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

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ARTICLE INFO

Article history:

Received 2 March 2016

Revised 18 April 2016

Accepted 25 April 2016

Available online xxxx

Keywords:

Volatile organic compounds (VOCs)

Phenol

Perovskite-type catalyst

Catalysis

Activation energy

Mineralization rate

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. LaMnO_3 catalyst is first prepared and further partially substituted with Sr and Cu to prepare $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$, and catalytic activities and fundamental characteristics of these three catalysts are compared. The results show that phenol removal efficiency achieved with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ 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 $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and LaMnO_3 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 $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$, and further increases mobility or availability of lattice oxygen. The results indicate that $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ 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 LaMnO_3 . Apparent activation energy of 48 kJ/mol is calculated by Mars–Van Krevelen Model for phenol oxidation with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_3$ 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 ($\text{C}_6\text{H}_5\text{OH}$) 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

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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/nocatalytic wet air oxidation, wet oxidation, electrochemical oxidation, photocatalytic oxidation, supercritical wet gasification, destruction with energetic electrons 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 absorption, 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 these cations give rise to multi-component oxides (A_{1-x}A'_xB_{1-y}B'_yO₃). Partial substitution may create oxygen vacancies in the perovskite structure and increases catalytic oxidation activity (Irusta et al., 1998; Pena and Fierro, 2001). Perovskite-type metal oxides which are easy to synthesize at a low cost and show great thermal stability at high temperatures have been regarded as good replacement to supported noble metals catalysts (Merino et al., 2006). Especially much attention has been paid to LaMnO₃ catalyst for its high catalytic activity and thermal stability in catalytic oxidation of hydrocarbons substances. Spinicci et al. (2003) pointed out that some Mn⁴⁺ exist besides Mn³⁺ in the LaMnO₃ catalyst, therefore, LaMnO₃ catalyst holds a superior oxidation-reduction characteristic and oxygen vacancy (Spinicci et al., 2003). With LaMnO₃ catalyst, oxygen exhibits good mobility and easy desorption, resulting in high oxidation activity. Moreover, a research conducted by Niu et al. (2007) discovered that partially replacing La with Sr at position "A" raises the reaction activity of perovskite-type catalyst. The addition of Sr to LaMnO₃ crystal lattice increases the concentration of Mn⁴⁺ which further strengthens the redox activity (Niu et al., 2007). Buciuman et al. (2002) also pointed out that the Cu substituted perovskite displays a high 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, La_{0.8}Sr_{0.2}MnO₃ and La_{0.8}Sr_{0.2}Mn_{0.8}Cu_{0.2}O₃ 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 the 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

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