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Development of an Analytical Method for Evaluating the Catalytic Active Sites of Titanium Silicalite Zeolite

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Abstract

A simple, quick, sensitive, accurate and precise method has been developed for evaluating the catalytic active sites of titanium silicalite-1 (TS-1). The catalytic active sites of titanium silicalite zeolite depend on the effectively active species (EAS) in TS-1 which react with specific substrates quickly. However, the EAS was hard to be evaluated with conventional instruments and techniques in the past. In this paper, the EAS was formed in TS-1 upon interaction with H_2O_2, and its presence could be confirmed by UV-vis spectroscopy which has an absorption peak at 385 nm. The absorbance at 385 nm was found to be linearly related to time, and when the absorbance and the increasing rate of absorbance (k) increased, the catalytic performance of TS-1 enhanced.

Keywords

1. Introduction

Titanium silicalite-1 (TS-1) was first reported by Taramasso in 1983 [1], which belonged to the MFI structure group. TS-1 possesses interesting catalytic properties, especially in reaction involving the use of H_2O_2 as the oxidant, such as the hydroxylation of phenol [2]-[5], thiophene oxidation [6], epoxidation of cyclohexene [7], epoxidation of styrene [8], cyclohexane oxidation [9], epoxidation of propene [10] [11], ammoximation of cyclohexanone [12] [13]. Many studies have focused on the catalytic performance of TS-1, however, only a few works have tried to investigate the nature and the properties of the active species formed in TS-1 upon interaction with H_2O_2 [14]-[16], and not all the framework titanium can contact with substrates quickly, due to the diffusion limitation by the size of the channels (0.56 nm × 0.53 nm). This lack can be ascribed to severe experimental problems, mainly due to the presence of H_2O and the lability of complexes formed by H_2O_2 on framework titanium in TS-1. Therefore, the effectively active species (EAS) in TS-1 is hard to be evaluated with IR

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and NMR. The most probable technique to evaluate EAS in TS-1 is UV-vis spectroscopy because it is not affected by the presence of H_2O. According to the literature, TS-1 contact with H_2O_2 water solution, a new band appears around 385 nm in the UV-vis spectrum. This band has already been assigned to the TiOOH on TS-1 [15] [16].

Herein we have dealt TS-1 with the mixed solution of H_2O_2 and methanol, the presence of the EAS has been confirmed by UV-vis spectroscopy. Epoxidation of propylene was used to assess the catalytic performance directly. The relationship between EAS in TS-1 and the catalytic performance has been systematically investigated to develop a quick analytical method for evaluating the catalytic active sites of titanium silicalite zeolite

2. Experimental

2.1. Chemicals and Reagents

Hydrogen peroxide AR grade (H_2O_2), methanol AR grade (CH_3OH), propene (C_3H_6), ammonia AR grade (NH_3) were purchased from Tianjin chemical reagent factory. TS-1 was prepared following the procedure reported by Thangaraj [17].

2.2. Instrumentation

UV-vis spectra of the samples were obtained on Agilent Cary 5000 Spectrometer.

2.3. Preparation of Samples

2.3.1. Preparation of Standard Samples

A 0.5 g of sample was weighed and transferred into the sample cell. 0.6 g H_2O and 0.3 g methanol were added to the sample at 298 K, and the mixture was confirmed by UV-vis spectroscopy. The propylene epoxidation was carried out in a stainless steel autoclave. In a typical run, 0.1 g of catalyst, 3.0 ml 27.5wt % H_2O_2 and 24 ml of methanol were fed into the reactor. The propylene was charged at constant pressure (0.6 MPa). The reaction was performed at 318 K under magnetic agitation for 60 min. The residual H_2O_2 was checked by iodometric titrating and the product of epoxidation of propylene was analyzed on a GC 7890II gas chromatograph, using a flame ionization detector and a capillary column (50 m × 0.25 mm × 0.25 μm, HT-superwax).

2.3.2. Preparation of Samples

At 298 K, 0.5 g of TS-1 powder was mixed with solution of 0.6 g (43.8 wt%) H_2O_2 and 0.3 g methanol, the paste fomed is placed in the sample holder. Then the UV-vis spcctrum of the paste mixture was quickly recorded on Agilent Cary 5000 Spectrometer and taken the change of the UV-vis spectrum every 2 minutes in the first 10 minutes.

2.4. Analytical Method Validation

The developed method was validated with respect to specificity, linearity, accuracy and reproducibility.

2.4.1. Specificity

Specificity is the degree to which the procedure applies to a single analyte and is checked in each analysis by comparing the blank UV-vis spectrum with the UV-vis spectrum obtained for the sample spiked with internal standard to trace out the interfering peaks. The specificity of the method was investigated by the analysis of the blank preparation spiked with sample, H_2O and methanol were added.

2.4.2. Linearity

The linearity of the peak height response was determined by taking the change of the UV-vis spectrum at 385 nm every 2 minutes in the first 10 minutes. The linear regression coefficient and correlation coefficient were calculated.

2.4.3. Accuracy

The accuracy was assessed by studying the proportional relations between the absorbance at 385 nm and the

catalytic performance of TS-1 by using two different catalytic performance of TS-1 in the range of 80% to 100%, and recovery study by standard addition method.

2.4.4. Reproducibility

Reproducibility of the method was determined by analyzing two times of TS-1 samples. The mean, relative standard deviation (RSD) and sample of reproducibility were calculated.

3. Results and Discussion

3.1. Specificity

Finally, the specificity was established by comparing the blank UV-vis spectrum with the UV-vis spectrum obtained for the sample spiked with internal standard to trace out the interfering peaks. The specificity of the analytical procedure was achieved since no interference peak was observed (**Figure 1**, UV-vis spectrum 1). This band at 385 nm has already been assigned to the TiOOH on TS-1 [15] [16].

3.2. Linearity

The linearity of this method was determined by taking the change of the UV-vis spectrum at 385 nm every 2 minutes in the first 10 minutes. The plot of peak height against respective time of sample was found to be linear (**Figure 2**). The linearity was evaluated by linear regression analysis using least square method. The regression equations were found to be $Y = aX + b$ for samples and correlation coefficient of the standard curves were found to be more than 0.99.

3.3. Accuracy

Accuracy of the method was found out by studying the proportional relations between the absorbance at 385 nm and the catalytic performance of TS-1 by using two different catalytic performance of TS-1 in the range of 80% to 100%, and recovery study by standard addition method. It was observed (**Table 1**) that when the increasing rate k of absorbance at 385 nm increased, which means the forming rate of active species TiOOH, the yield of propylene oxide improved and the absorbance increased, the conversion of H_2O_2 enhanced. And the conversion of H_2O_2 to the increasing rate of absorbance ratio was around 2.18, the yield of propylene oxide to the absorbance at 385 nm ration was around 152, the relative standard deviation (RSD) of ratio was 9.9% and 5.1%, respectively. The known standard was added to sample-3 and the results of recovery studies were shown in **Table 2**, the percentage recovery of the absorbance at 385 nm was 98.1% and the percentage recovery of the increasing rate k of absorbance was 99.5% which demonstrated that the method was highly accurate.
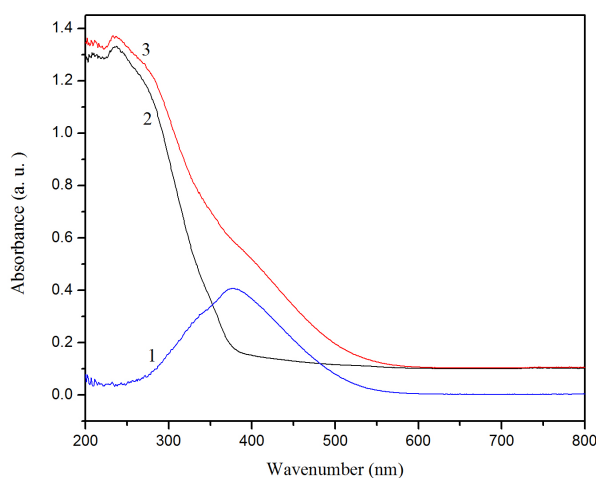

Figure 1. UV-vis spectra of the TS-1 samples. 1: the effectively active species; 2: H_2O, methanol and TS-1; 3: H_2O_2, methanol and TS-1.

3.4. Reproducibility

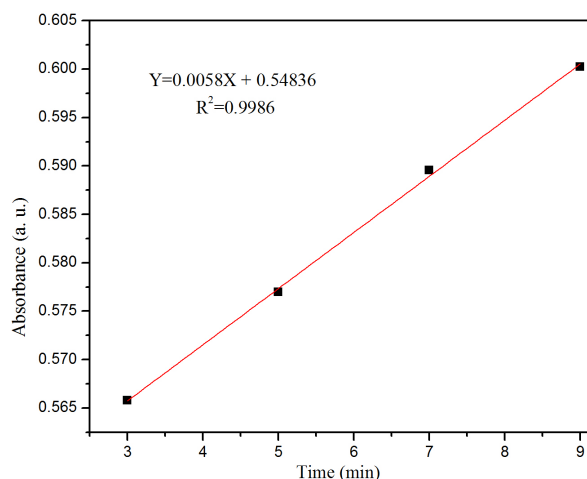Reproducibility data of sample is shown in **Table 3**. The relative standard deviation (RSD) of k was 1.02% and

Figure 2. Linearity of the increasing rate of absorbance.

Table 1. Accuracy for evaluating the catalytic performance of TS-1.

TS-1	A	k (min^{-1})	C (%)	Y (%)	C/A	Y/k
1	0.495	0.00559	99.7	87.8	2.01	157
2	0.423	0.00620	99.1	90.3	2.34	146
		Mean			2.18	152
		RSD (%)			9.9	5.1

A stand for the absorbance at 385 nm; k stand for the increasing rate of absorbance; C stand for the conversion of H_2O_2; Y stand for the yield of propylene oxide; RSD stand for relative standard deviation.

Table 2. Accuracy for the absorbance at 385 nm.

TS-1	3	4	5	Recovery (%)
A	0.437	0.189	0.307	98.1
k	0.00360	0.00170	0.00264	99.5

A stand for the absorbance at 385 nm; k stand for the increasing rate of absorbance; 3: sample-3; 4: standard sample; 5: 50 wt.% sample-3 and 50 wt.% standard sample.

Table 3. Reproducibility for the increasing rate of absorbance and absorbance.

TS-1	6	7
k^a (min^{-1})	0.004900	0.00640
k^b (min^{-1})	0.004830	0.00650
Mean of k (min^{-1})	0.004865	0.00645
RSD of k (%)	1.02	1.10
Absorbance^a	0.45304	0.41476
Absorbance^b	0.45780	0.41232
Mean of absorbance	0.45542	0.41354
RSD of absorbance (%)	0.739	0.417

k^a and k^b stand for the increasing rate of absorbance that the first and second measured, respectively; Absorbance^a and Absorbance^b stand for the absorbance at 385 nm that the first and second measured, respectively. RSD stand for relative standard deviation.

1.10%, respectively. The relative standard deviation (RSD) of absorbance was 0.739% and 0.417%, respectively. The results indicated that this method was highly precise.

4. Conclusion

A rapid analytical method for evaluating the catalytic active sites of titanium silicalite zeolite has been developed. The method was found to be simple, quick, sensitive, accurate and precise. The catalytic performance of TS-1 showed a good relationship with the effectively active species in TS-1 which helped to appraise the catalytic performance of TS-1 quickly.

Acknowledgements

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