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The Effect of Al^{3+}, Na^+, NH_4^+ on Ti Content in the Preparation of Ti-ZSM-5

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Abstract: The effect of Al^{3+}, NH_4^+, Na^+ on the Ti content in the preparation of Ti-ZSM-5 by the isomorphous substitution of ZSM-5 using gaseous $TiCl_4$ as titanium resource has been investigated. It is surprisingly found that although the direct ratio exists between the Ti content and the content of the skeletal Al: $y=0.08x^2+0.57x+1.23$ (here y represents TiO_2% and x represents Al_2O_3%), but the catalytic activities of Ti-ZSM-5 for the oxidation of styrene sharply rise with the decrease of TiO_2%. The skeletal Al hinders the Ti incorporation into the framework of molecular sieves characterized by FT-IR technique. At the same time, NH_4^+ ion has no effect on the Ti incorporation, but Na^+ ion does.

Keywords: Ti-ZSM-5; Ti content; styrene; catalytic oxidation.

Titanium-Silicalite (TS), which was first synthesized by Taramasso in 1983[1], is a catalyst with quite remarkable properties in the shape-selective oxidation of organic compounds with aqueous H_2O_2. During the recent decade, more papers on the hydrothermal synthesis of TS were reported[2, 3, 4]. Most of their aims were to search cheaper templates, but there were few papers about the gas-solid isomorphous substitution, namely secondary synthesis which was a good way of obtaining cheaper TS. In this paper, we showed the effect of Al^{3+}, NH_4^+ and Na^+ on the Ti content in the preparation of Ti-ZSM-5 from the isomorphous substitution of ZSM-5 using gaseous $TiCl_4$ as titanium source, characterization of skeletal titanium by FT-IR and the catalytic activity of Ti-ZSM-5 in the oxidation of styrene.

Experimental

Ti-ZSM-5 was synthesized by the reaction of ZSM-5 with gaseous $TiCl_4$ carried by the dried N_2 flow. This process was carried out in a quartz reactor for 12 h at 973K after being dried for 3 h at 773K. The Al_2O_3% and TiO_2% were analyzed by chemical methods. The skeletal titanium of Ti-ZSM-5 were characterized by FT-IR spectra, which were performed on a Nicolet 200SXV FT-IR (USA) spectrometer using KBr wafer technique at room temperature.

The catalyst (0.35g), acetone (12.00ml, as solvent), styrene (4.00ml) and aqueous H_2O_2 (31.26wt%) solutions (1.28ml) were added to a 50ml round-bottomed flask equipped with a condenser and a magnetic stirrer. The catalytic oxidation was

performed for 6 h at 333K under ambient atmosphere. Products were separated from catalyst and analyzed using a 102G series gas chromatograph equipped with a thermal conductivity detector and Paropak Q column (1.5m×3mm i.d.) with the column temperature at 503K and H_2 as the carrier gas.

Effect of skeletal Al on the Ti content of Ti-ZSM-5

Figure 1 The relation between Ti content and Al_2O_3% in ZSM-5.
Reaction time 12h, Reaction temperature: 973K

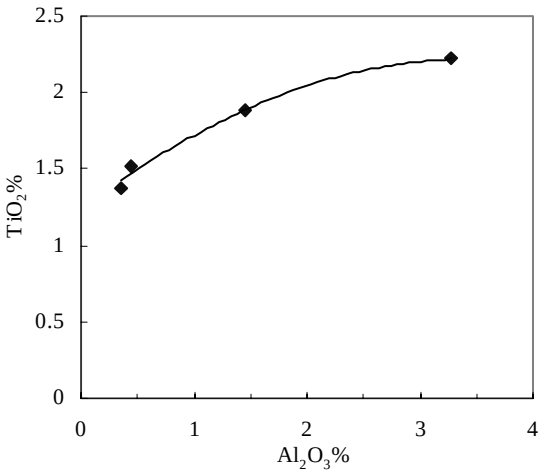
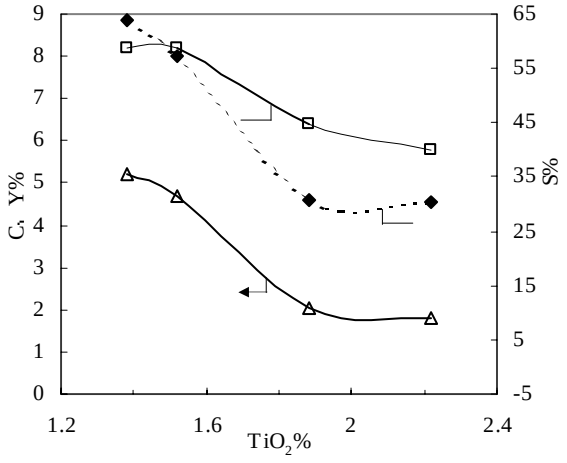


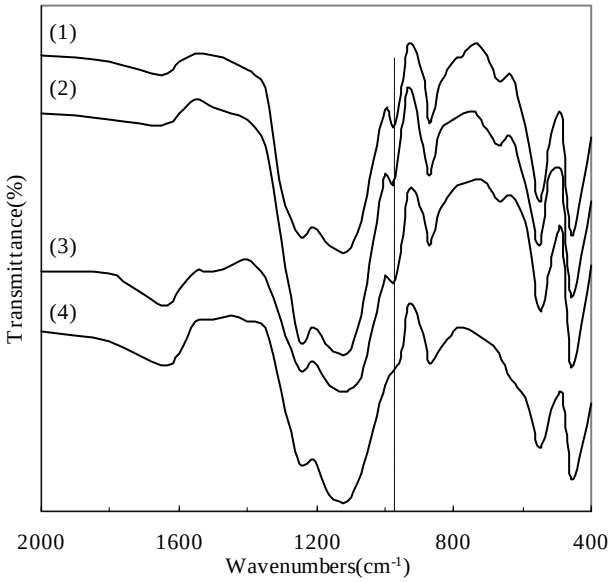
Figure 2 The oxidation results of styrene catalyzed by Ti-ZSM-5 with different Ti content.
Conversion of styrene Selectivity of $PhCH_2CHO$ Yield of $PhCH_2CHO$



From **Figure 1** and **2** it is surprisingly found that although the titanium content of Ti-ZSM-5 rises with the increase of skeletal Al in the isomorphous substitution of ZSM-5 by $TiCl_4$ with the formula: $y=0.08x^2+0.57x+1.23$ (here y represents TiO_2% and x

represents Al_2O_3%, R^2=0.9905), the catalytic activities of Ti-ZSM-5 for the oxidation of styrene sharply rise with the decrease of TiO_2%. It may imply skeletal Al, which provides Bronsted acid sites on the surface of molecular sieves, can adsorb Ti^{4+} ions *i.e.*, not all of Ti^{4+} ions are incorporated into the framework of molecular sieves. Using FT-IR technique to characterize the skeletal titanium, the results of FT-IR (**Figure 3)** show that the intensity of the adsorption band at 975cm^{-1} (a specific peak of the skeletal titanium) decreases with the increasing content of skeletal Al, which indicates that the content of skeletal Ti in the Ti-ZSM-5 decreases with the increasing Al content. From above results, we draw a conclusion that not all Ti incorporated into molecular sieves is used to substitute the skeletal Al, and the skeletal Al can hinder the Ti incorporation into the framework of ZSM-5.

Figure 3 The FT-IR spectra of Ti-ZSM-5 with Al_2O_3% being (1) 1.81%, (2) 2.06%, (3) 4.71%, (4) 5.2% and TiO_2% being (1) 1.38%, (2) 1.52%, (3) 1.88%, (4) 2.22%.



Effect of NH_4^{+} ions on Ti content

Table 1. The effect of NH_4^{+} ions on Ti content

Raw materials	Composition of Ti-ZSM-5		Catalytic activity of Ti-ZSM-5	
	Al_2O_3%	TiO_2%	C%*	S%**
HZSM-5	0.34	1.53	7.84	58.72
NH_4ZSM-5	0.34	1.52	7.65	58.13

* Conversion of styrene ** Selectivity of $PhCH_2CHO$

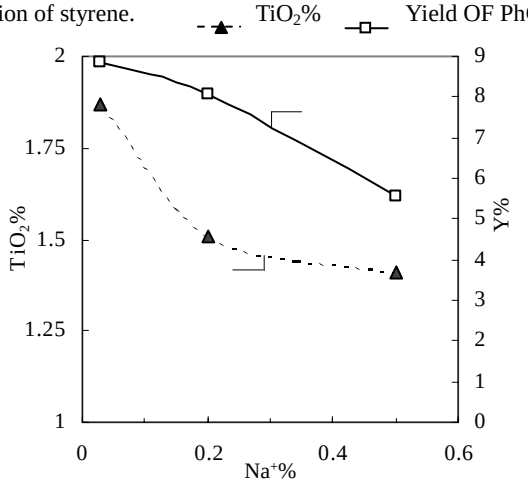
Table 1 shows there are no differences about the Ti content using HZSM-5 and NH_4ZSM-5 to react with $TiCl_4$, and their catalytic activities are also identical. The

reason is that NH_4ZSM-5 can change into HZSM-5 at above 811K, so NH_4^+ ions do not affect Ti content of Ti-ZSM-5

Effect of Na^+ ions on the Ti content

The Ti content decreases with the increasing Na^+% in the ZSM-5 (**Figure 4)**, Na^+ ions can impede the Ti incorporation into the framework. Their catalytic activities in the oxidation of styrene also prove the above results.

Figure 4. The effect of Na^+ on the Ti content by ZSM-5 and the catalytic activity of Ti-ZSM-5 in the oxidation of styrene.



Conclusion

In the isomorphous substitution of ZSM-5 by $TiCl_4$, both the skeletal Al and Na^+ ions can impede the Ti incorporation into the framework of the molecular sieves. NH_4^+ does not affect the formation of skeletal titanium at the isomorphous substitution temperature of 973K.

References

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