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Catalyzing the oxidation of sulfamethoxazole by permanganate using molecular sieves supported ruthenium nanoparticles

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HIGHLIGHTS

- Molecular sieve supported Ru increases the oxidation rate of SMX by 27–1144 times.
- XAFS analysis reveals that Ru catalyst acting as an electron shuttle.
- The catalytic ability of Ru/ZSM-5A drops in ten runs due to MnO_2 deposition.
- Partially deactivated Ru/ZSM-5A catalyst can be completely regenerated by $NH_2OH{\cdot}HCl$.

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ABSTRACT

This study developed a heterogeneous catalytic permanganate oxidation system with three molecular sieves, i.e., nanosized ZSM-5 (ZSM-5A), microsized ZSM-5 (ZSM-5B) and MCM-41, supported ruthenium nanoparticles as catalyst, denoted as Ru/ZSM-5A, Ru/ZSM-5B and Ru/MCM-41, respectively. The presence of 0.5 g L^{-1} Ru/ZSM-5A, Ru/ZSM-5B and Ru/MCM-41 increased the oxidation rate of sulfamethoxazole (SMX) by permanganate at pH 7.0 by 27–1144 times. The catalytic performance of Ru catalysts toward SMX oxidation by permanganate was strongly dependent on Ru loading on the catalysts. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses confirmed that Ru catalyst acted as an electron shuttle in catalytic permanganate oxidation process. Ru^{III} deposited on the surface of catalysts was oxidized by permanganate to its higher oxidation state Ru^{VII}, which could work as a co-oxidant with permanganate to decompose SMX and was then reduced to its initial tri-valence. During the successive runs, Ru/ZSM-5A could not maintain its catalytic activity due to the deposition of MnO_2, which was the reductive product of permanganate, onto the surface of Ru/ZSM-5A. Thus, the regeneration of partially deactivated Ru catalysts by reductant $NH_2OH{\cdot}HCl$ or ascorbic acid was proposed. Ru/ZSM-5A regenerated by $NH_2OH{\cdot}HCl$ displayed comparable catalytic ability to its virgin counterpart, while ascorbic acid could not completely remove the deposited MnO_2. A trace amount of leaching of Ru into the reaction solution was also observed, which would be ameliorated by improving the preparation conditions in the future study.

1. Introduction

Permanganate oxidation has been already widely used in water utilities over the past decades for control of dissolved Mn(II), taste and odor compounds, and cyanotoxins, due to its comparative stability, ease of handling, and relatively low cost (Vanbenschoten et al., 1992; Dietrich et al., 1995; Rodriguez et al., 2007). In recent years, the potential application of permanganate for oxidative removal of emerging pollutants during water and wastewater treatment has received great attention (Jiang et al., 2009, 2010; Jiang et al., 2012; Zhang et al., 2013a). Jiang et al. reported that permanganate was much more effective for oxidative removal of phenolic endocrine disrupting chemicals (EDCs) in real water at pH 8.0 compared to ozone, chlorine, and ferrate, mainly due to its relatively high stability as well as selectivity therein (Jiang et al., 2012). But considering the unpleasant color of permanganate, only very low inlet concentration was allowed to avoid the appearance

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of chromaticity in the treated water. Thus, catalyzing this process is becoming a necessity to achieve high organics removal with low permanganate dosage.

Among the catalysts which have potential for use in selective oxidations, ruthenium (Ru) takes a special position owing to its versatility. Therefore, CeO_2 and TiO_2 supported ruthenium nanoparticles, namely Ru/CeO_2 and Ru/TiO_2, were synthesized to catalyze permanganate oxidation (Zhang et al., 2013b, 2014a). The presence of $1.0\ g\ L^{-1}$ Ru/CeO_2 increased the oxidation rate of butylparaben by 3–96 times at pH 4.0–8.0 (Zhang et al., 2013b), while $1.0\ g\ L^{-1}$ Ru/TiO_2 increased the reaction rates of bisphenol A, diclofenac, acetaminophen, sulfamethoxazole, benzotriazole, carbamazepine, butylparaben, diclofenac, ciprofloxacin and aniline by 0.3–119 times at pH 7.0 (Zhang et al., 2014a). However, the dependence of the performance of catalysts on the specific area, pore size and diameter of supports and Ru loading has not been clarified. Neither were the performances of Ru catalysts with different supports compared.

It is also well known that the performance of catalyst largely depends on the surface area and pore size of support. Higher surface area can provide more active sites according to Chaliha and Bhattacharyya (2008). Molecular sieves have been employed as the support of various catalysts widely used in industrial processes due to their high surface areas and highly ordered porous structure (Elias et al., 2010). Especially, ZSM-5 with a uniform micropore size of 0.74 nm (Tang et al., 2012), and MCM-41 with a mesopore size of 1.5–10 nm, both of which have very high surface area (Li et al., 2003), have been widely used as catalyst or catalyst support (Huang et al., 2002; He et al., 2010). To the best of our knowledge, no study had systematically explored the performance of ZSM-based or MCM-41-based Ru catalysts in permanganate oxidation for degradation of organic pollutants in water. Therefore, both ZSM-5 and MCM-41 were chosen as supports for preparing the catalysts bearing Ru. The crystal/particle size of ZSM-5 can also influence its catalytic performance. Smaller crystals/particles offer shorter intracrystalline diffusion path for the reactants and products, and possess a higher number of external active sites compared to larger crystals (Triantafyllidis et al., 2004). Thus both the nanosized and microsized ZSM-5, namely, ZSM-5A and ZSM-5B, were employed in this study. The antibiotic drug sulfamethoxazole (SMX) is frequently detected in surface water and groundwater worldwide due to their incomplete removal during biological wastewater treatment (Jasper and Sedlak, 2013; Karaolia et al., 2014). In this paper, SMX was chosen as the target contaminant to investigate the catalytic performance of Ru/ZSM-5A, Ru/ZSM-5B and Ru/MCM-41 in permanganate oxidation processes.

The *in situ* XANES analysis revealed that Ru/CeO_2 acted as an electron shuttle in catalytic permanganate oxidation process (Zhang et al., 2013b). Ru^{III}, deposited on the surface of CeO_2 was oxidized by permanganate to its higher oxidation state Ru^{VI} and Ru^{VII}, which acted as the co-oxidants in organics oxidation. Then, Ru^{VI} and Ru^{VII} were reduced by organics to its initial state of Ru^{III} (Zhang et al., 2013b). In our previous study, the identification of Ru^{VII} and Ru^{VI} was only based the *K*-edge positions of Ru of different oxidation states reported in literature (Choy et al., 2000; Hosokawa et al., 2005). The EXAFS spectra of Ru/CeO_2 were very noisy, which may be due to the low Ru content and the amorphousness of Ru hydroxide on the CeO_2 support, and thus was discarded although the EXAFS spectra could offer electronic and local structural information on the ruthenium upon the change of its oxidation state. In this study, we bought commercial $KRu^{VII}O_4$ and synthesized $K_2Ru^{VI}O_4$ in our lab following the method reported by Greenwood and Earnshaw (1997), and collected the XANES spectra of Ru^{VII} and Ru^{VI} to verify the change of oxidation state of Ru in the process Ru/ZSM-5A catalyzed permanganate oxidation. Furthermore, EXAFS spectra were employed to get the electronic and local structural information of ruthenium upon the change of its oxidation states so as to support the information obtained from the XANES spectra. The drop of catalytic performance of Ru/TiO_2 and Ru/CeO_2 toward permanganate oxidation during successive runs was observed in our previous studies but no effort had been made to recover the reactivity of used catalyst.

Therefore, the objectives of this work were to (1) synthesize Ru/ZSM-5A, Ru/ZSM-5B and Ru/MCM-41 catalysts, and examine their performance and compare their performance to that of Ru/CeO_2 (Zhang et al., 2013b) and Ru/TiO_2 (Zhang et al., 2014a); (2) verify the role of Ru^{III} in catalytic permanganate oxidation process with both XANES and EXAFS spectra; (3) assess the stability of synthesized catalyst and develop a regeneration methodology for the partially deactivated catalyst.

2. Experimental section

2.1. Materials

SMX of analytical grade was purchased from Sigma–Aldrich. Methanol for chromatographic analysis was of HPLC grade and obtained from J&K Chemical Co., China. The supports ZSM-5A, ZSM-5B and MCM-41 were supplied by Catalyst Plant of Nankai University, while the precursor $RuCl_3$ by Acros Co. Ascorbic acid and hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), were purchased from Sinopharm Chemical Reagent Co., and their stock solutions were freshly prepared before use to avoid their oxidation. All solutions were prepared using Milli-Q water from a Millipore system. Filters used were Millipore Millex syringe-driven 0.22 μm (pore size) cellulose acetate membrane filters.

2.2. Catalyst preparation and characterization

The preparation methods for Ru/ZSM-5A, Ru/ZSM-5B and Ru/MCM-41 were totally the same to those for Ru/CeO_2 and Ru/TiO_2, except that different supports were employed (Zhang et al., 2013b, 2014a), as shown in Text S1. The morphology and particle size of Ru on ZSM-5A, ZSM-5B and MCM-41 were observed with transmission electron microscope (TEM, JEM-2100). The energy-dispersive X-ray spectroscopy (EDAX) analyses were also performed in the TEM analysis on Ametek Genesis XM in order to identify the presence of Ru on the surface of support. The particle size of ZSM-5A ZSM-5B and MCM-41 was determined with laser particle size analyzer. The BET surface areas for different supports were measured with the N_2 gas adsorption method on an ASAP analyzer (Micromeritics, USA). Prior to the adsorption–desorption measurements, the fresh molecular sieves were degassed at 300 °C in a N_2 flow for 2 h. Surface area, pore volume and mean pore size were obtained by measuring the volume adsorbed at different P/P_0 values and by applying different methods. The total pore volume was estimated by measuring the volume of gas adsorbed at P/P_0 of 0.998, whereas, *t*-plot method was used to calculate the micropore surface area (<2 nm) using the Harkins–Jura equation (Viswanadham et al., 2009). The volume distribution in mesopores was obtained from the adsorption branch of the isotherm by applying the Barrett–Joyner–Halenda (BJH) method. Total micropore volume (<2 nm) was obtained using the Horvath-Kawazoe method. In order to clarify the valence of Ru on ZSM-5A, the X-ray photoelectron spectrum (XPS) of Ru/ZSM-5A was collected on a PHI 5700 ESCA System using monochromatic Al Kα radiation (225 W, 15 mA, 1486.6 eV). Ru *K*-edge X-ray absorption fine structure (XAFS) spectra of the prepared catalysts were collected at BL14W1 beamline of Shanghai