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Rational design of $CrO_x/LaSrMnCoO_6$ composite catalysts with superior chlorine tolerance and stability for 1,2-dichloroethane deep destruction



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ABSTRACT

1,2-dichloroethane (1,2-DCE) is a representative industrial chlorinated volatile organic compound (CVOC) making great hazardous to the environment and human health. In this work, LaSrMnCoO₆ (LSMC) double perovskite-type materials with high thermal stability and coke resistance in 1,2-DCE oxidation were prepared by a facile sol-gel method. Based on this, a series of $CrO_x/LaSrMnCoO_6$ catalysts (Cr/LSMC, CrO_x loading = 5 to 20 wt.%) which combine the merits of CrO_x (high activity and chlorine tolerance) and LaSrMnCoO₆ were synthesized and adopted in deep oxidation of 1,2-DCE for the first time. As expected, obvious synergistic effects between CrO_x and LSMC on 1,2-DCE destruction were observed. Amongst, 10 wt.% $CrO_x/LaSrMnCoO_6$ (10Cr/LSMC) shows the best catalytic activity with 90% of 1,2-DCE destructed at 400 °C. Furthermore, the outstanding catalytic durability and water resistance of 10Cr/LSMC in 1,2-DCE oxidation were also demonstrated. In addition to this, the reaction pathway of 1,2-DCE decomposition over Cr/LSMC materials was discussed based on the results of online product analysis. We found that the enhanced catalytic performance of Cr/LSMC materials can be reasonably attributed to their high reducibility, excellent 1,2-DCE adsorption capability, and large amounts of Surface active lattice oxygen species. It can be anticipated that the Cr/LSMC catalysts are promising materials for CVOC elimination and the results from this work could also provide some new insights into the design of catalysts for CVOC efficient destruction.

1. Introduction

1,2-dichloroethane (1,2-DCE) regarded as one of typical chlorinated volatile organic compounds (CVOCs) is commonly used as an industrial solvent or an intermediate in organic synthesis process [1]. However, its high volatility and toxicity and great contributions to the formation of secondary pollutants and photochemical smog have caught much attention of researchers [2]. Various control approches such as absorption, hydrodechlorination, pyrolysis and catalytic decomposition have been investigated for CVOC destruction [3–7]. Conventional thermal incineration requires very high temperature (> 850 °C), leading to the formation of more toxic polychlorinated aromatic byproducts such as polychlorinated dibenzofurans (PCDFs) and dibenzodioxins (PCDDs) [8,9]. In comparison, catalytic oxidation operated at

much lower temperatures is considered as a more proper approach for the decomposition of CVOCs [10].

Supported noble metal catalysts, zeolites, and transitional metal oxides are usually studied in catalytic oxidation of CVOCs [11,12]. Noble metal-based catalysts are proved to be highly active materials in most of catalytic oxidation reactions. However, their high cost and low resistance to halide limit their wide applications in CVOC destruction [13]. H-zeolites (*e.g.*, H-ZSM-5, H-MOR, and H-BEA) were also usually investigated as the oxidation catalysts for CVOC destruction [14], while the Brønsted acid sites in H-zeolites usually lead to surface/structural coke deposition and catalyst deactivation [15]. Transition metal oxides (*e.g.*, V₂O₅, CrO_x, and MnO_x) exhibit high resistance to chlorine species during CVOC destruction, but their catalytic activities are usually lower than those of the noble metal-based catalysts [16–18]. Compared with

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other transition metal oxides, Cr_2O_3 is one of the most active and chlorine-tolerant catalysts for CVOC destruction [13], however, the loss and aggregation of Cr during long-term reactions should be considered [16].

In general, mixed transition metal oxides usually possess better catalytic activity and structure stability than their single phase counterparts [19-21]. Double perovskite-type oxides (DPOs; AA'BB'O₆, A2BB'O6, or AA'B2O6) as one kind of perovskite materials have been attracted extensive attentions in recent years due to their unique structure and properties such as providing more expansive combination spaces between different matching of A/A' and B/B' metals, excellent thermal stability, and coke resistance, which make them being highly desirable for catalytic applications [22]. Catalytic oxidation of methane over $Sr_2Mg_{1-x}Fe_xMoO_6.\delta$ was reported by Chen and co-workers [23], and results showed that the DPOs had excellent catalytic activity attributing to high contents of Fe-related surface lattice oxygen. Ding et al. [24] found that La2MnNiO6-MgO composite oxides with biphasic intergrowth effects achieved good performance and exceptional thermal stability for catalytic combustion of methane. La_{2-x}Sr_xFeCoO₆ oxides reported by Zhao et al. [25] were used to produce syngas and hydrogen and the oxygen mobility of DPOs was considered to be a potentially effective oxygen carrier for industrial applications of chemical looping. However, the catalytic oxidation of CVOCs over DPOs was not reported yet. As such, the study regarding catalytic destruction of CVOCs over DPOs may provide valuable insights for the future design and optimization of catalysts for this reaction.

In the present work, $CrO_x/LaSrMnCoO_6$ catalysts (Cr/LSMC) with CrO_x loadings varied from 5 to 20 wt.% were prepared by a wet impregnation protocol. The effects of structural, textural, and surface chemical properties of synthesized samples on their activity, product yield, and reaction durability in catalytic destruction of 1,2-DCE were investigated. In addition to this, the influence of water vapor on the oxidation of 1,2-DCE over prepared catalysts was also studied. Moreover, the reaction products distribution of 1,2-DCE destruction over Cr/LSMC were further explored. We believe that the $CrO_x/LaSrMnCoO_6$ catalysts are potential and promising materials for CVOC removal and the results from the present work could also provide new insights into the design of efficient catalysts for CVOC destruction.

2. Experimental

2.1. Catalyst preparation

LaSrMnCoO₆ double perovskite-type oxide was prepared by the solgel method. Stoichiometric amount of La(NO₃)₃6H₂O, Sr (CH₃COO)₂·0.5H₂O, Mn(CH₃COO)₃·4H₂O, and Co(NO₃)₂·6H₂O was firstly dissolved in 10 mL of deionized water and stirred at room temperature for 30 min. Then, a certain amount of critic acid (1.5 times of total metal ions) was added to the above transparent solution. After stirring for 1 h, the mixture was heated to 70 °C and maintained under continuous stirring until a sol was formed. Then, the obtained sol was dried at 100 °C for 24 h to obtain a dried gel. Finally, the resulting powder was calcined at 500 °C for 3 h and 1100 °C for 3 h in sequence under air atmosphere to obtain the LaSrMnCoO₆ support (denoted as LSMC).

 $CrO_x/LSMC$ catalysts were prepared by impregnation of synthesized LSMC with the solution of $Cr(NO_3)_3$ ·9H₂O. The impregnated solids were dried at 80 °C for 12 h and then calcinated at 500 °C for 5 h. $CrO_x/LSMC$ catalysts with CrO_x loadings of 5, 10, 15, and 20 wt.% (calculated as the weight percent of chromium on LSMC; the practical Cr loading measured by XRF analysis is shown in Table S2) are named as 5Cr/LSMC, 10Cr/LSMC, 15Cr/LSMC, and 20Cr/LSMC, respectively. For comparison, pure CrO_x , MnO_x, and CoO_x oxides were also prepared by calcination the corresponding metal precursors at 500 °C for 5 h. It's worth noting that the active content CrO_x introduced into the LSMC was also calcinated at 500 °C for 5 h. Therefore, the physicochemical properties

of Cr/LSMC can be compared with the chemical species of metal oxides because of the same calcinated conditions.

2.2. Catalyst characterizations

XRD measurements were performed on a powder diffractrometer (PANalytical B.V., Netherlands) with Cu-Ka radiation in 20 range of 20- 80° with a scanning rate of 10° /min. The tube voltage was 45 kV, and the current was 40 mA. Fourier transform infrared spectra (FTIR) were conducted on a Bruker Tensor 37 spectrometer. N₂ sorption isotherms were studied at 77 K on a Builder SSA-6000 apparatus. Before the measurements, the samples were processed for 4 h under vacuum at 473 K. The total pore volume was measured from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of ca. 0.99. The specific surface area and the pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively. Field emission scanning electron microscopy (FE-SEM) images were analyzed by the JEOL 7800 F microscope. High resolution transmission electron microscopy (HR-TEM) images were recorded on a FEI G2F30 microscope operating at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) experiments were conducted on an AXIS ULtrabld instrument (Kratos, UK) with Mg-K α radiation ($h\nu$ = 1253.6 eV). The X-ray anode was run at 250 W and the high voltage was maintained at 14.0 kV with a detection angle of 54°. The pass energy was fixed at 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was approximately 5×10^{-8} Pa. The spectra of all elements were recorded with extremely high resolution by using a RBD 147 interface (RBD Enterprises, USA) through the XPS Peak 4.1 software. The containment carbon (C 1s = 284.8 eV) was used as the calibrated binding energies. H₂-TPR experiments were performed on a TP-5080 (Xianquan, China) equipped with a thermal conductivity detector (TCD). In each test, 50 mg of catalyst was pretreated in a N₂ flow (30 mL/min) from 30 to 500 °C and kept at 500 °C for 1 h, then cooled down to the ambient temperature. The sample was reduced in a 5% vol.% H₂/Ar flow (30 mL/min) from 30 to 800 °C with a heating rate of 10 °C/min. Temperature programmed desorption of O₂ (O₂-TPD) and 1,2-DCE (1,2-DCE-TPD) were investigated on the same equipment as H₂-TPR. 100 mg of catalyst was pretreated in a N2 flow (30 mL/min) from 30 to 400 °C and kept at 400 °C for 1 h and then cooled to the room temperature prior to adsorption of O₂ or 1,2-DCE (500 ppm) for 2 h. After being saturated with O2 or 1,2-DCE, the catalyst was treated in a pure N2 flow (30 mL/min) for 1 h at room temperature. The desorption profiles of O₂-TPD or 1,2-DCE-TPD were recorded online from 30 to 700 °C with a heating rate of 10 °C/min. Thermogravimetric analysis (TG) of the aged catalysts was studied on an HCT-2TGA/DSC-1analyzer (Beijing Permanent, China) in temperature range of 35–700 °C with a heating rate of 10 °C/min under a continuous air flow of 50 mL/min.

2.3. Catalytic activity

All catalytic activity tests were performed in a continuous-flow fixed-bed reactor, which consists of a quartz tube that was filled with the prepared catalyst. The 1,2-DCE-contained gas was produced by bubbling air through a VOC (volatile organic compound) saturator, and then further diluted with another air stream (1000 ppm of 1,2-DCE). Temperatures of the fixed-bed and tubular electric furnace were monitored automatically by temperature programmed controller. In each test, 50 mg of catalyst (40–60 mesh) was putted into the tube reactor and the total gas flow rate was kept at 400 mL/min (gas hourly space velocity (GHSV) of *ca.* 48,000 mL/(gh)). Besides, the temperature of catalyst bed was firstly raised to 100 °C with the 1,2-DCE feed stream passing and stabilized for 30 min, followed by a second temperature ramp of 5 °C/min up to 550 °C. The 1,2-DCE, Cl-contained by-products, CO, and CO₂ in outlet gas were analyzed online by gas chromatograph (GC9890B, China) equipped with an electron capture detector (ECD) and a flame ionization detector (FID) coupled with an Ni-converter. Other by-products were identified by online mass spectrometer (SHP8400PMS, China).

The conversion of 1,2-DCE ($X_{1,2-DCE}$) was calculated by Eq. (1):

$$X_{1,2-DCE} = \frac{C_{\rm in} - C_{\rm out}}{C_{\rm in}} \times 100\%$$
(1)

where $C_{\rm in}$ and $C_{\rm out}$ are the inlet and outlet concentrations of 1,2-DCE, respectively.

The yields of CO, CO₂, HCl, and Cl₂ (respectively denoted as Y_{CO} , Y_{CO2} , Y_{HCl} , and Y_{Cl2}) were calculated by Eqs. (2)–(5), respectively:

$$Y_{\rm co} = \frac{C_{\rm co}}{2C_{\rm in} \times X_{\rm 1,2-DCE}} \times 100\%$$
(2)

$$Y_{\rm co_2} = \frac{C_{\rm co_2}}{2C_{\rm in} \times X_{\rm 1,2-DCE}} \times 100\%$$
(3)

$$Y_{\rm HCl} = \frac{C_{\rm HCl}}{2C_{\rm in} \times X_{\rm 1,2-DCE}} \times 100\%$$
(4)

$$Y_{\rm Cl_2} = \frac{2C_{\rm Cl_2}}{2C_{\rm in} \times X_{\rm l,2-DCE}} \times 100\%$$
(5)

where $C_{\rm CO}$, $C_{\rm CO2}$, $C_{\rm HCl}$, and $C_{\rm Cl2}$ are the outlet concentrations of CO, CO₂, HCl, and Cl₂, respectively. Stability test was carried out at 550 °C after a heating processing for 1,2-DCE combustion. To investigate the effect of water vapor on catalytic activity, the time-on-stream 1,2-DCE oxidation experiments were carried out in the presence and absence of 2 *vol.*%, 3 *vol.*%, and 5 *vol.*% of water vapor, which were introduced by automatic sample injector through pretreatment processor at 100 °C. Activity test was performed under the condition of 1,2-DCE of 1000 ppm, GHSV of 48,000 mL/(g·h), and reaction temperature of 550 °C.

3. Results and discussion

3.1. Catalytic performance of synthesized samples

3.1.1. Catalytic activity

Catalytic activity of all prepared samples for 1,2-DCE oxidation is displayed in Fig. 1A. All CrO_x supported catalysts possess much higher 1,2-DCE oxidation activity ($T_{90} = 400-537$ °C) than that of LSMC support ($T_{90} > 550$ °C). Amongst, 10Cr/LSMC shows the best oxidation activity with 90% of 1,2-DCE converted at 400 °C, much better than some typical catalysts for 1,2-DCE oxidation reported in the literature, as rod-like Co_3O_4 ($T_{90} = 420$ °C), Co/hydroxyapatite such $(T_{90} = 460 \text{°C})$, and 10Ba/Al2O3 $(T_{90} = 460 \text{°C})$ [18,26,27]. Pure CrO_x oxide also shows good catalytic activity in 1,2-DCE oxidation $(T_{90} = 463 \degree \text{C})$ compared with that of MnO_x $(T_{90} = 494 \degree \text{C})$ and CoO_x $(T_{90} = 516 \text{°C})$. By comparing with T_{90} values, the activity of all synthesized catalysts is in order of 10Cr/LSMC (400 $^{\circ}$ C) > CrO_x (494 °C) > 15Cr/LSMC $(463 \degree C) > MnO_x$ $(510 \degree C) > CoO_x$ (516 °C) > 20Cr/LSMC (525 °C) > 5Cr/LSMC (537 °C).

The oxidation of 1,2-DCE over perovskite-type oxides and transition metal oxides obeys a first-order reaction mechanism with respect to 1,2-DCE concentration (c): $r = -kc = (-A \exp(-E_a/RT))c$, where r, k, A, E_a are the reaction rate (mol/s), rate constant (s^{-1}), pre-exponential factor, and apparent activation energy (kJ/mol), respectively [28,29]. The reaction rates of 1,2-DCE over composite catalysts at 250 °C are displayed in Fig. 1B. It can be observed that the reaction rates over catalysts are in sequence of 10Cr/LSMC $(2.73 \times 10^{-11} \text{ mmol/(g·s)}) >$ 20Cr/LSMC $(2.50 \times 10^{-11} \text{ mmol/(g·s)}) > 15Cr/LSMC (2.44 \times 10^{-11} \text{ mmol/(g·s)})$ (1.96×10^{-11}) $mmol/(g \cdot s)) > LSMC$ $mmol/(g \cdot s)) > 5Cr/LSMC$ (1.88 \times 10 11 mmol/(g·s)). Results reveal that the reaction rates of 1,2-DCE over 10Cr/LSMC are obviously higher than that of LSMC catalyst, which indicates that the introduction of CrO_x is favorable for 1,2-DCE oxidation.



Fig. 1. (A) Catalytic activity of the synthesized catalysts for 1,2-DCE oxidation; (B) 1,2-DCE oxidation rates at 250 °C.

3.1.2. Reaction product distribution

The reaction products of prepared catalysts in the oxidation of 1,2-DCE are analyzed by online gas chromatography and online MS. The relationship between chlorinated by-products distribution and reaction temperature is shown in Figs. 2 and S4. As shown in Fig. 2, several Clcontaining by-products (1,1,2-trichloroethane, trichloroethene, and perchloroethylene) can be found in reaction process. 1,1,2-trichloroethane was firstly detected at about 200 °C. The concentration of 1,1,2-trichloroethane increases with the increasing of temperature and reaches the maximum value at about 500 °C, and then decreases with the further increasing of temperature. LSMC owns the smallest amount of 1,1,2-trichloroethane, which is associated with its low catalytic activity. The concentration of 1,1,2-trichloroethane over Cr/LSMC samples is higher than that of LSMC and follows the order of 5Cr/ LSMC > 10Cr/LSMC > 15Cr/LSMC > 20Cr/LSMC, indicating that the incorporation of CrOx enhances the catalytic activity of LSMC and facilitates the oxidation of 1,2-DCE. Small amounts of trichloroethene and perchloroethylene species are also detected in the reaction, which is ascribed to the dehydrochlorination of 1,1,2-trichloroethane (Fig. 2). Additionally, the formation of trichloroethene and perchloroethylene is attributed to the chlorination reaction and the generation of hydrogen chloride at high temperature.

The by-products distribution over 10Cr/LSMC was also analyzed by online MS, as shown in Fig. S4. The mass peaks of main fragment ions were determined based on the National Institute of Standards and Technology (NIST) chemistry database, and the mass ions of m/z = 62, 27, 44, 36, 70, and 29 represent for 1,2-DCE, vinyl chloride, CO₂, HCl, Cl₂, and acetaldehyde, respectively. As revealed in Fig. S4 (left part), the concentrations of vinyl chloride and 1,2-DCE show a decline trend



Fig. 2. Distribution of reaction by-products and yield of CO and CO₂ during 1,2-DCE oxidation.



Fig. 3. Stability of 10Cr/LSMC and CrO_x for 1,2-DCE oxidation.

with the increasing of reaction temperature, suggesting that the dehydrochlorination process is the first step in 1,2-DCE destruction, similar to previous report [13]. Besides, a fragment ion signal corresponding to acetaldehyde can be detected in the whole temperature range for activity test (the maximum concentration of acetaldehyde occurred at 500 °C), illustrating the occurrence of oxidation processes, as shown in Fig. S4 (right part). CO, CO₂, HCl, and Cl₂ as the main products were also observed during 1,2-DCE oxidation, and it is worth noting that the signal of Cl₂ obviously enlarges at temperature higher than 350 °C, indicating that the Deacon reaction (HCl + $O_2 \rightarrow H_2O + Cl_2$) determined by the high catalytic activity is proceeded [30]. Consequently, the forming of Cl_2 can be considered to follow direct decomposition of 1,2-DCE and the Deacon reaction in reaction process.

CO and CO₂ can be also detected during the oxidation process (Fig. 2). The CO₂ yield of samples enhances with the increasing of reaction temperature and reaches at around 90% at 550 °C, while the CO yield shows an opposite tendency at the temperature range of 400–550 °C (CO yield < 20% at 550 °C), indicating that the produced CO is oxidized to CO₂ at temperature higher than 400 °C. Both HCl and Cl₂ are considered as the deep oxidation products of 1,2-DCE, and Cl₂ is mainly formed through the Deacon reaction at high temperatures (> 350 °C). The chlorine balance of LSMC (102.88) and 10Cr/LSMC (99.71) is shown in Table S3. Fig. 2 shows that the CO₂ yield of LSMC support (82%) and CrO_x catalysts (86%) are less than that of 10Cr/LSMC (87%) at 550 °C, suggesting that the introduction of CrO_x improves catalytic performance of LSMC and enhances the oxidation of 1,2-DCE over the materials.

3.1.3. Stability and coke formation

It is of great importance to study the stability of a catalyst for catalytic oxidation of CVOCs due to chlorine poisoning and/or coke deposition, especially for industrial applications. The reaction stability of two active catalysts (10Cr/LSMC and CrO_x) was evaluated at 550 °C, as displayed in Fig. 3. It can be found that the long-term stability of 10Cr/LSMC catalyst is much better than that of CrO_x . The conversion of 1,2-DCE over 10Cr/LSMC can keep at around 99% in the first 2 h, and then slowly decreases and keeps at about 80% in the following 98 h. CrO_x oxide shows an obvious activity loss and deactivation in the whole test period, over which the conversion of 1,2-DCE sharply decreases to about 70% after 7 h and then further reduces to around 40% after 12 h. Above results demonstrate that Cr/LSMC catalysts possess excellent reaction durability for the destruction of 1,2-DCE attributed to the



Fig. 4. TG profiles of 10Cr/LSMC and CrO_x materials.

synergistic effect of perovskite-type oxides (good thermal stability) and CrO_x active sites (excellent activity).

The amount of coke deposited on the used catalyst (after 100 h of stability reaction) was investigated by TG technology. Fig. 4 shows the detailed TG profiles of 10Cr/LSMC and CrOx. 10Cr/LSMC has weight loss (0.15 wt.%) at around 280 °C, which is mainly associated with the adsorbed species (CO₂, H₂O, or chlorinated species). No coke deposition that can be decomposed above 400 °C over 10Cr/LSMC is detected [31]. As depicted in Fig. 4, CrO_x has three weight loss processes. The weight losses of the materials at the temperature lower than 200 °C including two stages are attributed to the physically adsorbed molecular water [32]. The weight loss of coke and adsorbed species disintegration over CrO_x (about 0.66 wt.%) at the temperature of 375 °C is higher than that of 10Cr/LSMC, indicating that the 10Cr/LSMC has better resistance to coke deposition. The TG profiles of all the catalysts are displayed in Fig. S5. It can be observed that all the catalysts except 10Cr/LSMC own three weight loss stages. The desorbed of CO₂, H₂O, or chlorinated species can result in the weight losses of the materials at the temperature lower than 200 °C. The weight losses of the materials at temperature above 400 °C are associated with the decomposed of coke deposition.

3.1.4. Effect of water vapor

Water vapor is a common component in industrial tail gas. In most cases, the water molecular in catalytic oxidation reactions is characterized as a competitive role, which can take up the active sites over catalysts [33,34]. Herein, the effect of water with different inlet concentrations varied from 2 to 5 vol.% on 10Cr/LSMC catalyst was investigated, as shown in Fig. 5. The conversion of 1,2-DCE is obviously inhibited when water vapor injected into the reaction system, and the activity of 10Cr/LSMC catalyst decreases continuously in the first 2.5 h with the increasing of water vapor concentration, especially when the water content increases from 3 to 5.0 vol.%. Then, the conversion of 1,2-DCE respectively stabilizes at around 95%, 92%, and 87% in the presence of 2, 3, and 5 vol.% of water vapor. Remarkably, the 1,2-DCE conversion rates are obvious recovered in all cases when shutting down the water vapor, suggesting that the 10Cr/LSMC catalyst possesses superior water-resistance in catalytic oxidation of 1,2-DCE. It's surprised to observe that the most active 10Cr/LSMC sample deactivates from 100% to 80% of 1,2-DCE conversion at 550 °C in dry atmosphere during durability test just after 350 min (Fig. 3), but 1,2-DCE conversion over 10Cr/LSMC just decreases from 100% to 87%-95% in humid atmosphere during durability test. Different results obtained in dry and humid atmospheres are owing to that the chlorinated species attack results in the inactivation of partial active sites on 10Cr/LSMC in dry atmosphere (Fig. 3), but the competitive adsorption of water molecule on the active content decreases the exposure ratio of active components resulting in the decreasing catalytic activity of 10Cr/LSMC in humid



Fig. 5. Effect of water feeding concentration on 1,2-DCE oxidation over 10Cr/LSMC catalyst.

atmosphere and the recovered 1,2-DCE conversion can be contributed to the covered active components is totally exposed to 1,2-DCE when turn off the feeding water.

3.2. Catalyst characterizations

3.2.1. Structural and textural properties

Crystal structure of all prepared catalysts was characterized by XRD, as shown in Fig. 6. The peaks centered at 35.0° and 40.7° over MnO_x can be assigned to the diffraction of MnO (PDF No.: 01-089-2804) and the other peaks over MnOx can be attributed to the diffraction of Mn₃O₄ (PDF No.: 01-075-1560) (Fig. 6g). Similarly, two different oxide phases (Cr₂O₃ (PDF No.: 01-084-0315) and CrO₂ (PDF No.: 01-071-0869)) can be found in CrO_x oxide (Fig. 6f). However, CoO_x oxide just has narrow and intensive diffraction peaks attributing to the presence of Co₃O₄ phase (PDF No.: 00-042-1467) (Fig. 6h). All Cr/LSMC catalysts have similar diffraction peaks at $2\theta = 23.0^{\circ}$, 32.8° , 40.5° , 46.6° , 58.6° , and 68.9°, corresponding to the typical diffraction peaks of DPOs (Fig. 6a-e) [24,35]. There are some small diffraction peaks appeared over Cr/ LSMC catalysts when CrO_x loading is higher than 5 wt.% (Fig. 6c-e). The diffraction peaks at 28.0° and 38.4° can be assigned to the Mn_3O_4 phase, and weak diffraction peaks at 20 of 26.0° and 71.7° can be respectively attributed to the existence of CrO₃ (PDF No.: 3-065-1388) and Cr₂O₃, indicating that the highly dispersed chromium oxides are successfully introduced to LSMC. The appearance of Mn₃O₄ peaks in the LSMC samples can be contributed to the interaction between CrO_x and LSMC, which results in the exposure of the Mn₃O₄ crystal phase. FTIR



Fig. 6. XRD patterns of (a) LSMC, (b) 5Cr/LSMC, (c) 10Cr/LSMC, (d) 15Cr/LSMC, (e) 20Cr/LSMC, (f) CrO_x, (g) MnO_x, and (h) CoO_x.

was also used to prove the formation of doped oxides as the vibration frequencies of metal-oxygen bonds are sensitive to be detected [36]. As displayed in Fig. S1, the broad band at around 600 cm⁻¹ is assigned to the stretching vibration of O-C=O functional group in plane and out of plane bending modes [37]. The band corresponding to Cr–O in the framework is observed at 933 cm⁻¹, confirming the incorporation of Cr in LSMC [38]. The band at 1383 cm⁻¹ is associated with the stretching vibration of C–OH or bending vibrations of –OH [39].

Results of specific surface area and pore structure of synthesized catalysts are illustrated in Table 1. CrO_x has the largest specific surface area $(24.4 \text{ m}^2/\text{g})$ and pore volume $(0.14 \text{ cm}^3/\text{g})$, while the related parameters of MnO_x ($6.2 \text{ m}^2/\text{g}$ and $0.05 \text{ cm}^3/\text{g}$) and CoO_x ($4.9 \text{ m}^2/\text{g}$ and $0.09 \text{ cm}^3/\text{g}$) are much smaller. All Cr/LSMC catalysts possess larger specific surface area $(5.5-8.7 \text{ m}^2/\text{g})$ and pore diameter (14.4-27.2 nm)than those of LSMC ($< 1.0 \text{ m}^2/\text{g}$ and 12.7 nm), which are favorable for the diffusion of reactant molecules and further accelerate the oxidation rate. As listed in Table 1, the specific surface area of Cr/LSMC decreases with the increasing of Cr content when CrOx loading is lower than 15 wt.%. However, 5Cr/LSMC and 20Cr/LSMC samples are characterized with very close specific surface area values of 8.7 and 8.3 m^2/g , respectively. 5Cr/LSMC sample owns higher specific surface area compared to 10Cr/LSMC and 15Cr/LSMC catalysts attributed to the highly dispersion of CrO_x on the surface of LSMC. 20Cr/LSMC also has a large specific surface area of $8.3 \text{ m}^2/\text{g}$ due to the large specific surface area of CrO_x (24.4 m²/g) although the 20Cr/LSMC sample is obviously agglomerated compared with 5Cr/LSMC.

| Table 1 |
|--|
| Physicochemical properties and catalytic performance of synthesized catalysts. |

| Samples | $S_{\rm BET}^{a}$ (m ² /g) | D_v^b (cm ³ /g) | D _p ^c (nm) | T ₅₀ ^d (°C) | T ₉₀ ^d (°C) |
|------------------|--|---------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|
| 5Cr/LSMC | 8.7 | 0.12 | 27.2 | 441 | 537 |
| 10Cr/LSMC | 7.0 | 0.08 | 17.7 | 315 | 400 |
| 15Cr/LSMC | 5.5 | 0.07 | 24.8 | 378 | 510 |
| 20Cr/LSMC | 8.3 | 0.10 | 14.4 | 400 | 525 |
| LSMC | < 1.0 | 0.07 | 12.7 | 478 | > 550 |
| CrO _x | 24.4 | 0.14 | 7.2 | 362 | 463 |
| MnO _x | 6.2 | 0.05 | 9.4 | 383 | 494 |
| CoO _x | 4.9 | 0.09 | 5.1 | 336 | 516 |
| | | | | | |

Note: ^a BET specific surface area calculated at $P/P_0 = 0.05$ -0.30; ^b Total pore volume estimated at $P/P_0 = 0.99$; ^c BJH pore diameter calculated from the absorption branch; ^d Temperatures at which 50% and 90% conversion of 1,2-DCE.

3.2.2. Catalyst morphology

FE-SEM micrographs of the synthesized materials are presented in Fig. 7. It is shown that LSMC has shaggy surfaces with irregular morphologies, composed of heterogeneous particles with different diameters (50-200 nm), and some particle aggregates can be found (Fig. 7a). Comparatively, 5Cr/LSMC (Fig. 7b) and 10Cr/LSMC (Fig. 7c) display more shaggy morphologies composed of small and regular balllike particles with average diameter around 150 nm. However, the particles of 15Cr/LSMC (Fig. 7d) and 20Cr/LSMC (Fig. 7e) are obviously aggregated. CrOx mainly consists of bar-like particles with average diameter of about 500 nm (Fig. 7f). The morphology of catalysts after stability tests (10Cr/LSMC-used and CrOx-used) was further investigated, as shown in Fig. 7g and h. Comparing with the fresh CrO_v, the particles of CrO_x-used catalyst are severely sintered and lots of large aggregates can be found, leading to an obvious activity loss. In contrast, the 10Cr/LSMC-used catalyst possesses a shaggy morphology and no obvious particle aggregate can be observed even after 100 h of continuous reaction at 550 °C, which indicates the excellent durability of 10Cr/LSMC catalyst.

As shown in Fig. 7i, two types of lattice distances (0.288 and 0.257 nm) respectively assigned to the (200) plane of Mn_3O_4 (main crystal plane) and (111) plane of MnO can be distinguished in LSMC, indicating the co-existence of Mn^{3+} and Mn^{2+} . Three different lattice planes can be found in 10Cr/LSMC, as displayed in Fig. 7k. (200) and (122) planes with lattice distance of 0.287 and 0.196 nm can be assigned to the CrO₃ phase, and (104) plane with lattice distance of 0.264 nm belongs to the Cr₂O₃ phase, in accordance with the XRD results (Fig. 6). However, just two kinds of lattice fringes with distance of 0.287 nm ((200) plane of CrO₃) and 0.276 nm ((103) plane of Mn_3O_4) can be observed in 20Cr/LSMC (Fig. 7l). Above results suggest that the crystal structure of Cr/LSMC catalysts can be obviously changed when alter the CrO_x loading.

3.2.3. Surface status

Deconvolution of La 3d, Sr 3d, Mn 2p, Co 2p, Cr 2p, and O 1 s, was performed by fitting a Gaussian-Lorentzian (GL) function with a Shirley background, as shown in Fig. 8. The results from deconvolution are presented in Tables 2 and 3. As shown in Fig. 8, both La 3d_{3/2} and La 3d_{5/2} display doublet peaks for 10Cr/LSMC (La 3d_{3/2}: 854.5 and 851.1 eV; La 3d_{5/2}: 838.2 and 834.8 eV) and LSMC (La 3d_{3/2}: 854.4 and 850.7 eV; La 3d_{5/2}: 837.5 and 834.1 eV), suggesting the presence of La³⁺ [24,40]. The Sr 3d XPS spectra of 10Cr/LSMC and LSMC can be divided into three peaks. The peaks at 131.8 and 134.0 eV are respectively associated with the bulk Sr²⁺ and surface-bound SrCO₃ species, indicating the presence of Sr²⁺ in the formation of perovskite phase [41]. The bonding energy (BE) measured at 133.2, 134.6, and 134.8 eV are ascribed to the presence of SrO [42]. The BE of Sr 3d at 136.1 eV is related to the existence of SrCO₃, and the formation of which is due to the influence of susceptible surface of the oxide system [42,43]. As shown in Fig. 8, Sr element in LSMC and 10Cr/LSMC samples exists as Sr²⁺. Table 3 exhibits the BE positions of Sr 3d XPS spectra. In addition, the distributions of Mn and Co species are also analyzed by XPS (Table 2), and the results suggest that the ratio of Mn and Co species is 0.92 and 0.93 (molar ratio of Mn and Co is 1:1), respectively, demonstrating that the sample (LaSrMnCoO₆) is successfully synthesized.

Mn $2p_{3/2}$ XPS spectra of LSMC and 10Cr/LSMC are displayed in Fig. 8. The Mn $2p_{3/2}$ can be divided into two peaks centered at 643.0 and 641.4 eV, corresponding to Mn⁴⁺ and Mn³⁺, respectively [44]. The Mn⁴⁺/Mn³⁺ ratio on the surface of 10Cr/LSMC (1.13) is higher than that of LSMC (0.96), and redox capability of CrO_x sites can be strongly enhanced by the large numbers of high valence Mn⁴⁺ cations on the surface of LSMC [45]. The chemical state of Co is also examined by XPS. As the Co $2p_{3/2}$ binding energy of Co²⁺ and Co³⁺ closes to each other, the spin-orbit splitting of Co 2p peaks ($\Delta E = E$ (Co $2p_{1/2}$) – E (Co $2p_{3/2}$)) is usually used to correlate with the cobalt oxidation state [46,47]. The ΔE values of 16.0, 15.0, and 15.2 eV stand for CoO, Co₂O₃, and



Fig. 7. FE-SEM images of (a) LSMC, (b) 5Cr/LSMC, (c) 10Cr/LSMC, (d) 15Cr/LSMC, (e) 20Cr/LSMC, (f) CrO_x, (g) 10Cr/LSMC-used, and (h) CrO_x-used; HR-TEM images of (i) LSMC, (*j*,k) 10Cr/LSMC, and (l) 20Cr/LSMC.

 Co_3O_4 , respectively [48,49]. In this work, the spin-orbit values of LSMC and 10Cr/LSMC are 15.4 and 15.6 eV, respectively, indicating that the cobalt state in these catalysts are mainly present as Co^{3+} .

It has been reported that Cr ions exist in various oxidation states in supported Cr materials and Cr cations (Cr^{3+} and Cr^{6+}) play important roles in redox processes [50]. The Cr $2p_{3/2}$ XPS peaks with BE at around 577 and 580 eV can be respectively assigned to Cr^{3+} and Cr^{6+} species [43,51–53]. Fig. 8 displays that the Cr element in CrO_x oxide is primary existed in the form of Cr^{3+} with BE of 576.4 eV, while both Cr^{3+} and Cr^{6+} species with BE values respectively centered at 576.5 and 579.6 eV can be observed in 10Cr/LSMC, indicating the co-existence of Cr_2O_3 and CrO_3 , in agreement with the results of XRD (Fig. 6). The percentage of Cr^{6+} and Cr^{3+} is about 85% and 15% in 10Cr/LSMC according to the corresponding XPS peak areas (Table 2), and the presence of large amounts of high-valent Cr^{6+} can enhance the oxidation ability of catalyst [54,55].

The fitted O 1 s spectra display three major oxygen contributions with the corresponding peaks centered at BE of 528.8–530.1, 531.3–532.0, and ~533.3 eV, attributed to the surface lattice oxygen (O_{α}) , surface adsorbed oxygen (O_{β}) , and carbonates/adsorbed molecular water (O_{γ}) , respectively (Fig. 8) [56,57]. The oxygen species distribution over 10Cr/LSMC, CrO_x, and LSMC catalysts are investigated, as documented in Table 2. The ratio of O_{α}/O_{β} in above catalysts is in sequence of 10Cr/LSMC (0.67) > CrO_x (0.35) > LSMC (0.06), in accordance with the activity of catalysts and indicates that surface lattice oxygen species play a significant role in the oxidation of 1,2-DCE. The effects of surface lattice oxygen species in oxidation process can be concluded that the lattice oxygen species of catalyst firstly oxidize the VOC leaving behind oxygen vacancies on catalyst surface, and then the adsorption of O₂ at vacancies is produced. Whereafter, the O-atom produced by the dissociation of O₂ to replenish the vacancies in the process [58].

The surface property of catalysts after stability tests (10Cr/LSMCused and CrO_x-used) were further characterized by XPS. The Cl 2p spectra and related results from deconvolution are respectively displayed in Fig. 9 and Table 3. Both Cl 2p XPS spectra can be further decomposed into two sub-peaks centered at 198.5/198.7 and 200.1/ 200.2 eV, respectively. The binding energy at 198.5/198.7 eV can be ascribed to the adsorption of HCl and/or Cl₂ from the decomposition of 1,2-DCE, and the binding energy at 200.1/200.2 eV can be attributed to the adsorption of 1,2-DCE on catalyst surface [51]. Results from Table 3 reveal that 1,2-DCE, HCl and/or Cl₂ species can be detected both on the



Fig. 8. La 3d, Sr 3d, Mn 2p, Co 2p, Cr 2p, and O1 s XPS spectra of synthesized catalysts.

Table 2

XPS results of Cr 2p, Mn 2p, Co 2p and O 1 s.

| Samples Cr 2p _{3/2} | | Mn 2p _{3/2} | | Mn | 01s | | | | | | |
|---------------------------------------|-----------------------|----------------------|-------------------------------|-----------------------|----------------------|-------------------|-------------------|------------------------------|-------------------------------|------------------------------|------------------------|
| | Cr ³⁺ | Cr ⁶⁺ | $Cr^{6+}/(Cr^{3+} + Cr^{6+})$ | Mn ⁴⁺ | Mn ³⁺ | Mn^{4+}/Mn^{3+} | /00 | $O_{\alpha}{}^{a}$ | O_{β}^{b} | O_{γ}^{c} | O_{α}/O_{β} |
| 10Cr/LSMC CrO _x LSMC | 533.9 32598.7 / | 3056.6 / / | 0.85 / / | 1048.9 / 5190.2 | 926.2 / 4991.7 | 1.13 / 0.96 | 0.92 / 0.93 | 19941.3 14154.9 1536.8 | 29714.5 40938.6 25849.3 | 20076.5 9285.3 30801.9 | 0.67 0.35 0.06 |

Note: ^a O_{α} is surface lattice oxygen; ^b O_{β} is surface adsorbed oxygen species; ^c O_{γ} is carbonates/adsorbed molecular water species.

 Table 3

 XPS results of Sr 3d and Cl 2p.

| Samples | Sr 3d | | | Cl 2p | | | |
|---------------------------------------|------------------------|-------------------------------|-----------------------|---------------------|---------------------|-----------------------------|--|
| | SrCO ₃ (eV) | SrO (eV) | Sr ²⁺ (eV) | 1,2-DCE (eV) | | HCl/Cl ₂ (eV) | |
| 10Cr/LSMC CrO _x LSMC | 134.0 / / | 134.8 / 133.2/ 134.6 | 136.1 / 131.8 | 200.2 200.1 / | 198.7 198.5 / | | |



Fig. 9. Cl 2p XPS spectra of the used 10Cr/LSMC and CrO_x catalysts.

surface of $\rm CrO_x$ and 10Cr/LSMC, which could occupy and block the active sites, leading to the decrease of catalytic activity.

3.2.4. Reducibility

Reducibility of all prepared catalysts was studied, as displayed in Figs. 10A and S2. As shown in Fig. S2, the reduction of CrO_x begins at about 250 °C, and its reduction profile is characterized by a single H₂ consumption peak centered at 335 °C, assigning to the reduction of Cr^{6+} to Cr^{3+} species [52,53]. For MnO_x, the reduction peak at 449 °C is assigned to the reduction of Mn₃O₄ to MnO and the temperature over 506 °C is corresponding to the reduction of MnO to metallic Mn in spinel oxides [20,44,59]. The H₂ consumption peaks at 359 °C over CoO_x can be attributed to the reduction of Co_3O_4 to Co^{2+} species

[47,60], and the reduction signal between 400 and 500 °C (with a small shoulder at 480 °C) can be assigned to the reduction of Co^{2+} species to metallic cobalt [20]. As shown in Fig. 10A, all DPOs (LSMC and Cr/ LSMC) exhibit similar reduction profiles with two different reduction regions of 414-474 and 643-664 °C (Fig. 10a-e), which is similar to the previous work [24]. The metal elements at A-site of DPOs usually have stable valence (e.g., La^{3+} and Sr^{2+}) and are hard to be reduced [61]. And the catalytic activities of the perovskites are mainly determined by the B site element properties [62]. Therefore, the changes of metallic valence states at B-site of DPOs have a crucial effect in the redox process. As shown in Fig. 10A, the first reduction region corresponds to the overlapping reduction of Cr^{6+} to Cr^{3+} , Mn^{4+}/Mn^{3+} to MnO, and Co^{3+}/Co^{2+} to Co° [14,15,20]. The second reduction region can be assigned to the reduction of Mn³⁺ to Mn²⁺ [20]. Compared with LSMC, all reduction peaks of Cr/LSMC catalysts shift towards lower temperatures, indicating the interaction between CrO_x and LSMC enhances the reducibility of catalysts. Amongst, 10Cr/LSMC possesses the best lowtemperature reducibility with reduction peaks centered at 414 and 643 °C, endowing the superior activity of 10Cr/LSMC.

Fig. 10B shows the reducibility of the used CrO_x and 10Cr/LSMC materials. No obvious reduction peak over the used CrO_x can be detected, indicating the active contents of single-metal oxides CrO_x are almost used up but incomplete recovery after 100 h of 1,2-DCE oxidation due to the deposition of chlorinated species or coke. The H₂ consumption peak of the used 10Cr/LSMC catalyst appears at higher temperature (centered at 564 °C) and owns a smaller amount of H₂ consumption compared to fresh 10Cr/LSMC catalyst, which suggests that the catalytic active sites (Cr^{6+} , Mn^{4+} , and Co^{3+}) take part in 1,2-DCE oxidation reaction and are consumed in the oxidation process. Compared to used CrO_x , a larger amount of H₂ consumption of used 10Cr/LSMC demonstrates the interaction and existence of electron transfer between CrO_x and LSMC.

3.2.5. Oxygen mobility

In general, the oxygen desorption peaks below 400 °C can be attributed to the surface adsorbed oxygen (O_{β}) , while the peaks appearing above 400 °C are due to the desorption of surface lattice oxygen (O_{α}) [63]. The oxygen desorption peaks below 200 °C are considered to be physically adsorbed oxygen species bound to the surface of the catalysts [64], and the chemically adsorbed oxygen $(O_2^- \text{ and } O^- \text{ species})$ desorbs between 200 and 400 °C [65]. Despite the similarity of the systems, differences in the desorbed oxygen can be found obviously. As shown in Fig. 11, very weak peaks corresponding to the desorption of lattice oxygen can be observed over LSMC (Fig. 11a), suggesting the presence of a small amount of surface lattice oxygen, in accordance with the XPS results (Fig. 8 and Table 2). Among Cr/LSMC catalysts, the desorption



Fig. 10. (A) H₂-TPR profiles of (a) LSMC, (b) 5Cr/LSMC, (c) 10Cr/LSMC, (d) 15Cr/LSMC and (e) 20Cr/LSMC; (B) H₂-TPR profiles of the fresh and used CrO_x, and 10Cr/LSMC samples.



Fig. 11. O_2 -TPD profiles of (a) LSMC, (b) 5Cr/LSMC, (c) 10Cr/LSMC, (d) 15Cr/LSMC, and (e) 20Cr/LSMC.

temperature of surface lattice oxygen increases in order of 10Cr/LSMC (457 °C) < 15Cr/LSMC (561 °C) < 5Cr/LSMC (575 °C) < 20Cr/LSMC (578 °C). The lower desorption temperature of surface lattice oxygen of 10Cr/LSMC indicates that the active lattice oxygen species in 10Cr/LSMC are transferred and released more readily [66]. It is generally accepted that the total oxidation of VOCs over reducible oxide catalysts occur *via* a two-stage redox cycle, and the attack of O_{α} can lead to the occurrence of this reaction [66], which indicates that the surface lattice oxygen species play a vital role in the oxidation of 1,2-DCE and can promote catalytic performance of the materials.

The adsorption/desorption performances of catalysts are crucial for 1,2-DCE oxidation, which were investigated by 1,2-DCE-TPD. As shown in Fig. S3, it can be observed that the 1,2-DCE desorption peak areas and the corresponding desorption temperatures over 10Cr/LSMC are higher than those of CrO_x and LSMC, indicating that the loaded-CrO_x enhances the 1,2-DCE adsorption capacity of catalyst. In detail, the temperature of first desorption peak of 1,2-DCE is in sequence of LSMC (195 °C) < CrO_x (323 °C) < 10Cr/LSMC < (476 °C), and this phenomenon can be reasonably assigned to the higher surface lattice oxygen in 10Cr/LSMC than that in CrO_x and LSMC. Compared with CrO_x and LSMC, 1,2-DCE strongly combines with active sites over 10Cr/LSMC so that it is hard to desorption from the surface of catalyst (Fig. S3), which is in well agreement with the order of catalytic activity. This indicates that the desorption capacity of 1,2-DCE molecules over DPOs is an important factor in 1,2-DCE decomposition.

4. Conclusions

A series of CrO_x/LaSrMnCoO₆ composite materials were synthesized and adopted for eliminating of 1,2-DCE. Results demonstrate that the interaction between CrO_x and LSMC plays an important positive role in the oxidation of 1,2-DCE by enhancing the reducibility and oxygen mobility of CrO_x/LSMC materials. High-valent Cr⁶⁺ is more active than Cr^{3+} as the existence of Cr^{6+} facilitates the surface lattice oxygen reacting with the LSMC. 10Cr/LSMC is the most active material among all prepared materials due to larger amount of Cr⁶⁺ species and surface lattice oxygen species, higher reducibility, and better 1,2-DCE adsorption capability. Vinyl chloride, 1,1,2-trichloroethane, trichloroethene, and perchloroethylene as primary reaction by-products over 10Cr/ LSMC are detected in 1,2-DCE oxidation, which can be totally oxidized to CO, CO₂, H₂O, HCl, and Cl₂. The introduction of CrO_x to LSMC accelerates the oxidation of 1,2-DCE and decreases the generation of byproducts. It can be rationally anticipated that the Cr/LSMC materials with superior catalytic activity, excellent stability, and water-resistance are one type of promising materials for industrial CVOC destruction.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2018.11.008.

References

- [1] Y. Wang, H.H. Liu, S.Y. Wang, M.F. Luo, J.Q. Lu, J. Catal. 311 (2014) 314–324.
- [2] H. Pan, Y. Jian, C. Chen, C. He, Z. Hao, Z. Shen, H. Liu, Environ. Sci. Technol. 51 (2017) 6288–6297.
- [3] Y.I. Bauman, I.V. Mishakov, D.V. Korneev, Y.V. Shubin, A.A. Vedyagin, R.A. Buyanov, Catal. Today 301 (2018) 147–152.
- [4] Y.I. Bauman, S.S. Sigaeva, I.V. Mishakov, A.A. Vedyagin, P.G. Tsyrulnikov, D.V. Korneev, R.A. Buyanov, React Kinet, Mech. Catal. 120 (2017) 691–701.
- [5] A.F. Bedilo, E.I. Shuvarakova, A.M. Volodin, E.V. Ilyina, I.V. Mishakov, A.A. Vedyagin, V.V. Chesnokov, D.S. Heroux, K.J. Klabunde, J. Phys. Chem. C 118 (2014) 13715–13725.
- [6] I.V. Mishakov, Y.I. Bauman, D.V. Korneev, A.A. Vedyagin, Top. Catal. 56 (2013) 1026–1032.
- [7] E.V. Ilyina, I.V. Mishakov, A.A. Vedyagin, A.F. Bedilo, K.J. Klabunde, Microporous Mesoporous Mater. 175 (2013) 76–84.
- [8] L. Champoux, J.F. Rail, R.A. Lavoie, Environ. Pollut. 222 (2017) 600–608.
 [9] Y.M. Chang, W.P. Fan, W.C. Dai, H.C. Hsi, C.H. Wu, C.H. Chen, J. Hazard. Mater.
- 192 (2011) 521–529.
 [10] M. Tian, M. Ma, B. Xu, C. Chen, C. He, Z. Hao, R. Albilali, Catal. Sci. Technol. 8
- (2018) 4503–4514.
- [11] C. He, Z. Jiang, M. Ma, X. Zhang, M. Douthwaite, J.-W. Shi, Z. Hao, ACS Catal. 8 (2018) 4213–4229.
- [12] M. Ma, H. Huang, C. Chen, Q. Zhu, L. Yue, R. Albilali, C. He, Mol. Catal. 455 (2018) 192–203.
- [13] P. Yang, S. Yang, Z. Shi, Z. Meng, Appl. Catal. B: Environ. 162 (2015) 227-235.
- [14] A. Campanella, M.A. Baltanás, Catal. Today 107-108 (2005) 208–214.
 [15] A. Aranzabal, J.A. González-Marcos, M. Romero-Sáez, J.R. González-Velasco,
- M. Guillemot, P. Magnoux, Appl. Catal. B: Environ. 88 (2009) 533–541.
- [16] P. Yang, Z. Shi, S. Yang, R. Zhou, Chem. Eng. Sci. 126 (2015) 361–369.
- [17] P. Yang, S. Zuo, Z. Shi, F. Tao, R. Zhou, Appl. Catal. B: Environ. 191 (2016) 53–61.
 [18] B. de Rivas, R. López-Fonseca, C. Jiménez-González, J.I. Gutiérrez-Ortiz, J. Catal. 281 (2011) 88–97.
- [19] Q. Dai, S. Bai, H. Li, W. Liu, X. Wang, G. Lu, Appl. Catal. B: Environ. 168-169 (2015) 141–155.
- [20] M.H. Castaño, R. Molina, S. Moreno, Appl. Catal. A Gen. 492 (2015) 48-59.
- [21] M.H. Castaño, R. Molina, S. Moreno, J. Mol. Catal. A Chem. 370 (2013) 167–174.
 [22] K. Zhao, L. Li, A. Zheng, Z. Huang, F. He, Y. Shen, G. Wei, H. Li, Z. Zhao, Appl.
- Energy 197 (2017) 393–404.
- [23] C. Li, W. Wang, C. Xu, Y. Liu, B. He, C. Chen, J. Nat. Gas Chem. 20 (2011) 345–349.
- [24] R. Ding, C. Li, L. Wang, R. Hu, Appl. Catal. A Gen. 464-465 (2013) 261-268.
- [25] K. Zhao, L. Li, A. Zheng, Z. Huang, F. He, Y. Shen, G. Wei, H. Li, Z. Zhao, Appl. Energy 197 (2017) 393–404.
- [26] S. Bai, Q. Dai, X. Chu, X. Wang, RSC Adv. 6 (2016) 52564-52574.
- [27] Z. Boukha, J. González-Prior, Bd. Rivas, J.R. González-Velasco, R. López-Fonseca, J.I. Gutiérrez-Ortiz, Appl. Catal. B: Environ. 190 (2016) 125–136.
- [28] H. Arandiyan, H. Dai, J. Deng, Y. Liu, B. Bai, Y. Wang, X. Li, S. Xie, J. Li, J. Catal. 307 (2013) 327–339.
- [29] H. Yang, J. Deng, Y. Liu, S. Xie, Z. Wu, H. Dai, J. Mol. Catal. A Chem. 414 (2016) 9–18.
- [30] F. Hess, H. Over, ACS Catal. 7 (2016) 128–138.
- [31] P. Yang, S. Zuo, R. Zhou, Chem. Eng. J. 323 (2017) 160–170.
- [32] C.J. Van Oers, W.J.J. Stevens, E. Bruijn, M. Mertens, O.I. Lebedev, G. Van Tendeloo, V. Meynen, P. Cool, Microporous Mesoporous Mater. 120 (2009) 29–34.
- [33] Z. Jiang, C. He, N.F. Dummer, J. Shi, M. Tian, C. Ma, Z. Hao, S.H. Taylor, M. Ma, Z. Shen, Appl. Catal. B: Environ. 226 (2018) 220–233.
- [34] B. de Rivas, R. Lopez-Fonseca, M.A. Gutierrez-Ortiz, J.I. Gutierrez-Ortiz, Chemosphere 75 (2009) 1356–1362.
- [35] R. Hu, R. Ding, J. Chen, J. Hu, Y. Zhang, Catal. Commun. 21 (2012) 38–41.
- [36] G. Liu, L. Sun, J. Liu, F. Wang, C.J. Guilde, Mol. Catal. 440 (2017) 148–157.
- [37] S. Pourebrahimi, M. Kazemeini, L. Vafajoo, Ind. Eng. Chem. Res. 56 (2017) 3895–3904.
 [38] D. Alcheinel, G. Machala, and J. Ding, Chem. 2014, 1997 (2016).
- [38] P. Sakthivel, S. Muthukumaran, J. Phys. Chem. Solids 120 (2018) 183–189.
- [39] J. Lu, F. Fu, L. Zhang, B. Tang, Chem. Eng. J. 346 (2018) 590–599.

- [40] J.M. Giraudon, A. Elhachimi, F. Wyrwalski, S. Siffert, A. Aboukaïs, J.F. Lamonier, G. Leclercq, Appl. Catal. B: Environ. 75 (2007) 157–166.
- [41] P.A.W. van der Heide, Surf. Interface Anal. 33 (2002) 414–425.
- [42] K. Kim, J. Jeong, A.K. Azad, S.B. Jin, J.H. Kim, Appl. Surf. Sci. 365 (2016) 38-46.
- [43] C. Norman, C. Leach, J. Membrane Sci. 382 (2011) 158–165.
- [44] Y. Jian, M. Ma, C. Chen, C. Liu, Y. Yu, Z. Hao, C. He, Catal. Sci. Technol. 8 (2018) 3863–3875.
- [45] S. Zhang, Y. Zhao, J. Yang, J. Zhang, Chem. Eng. J. 348 (2018) 618–629.
- [46] J. Luo, M. Meng, X. Li, X. Li, Y. Zha, T. Hu, Y. Xie, J. Zhang, J. Catal. 254 (2008) 310–324.
- [47] L.Y. Lin, H. Bai, RSC Adv. 6 (2016) 24304-24313.
- [48] Y. Yu, Q. Zhong, W. Cai, J. Ding, J. Mol. Catal. A Chem. 398 (2015) 344-352.
- [49] N. Weidler, S. Paulus, J. Schuch, J. Klett, S. Hoch, P. Stenner, A. Maljusch, J. Brotz, C. Wittich, B. Kaiser, W. Jaegermann, Phys. Chem. Chem. Phys. 18 (2016) 10708–10718.
- [50] L. Zhang, Y. Zhao, H. Dai, H. He, C.T. Au, Catal. Today 131 (2008) 42-54.
- [51] Q. Dai, S. Bai, J. Wang, M. Li, X. Wang, G. Lu, Appl. Catal. B: Environ. 142-143 (2013) 222-233.
- [52] L. Xu, Y. Zhang, Y. Deng, Y. Zhong, S. Mo, G. Cheng, C. Huang, Mater. Res. Bull. 48 (2013) 3620–3624.
- [53] S. Yang, E. Iglesia, A.T. Bell, J. Phys. Chem. B 109 (2005) 8987-9000.
- [54] P. Yang, S. Zuo, R. Zhou, Chem. Eng. J. 323 (2017) 160-170.

- [55] T.-T. Zhang, J.-D. Song, J.-X. Chen, A.-P. Jia, M.-F. Luo, J.-Q. Lu, Appl. Surf. Sci. 425 (2017) 1074–1081.
- [56] S. Xie, Y. Liu, J. Deng, J. Yang, X. Zhao, Z. Han, K. Zhang, Y. Wang, H. Arandiyan, H. Dai, Catal. Sci. Technol. 8 (2018) 806–816.
- [57] C. He, X. Liu, J. Shi, C. Ma, H. Pan, G. Li, J. Colloid. Interf. Sci. 454 (2015) 216–225.
 [58] M.A. Saqlain, A. Hussain, M. Siddiq, A.A. Leitão, Appl. Catal. A Gen. 519 (2016) 27–33
- [59] D. Döbber, D. Kießling, W. Schmitz, G. Wendt, Appl. Catal. B: Environ. 52 (2004) 135–143.
- [60] A. Zhang, W. Zheng, J. Song, S. Hu, Z. Liu, J. Xiang, Chem. Eng. J. 236 (2014) 29–38.
- [61] M. Tian, C. He, Y. Yu, H. Pan, L. Smith, Z. Jiang, N. Gao, Y. Jian, Z. Hao, Q. Zhu, Appl. Catal. A Gen. 553 (2018) 1–14.
- [62] J.A. Onrubia, B. Pereda-Ayo, U. De-La-Torre, J.R. González-Velasco, Appl. Catal. B: Environ. 213 (2017) 198–210.
- [63] C. Deng, Q. Huang, X. Zhu, Q. Hu, W. Su, J. Qian, L. Dong, B. Li, M. Fan, C. Liang, Appl. Surf. Sci. 389 (2016) 1033–1049.
- [64] R. Dinamarca, X. Garcia, R. Jimenez, J.L.G. Fierro, G. Pecchi, Mater. Res. Bull. 81 (2016) 134–141.
- [65] W. Song, Z. Ren, S.Y. Chen, Y. Meng, S. Biswas, P. Nandi, H.A. Elsen, P.X. Gao, S.L. Suib, ACS Appl. Mater. Interf. 8 (2016) 20802–20813.
- [66] W. Si, Y. Wang, S. Zhao, F. Hu, J. Li, Environ. Sci. Technol. 50 (2016) 4572-4578.