Titanium Species and Structure-performance Relationship in Boron-free Ti-MWW Zeolite Studied by UV Resonance Raman Spectroscopy

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Abstract: The titanium species and structure-performance relationship in boron-free Ti-MWW zeolite were thoroughly studied by 244 nm excited UV resonance Raman spectroscopy. It was surprisingly found out that acid treatment not only removed a part of the dominant non-framework TiO_m (m = 5, 6) species but also made most of them transformed into TiO_4 species. Only acid-treated and subsequently calcined Ti-MWW showed catalytic activity in 1-hexene epoxidation. The order of catalytic performance of TiO_4 species is: framework $Ti(OSi)_4$ species > framework $Ti(OSi)_3OH$ species >> TiO_4 species in amorphous SiO_2 matrix, which would be beneficial for development of highly efficient titanosilicate zeolites.
Keywords: Boron-free Ti-MWW zeolite, UV resonance Raman, Structure-performance relationship.

1. Introduction

Because of excellent catalytic performance in selective oxidation, Ti-MWW zeolite has attracted considerable attention in both academia and industry.[1,2] However, there are still many issues unclear due to the lack of powerful technique to characterize titanium species in depth. Such as why the catalytic performance of Ti-MWW zeolite is remarkably improved by acid treatment,[2,3] what kind of TiO_4 species is most effective. For the further study of Ti-MWW zeolite and development of highly efficient titanosilicate zeolite, it is of great significance to clarify these issues. UV resonance Raman spectroscopy (UVRRS) has proven to be efficient in studying low-content transition metal species in transition metal-containing (such as titanium, iron, vanadium) molecular sieves since the charge transfer transitions between oxygen ion and transition metal ion can be resonantly excited by UV lasers.[4,5] In this study, we have clearly elucidated the exact role of acid treatment and the underlying structure-performance relationship in boron-free Ti-MWW zeolite by powerful UVRRS with the excitation line at 244 nm.[6]

2. Experimental

Boron-free Ti-MWW precursors were hydrothermally synthesized and treated according to the references.[3] Besides routine characterizations, UV resonance Raman characterization excited at 244 nm was carried out on a triple spectrograph Raman system UV-Raman-100 with spectral resolution of 3 cm^{-1}. The liquid-phase oxidation reaction of 1-hexene with H_2O_2 was used as the model to investigate the relationship between the specific structure of titanium species and catalytic performance.

3. Results and discussion

As shown in Figure 1, UV resonance Raman spectroscopic characterization indicated that non-framework TiO_m (m = 5, 6) species were the dominant titanium species in as-made Ti-MWW materials synthesized by the boron-free dual SDAs strategy. Post-treatment, especially acid treatment, showed significant influence on the state of titanium species in final sample. Acid treatment not only removed a part of the non-framework titanium species but also made most of them transformed into TiO_4 species, which has never been pointed out in previous studies. Moreover, acid treatment of as-synthesized Ti-MWW samples resulted in the formation of framework TiO_4 species, while only TiO_4 species in amorphous SiO_2 matrix was formed when directly calcined Ti-MWW samples were treated with acid.

The samples with non-framework TiO_m (m = 5, 6) species and TiO_4 species in amorphous SiO_2 structure showed no catalytic activity in 1-hexene epoxidation. Only those with framework TiO_4 species showed excellent catalytic activity. Ti-MWW(50)-AT-C with much higher Si/Ti ratio unexpectedly showed better catalytic performance than Ti-MWW(30)-AT-C. Spectroscopic characterizations indicated that the main titanium species in Ti-MWW(50)-AT-C and Ti-MWW(30)-AT-C were framework $Ti(OSi)_4$ and $Ti(OSi)_3OH$ species, respectively. Due to the presence of hydrophilic hydroxyl, it would be more difficult for hydrophobic 1-hexene to access the corresponding active intermediate of framework $Ti(OSi)_3OH$ species in comparison with that of framework $Ti(OSi)_4$ species, which may be the reason for lower catalytic activity of Ti-MWW(30)-AT-C.

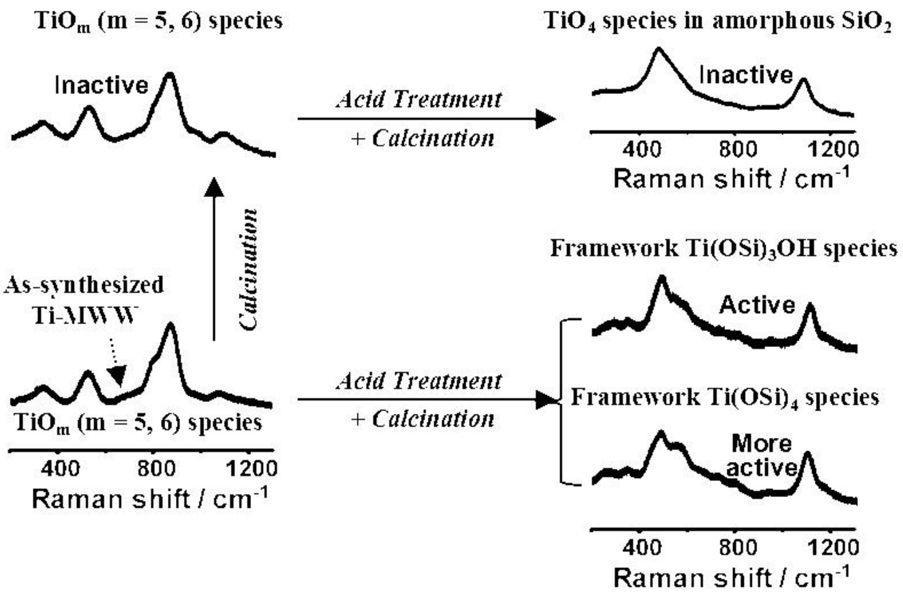

Figure 1. Titanium species and structure-performance relationship in boron-free Ti-MWW zeolite.

4. Conclusions

We have thoroughly investigated the titanium species and structure-performance relationship in boron-free Ti-MWW zeolite by 244 nm excited UVRRS for the first time. It was surprisingly found out that acid treatment not only removed a part of the dominant non-framework TiO_m (m = 5, 6) species but also made most of them transformed into TiO_4 species, which has never been reported before. Interestingly, acid treatment of as-synthesized and directly calcined Ti-MWW resulted in the formation of active framework TiO_4 species and inactive TiO_4 species in amorphous SiO_2 matrix, respectively. Only the samples obtained from acid treatment of as-synthesized Ti-MWW and subsequent calcination showed catalytic activity in 1-hexene epoxidation. Importantly, despite higher Si/Ti ratio, framework $Ti(OSi)_4$ species-dominant Ti-MWW showed better catalytic performance than the relatively hydrophilic framework $Ti(OSi)_3OH$ species-dominant one. These understandings would be beneficial for further study of Ti-MWW and development of highly efficient titanosilicate zeolites.

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