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Short Communication

Fine-tuning the local structure and catalytic activity of titanium-amine functionalized silica in oxidation of limonene by aqueous hydrogen peroxide

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ABSTRACT

Titanium-amine functionalized silica was successfully prepared by a so-called one-pot approach by using 3-aminopropyltrimethoxysilane (APTMS), tetraethoxysilane (TEOS) and titanium(IV) sulfate as precursors. It is demonstrated that the TEOS/APTMS molar ratio in the synthesis of titanium-amine functionalized silica affected the local coordination of titanium and its corresponding positive impact on catalytic activity in oxidation of limonene by aqueous hydrogen peroxide.

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1. Introduction

In nature, there are many minerals that contain titanium; unfortunately not all structures of them are being known [1]. From local structure point of view, titania has three types of structures: six-fold, five-fold and four-fold coordinated titanium. Six-fold coordinated titanium(IV) is the structure which is most likely to be found, as the oxygen octahedron around the titanium. It is well known that rutile, anatase and brookite phases of titanium dioxide contain six-fold coordinated structures. One of the examples of minerals that contain five-fold coordinated titanium(IV) is fresnoite [2]. Four-fold coordinated titanium(IV) is present in the framework position in TS-1 zeolite [3].

The coordination of titanium(IV) is intensively studied because the tetrahedral (four-fold coordination) and octahedral (six-fold coordination) titanium(IV) gives distinguishable effect to the reactivity in heterogeneous catalysis. From the previous works, it showed that the isolated tetrahedral Ti plays a significant role in the catalytic reactions [3–7]. In view that TS-1 zeolite is a very active catalyst in oxidation reactions by using aqueous hydrogen peroxide, the synthesis of materials with tetrahedral coordination of Ti has attracted a great deal of attention. Several methods have been reported to prepare materials containing Ti with tetrahedral coordination, such as incorporation of titanium within zeolites cavity and framework [3], loading NaY zeolite particles with TiO₂ [6] and impregnation of TiO₂ on ZrO₂ [5]. However, our strategy is different from those previously reported because the aim of this communication is to demonstrate fine-tuning of the local structure of Ti in titanium-amine functionalized silica. To examine this catalytic system, the oxidation of limonene by using aqueous H_2O_2 was chosen as a model reaction.

2. Experiment

2.1. Synthesis of titanium-amine functionalized silica

Titanium-amine functionalized silica with the TEOS/APTMS molar ratio of 1:1 was synthesized as follows. TEOS (5 mmol, 1.12 ml) was added into the mixture containing HCl (0.01 M, 0.156 ml), H₂O (0.75 ml), ethanol (4.98 ml) and hexane (30 ml). The mixture was then stirred for 1 hour to produce silica sols. APTMS (5 mmol, 0.93 ml) in ethanol (25 ml) and hexane (25 ml) was reacted with silica sols under reflux at 80 °C for 2 h and followed by stirring overnight to produce amine functionalized silica particles. Titanium(IV) sulfate (2.5 mmol, 0.54 ml) was added into the amine functionalized silica particles, and the mixture was stirred overnight at room temperature. Then the resulting powder was washed with water, hexane and ethanol, respectively. The solid particles were dried at 100 °C overnight. A similar procedure was also carried out to prepare titanium-amine functionalized silica with different composition of TEOS/APTMS for the molar ratio 1:2, 1:3, and 1:4, respectively.

Hydrolyzed TEOS and APTMS were also prepared for comparison. TEOS and APTMS were hydrolyzed under stirring with water. After washing with ethanol, the solid particles were then dried at 100 °C overnight.



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2.2. Characterizations

The solid catalysts obtained were characterized by Fourier transform infrared spectrometer (FTIR), diffuse reflectance ultraviolet–visible spectrometer (DR UV–vis), and ²⁹Si solid-state magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR) spectrometer.

The FTIR spectra of all samples were collected on a Perkin Elmer Spectrum One spectrometer with 10 scans and resolution of 4 cm^{-1} , in the range of $4000-400 \text{ cm}^{-1}$. By using these parameters, a very clear spectrum and low noise absorption bands were obtained. Potassium bromide (KBr) pellet technique was used to examine the functional groups of titanium-amine functionalized silica particles, where the samples were mixed with KBr in the weight ratio of 1:100. The samples were also recorded by Perkin Elmer Ultravioletvisible Spectrometer Lambda 900 and plotted using Kubelka–Munk function, in the range of 200–800 nm. The ²⁹Si MAS NMR experiments were performed using Bruker Avance 400 MHz 9.4 T spectrometer. The spectra were recorded at 79.44 MHz using 4 µs radio frequency pulses, a recycle delay of 60 s and spinning rate of 7.0 kHz using a 4 mm zirconia sample rotor. ²⁹Si MAS NMR chemical shifts were referred to external TMS at 0 ppm.

2.3. Catalytic activity of titanium-amine functionalized silica

All reactions were carried at 70 °C with limonene (0.83 ml), 30% H_2O_2 (0.38 ml), and acetonitrile (2 ml) as solvent and catalyst (50 mg) with stirring for 22 h. The products of reaction were analyzed by Agilent Gas Chromatography model 68900N equipped with Ultra-1 column and a Flame Ionization Detector (FID).

3. Results and discussion

Fig. 1 shows the infrared spectra of silica, 3-aminopropyltrimethoxysilane (APTMS), amine functionalized silica, and titaniumamine functionalized silica with various molar ratios of TEOS/APTMS. From all of the spectra, it is clear that the vibration bands of Si–O–Si appear at *ca.* 1030 cm⁻¹ in all samples which is in agreement with the previous reports [4–8]. The broad feature at 3445 cm⁻¹ of hydrolyzed TEOS was undoubtedly due to the Si–OH, while the two bands at 3435 and 3105 cm⁻¹ in titanium-amine functionalized silica are assigned to primary N–H vibration stretch. It has been generally accepted that the two bands represent asymmetrical and symmetrical N–H stretching vibrations [9]. This evidence reinforces our argument that the primary amines are present in titanium-amine functionalized silica. There is a peak absorption appearing at 2873 cm⁻¹ in hydrolyzed APTMS and titanium-amine functionalized silica samples which is the assignment of sp³ C–H stretch.

As shown in Fig. 1, a new band at 618 cm^{-1} has appeared in all titanium-amine functionalized silica samples suggesting the formation of Ti—N bonding [10]. Since the amount of Ti(IV) in the entire variation in experiment is the same, the intensity of the Ti–N (bending mode) should also be similar. It is worth noting that the N–H bending bands of the primary amine of titanium-amine functionalized silica, which are presented at absorption bands at 1624 and 1508 cm⁻¹, are shifting to lower frequencies compared to APTMS at absorption bands at 1644 and 1599 cm⁻¹. This shifting is due to the weakening of the N—H bond by the formation of Ti—N bond. The comparison between the FTIR spectra of pure TiO₂ (Fig. 1a) and titanium-amine functionalized silica, This evidence reinforced our argument that the Ti—N bond existed in titanium-amine functionalized silica.

Fig. 2 showed DR UV-vis spectra of titanium-amine functionalized silica in different molar ratio of TEOS/APTMS. Deconvolution of the broad peak at around 260–330 nm of the spectra showed the existence of titanium with tetrahedral and octahedral coordinations,



Fig. 1. The FTIR spectra of (a) titanium dioxide, (b) hydrolyzed TEOS, (c) hydrolyzed APTMS, (d) amine functionalized silica, and titanium-amine functionalized silica with the following molar ratios of TEOS/APTMS: (e) 1:1, (f) 1:2, (g) 1:3, and (h) 1:4.

which are centered at *ca.* 250 and 300 nm, respectively [11]. The decrease in peak area of deconvoluted tetrahedral to octahedral coordination of titanium with a decrease in the TEOS/APTMS molar ratio is clearly observed in titanium-amine functionalized silica. This suggests that the amount of tetrahedral titanium in titanium-amine functionalized silica from the molar ratio of TEOS/APTMS 1:1 to 1:4 has decreased by an increase the amount of the amine groups.

We have applied ²⁹Si MAS NMR to obtain independent information about the local structure of silicon in titanium-amine functionalized silica. As shown in Fig. 3, each of ²⁹Si spectrum of titanium-amine functionalized silica consists of four peaks, which are denoted as $T^2 = RSi(OH)(OSi)_2$ (-57 ppm), $T^3 = RSi(OSi)_3$ (-66 ppm), $Q^2 = (HO)_2 Si(OSi)_2$ (-90 ppm), $Q^3 = HOSi(OSi)_3$ (-110 ppm), and $Q^4 = Si(OSi)_4$ (-110 ppm) silicon species [12]. There are no peaks of T^2 and T^3 ; the characteristic peaks of the silane coupling agent are observed in the NMR spectrum of hydrolyzed TEOS (Fig. 3a), since TEOS is completely hydrolyzed into silica. It is also clearly observed that intensity of the Q³ and Q⁴ peaks decreased, while that of the T³ and T² peaks increased when the molar ratio of TEOS/APTMS in the synthesis of titanium-amine functionalized silica is decreased (Fig. 1b, c and d). Thus, it has proven that the numbers of Si-O-Si linkages are reduced with the increasing amount of APTMS. It is suggested that the amine group induced the changing of the titanium chemical environment from tetrahedral to octahedral with the increase in the amount of amine groups. Based on the above results, one expects that the change of titanium coordination in titaniumamine functionalized silica affects its catalytic activity in oxidation of limonene by using aqueous hydrogen peroxide.

Fig. 4 showed the effect of coordination of titanium on the catalytic activity in oxidation of limonene. Gas chromatography analyses indicated



Fig. 2. The DR UV-vis spectra of titanium-amine functionalized silica with various molar ratios of TEOS/APTMS: (a) 1:1, (b) 1:2, (c) 1:3, and (d) 1:4.

that 1,2-epoxylimonene, carveol and carvone were the products. It can be observed that titanium-amine functionalized silica with the TEOS/APTMS molar ratio of 1:1 has the highest turnover number (TON). TON is the number of moles of a limonene substrate consumed to yield given products and is normalized to the number of moles of titanium. It has shown that the increasing the environment of octahedral titanium is causing the ineffectiveness in the conversion of limonene. This argument is also supported by the fact that the catalytic activity of TEOS/APTMS complex, without the titanium addition, showed only 2% of limonene conversion. This result confirmed the catalytic action of Ti active site in of titanium-amine functionalized silica.

Based on the FTIR measurements, it is confirmed the formation of Ti—N bonding in titanium-amine functionalized silica. The formation of Ti—N bonding is possible since in the first step, the silica surface



Fig. 3. The ²⁹Si solid state MAS NMR spectra of (a) hydrolyzed TEOS, and titanium-amine functionalized silica with various molar ratios of TEOS/APTMS (b) 1:1, (c) 1:2, (d) 1:3, and (e) 1:4.

was functionalized by 3-aminopropyltriethoxy silane (APTMS). It is expected that all the –OH groups reacted with APTMS. So, the addition of $Ti(SO_4)_2$ in the next step makes Ti coordinate to amine and not to – OH group.



Fig. 4. The effect of tetrahedral and octahedral coordination of Ti on turnover number (TON) in oxidation of limonene by aqueous hydrogen peroxide by using titanium-amine functionalized silica as a catalyst. TON is the number of moles of a limonene substrate consumed to yield a given product and is normalized to the number of moles of titanium.

$(-NH_2)_n + Ti(SO_4)_2 \rightarrow [Ti(-NH_2)_n]^{4+} + 2SO_4^{2+}$



Low surface coverage of Tiamine functionalized silica

High surface coverage of Tiamine functionalized silica

Fig. 5. The possible local structure of Ti in titanium-amine functionalized silica.

One suggests the formation of $[\text{Ti}(-\text{NH}_2)_n]^{4+}$ complex in titanium-amine functionalized silica. Because the amine group (NH₂) has an electron pair, this group can act as a ligand, and Ti(IV) can be coordinated to NH₂. As a result, a cation complex is formed and neutralized by SO₄²⁻ in order to maintain electrical neutrality. This reaction is written as follows:

$$(-\mathrm{NH}_2)_n + \mathrm{Ti}(\mathrm{SO}_4)_2 \rightarrow [\mathrm{Ti}(-\mathrm{NH}_2)_n]^{4+} + 2\mathrm{SO}_4^{2-}$$

On the basis of these results, a model of the possible local structure of Ti in titanium-amine functionalized silica is proposed (see Fig. 5).

In summary, the Ti coordination could be fine-tuned by varying the molar ratio of tetraethoxysilane (TEOS), 3-aminopropyltrimethoxysilane (APTMS) and titanium(IV) sulfate as precursors in the synthesis of titanium-amine functionalized silica by a so-called one-pot approach. The spectroscopic analysis by using DR UV-vis, FTIR, and ²⁹Si MAS NMR, and catalytic activity results indicated strongly that Ti is in tetrahedral and octahedral environments of nitrogen. The results of limonene oxidation by using aqueous hydrogen peroxide showed that titanium-amine functionalized silica with the highest amount of tetrahedral Ti has the highest TON in oxidation of limonene by using aqueous hydrogen peroxide as an oxidant. Thus, local structure of tetrahedral Ti as the nitrogen tetrahedron around the titanium in titanium-amine functionalized silica is a potential active site that can be further explored in the future.

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