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Positron annihilation characteristics and catalytic performances of poly (vinyl alcohol) intercalated montmorillonite supported Pd^0 nanoparticles composites

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ABSTRACT

The microstructure of poly (vinyl alcohol)/ montmorillonite (PVA/MMT) matrices and Pd@PVA/MMT catalytic composite was characterized by positron annihilation spectroscopy (PAS) and other techniques, such as high resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and X-ray photo electron spectroscopy (XPS). XRD and HR-TEM results showed that 20% was the saturation loading percentage of PVA intercalation into MMT. Ortho-positronium (*o*-Ps) annihilations were mainly distributed in the interlayer spacing of MMT and/or open spaces (free volume) of PVA. Below the saturation loading percentage of PVA ($\leq$ 20%), it was found that the *o*-Ps annihilation lifetime became shorter after the intercalation of PVA chains into MMT layers. With further addition of PVA, the *o*-Ps annihilation lifetime became longer after the formation of exfoliated structure. The 20%-PVA/MMT matrix has been selected as the platform to further immobilize Pd specie for preparing novel 0.2%-Pd@20%-PVA/MMT catalytic composite. The effects of Pd immobilization on the microstructure of PVA/MMT matrices were also sensitively detected by PAS. The mean size of the micro-defects (from Tao-Eldrup model) increased from 0.28 nm (20%-PVA/MMT) to 0.29 nm (0.2%-Pd^{2+}@20%-PVA/MMT or 0.2%-Pd^0@20%-PVA/MMT), respectively. This increase in the size of the micro-defects of 20%-PVA/MMT matrix after Pd immobilization was mainly due to the replacement of the inter-molecular hydrogen bodings of PVA chains by the interactions formed between the PVA chains and Pd species. The prepared 0.2%-Pd^0@20%-PVA/MMT catalytic composite showed excellent catalytic efficiency and recyclability in both Heck-type and Sonogashira-type coupling reactions. The correlations between the microstructure and performance of the 0.2%-Pd^0@20%-PVA/MMT composite were thoroughly discussed.

1. Introduction

Nowadays, palladium (Pd) catalysis becomes one of the most important and attractive issues in organic synthesis (Balanta et al., 2011; Tsuji, 2004). In homogenous Pd catalysis process, Pd catalysts are put into the reaction mixture directly and have many difficulties in separation, recovery, and purification, etc (Cole-Hamilton and Tooze, 2006). However, in heterogeneous Pd catalysis process, Pd catalysts are well supported on solid matrices and usually have fairly good recyclability (Yin and Liebscher, 2007; Nasrollahzadeh et al., 2017). Therefore, the developments of heterogeneously supported Pd catalysts with excellent catalytic performances are crucial to most chemical processes. To this goal, many solid materials, including carbon materials (Nasrollahzadeh et al., 2018; Wang et al., 2013), inorganic compounds (Polshettiwar et al., 2009; Del Zotto and Zuccaccia, 2017), natural clay (Xu et al., 2014; Chavan et al., 2015), and polymers (Guibal, 2005; El Kadib, 2015), and so on, have been frequently used as supporting matrices for Pd active species for the development of heterogeneous catalysts.

Montorillonite (MMT), a kind of nature-rich mineral clay, is widely used to prepare catalytic nanocomposites. It is mainly attributed to the excellent properties of MMT, such as good molecular adsorption, extensive swelling, high cations-exchanging capabilities, and remarkable stabilities (Zhou, 2011). Typically, there are two strategies in the use of MMT-based materials as the supports for the immobilization of catalytically active Pd species. One strategy is the embedding of active Pd

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cations into the pores of acid pre-treated MMT supports. After acid treatment, cations (like Al^{3+}, Mg^{2+}, Na^{+}, etc) of the MMT layers can be dissolved out and lots of new pores will be induced. For example, as reported by Borah and Dutta (2013), the specific area of MMT supports was improved greatly after treatment with sulfuric acid, and Pd^0-nanoparticles supported on such modified MMT showed high activity as used in Heck reactions and Sonogashira reactions. The other strategy is the entrapping of the Pd species within the interlayer spacing of intercalated or pillared MMT layers by simple ion-exchange process. For example, as reported by Mitsudome et al. (2007), sub-nano ordered Pd clusters can be easily entrapped within the interlayer spacing of MMT by ion-exchange, and the prepared MMT-entrapped Pd clusters heterogeneous catalysts show high catalytic activity for various organic reactions. The catalytically active Pd species are usually immobilized through chelation with the polar groups (-OH groups) located on the surface of the silicate layer of MMT. However, due to the inorganic nature intrinsic of MMT, such chelation interactions are usually not strong enough. And the prepared Pd-MMT catalysts with both strategies show limited recyclability (can reuse 3 times) for the serious leaching of the active Pd species. Therefore, MMT is hardly used in its pure form for the applications as catalyst supports.

Recent developments in materials science have enabled ones to develop various inorganic clay-organic polymer hybrid functional materials by modifying the inorganic clay hosts with polar polymer chains, such as poly (vinyl alcohol) (PVA) (Strawhecker and Manias, 2000; Lebaron et al., 1999). On the one hand, PVA have excellent chelation capabilities with transition metals for the containing of plenty of –OH groups within its macromolecular backbone. On the other hand, PVA is definitely able to intercalate or exfoliate MMT layers by solution intercalation method for expansion the interlayer spacing of MMT. Therefore, the fabrication of PVA/MMT hybrid materials could realize the combination of the advantages of both the inorganic MMT and the organic polar polymer of PVA components within a same solid, making it possible in designing ideal supporting materials for transition metal of Pd catalysts. As we know, understanding the microstructure-catalysis relationship is very crucial for improving the catalytic performances of heterogeneous catalysts (Sun et al., 2015). Thus, it is necessary to investigate the fine microstructure of PVA/MMT matrices and Pd supported on PVA/MMT catalytic composites. A number of characterization methods, such as X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), N_2 adsorption/desorption methods have been used in the characterization of the catalytic nanocomposites. And valuable information on the microstructure can be obtained with these techniques, such as crystalline structure, interlayer distances, surface area, and so on. However, the characterization of the atomic and molecular defects of the catalytic nanocomposites is still very necessary and challengeable, which is due to the fact that sub-nano level defects can be detected only by few unique characterization techniques, like positron annihilation spectroscopy (PAS).

Actually, as a novel and unique method, PAS has been successfully used to characterize the atomic and molecular defects, such as free volume holes, microvoids, and interfacial properties of nanocomposites (Jean, 1990; Jean et al., 2013; Pethrick, 1997; Fuioka et al., 2015). Positrons are extremely sensitive to various structural defects in materials. In the defects with loose structure where the density of free electrons is relatively low, positron can combine with an electron to form a metastable atom, which is called positronium (Ps), and then annihilate in the defects. According to the different electron and positron spin states, Ps are classified into two types, i.e. para-positronium (*p*-Ps, singlet state, with antiparallel spins), and ortho-positronium (*o*-Ps, triplet state, with parallel spins). The lifetime of *p*-Ps is 0.125 ns. In vacuum, o-Ps has a lifetime of 142 ns, shortened inside a cavity due to the possible annihilation with an external electron in singlet state ('pick off' process). The smaller is the cavity, the shorter is the *o*-Ps lifetime, owing to an increased density of external electrons surrounding Ps. In PAS analysis, the *o*-Ps lifetime (τ_3, longest lifetime) is decided by the size of the defects, and its intensity (I_3) is directly related to the number of the defects. Using Tao-Eldrup free volume model (Tao, 1972; Eldrup et al., 1981), we can calculate the mean radius of the defects, R, from the *o*-Ps lifetime τ_3 through Eq. (1), where ΔR (=0.1656 nm) is the thickness of fitted empirical electron layer. Therefore, *o*-Ps can be used as a sensitive probe to detect the micro-defects in complex matters.

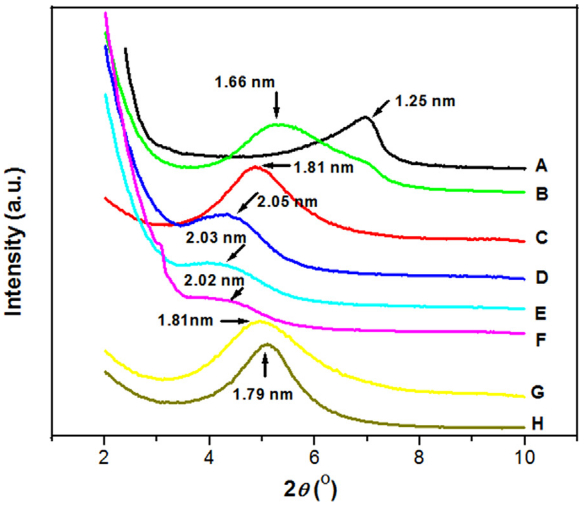

Fig. 1. XRD patterns of MMT, PVA/MMT matrices and Pd@PVA/MMT catalytic composites. A. MMT; B. 10%-PVA/MMT; C. 20%-PVA/MMT; D. 30%-PVA/MMT; E. 40%-PVA/MMT; F. 50%-PVA/MMT; G. 0.2%-Pd^{2+}@20%-PVA/MMT; H. 0.2%-Pd^0 @ 20%-PVA/MMT.

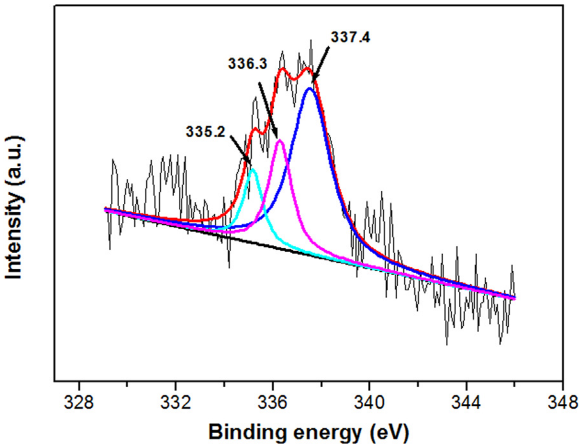

Fig. 2. XPS spectra of the 0.2%-Pd^0 @ 20%-PVA/MMT catalytic composite.

$$\frac{1}{\tau_3} = 2\left\{1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right\} \tag{1}$$

Recently, more and more attention is focused on the using of PAS to characterize the size and distribution of the micro-defects in layered-structure materials, namely MMT. Pujari et al. (Joshi et al., 1998), for the first time, used PAS to investigate the microstructure of Al-pillared MMT and found that the calcination temperature had great effects on the formation of *o*-Ps. Ichimura et al. (Sano et al., 1999) found that Ps atoms are predominantly distributed in the interlayer spacing of MMT rather than in the crystalline silicate layers. Our preliminary results (Zeng et al., 2016; Liu et al., 2018; Xu et al., 2018) also confirmed that *o*-Ps annihilation mainly take place in the expanded interlayer spacing of MMT intercalated with polymer chains, like chitosan and poly (vinyl pyrrolidone). On the basis of these studies, PAS is expected to be a useful technique to study the PVA/MMT matrices and Pd supported on PVA/MMT catalytic composites. Depending on the composition, the