Novel metal loaded KIT-6 catalysts and their applications in the catalytic combustion of chlorobenzene

Fei He [a], Jiaqi Luo [a], Shantang Liu [a,b,*]

[a] Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430074, PR China
[b] Wuhan Industrial Institute for Chemical Advanced Material Limited Liability Company, Wuhan 430074, PR China

HIGHLIGHTS

- Metal loaded KIT-6 catalysts are prepared by incipient-wetness impregnation method.
- Catalytic activity for CB degradation is correlating with the redox properties.
- With increasing Mn content, the amount of Mn in the channels of KIT-6 increases.
- T90 temperature of Mn3/KIT-6 was as low as 210.7 °C.
- CB conversion of Mn3/KIT-6 at T90 temperature was maintained at 90% for 1000 min.

GRAPHICAL ABSTRACT
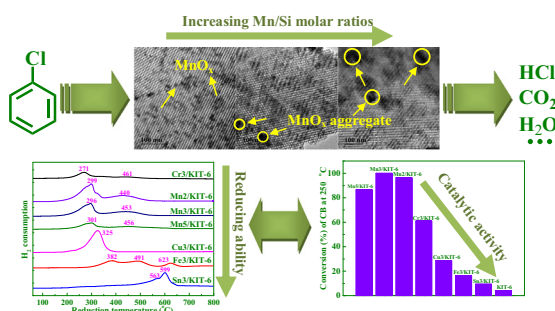
ABSTRACT

A series of metal-loaded mesoporous silica catalysts, M/KIT-6 (M = Mn, Cu, Fe, Cr, Sn), were prepared by incipient-wetness impregnation method, and tested in the catalytic combustion of chlorobenzene (CB) as a model of chlorinated aromatics. The effects of metal oxide species and concentration on the textural structure and catalytic properties were studied in detail. It was found that the dispersion, specific surface area and reducibility are the main factors influencing the catalytic activity. On the basis of T50 (temperature at which 50% conversion is attained), the catalytic activity for the CB degradation decreases in the following order: Mn/KIT-6 > Cr/KIT-6 > Cu/KIT-6 > Fe/KIT-6 > Sn/KIT-6, correlating with the redox properties of the catalysts. Mn/KIT-6 catalysts having different molar ratios of Mn/Si were found to possess high catalytic activity for catalytic combustion of CB. Among these, Mn3/KIT-6 was the most active catalyst, for which the complete combustion temperature (T90) of chlorobenzene was 210.7 °C. By increasing the Mn/Si molar ratio to 1/2, T90 was raised to 238.5 °C. This is due to the decrease of pore volume and specific surface area caused by increase in the amount of Mn in the channels of KIT-6, increased agglomeration of Mn, and the lowering of $O_{ads}/(O_{latt} + O_{ads} + O_{wat})$ concentration ratio. Conversion of CB over the Mn3/KIT-6 catalyst was maintained at 90% or more for 1000 min, indicating the excellent stability of this catalyst.

© 2016 Published by Elsevier B.V.

1. Introduction

Aryl chlorides continue to attract considerable public concern because of their persistence in the environment, bioaccumulation in the tissues and potential toxicity as carcinogens and teratogens [1]. Therefore, it is important to develop convenient, practical and

* Corresponding author at: Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430074, PR China. Tel.: +86 27 87195001.
  E-mail address: liushantang@mail.wit.edu.cn (S. Liu).

cost effective methods to remove aryl chloride pollutants. Among various available detoxification techniques, catalytic combustion has been proven to be a promising and emerging technology, due to its highly effective character (between 250 and 550 °C) and low use of energy (without additional fuel) when compared to a thermal process [2]. Vanadium oxide catalysts have been reported to be active for this technology, and are being commercially adopted for the practical application [3–5]. However, these catalysts have some unavoidable drawbacks, such as high light-off temperature, the toxicity of vanadium, and low specific surface area [6,7]. Thus, there is a major research interest to develop suitable alternatives for vanadium oxide.

There are various reports on catalysts for catalytic oxidation of chlorinated volatile organic compounds (CVOCs), and most of them are focused on three types of catalysts based on noble metals, metal oxides and zeolites [8–10]. Metal catalysts have been widely used for the effective catalytic combustion of CVOCs, however they are susceptible to the adsorption of Cl species on the active sites and also lead to the formation of undesirable polychlorinated compounds during the reaction process [11]. Most of the catalysts that have been reported for catalytic combustion showed good activity only at high reaction temperatures over 500 °C [12], which requires specialized equipment and additional fuel consumption. Therefore, the development of new and improved catalysts having high activity in converting aryl chlorides is of great significance. The key to solve this problem is to develop more active metal oxides and enhance the specific surface area of catalysts.

Among all the catalysts studied in the past few years, much attention has been focused on zeolite catalysts, mainly due to their special three-dimensional channel structure, shape-selective catalyzing effects, high internal surface area, good thermal stability and large ion-exchange capacity [13]. It has been reported that some zeolites, such as SBA-15, ZSM-5, MCM-41 and Beta zeolite, display good catalytic combustion activity [14–17]. Also, the surface characters of mesoporous supports are related to the dispersion of metal oxides. Better dispersion of the active species will be favorable for enhancing the redox capability of metal oxides as well their reactivity. In 2003, Kleitz et al. have synthesized a novel type of mesoporous silica, called KIT-6, with three-dimensional cubic Ia3d symmetry [18]. Recently, it has been usually used as a hard template for crystal growth of ordered mesoporous metal oxides, such as porous crystals of TiO_2 [19], Mn_3O_4 [20], CuO [21], etc. However, the product yield with this method is low, and the preparation process is complex, thus limiting its large-scale application. In addition to being used as a template, KIT-6 is a kind of mesoporous silica and shows excellent adsorption and desorption performance for various gases [22]. These properties would be very helpful for building adsorption-catalytic bi-functional catalyst systems in the near future. Therefore, mesoporous KIT-6 is a good choice as the support to achieve high dispersion of metal oxides and a better diffusion of reactants.

To the best of our knowledge, there is no report to date on evaluating the catalytic activity of KIT-6 supported metal oxides for oxidation of chlorobenzene. In this paper, a series of M/KIT-6 derivatives (M = Mn, Cu, Fe, Cr, Sn) were synthesized through an incipient-wetness impregnation method, and the effects of metal oxide species and concentration on the textural structure and catalytic properties have also been explored.

2. Experimental

2.1. Materials preparation

The synthesis of KIT-6 was carried out according to a previously reported procedure [18]. About 6 g of P123 (EO20PO70EO20, poly (ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethylene glycol), average molecular weight = 5800, Sigma–Aldrich) was dissolved in 11.8 g of HCl (35%) and 217 g of H_2O. Then, 6 g of n-butanol was added and the solution was stirred for 1 h at 35 °C. Then, 12.9 g of tetraethyl orthosilicate (TEOS) was added, and the resultant solution was stirred for 24 h at 35 °C. It was then transferred to a Teflon-lined stainless steel autoclave and placed in an oven at 100 °C for 24 h. The resulting precipitate was filtered, washed with deionized water, and dried at 100 °C overnight. The obtained powder was finally heated up to 550 °C at a ramp rate of 2 °C/min and calcined at this temperature in air for 5 h.

A series of metal modified KIT-6 mesoporous catalysts were prepared by an incipient-wetness impregnation method. In a typical procedure, a certain amount of the metallic precursor (50 wt % $Mn(NO_3)_2$ aqueous solution, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 5H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ or $SnCl_4 \cdot 4H_2O$) was dissolved into deionized water, and then the above aqueous solution was added to KIT-6. The M/Si molar ratio was kept as 1/3. Following impregnation, the catalysts were kept at room temperature for 24 h, dried at 80 °C in air overnight, and then calcined at 400 °C for 4 h. For studying the effect of metal content, the M/Si molar ratio of catalyst prepared with 50 wt% $Mn(NO_3)_2$ aqueous solution was kept as 1/5, 1/3, and 1/2. The catalysts were denoted by Mx/KIT-6, where M represents the type of metal used, and x represents the reciprocal of M/Si molar ratio. For example, Mn3/KIT-6 represents the Mn/KIT-6 catalyst with the Mn/Si molar ratio of 1/3. For comparison, the Mn3/KIT-6 catalyst was also prepared by a mechanical blending method, and this sample is denoted by mix-Mn3/KIT-6.

2.2. Characterization

The phase structures of the catalysts were analyzed by X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku MiniFlex 600) with Cu Kα radiation (40 kV and 40 mA). Nitrogen adsorption and desorption isotherms were measured on a Micromeritics ASAP 2460 nitrogen-adsorption apparatus. The specific surface areas of samples were measured using the Brunauer–Emmett–Teller (BET) method, and the pore volumes and pore size distributions were determined using the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) images were acquired using a JEOL JEM-2100 microscope. The samples were ground up using a mortar, suspended in ethanol and mounted onto Cu grids. The surface atomic states of the catalysts was analyzed by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha XPS). The temperature-programmed reduction (TPR, Micro 2920) runs were conducted with a linear heating rate (10 °C/min) in a flow of 10% H_2 in argon at a flow rate of 40 mL/min.

2.3. Catalytic activity test

Catalytic combustion reactions were performed at atmospheric pressure in a continuous flow micro-reactor, which was made of a quartz tube with an 8 mm inner diameter, with 0.2 g of catalyst packed in the center of the reactor. CB was introduced into the reactor by a carrier gas of N_2 through a saturator maintained at 0 °C, and then it was mixed with N_2 and O_2 in a mixing drum. The feed flow through the reactor was set with a CB concentration of 5000 ppm and gas hourly space velocity (GHSV) of 20,000 h^{-1}. The reaction temperature was measured and controlled with a thermocouple located at the thermal part of the reactor. Catalytic tests were performed at temperature range of 100–250 °C in a step mode, the catalysts being stabilized for 20 min at each temperature. The effluent gases were analyzed on-line at a given temperature by using two gas chromatographs (GC), one equipped with FID for organic chlorinated reactant, and the other with TCD for CO and CO_2. The concentrations of Cl_2 and HCl were analyzed by the