The influence of titanium content on the structure of TS-1 and the activity for the direct hydroxylation of toluene to cresols

Conglin Pang, Guiying Li*, Changwei Hu

Key Laboratory of Green Chemistry and Technology, MOE, College of Chemistry, Sichuan University, Chengdu, 610064, China

**Fax: 028-85411105, E-mail: gchem@scu.edu.cn (G. Li).*

Abstract: A series of TS-1 samples with different Ti content has been prepared and evaluated in the hydroxylation of toluene to cresols with H_2O_2 as oxidant. The activity results have been correlated with the state of Ti species. The morphology and structure of the catalysts were examined by nitrogen adsorption/desorption, UV-vis, XPS and TEM. The results showed that the framework Ti was responsible for the ring C-H bond activation, resulting in toluene hydroxylation; while the extra-framework Ti species was advantageous to the formation of side chain oxidation products.

Keywords: Titanium silicalite-1 (TS-1), Toluene hydroxylation, Titanium species.

1. Introduction

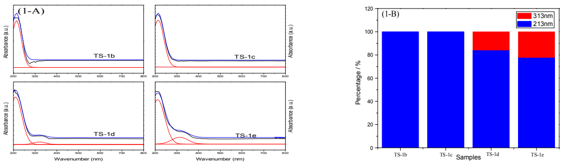
Cresols are important intermediates for fine chemicals. Generally, worldwide industrial production of cresols is carried out by multistep reaction processes using toluene as the starting material. The multistep processes have many disadvantages, for example, it is energy and time consuming, low atom efficiency, massive by-products and serious environmental pollution. The catalysts investigated in the direct oxidation of toluene are mostly porous zeolite materials, such as SBA-15, ZSM-5, MCM-41, and so on. However, as the catalyst support, because of their energy consuming and metal's leaching by conventional impregnation, they are used restrictedly. Among them, titanium-modified MCM-41 (TS-1) has inestimable advantages, for the active Ti species could be obtained by hydrothermal direct synthesis, getting rid of the impregnation of metal wastage. In addition, TS-1 shows good selective ring oxidation, and has great potential for the study of toluene hydroxylation. It is well known that titanium plays an important role for the catalytic performance in TS-1. In fact, there exist two types of Ti species in TS-1 zeolite, that is, the [TiO_4] species in the framework, and the TiO_2 species in the extra-framework. Among them, the framework Ti species is considered to be the active center for selective oxidation. However, the effective way to increase the framework Ti and reduce extra-framework Ti is still a challenge. Various TS-1 samples were synthesized with different Ti content in the present work to investigate the performance of different Ti species in toluene hydroxylation system with emphasis on the competitive reactions between ring C-H bond activation and side chain oxidation.

2. Experimental

Various TS-1 samples were synthesized following the procedures reported in the literature[1]. The Ti/Si molar ratios (%) were controlled to be 0, 0.89, 1.48, 2.96, 5.92, and the corresponding samples were named as TS-1a, TS-1b, TS-1c, TS-1d and TS-1e, respectively. All of the catalysts were characterized by BET, UV-vis, XPS and TEM.

3. Results and discussion

The DR UV-vis results were shown in Fig.1-A. The bands at 213nm and 313nm corresponded to framework Ti and extra-framework Ti, respectively. The percentages of the two peaks were calculated and shown in Fig.1-B, it is implied that the percentage of framework Ti species in TS-1b and c is higher than TS-1d and e. That is to say, the excessive Ti species have been transformed into extra-framework Ti species for TS-1d and e. Apparently, this view is well relevant to the XPS of the Ti_{2p} peak (Fig.2-A). It can be seen that two major peaks were found at 460.0 eV and 457.5 eV, which were assigned to framework Ti and extra-framework Ti, respectively. And the corresponding quantified results were illustrated in Fig.2-B. It is indicated that all of the Ti species in TS-1b and c was shown as tetrahedral framework Ti species, in other words, framework Ti is further generated from b to c. In contrast, the extra-framework Ti was observed in TS-1d and e, and increasing Ti content would lead to an increase in the percentage of the extra-framework Ti. Overall, both UV-vis and XPS results shown that with the introduction of Ti, it entered the framework firstly (a to c), when got to a critical value of 1.48%, the extra-framework Ti began to generate (d to e). The percentage of framework Ti species had the following order TS-1a< TS-1b= TS-1c> TS-1d> TS-1e. So on TS-1c the framework Ti was the highest, while no extra-framework Ti was observed.



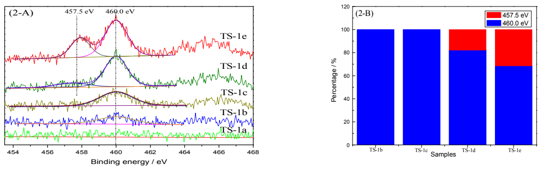


Figure 1. (A)UV-Vis spectra of TS-1 after deconvolution; (B)The corresponding quantified ratio between the two state of Ti species.

Figure 2. (A)Ti_{2p} XPS results of TS-1 samples; (B)The corresponding distributions of framework Ti and extra-framework Ti.

TEM images were shown in Fig. 3. It was shown that the TS-1a and b and c exhibit similar lumps morphology with mean dimensions approximate to 100nm. However, a petal morphology for TS-1d and e was observed, and the crystal diameter increased to about 200nm, suggesting that with the increase of Ti content, the active components might not be dispersed on the surface of TS-1 zeolite and the extra-framework Ti species was produced.

The results of physicochemical property and catalytic test were list in Table 1. Obviously, the TS-1c has the best pore structure features, owing to all of the Ti species were distributed within the framework. Because of the bigger S_{BET} was beneficial to the mass diffusion as well as the most framework-Ti, TS-1c showed best catalytic property in toluene hydroxylation. Furthermore, because the excessive Ti would form extra-framework Ti, which had negative impact on the catalytic activity, TS-1d and e shown a poor catalytic activity. Thus, the framework Ti is favorable to the formation ring C-H bond activation products, whereas extra-framework Ti is advantageous to the formation of side chain oxidation products.

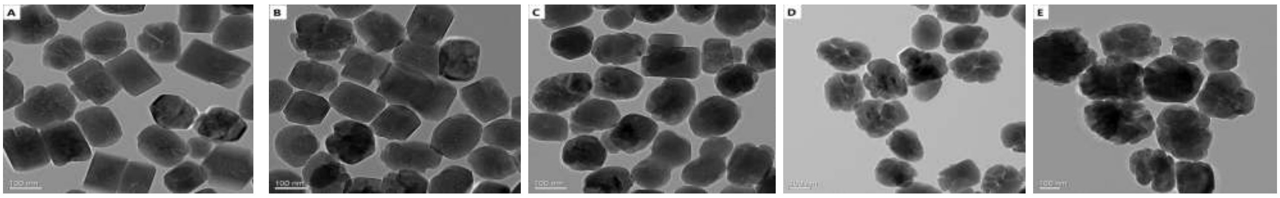


Fig.3. TEM of TS-1 samples with different Ti content: (A)TS-1a; (B)TS-1b; (C)TS-1c; (D)TS-1d; (E)TS-1e.

Table 1. The effect of Ti content on the catalytic hydroxylation of toluene

Sample	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	D_{avg} (Å)	Yield (mol %)					$C_{toulene}$	$Y_{cresols}$	$S_{cresols}$	S_{ring}
				o-Cresol	p-Cresol	BM	HA	MQ				
TS-1a	383.04	0.261	27.29	1.5	7.2	0.61	0.6	1.9	11.8	8.7	73.7	89.8
TS-1b	419.55	0.265	25.24	4.0	15.8	3.1	0.3	0.8	24.0	19.8	82.5	85.8
TS-1c	463.54	0.268	23.11	6.8	26.0	4.7	0.7	0.7	38.9	32.8	84.3	86.1
TS-1d	399.48	0.202	20.19	6.2	22.7	8.5	0.7	1.2	39.3	28.9	73.5	76.6
TS-1e	388.18	0.190	19.62	4.5	17.8	11.4	1.5	2.3	37.5	22.3	59.5	65.6

4. Conclusions

In conclusion, several TS-1 samples with different Ti content had been systematically investigated for the direct hydroxylation of toluene to cresols. For TS-1, the framework Ti is limited, the maximum ratio of Ti/Si is 1.48% (TS-1c). TS-1c contained the biggest S_{BET} and highest concentration of framework Ti, thus reaction substrates could easily diffuse and get in touch with the active [TiO_4] sites. Framework Ti and extra-framework Ti have different contributions to the reaction: the framework Ti is responsible for the ring C-H bond activation, while the extra-framework Ti is advantageous to the formation of side chain oxidation.

References

1. Yu, T., et al., *Direct amination of benzene to aniline by reactive distillation method over copper doped hierarchical TS-1 catalyst.* Catal. Sci. Technol., 2014. **4**(3): p. 639-647.