Preparation of metal-doped Cu–Mn/HTS-1 catalysts and their mechanisms in efficient degradation of toluene

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ABSTRACT

In order to study their synergistic catalytic effects in toluene degradation, CuMn₂O₄/HTS-1 (HTS-1 was a titanium silicon molecular sieve), Cu₀.₇Mn₂₅Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂₅Ce₀.₃Oₓ/HTS-1 catalysts were prepared by the impregnation method. The textural properties, redox properties and acidity of the catalysts were characterized by X-ray diffractometer (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), H₂ temperature-programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS), frustrated total internal reflection (FT-IR), ammonium temperature-programmed desorption (NH₃-TPD) and pyridine adsorption internal reflection (Py-IR) measurements. The potential roles of Lewis acid sites (activating dioxygen) were discussed, and the experimental results indicated that the most efficient route for toluene degradation over Cu₀.₇Mn₂₅Ce₀.₃Oₓ/HTS-1 (toluene conversion rate of 90% (T₉₀) = 295°C) was ascribed to regulation of the synergistic effects of redox properties (activating molecular toluene) and Lewis acid sites (activating dioxygen). The Mars–Van–Krevelen (MVK) model was adopted to describe the reaction process of toluene oxidation, which gave an in-depth view into the toluene degradation over CuMn₂O₄/HTS-1, Cu₀.₇Mn₂₅Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂₅Ce₀.₃Oₓ/HTS-1. In addition, the synergistic effects between redox properties and Lewis acid sites were studied in detail.

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Keywords:
- Toluene degradation
- Redox property
- Lewis acid sites
- Synergistic effect
- Mars–Van–Krevelen (MVK) model

Introduction

Volatile organic compounds (VOCs), which are important gaseous pollutants in the atmosphere, are among the important precursors of air pollution (Zheng et al., 2012). VOCs can be eliminated in many ways, including adsorption, catalytic combustion (Bonelli et al., 2011), photocatalytic degradation (Higashimoto et al., 2008) and physical separation (Modelski et al., 2011). Catalytic combustion is one of the most economical methods to completely destroy VOCs due to its high efficiency (Feng et al., 2018a, 2018b). Among many VOCs, toluene is often utilized as a characteristic pollutant to investigate the performance of catalysts (Aziz and Kim, 2017; Lu et al., 2015). The catalytic oxidation of toluene is carried out at the gas-solid interface, and the adsorption process is best achieved with catalysts that have a uniform pore structure and large...
surface area (Chisholm et al., 2018; Farmanzadeh and Valipour, 2018; Kraus et al., 2018). For this reason, zeolite-based catalysts are widely applied in the catalytic oxidation of toluene. Especially in recent years, ZSM-5 has been investigated extensively to improve its catalytic activity and stability. Niwa (Maeda et al., 1997) found that for methane combustion on H-ZSM-5 with different Al concentrations, catalysts with high Si/Al ratio exhibited better performance due to the hydrophobicity of the supports. To improve the hydrophobicity of catalysts, HTS-1 (H type Ti–Si zeolite) materials can be applied as catalyst support due to the absence of strongly hydrophilic Al³⁺ in the framework structure (Du et al., 2017a, 2017b; Ni et al., 2018).

The two key steps in the oxidation of toluene are benzene cleavage and deep oxidation processes (Cen et al., 2014; Wang et al., 2015). It is best achieved with the use of catalysts that have good redox properties. Transition metal oxides (Li et al., 2014; Suárez-Vázquez et al., 2018; Tsoncheva et al., 2013; Zhang et al., 2017b) (CuO, MnO₂) are typically selected for this purpose (Li et al., 2017; Machej et al., 2014; Morales et al., 2017). CuMn₂O₄ spinel is particularly well known for its flexibility in the role of rare earth elements. When the amount of rare earth elements is larger, it will seriously destroy the redox properties of the system, but also provide suitable redox properties of the catalyst. Unfortunately, the acid properties of CeO₂ were not fully characterized in these studies and possible correlations between acidity and redox properties was not directly discussed (Fan et al., 2012; Zheng et al., 2012). The introduction of CeO₂ can not only enhance the redox properties of the system, but also provide suitable acid sites (Liu et al., 2013). Bronsted acid and Lewis acid sites on the catalyst surface are regarded as the active centers for the redox reaction. In practical research studies, Cerium oxide (CeO₂) has been doped into CuMn₂O₄ spinel to enhance the redox properties of the catalysts.}

1. Materials and methods

1.1. Catalyst preparation

HTS-1 was directly used as carrier, and supported CuMn₂O₄, Cu₀.₇Mn₂Y₀.₃Oₓ and Cu₀.₇Mn₂Ce₀.₃Oₓ catalysts were prepared by the impregnation method. Taking Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1 as an example, 5.9 g Cu(NO₃)₂·3H₂O, 25.1 g 50% Mn(NO₃)₂ solution and 13.0 g Ce(NO₃)₃·6H₂O were weighed and dissolved in 500 mL distilled water, and thoroughly mixed. HTS-1 (10 g) was added to the solution, and the mixture was stirred under magnetic stirring for 24 hr. The solution was filtered and the filter cake was dried in a vacuum oven at 60°C for 24 hr. The cake was ground to 60–80 mesh and calcined in a muffle furnace. The temperature program of the calcining process was: heat to 500°C at a heating rate of 5°C/min and dwell 3 hr. The inductively coupled plasma mass spectrometry (ICP-MS, 7900, Agilent Technologies, USA) results are shown in Appendix A Table S2.

1.2. Catalyst characterization

The textural properties, redox properties and acidity of catalysts were characterized by XRD, TEM, SEM, H₂-TPR, XPS, FT-IR, NH₃-TPD and Py-IR measurements. Related instrument parameters and test conditions are provided in Appendix A. Supplementary data.

1.3. Catalytic activity measurement

An online device system was used to test the catalytic activity of samples. In addition, 2000 ppmV toluene in air balance with a total flow rate of 120 mL/min controlled by a mass flow controller (accuracy: 1.5%) was used as the reactant. The quartz reactor (11 mm diameter) was loaded with 200 mg of the catalysts (60–80 mesh), and the gas hourly space velocity (GHSV) was 10,000 mL/(g·hr). The inlet and outlet concentration of toluene were analyzed by a gas chromatograph (GC7900, Techcomp, China) with a flame ionization detector (FID) and a chromatographic column (Carbowax 20M/ Chromosorb W, Agilent, USA) at the chromatographic temperature of 150°C. The toluene conversion (Y) was defined as:

\[
Y = \left(\frac{C_{\text{toluene, inlet}} - C_{\text{toluene, outlet}}}{C_{\text{toluene, inlet}}}\right) \times 100\%
\]

where, \(C_{\text{toluene, inlet}}\) and \(C_{\text{toluene, outlet}}\) are import and export of toluene concentration, respectively.
2. Results and discussion

2.1. Catalytic activity for toluene

As shown in Fig. 1, Cu_{0.7}Mn_{2}Ce_{0.3}O_x/HTS-1 showed the highest performance for toluene degradation at the temperature of 295°C. The catalytic performance varied as follows: Cu_{0.7}Mn_{2}Ce_{0.3}O_x/HTS-1 > Cu_{0.7}Mn_{2}Y_{0.3}O_x/HTS-1 > CuMn_{2}O_{4}/HTS-1. Compared with pure HTS-1, the performance of other catalysts was significantly enhanced when CuMn_{2}O_{4} spinel was introduced. For Cu_{0.7}Mn_{2}Ce_{0.3}O_x/HTS-1 and Cu_{0.7}Mn_{2}Y_{0.3}O_x/HTS-1, the catalytic activity of the toluene degradation heightened due to Y and Ce introduction into CuMn_{2}O_{4}/HTS-1. The lifetime of Cu_{0.7}Mn_{2}Ce_{0.3}O_x/HTS-1 was tested (Appendix A Fig. S2), and showed that the catalytic activity of the catalyst was not changed after 100 hr, and the catalytic efficiency decreased only 2.9% (Scheme 1).

The toluene degradation process was derived from the GC-MS data; as shown in Scheme 2, the methyl group in toluene is first oxidized to form benzoic acid, and decarboxylation of benzoic acid produces benzene. The C-H bonds react with oxygen free radicals, which eventually oxidize the reactants to H_2O and CO_2. The two key steps in the oxidation of toluene are benzene cleavage and deep oxidation processes. As shown in Fig. 2, benzene and carbon monoxide are two important by-products that can be used to determine the process of benzene ring cleavage and deep oxidation. Compared with CuMn_{2}O_{4}/HTS-1, the complete conversion temperature of benzene was lower over Cu_{0.7}Mn_{2}Y_{0.3}O_x/HTS-1 and Cu_{0.7}Mn_{2}Ce_{0.3}O_x/HTS-1, which indicated that it was easier to open and crack the benzene ring with these catalysts. The catalysts...
with Lewis acid sites were expected to have high activity in the catalytic oxidation of toluene, and the Lewis acid sites were considered to be the active sites for the adsorption and activation of oxygen molecules. Although the introduction of Y and Ce can increase the active sites of catalysts and promote aromatic ring cleavage, more oxygen vacancies are needed to ensure the deep oxidation of by-products to CO₂ and H₂O. Compared with CuMn₂O₄/HTS-1, the conversion temperature of carbon monoxide is lower over Cu⁰.⁷Mn₂Ce⁰.³Oₓ/HTS-1, which may be explained by the fact that the introduction of Ce provides oxygen vacancies for the catalysts because of the electron transfers between Ce⁴⁺ and Mn³⁺. To explain the phenomenon whereby the introduction of Ce is conducive to the degradation of toluene, the properties of catalysts were characterized and the MVK kinetic model was adopted to investigate the synergism between redox properties and acidic sites.

2.2. Textural properties of catalysts

The wide-angle XRD patterns of HTS-1 and the corresponding supported catalysts are shown in Fig. 3. The characteristic peaks for the MFI structure of zeolite could be observed in all of the samples, indicating that the catalysts were single-phase HTS-1 (JCPDS-ICDD 43-0055). The characteristic peaks (JCPDS-ICDD 74-2422) of CuMn₂O₄ spinel were observed in CuMn₂O₄/HTS-1, Cu₀.⁷Mn₂Y₀.³O₅-HTS-1 and Cu₀.⁷Mn₂Ce₀.³O₅-HTS-1. Moreover, the doping of Y and Ce resulted in introduction of defects in the CuMn₂O₄ crystal structure for Cu₀.⁷Mn₂Y₀.³O₅-HTS-1 and Cu₀.⁷Mn₂Ce₀.³O₅-HTS-1, in which the characteristic peaks of the two samples became weaker and had a small angle shift. The reason is that with the decrease of Cu content in the catalysts, the Mn species in CuMn₂O₄ spinel become unstable (Niu et al., 2018). Part of the Mn species remains inside the spinel to maintain the electrical neutrality of the spinel structure, resulting in low crystallinity for the spinel. Other Mn species were introduced into the lattice of Y₂O₅ or CeO₂. Additionally, a charge imbalance was produced due to the valences of Cu and the doping element. For the multiple composite oxides, acidic sites were produced when the electric charge was unbalanced. Diffraction peaks of other phases, such as Y₂O₃ and CeO₂, were not observed in the catalysts, which can be explained by the doping of Y₂O₃ and CeO₂ being relatively low and the oxides evenly dispersed on HTS-1.

As shown in Fig. 4a and b, the microscopic morphology of HTS-1 is spherical, and the diameter of the spheres is 300–400 nm. Cu₀.⁷Mn₂Ce₀.³O₅ was loaded on the surface of the spherical HTS-1. Energy dispersive X-ray spectroscopy (EDX) analysis (Fig. 4c and d) was carried out on the surface elements of the spheres and the loaded particles, respectively. Results confirmed that Cu₀.⁷Mn₂Ce₀.³O₅ adhered to the surface of the microspheres in the form of small particles. The elemental distribution of Cu₀.⁷Mn₂Ce₀.³O₅ on HTS-1 is shown by mapping images (Fig. 5). As a carrier of catalysts, HTS-1 showed excellent dispersion properties for Cu₀.⁷Mn₂Ce₀.³O₅.

As shown in Fig. 6a, the Cu₀.⁷Mn₂Ce₀.³O₅ particles were uniformly attached to the surface of HTS-1 microspheres, which indicated that Cu₀.⁷Mn₂Ce₀.³O₅ was highly and uniformly dispersed. Unambiguous crystal lattice fringes emerged with interplanar distances of 0.31, 0.48 and 1.15 nm, demonstrating that CeO₂, CuMn₂O₄ and HTS-1 (Fig. 6b–d) were present. The microscopic grain size of the Cu₀.⁷Mn₂Ce₀.³O₅ was calculated. It can be seen from the Fig. 6e and f that the grain size range is mainly between 8 and 20 nm.

2.3. Redox properties and oxidation states of catalysts

In general, the improvement of the redox properties of catalysts is beneficial to the deep oxidation of toluene. The redox properties of CuMn₂O₄/HTS-1, Cu₀.⁷Mn₂Y₀.³O₅-HTS-1 and Cu₀.⁷Mn₂Ce₀.³O₅-HTS-1 were evaluated by H₂-TPR. As shown in Fig. 7, H₂ consumption peaks in the range of 250–300°C could be observed, which originated from the reduction of Mn⁴⁺ to Mn³⁺ and Mn³⁺ to Mn²⁺ in the catalysts (Li et al., 2018). For the Cu₀.⁷Mn₂Ce₀.³O₅/HTS-1 catalyst, a weak reduction peak at about 400–500°C (Appendix A Fig. S3) was found, which was attributed to the reduction of CeO₂ in
Fig. 2 – Toluene conversion and production of carbon monoxide and benzene versus temperature for (a) CuMn₂O₄/HTS-1, (b) Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and (c) Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1.
Cu_{0.7}Mn_{2}Ce_{0.3}O_{x}. It can be seen that the Cu_{0.7}Mn_{2}Ce_{0.3}O_{x}/HTS-1 catalyst had more excellent redox performance than the CuMn_{2}O_{4}/HTS-1 and Cu_{0.7}Mn_{2}Y_{0.3}O_{x}/HTS-1, because a low-temperature peak shift was observed for the catalysts. This could be a result of the excess Mn in spinel doped into the CeO_{2} lattice leading to an increase in the amount of Mn^{4+}, which makes the lattice oxygen in the system more active and easier to reduce. The interaction between CuMn_{2}O_{4} and CeO_{2} intensified the electron cycle between Ce^{3+} and Ce^{4+} and induced electron transfer between Ce^{4+} and Mn^{3+} (Hussain et al., 2001).

The Mn species located in the CuMn_{2}O_{4}/HTS-1, Cu_{0.7}Mn_{3}Y_{0.3}O_{x}/HTS-1 and Cu_{0.7}Mn_{2}Ce_{0.3}O_{x}/HTS-1 catalysts were characterized by XPS (Fig. 8). The percentage of Mn^{4+} on the surface of CuMn_{2}O_{4}/HTS-1, Cu_{0.7}Mn_{2}Y_{0.3}O_{x}/HTS-1 and Cu_{0.7}Mn_{2}Ce_{0.3}O_{x}/HTS-1 catalysts were approximately 15.7%, 24.8%, and 31.1%, respectively (Table 1). The Cu_{0.7}Mn_{2}Ce_{0.3}O_{x}/HTS-1 catalyst had a relatively higher Mn^{4+} mol.% than CuMn_{2}O_{4}/HTS-1 and Cu_{0.7}Mn_{2}Y_{0.3}O_{x}/HTS-1. This implies that the electron cycle between Ce^{3+} and Ce^{4+} was intense and induced electron transfer between Ce^{4+} and Mn^{3+}, which led to a higher Mn^{4+} mol.% in the Cu_{0.7}Mn_{2}Ce_{0.3}O_{x}/HTS-1 catalyst.
In our previous work (Niu et al., 2018), we calculated the valence distribution of Mn species through the counter-evidence method, and further explored the cause for the increase of Mn$^{4+}$ content in the Cu_{0.7}Mn$_2$Y$_{0.3}$O$_x$/HTS-1 and Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1 catalysts. In this study, we also determined the valence distribution of Mn species through the counter-evidence method.

Fig. 5 – Mapping images of Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1.

Fig. 6 – (a–d) transmission electron microscopy (TEM) morphologies of Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1 and (e, f) the particle size distribution of over Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1. d: lattice distance.
counter-evidence method. Related calculations and discussions are provided in the supplemental information. By way of proof, we can conclude that Mn species exist in $\text{Y}_2\text{O}_3$ in the form of Mn$^{3+}$ and Mn$^{4+}$. For the Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1 catalyst, the Mn species exist only in the form of Mn$^{4+}$ in the CeO$_2$ lattice. This is the major reason why there were large amounts of Mn$^{4+}$ on the surface of the Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1 catalyst. It appears that higher amounts of exposed Mn$^{4+}$ sites in the sample make oxidation more favorable, which will generate more oxygen vacancies and improve the lattice oxygen (O$_{\text{latt}}$) mobility. Finally, the catalytic activity will be increased. The XPS analysis of O$_{1s}$ is shown in Appendix A Fig. S4 and Table S6.

Suitable acid sites can effectively promote the adsorption and activation of molecular oxygen, thereby supplementing the consumption of lattice oxygen in the reaction. The synergistic effect between redox properties (activating molecular toluene) and Lewis acid sites (activating dioxygen) was considered to occur during the catalytic oxidation of toluene.

Therefore, the surface acidity of catalysts was also analyzed in this study.

2.4. Acidity of catalysts

The interaction between the metal oxide and HTS-1 was characterized by FT-IR (Fig. 9). In general, bands at approximately 550 and 1225 cm$^{-1}$ were related to HTS-1, indicating the presence of an MFI topology. There was a slight redshift observed for CuMn$_2$O$_4$/HTS-1, Cu$_{0.7}$Mn$_2$Y$_{0.3}$O$_x$/HTS-1 and Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1, which was ascribed to the introduction of CuMn$_2$O$_4$. The bands at approximately 3424 cm$^{-1}$ were assigned to Si–OH of the zeolite, which can adjust the acidity by hydrogen bonding. The redshift in the peak at 3424 cm$^{-1}$ for Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1 suggests that the Si–OH group became unstable. For the multiple oxide composites, the acidic sites would change when the electrical neutrality is destroyed.

The surface acidity of HTS-1, CuMn$_2$O$_4$/HTS-1, Cu$_{0.7}$Mn$_2$Y$_{0.3}$O$_x$/HTS-1 and Cu$_{0.7}$Mn$_2$Ce$_{0.3}$O$_x$/HTS-1 was investigated
using NH₃-TPD (Fig. 10a). The catalysts showed weak peaks at 140–200°C (Dai et al., 2018), which should be due to the physical adsorption of NH₃ in the hierarchical channel or weak hydroxyls. Compared with HTS-1 and CuMn₂O₄/HTS-1, the absence of desorption peaks at 478 and 481°C implied the absence of strong acid sites on Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1, respectively. Moreover, a new peak at 348, 360 and 346°C was observed on CuMn₂O₄/HTS-1, Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1, respectively, which was ascribed to the adsorption of NH₃ on the CuMn₂O₄ spinel, because the spinel can be considered as a Lewis acid according to the generalized theory of acids and bases. Compared with the CuMn₂O₄/HTS-1 catalyst, Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1 have significantly more acidity because Y₂O₃ and CeO₂ were introduced into the catalyst as Lewis acids. In particular, compared with the Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 catalyst, the Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1 catalyst showed enhanced Lewis acidity. This implied that the electron cycle between Ce³⁺ and Ce⁴⁺ was intense and

### Table 1 – X-ray photoelectron spectroscopy (XPS) analysis of Mn₂p in CuMn₂O₄/HTS-1, Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mn²⁺ (mol.%)</th>
<th>Mn³⁺ (mol.%)</th>
<th>Mn⁴⁺ (mol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuMn₂O₄/HTS-1</td>
<td>84.3</td>
<td>15.7</td>
<td></td>
</tr>
<tr>
<td>Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1</td>
<td>75.2</td>
<td>24.8</td>
<td></td>
</tr>
<tr>
<td>Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1</td>
<td>68.9</td>
<td>31.1</td>
<td></td>
</tr>
</tbody>
</table>

*: not detected.

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Fig. 9 – Frustrated total internal reflection (FT-IR) spectra of HTS-1, CuMn₂O₄/HTS-1, Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1.

Fig. 10 – (a) ammonium temperature-programmed desorption (NH₃-TPD) curves and (b) pyridine adsorption internal reflection (Py-IR) spectra of HTS-1, CuMn₂O₄/HTS-1, Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1. L-acid: Lewis acid; B-acid: Brønsted acid.
induced electron transfer between Ce⁴⁺ and Mn³⁺, which led the electric charge becoming unbalanced in the Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1 catalyst. For the multiple oxide composites, the acidic sites were produced when the electric charge was unbalanced.

The coexistence of Brønsted and Lewis acid sites was also confirmed by the Py-IR technique (Fig. 10b). Classically, the bands at 1578 and 1635 cm⁻¹ on materials are considered as due to the adsorption of pyridine onto Brønsted sites, and the bands at 1499 and 1578 cm⁻¹ are considered as arising from the adsorption of pyridine on Lewis sites (Barzetti et al., 1996). The band at 1490 cm⁻¹ is related to the adsorption of pyridine on Brønsted and Lewis sites. As shown in Table 2, the Brønsted/Lewis (B/L) ratios of Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 and Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1 were 0.08 and 0.12, respectively, much lower than that of CuMn₂O₄ (at approximately 0.19). The case can be considered that a charge imbalance was produced due to differences in the valences of Cu and the doping element. For the multiple oxide composites, the Brønsted/Lewis ratio would change when the electrical neutrality is destroyed. Compared with the Cu₀.₇Mn₂Y₀.₃Oₓ/HTS-1 catalyst, the Cu₀.₇Mn₂Ce₀.₃Oₓ/HTS-1 catalyst showed more Lewis acid sites, as the acid amount increased. This implied that the electron cycle between Ce³⁺ and Ce⁴⁺ was intense and induced electron transfer between Ce⁴⁺ and Mn³⁺, which contributed to creation of more Lewis acid sites. The Lewis acid sites are considered to be the active sites for catalytic oxidation (Wu et al., 2018). Oxygen can be regarded as a typical Lewis base, which can produce electron pairs adsorbed on catalysts due to the existence of strong Lewis acid sites, and then the adsorbed oxygen molecules on these active sites can dissociate into surface oxygen species (O²⁻, O²²⁻, or O¹⁻), thereby supplementing the consumption of lattice oxygen in the reaction.

2.5. Catalyst reaction kinetics

For our catalysts, the spinel valence and conduction bands are both of metal character, thus the requisite electrons are readily available. This allows for direct activation of dioxygen via electron transfer provided by the atomic dⁿ orbit (dⁿ) active centers and surface oxygen species such as O²⁻, O²²⁻, or O¹⁻ may be generated as a result (Zasada et al., 2017). These surface oxygen species react rapidly with the reduction sites on the catalyst surface to produce lattice oxygen. As a result, the MVK pathway is possible, which is an indirect oxidation process that involves lattice oxygen and is controlled by the kinetics of oxygen vacancy formation (Hung, 2008; Vannice, 2007).

The effects of internal diffusion, external diffusion, mass transfer limitations and thermal effects (Appendix A Fig. S5a, b and c) were considered to better adapt to the MVK model. The two steps (oxidation and reduction) of the MVK model can be expressed as follows:

\[
\text{Cat-O} + \text{HC} \rightarrow \text{Cat} + \text{HC-O} \quad k_{\text{tol}} \tag{2}
\]

\[
2\text{Cat} + O_2 \rightarrow 2\text{Cat-O} \quad k_{\text{o}} \tag{3}
\]

in which Cat is the catalyst, Cat-O is the oxide catalytic material, HC is the hydrocarbon, \(k_{\text{tol}}\) is reaction rate of toluene at temperature \(T\), and \(k_{\text{o}}\) is oxygen reaction rate at temperature \(T\). The relevant formulas are provided in Appendix A. Supplementary data.

The catalytic process of oxidation of toluene to benzoic acid was introduced into the MVK-1 model for further study. As shown in Scheme 3, the oxidation process was divided into two steps. In step (1), toluene reacted with the Cat-O (oxidation active sites), generated H₂O, benzoic acid (oxidation products) and Cat (reductive active sites); In step (2), Cat produced in step (1) continued to react with O₂, and Cat-O was obtained to participate in the reaction in step (1).

The equipotential diagram (Scheme 3) shows the surface potential distribution of toluene and oxygen molecules. As Zhang’s research found (Zhang et al., 2017a), the surface...
oxygen was less mobile and could be firmly held in the lattice matrix at low temperature. With these precedents in mind, the combination of the “fixed” surface oxygen was considered as a Lewis base. At the temperature (T ≥ 200°C) of catalytic reaction, the surface oxygen was more mobile and loss from the lattice matrix occurred. Oxygen as a new Lewis base can be adsorbed on the Cu0.7Mn2Y0.3Ox/HTS-1 and Cu0.7Mn2Ce0.3Ox/HTS-1 surfaces due to the existence of strong Lewis acid sites (Genty et al., 2018). Lewis acid sites can effectively adsorb and activate oxygen molecules to generate surface oxygen species. The surface oxygen species react with reducing active sites on the surface of the catalyst to form activated lattice oxygen for oxidation of toluene.

Raw data for kinetic calculations are provided in Appendix A Table S4. The Arrhenius fitting curves of CuMn2O4/HTS-1, Cu0.7Mn2Y0.3Ox/HTS-1, and Cu0.7Mn2Ce0.3Ox/HTS-1 for the Mars–Van-Krevelen-1 (MVK-1) model are shown in Fig. 11. The values of the activation energy for surface oxidation and surface reduction over catalysts are shown in Table 3. We can notice that the surface reduction activation energy is much lower than surface oxidation activation energy. This is consistent with the MVK-1 mechanism, where the surface oxidation step is the key step. Compared with Cu0.7Mn2Y0.3Ox/HTS-1, the oxidation activation energy of Cu0.7Mn2Ce0.3Ox/HTS-1 was significantly reduced due to the higher lattice oxygen density on the catalyst surface, which benefited from the fact that the electron cycle between Ce3+ and Ce4+ was intense and induced electron transfer between Ce4+ and Mn3+. The decrease in the surface reduction activation energy for Cu0.7Mn2Ce0.3Ox/HTS-1 was caused by the distribution of Lewis acid sites, which can effectively adsorb and activate oxygen molecules to generate surface oxygen species.

Another MVK-2 model was tested. In this model, the chemical reaction was the oxidation of toluene to CO2 and H2O. Raw data for kinetic calculations is provided in Appendix A Table S5. The mathematical expression of the MVK-2 mechanism is shown in Table 4. The Arrhenius fitting curves of CuMn2O4/HTS-1, Cu0.7Mn2Y0.3Ox/HTS-1, and Cu0.7Mn2Ce0.3Ox/HTS-1 for MVK-1 model are shown in Fig. 12.

Compared with CuMn2O4/HTS-1, the values of the activation energy for surface oxidation and surface reduction over Cu0.7Mn2Ce0.3Ox/HTS-1 and Cu0.7Mn2Y0.3Ox/HTS-1 dropped significantly. This phenomenon reflected the synergistic effect of redox properties and Lewis acid sites on the complete oxidation of toluene. Oxygen vacancies generated by electron transfer are beneficial to the oxidation of toluene, and the lattice oxygen on the catalyst surface reacts with toluene molecules to produce a highly reducible catalyst. The reducible catalyst activates oxygen molecules under the effect of Lewis acid sites to form surface oxygen species (O2−, O22−, or O−).

Table 3 – Summary of the kinetics values from the MVK-1 model.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate parameters</th>
<th>Activation energy (Ea (kJ/mol))</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuMn2O4/HTS-1</td>
<td>[k_{\text{toil}} = 4534 \times e^{-\frac{41559}{RT}}]</td>
<td>41.559</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>[k_o = 58748 \times e^{-\frac{134.747}{RT}}]</td>
<td>134.747</td>
<td>0.982</td>
</tr>
<tr>
<td>Cu0.7Mn2Y0.3Ox/HTS-1</td>
<td>[k_{\text{toil}} = 1178 \times e^{-\frac{32375}{RT}}]</td>
<td>32.375</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>[k_o = 44248 \times e^{-\frac{57551}{RT}}]</td>
<td>57.551</td>
<td>0.962</td>
</tr>
<tr>
<td>Cu0.7Mn2Ce0.3Ox/HTS-1</td>
<td>[k_{\text{toil}} = 150 \times e^{-\frac{23639}{RT}}]</td>
<td>23.639</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>[k_o = 4317 \times e^{-\frac{49528}{RT}}]</td>
<td>49.528</td>
<td>0.966</td>
</tr>
</tbody>
</table>

R: gas constant.
to replenish the lattice oxygen lost by toluene oxidation. Although the content of Lewis acid sites in Cu0.7Mn2Y0.3Ox/HTS-1 is significantly higher than that of CuMn2O4/HTS-1, there are no more oxygen vacancies for Cu0.7Mn2Y0.3Ox/HTS-1 to maintain the surface oxidation of the toluene. Compared with Cu0.7Mn2Y0.3Ox/HTS-1, the values of the surface oxidation activation energy for Cu0.7Mn2Ce0.3Ox/HTS-1 dropped significantly.

### Table 4 – Summary of the kinetics values from the Mars–Van–Krevelen–2 (MVK-2) model.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Rate parameters</th>
<th>Activation energy (Ea [kJ/mol])</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuMn2O4/HTS-1</td>
<td>( k_{\text{tot}} = 24095 \times e^{\left( \frac{48562}{RT} \right)} )</td>
<td>48.562</td>
<td>0.993</td>
</tr>
<tr>
<td>Cu0.7Mn2Y0.3Ox/HTS-1</td>
<td>( k_{\text{tot}} = 6284486 \times 10^e^{\left( \frac{138979}{RT} \right)} )</td>
<td>138.979</td>
<td>0.984</td>
</tr>
<tr>
<td>Cu0.7Mn2Ce0.3Ox/HTS-1</td>
<td>( k_{\text{tot}} = 1159 \times e^{\left( \frac{32514}{RT} \right)} )</td>
<td>32.514</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>( k_{\text{so}} = 1789429 \times e^{\left( \frac{80375}{RT} \right)} )</td>
<td>80.375</td>
<td>0.944</td>
</tr>
<tr>
<td></td>
<td>( k_{\text{sa}} = 322 \times e^{\left( \frac{26875}{RT} \right)} )</td>
<td>26.875</td>
<td>0.982</td>
</tr>
<tr>
<td></td>
<td>( k_{\text{sa}} = 89786 \times e^{\left( \frac{53642}{RT} \right)} )</td>
<td>53.642</td>
<td>0.966</td>
</tr>
</tbody>
</table>

### 3. Conclusions

The CuMn2O4/HTS-1, Cu0.7Mn2Y0.3Ox/HTS-1 and Cu0.7Mn2Ce0.3Ox/HTS-1 catalysts were prepared by the impregnation method. The order of catalytic performance was as follows: Cu0.7Mn2Ce0.3Ox/HTS-1 > Cu0.7Mn2Y0.3Ox/HTS-1 > CuMn2O4/HTS-1. Regulation of the synergistic effects of redox properties and Lewis acid sites in the Cu0.7Mn2Ce0.3Ox/HTS-1 catalyst led to the best performance. The most efficient route for toluene degradation over Cu0.7Mn2Ce0.3Ox/HTS-1 (T\(_{\text{so}}\) = 295°C) was ascribed to regulation of the synergistic effects of redox properties (activating molecular toluene) and Lewis acid sites (activating dioxygen). For the catalytic oxidation process of toluene, the Lewis acid sites accelerate the adsorption and activation of molecular oxygen to form surface oxygen species (O\(_2^−\), O\(_2^{2−}\), or O\(^−\)) and the redox properties facilitate the deep catalytic oxidation of the intermediate products or by-products to CO\(_2\) and H\(_2\)O.

### Acknowledgments

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.08.019.

### REFERENCES


