different samples as a function of x ; and (D) TEM and HRTEM images of Ni₂Mn₄Ce₄.

to the lattice constant of pure CeO₂. For Ni₅Mn₁Ce₄ and Ni₆Ce₄, which had obvious NiO peaks, the NiO lattice constants were 0.2953 nm and 0.2955 nm, respectively, similar with pure NiO (0.2955 nm). This suggested that at a high nickel level, nickel and ceria were formed separate phases, similar with Zhu's report.²³ For Ni₂Mn₄Ce₄, TEM images (Fig. 2(D)) showed that ~10 nm NiO particles dispersed in CeO₂ matrix, and no evidence of MnO_x were observed. Combined with conclusion from peak shift study, at a low nickel content, nickel oxide was present in ceria, probably in the form of nano-clusters, and with an amount of Ni²⁺, as a result, there was no peak related to NiO. Based on above analysis, the lattice constants variation when $x < 3$ may probably due to manganese and nickel ions, which can enter ceria lattice to form solid solution, because the ionic radius of Mn⁴⁺ and Ni²⁺ are smaller than Ce⁴⁺. For Ni₂Mn₄Ce₄, manganese and part of nickel ions may enter ceria lattice to form solid solution, while NiO cluster may well dispersed in the matrix of solid solution.

As surface area and pore size of catalysts contributed much to catalytic activity, the N₂ adsorption-desorption isotherms and pore size distributions were shown in Fig. 3; the specific area and average pore size were also summarized in Table 2. All the catalysts showed a type IV isotherm with a H₃ hysteresis loop, indicating the existence of mesoporous structure. The specific surface area followed a sequence of Ni₂Mn₄Ce₄ > Ni₁Mn₅Ce₄ > Ni₃Mn₃Ce₄ > Ni₄Mn₂Ce₄ > Mn₆Ce₄ > Ni₄Mn₂Ce₄ > Ni₅Mn₁Ce₄ > Ni₆Ce₄. It can be seen that the surface area of the

catalysts firstly increased with nickel addition, and then decreased, indicating the three elements incorporated with each other. The Ni₂Mn₄Ce₄ catalyst had the largest surface area, which may also have more active sites for NO adsorption and oxidation, consistent with NO catalytic activity. It was interesting that when $x < 4$, nickel content increase could enlarge surface area; when $x > 4$, surface area decreased with further nickel addition. The results were consistent with XRD patterns, because when $x > 4$, the high crystallinity was a reason for surface area decrease. As the samples all presented only CeO₂ phase when $x < 4$, it was more meaningful to discuss these samples. The specific area of samples from Ni₁Mn₅Ce₄ to Ni₄Mn₂Ce₄ were larger than Mn₆Ce₄, so it is reasonable to attribute the change to the introduction of nickel into Mn-Ce system. The H₂-TPR and XPS results in the following parts would also support our hypothesis.

3.2.2 Temperature programmed reduction/desorption. The H₂-TPR was used to investigate redox properties of the catalysts, which were usually related to catalytic activities. As shown in Fig. 4(A), the Mn₆Ce₄ sample presented three main peaks, centered at 297 °C, 405 °C and 485 °C, which can be assigned to the reduction of Mn⁴⁺ → Mn³⁺, Mn³⁺ → Mn²⁺ and Ce⁴⁺ → Ce³⁺, respectively.²⁴ When x increased to 2, the peak related to Mn⁴⁺ → Mn³⁺ shifted to lower temperature range (262 °C and 234 °C), indicating the improvement of reduction properties; this may be caused by increase of high valance manganese species.²⁵ There was a new peak appeared at ~358 °C for Ni₂Mn₄Ce₄, and with increasing x , the peak intensity becomes stronger. We certainly ascribed the peak to the reduction of NiO_x.²⁶ When x was larger than 3, a new shoulder peak at ~300 °C appeared; however, the peak disappeared when manganese was fully substituted by nickel. This small shoulder peak may be related to the reduction of manganese species, indicating the further increase of manganese valence caused by nickel addition. There was a board peak at 365 °C for Ni₆Ce₆, which can be ascribed to the overlap of reduction of nickel species and ceria species. From the lower reduction temperature of different samples, it was interpreted that the corporation of Mn, Ce, Ni reached a maximum for Ni₂Mn₄Ce₄, therefore greatly enhanced the reducibility of catalysts.

The O₂-TPD spectra were shown in Fig. 4(B), and were used to determine the oxygen species in different samples. The O₂-desorption spectra were divided into three segments, according to their desorption temperature.²⁷ The peaks < 400 °C (denoted

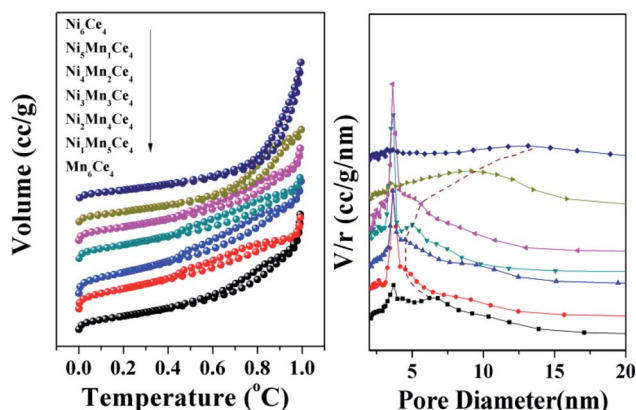


Fig. 3 N₂ adsorption-desorption isotherm and pore size distributions of composites, and their specific surface area data.

Table 2 Summarized physical properties and surface species ratios of all samples

Samples	BET ^a (m ² g ⁻¹)	Pore volume ^b (mL g ⁻¹)	Pore diameter ^a (nm)	O _{ads} ^c /(O _{latt} + O _{ads})	Ni ³⁺ /Ni ^{2+c}	Mn ³⁺ /Mn ^{4+c}	Ce ³⁺ /Ce ^{4+c}
Mn ₆ Ce ₄	152.116	0.3955	10.70	0.81	—	0.68	0.27
Ni ₁ Mn ₅ Ce ₄	208.031	0.3051	7.28	0.91	11.15	0.64	0.34
Ni ₂ Mn ₄ Ce ₄	221.013	0.3867	6.24	0.98	3.46	0.42	0.28
Ni ₃ Mn ₃ Ce ₄	160.861	0.2849	8.66	0.88	3.74	0.51	0.56
Ni ₄ Mn ₂ Ce ₄	159.982	0.3237	7.22	0.94	1.87	0.50	0.33
Ni ₅ Mn ₁ Ce ₄	122.246	0.3285	11.20	0.90	0.57	0.81	0.45
Ni ₆ Ce ₄	108.082	0.5125	17.64	0.91	0.35	—	0.41

^a Calculated by BET method, obtained from N₂ adsorption at 77 K. ^b Determined by adsorption capacity at relative pressure of $P/P_0 = 0.99$.

^c Calculated from XPS data.

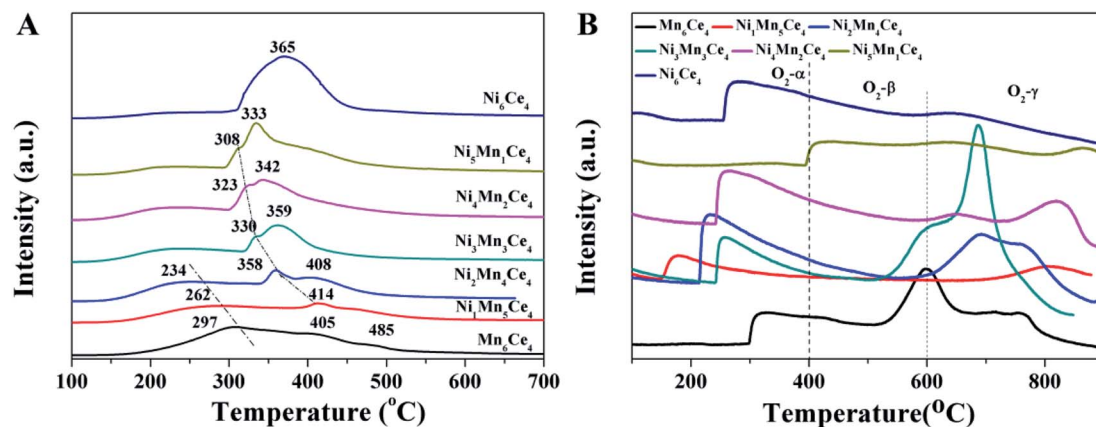


Fig. 4 (A) The H_2 -TPR and (B) O_2 -TPD profile of different catalysts.

as $\text{O}_2\text{-}\alpha$) was ascribed to the desorption of weakly adsorbed oxygen species. The peaks between 400 and 600 °C ($\text{O}_2\text{-}\beta$) were related to surface non-stoichiometric oxygen desorption.²⁸ And the peaks > 600 °C ($\text{O}_2\text{-}\gamma$) represented that the remained lattice oxygen was continuously declined, indicating higher valence of metal ions were reduced to lower valence. As the reaction temperature of NO oxidation in this study was lower than 400 °C, it was more meaningful to discuss $\text{O}_2\text{-}\alpha$. The peak areas related to $\text{O}_2\text{-}\alpha$ for samples $\text{Ni}_x\text{Mn}_{6-x}\text{Ce}_4$ (x from 0 to 6) were 6381, 7235, 8793, 6125, 5006, 236, and 6104, respectively. $\text{Ni}_2\text{Mn}_4\text{Ce}_4$ exhibited the most $\text{O}_2\text{-}\alpha$ species, and the result was consistent with XPS data in the next part.

3.2.3 Surface species valance analysis. In order to investigate details of surface species and obtain more information about cooperation among three elements, XPS spectra of different samples have been recorded and fitted, as shown in Fig. 5. The O 1s spectra can be fitted into three peaks as shown in Fig. 5(A). The peak centered at 529.7 eV was assigned to surface lattice oxygen (O_α), and the peaks at 531.4 eV and 533.1 eV can be assigned to surface adsorbed oxygen (O_β) and

surface weakly adsorbed water (O_γ), respectively.²⁹ Because of mesoporous structure, the intensity of O_γ peak of all catalysts was much stronger than O_α and O_β , indicating much weakly adsorbed water on surface. The ratios of $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ were shown in Table 2. It is accepted that surface oxygen species are important in catalytic oxidation process.³⁰ The $\text{Ni}_2\text{Mn}_4\text{Ce}_4$ catalyst exhibited the largest $\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$ ratio, leading to the maximum NO oxidation activity.

Fig. 5(B) showed the Mn 2p spectra of $\text{Ni}_x\text{Mn}_{6-x}\text{Ce}_4$ ($x = 0\text{--}6$), and Mn 2p_{3/2} can be de-convoluted into two peaks. The peaks at 643.2 eV and 641.4 eV can be assigned to Mn^{4+} and Mn^{3+} , indicating a mixed valence manganese state.³¹ As shown in Table 2, the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ was associated with Ni/Mn molar ratio. $\text{Ni}_2\text{Mn}_4\text{Ce}_4$ showed the smallest proportion of $\text{Mn}^{3+}/\text{Mn}^{4+}$, indicating more high valence Mn species in it. Furthermore, the catalytic performance sequence is consistent with $\text{Mn}^{3+}/\text{Mn}^{4+}$, indicating high valence manganese may be the active sites for NO oxidation.

The Ni 2p XPS spectra was convoluted into three peaks in Fig. 5(C). The peaks can be assigned to the main peak of Ni 2p

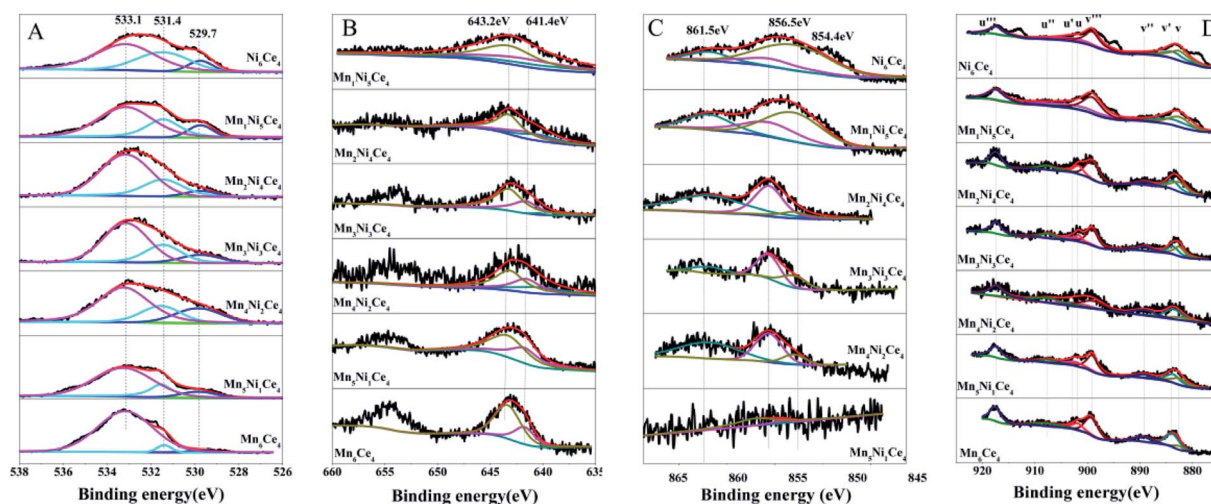


Fig. 5 The XPS spectra of $\text{Ni}_x\text{Mn}_{6-x}\text{Ce}$ catalysts, (A) O 1s, (B) Mn 2p, (C) Ni 2p and (D) Ce 3d.

and two satellite peaks, which were located at 854.4 eV, 856.5 eV and 861.5 eV, respectively. The peak at 854.4 eV (with satellite 861.5 eV) was corresponding to Ni²⁺ species;³² and the peak at 856.5 eV origins from Ni³⁺ species.³³ The Ni³⁺/Ni²⁺ ratios of different samples were summarized in Table 1. When *x* was less than 3, the Ni³⁺/Ni²⁺ firstly decreased and then increased. Ni₂Mn₄Ce₄ had the lowest Ni³⁺/Ni²⁺ and Mn³⁺/Mn⁴⁺, indicating the existence of Ni³⁺ + Mn³⁺ → Ni²⁺ + Mn⁴⁺. However, when *x* was more than 3, Ni³⁺/Ni²⁺ decreased sharply, indicating nickel species were mainly existed in the form of Ni²⁺. This was consistent with XRD results, with the appearance of NiO peaks. The results showed that the addition of nickel could regulate the manganese valence, especially when *x* < 3. When *x* > 3, nickel oxide was hard to form solid solution with ceria, therefore leading to separate phase of NiO and CeO₂.

The Ce 3d spectra can be decomposed into eight peaks, as shown in the assignments of Fig. 5(D). According to literatures, The two bands labeled as v' and u' corresponded to Ce³⁺, and the other six bands can be assigned to Ce⁴⁺.³⁴ The Ce³⁺/Ce⁴⁺ ratios were summarized in Table 1. Surprisingly, although molar ratio of cerium didn't change, the Ce³⁺/Ce⁴⁺ ratios varied among different samples. This indicated there was also an interaction between cerium, nickel and manganese. Compared with other samples, Ni₂Mn₄Ce₄ presented lowest Ce³⁺/Ce⁴⁺ ratio. More surface Ce⁴⁺ species would facilitate Ni²⁺ + Ce⁴⁺ → Ce³⁺ + Ni³⁺, therefore enhancing the reaction of Ni³⁺ + Mn³⁺ → Ni²⁺ + Mn⁴⁺.

From the above characterizations, it can be concluded Ni₂Mn₄Ce₄ exhibited biggest specific surface area, high ratio of Mn⁴⁺, which can make it more productive in NO catalytic oxidation.

3.3 In situ DRIFTS study

As Ni₂Mn₄Ce₄ presented the best NO catalytic oxidation activity, a series of *in situ* DRIFTS experiments were investigated in order to study NO and/or O₂ adsorption behaviors.

3.3.1 NO adsorption behaviors on Ni₂Mn₄Ce₄. Fig. 6(A) exhibited the *in situ* DRIFTS spectra of Ni₂Mn₄Ce₄ catalysts exposed to NO + O₂/N₂ for 30 min at different temperatures,

several bands at 1651, 1635, 1625, 1577, 1556, 1541, 1519, 1505, 1487 and 1309 cm⁻¹ were detected. The bands at 1651, 1635, and 1625 cm⁻¹ can be assigned to adsorbed NO₂.^{20,35} The bands at 1577, 1556, 1541, 1505, 1487 cm⁻¹ were ascribed to bidentate nitrate;³⁶ and the bands at 1519 and 1309 cm⁻¹ can be assigned to monodentate nitrate.²⁰ Different from previous reports, the intensity of bands related to adsorbed NO₂ were much high, which may be due to the large surface area of the catalyst. The NO₂ were adsorbed on the inner surface of the catalysts, and with temperature increased, its intensity decreased, indicating desorption of NO₂ at higher temperature. As the relative intensity of bidentate nitrate and monodentate nitrate species was not significant, the time-dependent spectra were obtained at ~180 °C to further investigate the NO and O₂ adsorption/desorption behaviors on catalyst, as shown in Fig. 6(B).

When 250 ppm NO (balanced with N₂) was introduced, the peaks intensity increased with time. The existence of NO₂ related peak indicated that NO can react with surface oxygen to form NO₂. The peak at 1288 cm⁻¹ can be assigned to monodentate nitrate and it shifted to 1341 cm⁻¹, which can be ascribed to *cis*-dimer nitroso. When O₂ was introduced to the flue gas, the nitrate peaks first increased and then decreased. However, the NO₂ peaks increased with time. This indicated nitrate may be an important intermediate to form NO₂, and it can be easily desorbed from the catalyst surface. Interestingly, the peaks related to *cis*-dimer nitroso disappeared after introducing O₂, suggesting it was rapidly oxidized by oxygen to form NO₂.

3.4 Proposed mechanism of NO catalytic oxidation on Ni₂Mn₄Ce₄

From the results of surface elements distribution, temperature programmed reduction analysis, we obtained that the existence of Ni³⁺ + Mn³⁺ → Ni²⁺ + Mn⁴⁺ and Ce⁴⁺ + Ni²⁺ → Ni³⁺ + Ce³⁺. Higher valence manganese was the main sites for NO catalytic oxidation. From the *in situ* DRIFTS, the main intermediates were bidentate nitrate and monodentate nitrate species. Therefore, a mechanism based on the above experimental results was proposed, as shown in Fig. 7. The surface -M-O-M-

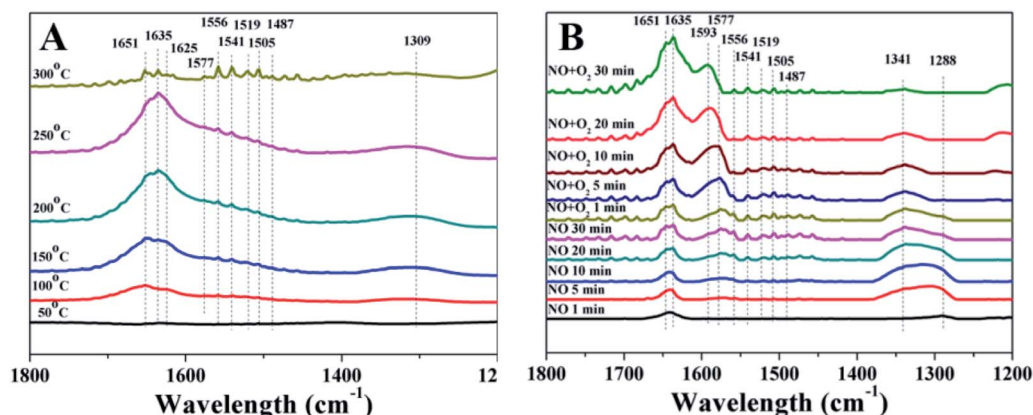


Fig. 6 *In situ* DRIFTS spectra of Ni₂Mn₄Ce₄ catalysts exposed to (A) NO + O₂/N₂ at different temperatures; (B) NO + N₂ and NO + O₂/N₂ at 200 °C.

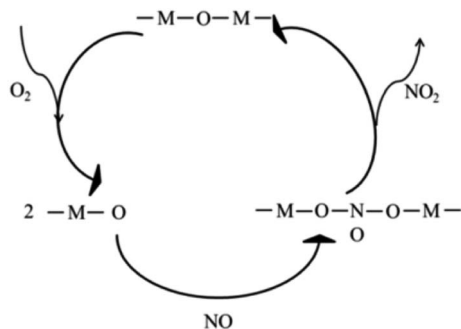


Fig. 7 A possible NO oxidation mechanism of as-prepared samples.

firstly reacted with oxygen to form $-M-O$, and then the later species was reacted with gaseous NO to form nitrates intermediates. At proper temperature, the nitrates intermediates were easily decomposed into gaseous NO_2 , and the metal-oxygen species was returned to original states to form a complete catalytic circle.

3.5 SO_2 resistance of different catalysts

In practical conditions, SO_2 that co-existed with NO may influence the catalytic oxidation of NO. Studies of NO oxidation in the existence of SO_2 ($Ni_2Mn_4Ce_4$ and Mn_6Ce_4) were conducted, and the results were shown in Fig. 8. When SO_2 was introduced, the NO conversion rate was decreased for both two catalysts. When the temperature was above $\sim 270^\circ C$, the activity decrease was not significant; mainly because the reaction is thermodynamic limited at higher temperature. However, at the lower temperature range, the NO conversion rate dropped drastically. For example, the NO conversion rate for Mn_6Ce_4 and $Ni_2Mn_4Ce_4$ dropped by 25.29% and 13.15% at $180^\circ C$, respectively. $Ni_2Mn_4Ce_4$ had a better SO_2 resistance compared with its counterpart without nickel, because nickel may decrease SO_2 adsorption, similar with our previous study.¹⁴

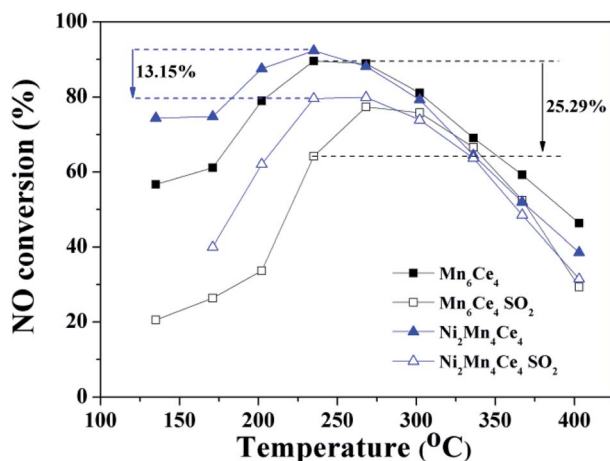


Fig. 8 NO oxidation performances of Mn_6Ce_4 and $Ni_2Mn_4Ce_4$ in presence of SO_2 (200 ppm).

4 Conclusions

In this paper, a series of mesoporous Ni-Mn-Ce ternary oxides were fabricated for NO catalytic oxidation, and the properties were characterized by various experiments. The $Ni_2Mn_4Ce_4$ catalyst showed a 95% NO conversion rate at $210^\circ C$. The introduction of nickel into Mn-Ce composites can regulate the ratio of surface oxygen and manganese species, therefore improving the NO catalytic oxidation. Compared with other catalysts, $Ni_2Mn_4Ce_4$ exhibited a higher specific surface area, lower reduction temperature, more surface Mn^{4+} species, which led to its higher NO oxidation activity. XPS results can provide proofs for $Ni^{2+} + Ce^{4+} \rightarrow Ce^{3+} + Ni^{3+}$, and $Ni^{3+} + Mn^{3+} \rightarrow Ni^{2+} + Mn^{4+}$. From the results of *in situ* DRIFTS, a possible mechanism was proposed, in which nitrates species were main intermediates. The SO_2 resistance experiments showed that nickel addition can increase SO_2 durability of catalysts, mainly because nickel may decrease SO_2 competitive adsorption on catalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The research was financially supported by the National Key Research and Development Plan (2016YFC0204100, 2016YFC0204103), Control Strategy and Technology Integrated Demonstration of Industrial Source Pollution in Guanzhong area of China (ZDRW-ZS-2017-6-2). The authors also acknowledge the analytical and testing center of Institute of Process Engineering, Chinese Academy of Sciences, for their extensive help in testing of samples.

References

- (a) G. Busca, L. Lietti, G. Ramis and F. Berti, *Appl. Catal., B*, 1998, **18**, 1; (b) P. G. Smirniotis, P. M. Srekanth, D. A. Peña and R. G. Jenkins, *Ind. Eng. Chem. Res.*, 2006, **45**, 6436.
- L. J. Alemany, L. Lietti, N. Ferlazzo, P. Forzatti, G. Busca, E. Giamello and F. Bregani, *J. Catal.*, 1995, **155**, 117.
- H. Hu, S. X. Cai, H. R. Li, L. Huang, L. Y. Shi and D. S. Zhang, *ACS Catal.*, 2015, **5**, 6069.
- S. Adjimi, J. M. García-Vargas, J. A. Díaz, L. Retailleau, S. Gil, M. Pera-Titus, Y. Guo and A. Giroir-Fendler, *Appl. Catal., B*, 2017, **219**, 459.
- C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee and B. Bandl-Konrad, *Chem. Commun.*, 2004, 2718.
- J. Li, W. H. Goh, X. Yang and R. T. Yang, *Appl. Catal., B*, 2009, **90**, 360.
- (a) Z. Wu, N. Tang, L. Xiao, Y. Liu and H. Wang, *J. Colloid Interface Sci.*, 2010, **352**, 143; (b) F. Meng, S. Zhang, X. Li, Y. Zeng and Q. Zhong, *Mol. Catal.*, 2019, **473**, 110393.
- W. Cai, Q. Zhong, J. Ding and Y. Bu, *Chem. Eng. J.*, 2015, **270**, 1.
- Z. Hong, Z. Wang and X. Li, *Catal. Sci. Technol.*, 2017, **7**, 3440.

- 10 (a) M. Machida, M. Uto, D. Kurogi and T. Kijima, *J. Mater. Chem.*, 2001, **11**, 900; (b) P. Sudarsanam, B. Hillary, M. H. Amin, S. B. A. Hamid and S. K. Bhargava, *Appl. Catal., B*, 2016, **185**, 213.
- 11 (a) N. Tang, Y. Liu, H. Wang and Z. Wu, *J. Phys. Chem. C*, 2011, **115**, 8214; (b) K. Li, X. Tang, H. Yi, P. Ning, D. Kang and C. Wang, *Chem. Eng. J.*, 2012, **192**, 99.
- 12 (a) H. Chen, Y. Wang and Y.-K. Lyu, *Mol. Catal.*, 2018, **454**, 21; (b) S. J. Ma, X. W. Wang, T. Chen and Z. H. Yuan, *Chem. Eng. J.*, 2018, **354**, 191.
- 13 T. Zhang, H. Li, Z. Yang, F. Cao, L. Li, H. Chen, H. Liu, K. Xiong, J. Wu, Z. Hong and W. Wang, *Appl. Catal., B*, 2019, **247**, 133.
- 14 W. M. Li, H. D. Liu and Y. F. Chen, *RSC Adv.*, 2019, **9**, 11912.
- 15 S. Lai, Y. She, W. Zhan, Y. Guo, Y. Guo, L. Wang and G. Lu, *J. Mol. Catal. A: Chem.*, 2016, **424**, 232.
- 16 Z. Liu, Y. Yi, S. Zhang, T. Zhu, J. Zhu and J. Wang, *Catal. Today*, 2013, **216**, 76.
- 17 F. Kleitz, S. Hei Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136.
- 18 Z. Wang, F. Lin, S. Jiang, K. Qiu, M. Kuang, R. Whiddon and K. Cen, *Fuel*, 2016, **166**, 352.
- 19 F. Gao, X. Tang, H. Yi, C. Chu, N. Li, J. Li and S. Zhao, *Chem. Eng. J.*, 2017, **322**, 525.
- 20 B. Zhao, R. Ran, X. Wu and D. Weng, *Appl. Catal., A*, 2016, **514**, 24.
- 21 X. Tang, J. Chen, X. Huang, Y. Xu and W. Shen, *Appl. Catal., B*, 2008, **81**, 115.
- 22 C. Lamonier, A. Ponchel, A. D'Huysser and L. Jalowiecki-Duhamel, *Catal. Today*, 1999, **50**, 247.
- 23 T. Zhu and M. Flytzani-Stephanopoulos, *Appl. Catal., A*, 2001, **208**, 403.
- 24 G. Long, M. Chen, Y. Li, J. Ding, R. Sun, Y. Zhou, X. Huang, G. Han and W. Zhao, *Chem. Eng. J.*, 2019, **360**, 964.
- 25 X. Hu, L. Huang, J. Zhang, H. Li, K. Zha, L. Shi and D. Zhang, *J. Mater. Chem. A*, 2018, **6**, 2952.
- 26 Y. Wan, W. Zhao, Y. Tang, L. Li, H. Wang, Y. Cui, J. Gu, Y. Li and J. Shi, *Appl. Catal., B*, 2014, **148–149**, 114.
- 27 X. Zhou, X. Lai, T. Lin, J. Feng, Z. Hou and Y. Chen, *New J. Chem.*, 2018, **42**, 16875.
- 28 H. Li, W. K. Ho, J.-j. Cao, D. Park, S. C. Lee and Y. Huang, *Environ. Sci. Technol.*, 2019, **53**, 10906.
- 29 Y. Xie, J. Wu, G. Jing, H. Zhang, S. Zeng, X. Tian, X. Zou, J. Wen, H. Su, C.-J. Zhong and P. Cui, *Appl. Catal., B*, 2018, **239**, 665.
- 30 W. Tang, M. Yao, Y. Deng, X. Li, N. Han, X. Wu and Y. Chen, *Chem. Eng. J.*, 2016, **306**, 709.
- 31 W. Xu, G. Zhang, H. Chen, G. Zhang, Y. Han, Y. Chang and P. Gong, *Chin. J. Catal.*, 2018, **39**, 118.
- 32 S. R. Kirumakki, B. G. Shpeizer, G. V. Sagar, K. V. R. Chary and A. Clearfield, *J. Catal.*, 2006, **242**, 319.
- 33 J. Liu, X. Li, R. Li, Q. Zhao, J. Ke, H. Xiao, L. Wang, S. Liu, M. Tadé and S. Wang, *Appl. Catal., A*, 2018, **549**, 289.
- 34 (a) C. Tang, J. Li, X. Yao, J. Sun, Y. Cao, L. Zhang, F. Gao, Y. Deng and L. Dong, *Appl. Catal., A*, 2015, **494**, 77; (b) J. Zhang, Y. Cao, C.-A. Wang and R. Ran, *ACS Appl. Mater. Interfaces*, 2016, **8**, 8670.
- 35 (a) G. Qi and R. T. Yang, *J. Phys. Chem. B*, 2004, **108**, 15738; (b) H. Wang, H. Chen, Y. Wang and Y.-K. Lyu, *Chem. Eng. J.*, 2019, **361**, 1161; (c) C. C. Dinerman and G. E. Ewing, *J. Chem. Phys.*, 1970, **53**, 626.
- 36 G. Zhou, B. Zhong, W. Wang, X. Guan, B. Huang, D. Ye and H. Wu, *Catal. Today*, 2011, **175**, 157.