Catalytic removal of phenol from gas streams by perovskite-type catalysts

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ABSTRACT

Three perovskite-type catalysts prepared by citric acid method are applied to remove phenol from gas streams with the total flow rate of 300 mL/min, corresponding to a GHSV of 10,000/hr. LaMnO₃ catalyst is first prepared and further partially substituted with Sr and Cu to prepare La₀.₈Sr₀.₂MnO₃ and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃, and catalytic activities and fundamental characteristics of these three catalysts are compared. The results show that phenol removal efficiency achieved with La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ reaches 100% with the operating temperature of 200°C and the rate of mineralization at 300°C is up to 100%, while the phenol removal efficiencies achieved with La₀.₈Sr₀.₂MnO₃ and LaMnO₃ are up to 100% with the operating temperature of 300°C and 400°C, respectively. X-ray photoelectron spectroscopy (XPS) analysis shows that the addition of Sr and Cu increases the lattice oxygen of La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃, and further increases mobility or availability of lattice oxygen. The results indicate that La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ has the best activity for phenol removal among three catalysts prepared and the catalytic activity of phenol oxidation is enhanced by the introduction of Sr and Cu into LaMnO₃. Apparent activation energy of 48 kJ/mol is calculated by Mars–Van Krevelen Model for phenol oxidation with La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ as catalyst.

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Introduction

Volatile organic compounds (VOCs) are one of the major contaminants which not only cause the deterioration of air quality of all urban and industrial areas but also pose adverse effects on human health. Each day, large quantities of VOCs are emitted into the atmosphere from both human activities and natural sources. Most VOCs are toxic and they can enter human body to harm respiratory, nervous, digestion and metabolic systems through skin contact, inhaling or ingestion (Rumchev et al., 2007). Besides, the term of VOCs also associates all VOCs capable of producing photochemical oxidants by means of reaction provoked by solar light, in the presence of nitrogen oxides (Ivanova et al., 2013). As some of VOCs are carcinogenic, more rigorous environmental regulations have to be followed to reduce the emissions and health effect.

Phenol (C₆H₅OH) is one of the most important organic pollutants. The earliest separation of phenol from tar was made in the year of 1834 by a German chemist Runge. It is an aromatic compound that remains a hygroscopic crystalline solid in room temperature and atmospheric pressure. It has a distinctive pungent sweet smell that also smells like tar sometimes. Being generated from a number of industrial factories such as refinery, textiles, pulp and paper, resin and plastics, pharmaceutical and petrochemical processes, phenol derivatives are widely distributed in atmosphere, groundwater and surface water. In the aviation industry, phenol is used...
as a paint remover for plane exterior surfaces (Schmidt, 2005). Additionally, it is also an important odor-causing substance, with a relatively low odor threshold (0.04 μg/L) (Amoore and Hautala, 1983; Busca et al., 2008). Also, phenol is one of the most common organic water pollutants and available technologies for reducing the discharge of phenol from wastewater are studied. Separation technologies such as distillation, extraction, adsorption, membrane pervaporation and membrane-solvent extraction have been developed (Tumakaka et al., 2007; Pinto et al., 2005; Greminger et al., 1982; Dąbrowski et al., 2005; Peng et al., 2003; Kujawski et al., 2004). Destruction technologies such as catalytic/noncatalytic wet air oxidation, wet oxidation, electrochemical oxidation, photocatalytic oxidation, supercritical wet gasification, destruction with energetic atmospheres as well as biochemical treatments have been considered (Bhargava et al., 2006; Chedeville et al., 2007; Chen, 2004; Gimeno et al., 2005; Dileo et al., 2007; He et al., 2005). To effectively remove VOCs from gas streams, various techniques including adsorption, condensation, biological treatment, thermal incineration, catalytic oxidation and photocatalytic oxidation have been developed. However, most of control technologies available for VOCs removal still have some limits for practical application. Therefore, development of a cost-effective and efficient method to remove VOCs via complete catalytic oxidation to harmless products such as H2O and CO2 is essential (Kołodziej and Łojewska, 2005). Perovskite-type oxides are excellent candidates as catalysts particularly suited for exhaust gas control (Alifanti et al., 2005; Niu et al., 2007; Oemar et al., 2014). Perovskite-type oxides have the general formula of ABO3 or A2BO4. Typically, “A” stands for alkali or alkaline earth metal while “B” can be any transition metal element (Hosseini et al., 2013). A wide range of chemical elements can occupy positions of A and B in the perovskite structure, and partial substitutions of the cations give rise to multi-component oxides (A1−xA′B1−xB′2O3). Partial substitution may create oxygen vacancies in the perovskite lattice which may further strengthen the activity of ABO3 perovskite-type catalysts. The addition of Sr to LaMnO3 crystal lattice increases the concentration of Mn4+, which further strengthens the reducibility in the low/medium temperature range (200–500°C) within which the oxidation reactions are generally performed.

Although many studies have been conducted for removing VOCs from gas streams, very few data can be found in the literature concerning the treatment of phenol-containing gaseous streams. This paper investigates the effect of partial substitution of strontium (Sr) and copper (Cu) on the catalytic activity of LaMnO3 in removing phenol from gas streams. The perovskite-type catalyst LaMnO3 synthesized using citric acid sol–gel process method is improved by the addition of Sr and Cu and the catalytic performances of three catalysts prepared were compared and the physical, chemical properties of the catalysts were characterized by SEM, EDS, XDR, BET and XPS.

1. Experimental

1.1. Catalyst preparation

Samples of LaMnO3, La0.8Sr0.2MnO3 and La0.8Sr0.2Mn0.8Cu0.2O3 were prepared by citrate sol–gel method. The corresponding metal nitrates were used for preparing a 1 mol/L aqueous solution. Citric acid was added into aqueous solution of nitrate metal in a designated proportion, the molar ratio of citric acid to total metal cations was 3 to 1, and the mixed aqueous solution was gradually heated to 85°C and maintained for 1 hr with stirring. Then, ethylene glycol was added into the solution at 90°C and stirred for four hours. Ethylene glycol was then added to the mixed aqueous solution to control the molar ratio of citric acid to ethylene glycol at 1:1. The mixed aqueous solution was then heated and stirred to evaporate the water to start the process of sol formation and the transformation of sol into gel. It was dried at 110°C for 24 hr, and then heat treated at 350°C for 2 hr in air, and finally calcined in air at 700°C for 5 hr. The synthesized particles were then pulverized to a 100 mesh size for use.

1.2. Characterization of catalysts

Brunauer Emmett Teller (BET) surface areas, pore diameter, and pore volume of catalysts prepared were measured using an ASAP2010 (ASAP2010 Micromeritics, USA). Sample morphology and dispersion were characterized by scanning electron microscopy (SEM, S80 JEOL, Japan). SEM and energy-dispersive X-ray spectroscopy (EDS) (JEOL, JSM-6700F) were used to determine the structures and the composition of the catalysts prepared.

X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (BRUKER, D8AXRD) over the range of 5° ≤ 2θ ≤ 80°, operated at 40 kV and 10 mA, using Cu-Kα radiation with a nickel filter. An X-ray photoelectron spectroscopy (XPS) spectrum was obtained with monochromatic Al anode X-ray which was equipped with a concentric hemispherical analyzer. Al Kα (1486.6 eV) X-ray source was used for excitation. The binding energies were referenced to the C1s line at 284.5 eV.

1.3. Catalytic activity measurement

Removal efficiency of phenol (C6H5OH) achieved with the catalysts prepared was evaluated in a fixed-bed reactor at atmospheric pressure. Fig. 1 illustrates the experimental
system for evaluating catalytic activity in removing phenol (C₆H₅OH) from gas streams. The total flow rate was controlled at 300 mL/min, corresponding to a GHSV (gas hourly space velocity) of 10,000/hr. The reactor consists of a quartz tube (i.d. = 20 mm) and the synthesized particles are pulverized to a 100 mesh size for use. The reaction temperature was varied from 50 to 600°C to evaluate the temperature effect. Phenol (C₆H₅OH)-containing gas stream is generated by passing air through pure liquid phenol kept in a water bath of a fixed temperature (45°C). Gas stream containing vaporized phenol then flows through two empty aerator bottles connected in series and immersed in a water bath of constant temperature 13°C. Further, phenol vapor that flows through the cold temperature will condense onto the aerator bottles wall and becomes supersaturated. As phenol containing gas stream reaches room temperature, the phenol (C₆H₅OH) state in piping is saturated. A mixture of air with 121 mg/L phenol (C₆H₅OH) was introduced into the reactor to serve as reagents. The CO₂ concentrations of exhaust were measured by using a CO₂ analyzer (Thermo 41C CO₂ Analyzer, USA). For sampling and analysis of exhaust phenol, dichloromethane is applied to absorb the phenol in gas stream, and then injected into the gas chromatograph-flame ionization detector (GC-FID) for analysis. Additionally, phenol (C₆H₅OH) and possible organic products were analyzed by an Agilent 6890N GC-FID. In addition, the influences of space velocity and water vapor (H₂O(g)) on phenol removal are also evaluated with a lab-scale experimental system. With H₂O(g) test, a peristaltic pump was used to inject H₂O(l) into the gas stream to control the H₂O(g) content. In addition, mass flow controllers (MFC) were used to control the gas flow rates. Phenol (C₆H₅OH) removal efficiency and CO₂ mineralization rate are calculated, respectively, by the following equations:

\[
\eta(\%) = \frac{[C_6H_5OH]_{\text{in}} - [C_6H_5OH]_{\text{out}}}{[C_6H_5OH]_{\text{in}}} \times 100\%
\]

\[
\text{CO}_2 \text{ mineralization rate (\%)} = \frac{[CO_2]_{\text{out}}}{6 \times [C_6H_5OH]_{\text{in}}} \times 100\%
\]

where, \([\ ]_{\text{in}}\), and \([\ ]_{\text{out}}\) are species concentrations measured before and after the reactor, respectively.

2. Results and discussion

2.1. Characterization of the catalysts

The phase structures of catalyst powders including La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃, La₀.₈Sr₀.₂MnO₃ and LaMnO₃ were examined by XRD, as shown in Fig. 2. All three catalysts reveal the peak value at 23°, 32°, 41°, 47°, 58°, 68° and 78°. Previous study indicates that peak values correspond to the characteristic peaks of perovskite crystalline phase, signifying that the study has succeeded in synthesizing the catalysts with perovskite crystalline phase (Sui et al., 2011). However, small differences exist in these diffraction patterns, especially for the sample of La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ with additional peaks of the La₂CuO₄ and CuO phases. Perovskite-type catalysts are with a general formula of ABO₃ or A₂BO₄. La₂CuO₄ structure belongs to A₂BO₄-type perovskite. Relevant study of Chen et al. (2014) indicates that formation of La₂CuO₄ may lead to small amount of residual CuO. Also, they point out that La₂CuO₄ and CuO have good catalytic activity for VOC oxidation at <300°C. However, La0.8Sr0.2Mn0.8Cu0.2O3 diffraction peaks are mainly assigned to ABO₃-type perovskite. Therefore, the effects of La₂CuO₄ and CuO on activity are not significant due to small diffraction peaks of La₂CuO₄ and CuO although La₂CuO₄ and CuO possess good activity. In order to understand the homogeneity of catalyst powders, the samples were examined by SEM. Fig. 3 exhibits the images of LaMnO₃, La₀.₈Sr₀.₂MnO₃ and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ catalysts, respectively, with the magnification of 80,000. LaMnO₃ (Fig. 3a) is in the form of spherical particles, mainly constituted by aggregates of particles, resulting in reducing SₐEₐ. The particle sizes of the three catalysts prepared. As expected from bulk materials
without much internal porosity, all the samples exhibit relatively low \( S_{\text{BET}} \) (in the range of 5.88–9.13 m\(^2\)/g). The \( S_{\text{BET}} \) of LaMnO\(_3\), La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) and La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\) are 5.88, 7.35 and 9.13 m\(^2\)/g, respectively. The addition of Sr and Cu into the LaMnO\(_3\) lattice induces the increase of \( S_{\text{BET}} \). La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\) catalyst possesses the largest specific surface area. Also, results of EDS are presented in Table 1, indicating that the elemental compositions of catalysts present a little divergence if compared with the formula of catalysts designated. However, elemental compositions of catalyst identified by EDS are mainly analyzed on portion of surface, which may cause a little divergence on elemental composition. However, three catalysts present good perovskite-type catalyst by XRD results.

2.2. XPS property analysis

XPS is used to analyze the chemical bonding displacement status. O, La, Mn, Sr and Cu elements in three catalysts including LaMnO\(_3\), La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) and La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\) are analyzed to understand element patterns. The peaks of all catalysts are synthesized by Origin software. The XPS spectra of O 1s are shown in Fig. 4. The peak at ca. 529 eV is identified as lattice oxygen, while that at 531.8 eV is assigned to the surface adsorbed oxygen (Tabata et al., 1998). It is interesting to know that the lattice oxygen could be increased by adding with Sr and Cu. As Sr is added to form La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)O\(_3\), the lattice oxygen as an active species could be increased. Sutthiumporn et al. (2012) point out that the lattice oxygen species in perovskite-based catalysts play important roles in oxidation. The perovskite catalysts with more lattice oxygen possess better mobility of oxygen as well as higher activity. According to Mars–Van Krevelen mechanism, reactant could react with lattice oxygen of catalyst to form oxygen vacancy, and then the catalyst is oxidized by oxygen, namely, activity of catalyst could be regenerated. Therefore, the higher lattice oxygen mobility of La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\) catalyst is the key to its higher activity. In addition, Fig. 4 presents XPS spectra of La 3d, the characteristic peaks of La are attributed to La\(^{3+}\). The results indicate that peak values of La 3d shift to lower energy as Sr and Cu are added due to improving oxidation capability. For Mn 2p spectrum, peak intensities are evaluated by applying a peak synthesis procedure that includes two components of Mn\(^{3+}\) and Mn\(^{4+}\). Chen et al. (2013) suggest that the characteristic peaks of Mn\(^{3+}\) and Mn\(^{4+}\) ions be located at ca. 641.2 and 642.5 eV, respectively (Chen et al., 2013). The addition of Sr into LaMnO\(_3\) catalyst forms La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\), the characteristic peaks are located at ca. 132.8 and 134.6 eV (Wu et al., 2005). Sr in La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) and La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\) appears in the form of Sr\(^{2+}\). Partial substitution of trivalent cation (La\(^{3+}\)) with divalent cation (Sr\(^{2+}\)) may produce oxygen vacancies by charge compensation, hence activity can be affected by changing average oxidation state of B-site cations and creating oxygen vacancy to maintain the balanced charge. The XPS graph of the copper element shows that characteristic peaks of Cu\(^{2+}\) are located at ca. 935 and 942 eV. This may be explained by the effect of the ionic coordinate structure of La\(_{0.8}\)Sr\(_{0.2}\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\) around Cu\(^{2+}\) ions. Lisi et al. (1999) point out that changes in the oxidation of Mn\(^{3+}\) to produce Mn\(^{4+}\) ion bring the charge compensation of Cu\(^{2+}\) to a balance (Lisi et al., 1999).
2.3. Catalytic activity of perovskite-type catalyst for phenol removal

In the process of VOCs catalytic oxidation, the reaction temperature at the catalyst bed is considered as the most crucial parameter. To understand the catalytic activities of three catalysts (LaMnO₃, La₀.₈Sr₀.₂MnO₃ and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃) for phenol removal at different temperatures, a temperature range of 50–600°C is chosen to test the oxidation of phenol with the inlet concentration of 121 mg/L, and GHSV of 10,000/hr. Fig. 5 shows the removal efficiencies of phenol achieved at different reaction temperatures. Increasing temperature not only provides more energy and probability of collision, but also excites oxygen deep in the catalyst lattice to the surface of the catalyst, forming oxygen vacancies. The phenol removal efficiency achieved with La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ reaches 100% at 200°C and the mineralization rate reaches 100% at 300°C. On the other hand, the phenol removal efficiencies achieved with La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ reach 100% at 300 and 400°C, respectively. The result shows that La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ must be operated at 300°C to ensure complete phenol (C₆H₅OH) oxidation. Efficiency curve is frequently characterized by T₁₀₀ which is the temperature needed to achieve 100% removal of pollutant. The T₁₀₀ values for the removal of phenol (C₆H₅OH) with LaMnO₃, La₀.₈Sr₀.₂MnO₃ and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ are 400, 300 and 200°C, respectively. Hence, the catalytic activities for phenol removal are arranged as: La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ > La₀.₈Sr₀.₂MnO₃ > LaMnO₃. Huang et al. (2008) used La₀.₈Sr₀.₂CoO₃ to convert toluene, and the result indicates that 99% conversion could be reached at 300°C. Hosseini et al. (2010) evaluate the catalytic activity of La₂Zn₀.₃Fe₀.₇O₃ for toluene conversion and indicate that conversion efficiency reaches 96% as temperature is controlled at 323°C. Recently, LaCoO₃ is investigated by Zhang et al. (2015) for toluene removal, and the result indicates that operating temperature needs to be controlled at 280°C to achieve 90% conversion. Overall, La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ shows good performance if compared with literature. Through the experiments in this study, it is proven that catalytic activity of LaMnO₃ catalyst can be enhanced by modification with Sr and Cu. The oxygen vacancy can be produced by charge compensation as a low-valence cation (Sr²⁺) occupies the frame at La³⁺-site, resulting in more lattice oxygen and good mobility of lattice oxygen. As mentioned previously, the lattice oxygen species in perovskite-based catalysts play important roles in oxidation, namely, perovskite catalysts with more lattice oxygen possess better mobility of oxygen as well as higher activity for VOC oxidation. Likewise, the addition of Cu could increase the ratio of Mn⁴⁺/(Mn⁴⁺ + Mn³⁺), and increasing Mn⁴⁺ ions raises oxygen adsorption and desorption capacities. Namely, redox of catalyst could be increased (Lisi et al., 1999). Also, previous study indicates that the addition of Sr into perovskite-type catalyst reveals the same effect (Niu et al. (2007), resulting in higher catalytic activity in converting VOC (Chen et al., 2014). The results show that La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ has the best activity for phenol removal among three catalysts prepared and the catalytic activity for phenol oxidation is enhanced by introduction of Sr and Cu into the lattice.

Fig. 5 shows the removal efficiencies of phenol achieved with La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ reaches 100% at 300°C. However, mineralization rate achieved with La₀.₈Sr₀.₂MnO₃ and LaMnO₃ are 96% and 87%, respectively, implying that at 300°C, there is enough energy to break C–C and C=C on the benzene ring and then oxidize phenol to yield CO₂. At 200°C, removal efficiencies achieved with three catalysts are all

<table>
<thead>
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<th>Catalyst</th>
<th>EDS (wt.%)</th>
<th>S_BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO₃</td>
<td>31.07</td>
<td>29.69</td>
</tr>
<tr>
<td>La₀.₈Sr₀.₂MnO₃</td>
<td>21.8</td>
<td>25.27</td>
</tr>
<tr>
<td>La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃</td>
<td>22.97</td>
<td>18.12</td>
</tr>
</tbody>
</table>

EDS: energy-dispersive X-ray spectroscopy.
above 90%, but CO₂ mineralization rates fall between 20%–30%. As the reaction temperature is fixed at 200°C, yellow substances are found at the tail end of the reaction tube after reaction. A further GC–MS analysis of the yellow substance after rinsing and collecting with dichloromethane reveals that it contains carbon-containing compounds of alkane, hydroxyl and phenoxy radicals. It is speculated that energy at 200°C is not adequate to completely break the benzene ring of phenol, causing a yield of other carbon-containing compounds and resulting in low CO₂ mineralization rate.

2.4. Effect of GHSV on catalytic activity of La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃

Space velocity is the volume of reactant flowing through a unit of catalyst bed volume within a unit of time, and is also referred to as GHSV for short. To investigate the effect of different GHSVs on phenol removal by perovskite-type catalysts, phenol concentration is fixed at 121 ppm, and the reaction temperature is controlled at 300°C. As shown Fig. 7, as GHSV is increased from 10,000 to 30,000/hr, phenol removal
efficiency decreases from 100% to 84% and mineralization rate decreases from 100% to 82%; all of these changes are related to the gas residence time. When the pressure and temperature are fixed, increasing GHSV increases the volume flow rate, resulting in a shorter residence time of reactants inside the reactor and the phenol removal efficiency is reduced.

2.5. Effect of H2O(g) on catalytic activity of La0.8Sr0.2Mn0.8Cu0.2O3

In order to investigate the effect of H2O(g) on phenol removal, 3%, 5% and 7% H2O(g) are introduced into the system, respectively. Fig. 8 shows the effects of 3%–7% H2O(g) on phenol removal achieved with La0.8Sr0.2Mn0.8Cu0.2O3 at 300°C. The results indicate that phenol removal efficiency and mineralization rate decrease from 100% to 96.3% and 100 to 95.5%, respectively, as 3% H2O(g) is introduced. As H2O(g) is further increased to 7%, the phenol removal efficiency and mineralization rate decrease further to 89.3% and 88.4%. It is clear that activities of La0.8Sr0.2Mn0.8Cu0.2O3 suffer from H2O(g) slightly. H2O(g) could be adsorbed on metal oxides and it causes the reduction of active sites for phenol removal. However, the phenol removal efficiency achieved with La0.8Sr0.2Mn0.8Cu0.2O3 still maintains at about 90% with 7% H2O(g) in the gas stream. The results indicate that La0.8Sr0.2Mn0.8Cu0.2O3 has good tolerance for H2O(g) when operated at 300°C.

2.6. Stability of La0.8Sr0.2Mn0.8Cu0.2O3 catalyst for catalytic oxidation

Catalyst activity and stability are two important factors that decide whether the catalyst can be practically utilized or not. After being used for a certain time, the catalyst may lose its initial activity, i.e., a deactivating phenomenon. To evaluate the long-term activity, a stability test for phenol oxidation over La0.8Sr0.2Mn0.8Cu0.2O3 catalyst was carried out for 36/hr at 300°C, and phenol conversion efficiencies versus time are shown in Fig. 9.

Fig. 9 – Phenol removal efficiency as a function of time with La0.8Sr0.2Mn0.8Cu0.2O3 as catalyst. Conditions: C6H5OH = 121 ppm, GHSV = 10,000/hr, Temperature = 300°C.

Fig. 10 – Arrhenius plot for rate constants of phenol conversion with LaMnO3, La0.8Sr0.2MnO3, and La0.8Sr0.2Mn0.8Cu0.2O3, respectively.

Earlier studies have shown that LaMnO3, La0.8Sr0.2MnO3, and La0.8Sr0.2Mn0.8Cu0.2O3 have different activities in the phenol oxidation process. To further investigate the catalytic activities of these catalysts, rate constants were determined using the Arrhenius equation. The Arrhenius plot for rate constants of phenol conversion with these catalysts is shown in Fig. 10. The results indicate that La0.8Sr0.2Mn0.8Cu0.2O3 has the highest activity, followed by La0.8Sr0.2MnO3 and LaMnO3.

Fig. 10 – Arrhenius plot for rate constants of phenol conversion with LaMnO3, La0.8Sr0.2MnO3, and La0.8Sr0.2Mn0.8Cu0.2O3, respectively.
2.7. Activation energy of phenol oxidation

This study also investigates the activation energy of phenol oxidation with LaMnO₃, La₀.₈Sr₀.₂MnO₃, and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃. The kinetics of catalytic oxidation of phenol were studied using the Mars-Van Krevelen Model. First, the system is assumed in steady-state, and the reaction rate (−ri) could be determined with a differential-type reactor. Then different temperatures (T) and inlet phenol concentrations (Ci), various values of −ri can be calculated. Then, the values of rate constant (k) at different temperatures are obtained by regression straight line of 1/ri versus 1/T. Finally, a regression straight line was by obtained plotting ln (k) versus 1/T, and activation energy (Ea) could be calculated by Arrhenius equation (See Fig. 10). Detailed results of the regression analysis of the data obtained are presented in Table 2. The results indicate that rate constant of all catalysts prepared increase with increasing temperature. Moreover, the activation energies of phenol oxidation with LaMnO₃, La₀.₈Sr₀.₂MnO₃, and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ are calculated as 53, 51, and 48 kJ/mol. It is found that La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ possesses the lowest activation energy. To compare with literature, Buciuman et al. (2002) investigated the activation energies for phenol oxidation is proven to be superior to the predecessors including LaMnO₃ and La₀.₈Sr₀.₂MnO₃.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>LaMnO₃</th>
<th>La₀.₈Sr₀.₂MnO₃</th>
<th>La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃</th>
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<tr>
<td>T (°C)</td>
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<td></td>
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</tr>
<tr>
<td>80</td>
<td>150</td>
<td>200</td>
<td>250</td>
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<tr>
<td>k (1/sec)</td>
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<td>0.26</td>
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<tr>
<td>Ea (kJ/mol)</td>
<td>53</td>
<td>51</td>
<td>48</td>
</tr>
</tbody>
</table>

3. Conclusions

Three catalysts including LaMnO₃, La₀.₈Sr₀.₂MnO₃ and La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ are prepared using citric acid sol–gel method. BET analysis indicates that specific surface areas of these catalysts fall between 5 and 10 m²/g. XRD crystalline phase analysis shows that all three catalysts prepared conform to Perovskite-type properties. The addition of Sr and Cu increases the catalyst activity and stability as demonstrated by XPS analysis. Comparison of three catalysts reveals significant improvements in the physicochemical properties of modified La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃.

In terms of catalyst activity, the removal efficiency of phenol achieved with La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ is superior to two other catalysts. At a mere 200°C, phenol can be completely removed and, 100% of mineralization rate can be achieved at 300°C. The results of catalyst testing prove that the modified La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ exhibits the best activity for phenol removal. Hence, the performance of La₀.₈Sr₀.₂Mn₀.₈Cu₀.₂O₃ for phenol oxidation is proven to be superior to the predecessors including LaMnO₃ and La₀.₈Sr₀.₂MnO₃.

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