Tuning the acidity and dehydration activity of Si-Zr mixed oxides

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In a number of catalytic reactions, mixed oxides show better performance than the single oxide [1]. Another benefit of mixed oxides is enhanced thermal stability by intermixing of a major component with a minor counterpart [2]. The typical example is ZrO_2-based mixed oxides because amphiphilic (both acidic and basic) character of ZrO_2 can be tuned by addition of another metal oxide. It was reported that the introduction of SiO_2 leads to stabilization of ZrO_2 structure and precise control of Brönsted and Lewis acid concentrations [3].

Herein the Si-Zr mixed oxides with different Si/(Si+Zr) molar ratios were prepared and tested in the dehydration of *iso*-propanol. The catalyst preparation starts from ageing an aqueous solution of tetraethyl-orthosilicate and zirconium oxynitrate hydrate with a desired molar ratio at 75 ℃ for 48 h, followed by calcination at 500 ℃ for 6 h. The final Si-Zr oxide samples are characterized by XRD, N_2 physisorption, SEM, *iso*-propanol TPD (IPA-TPD), pyridine-chemisorbed IR and XPS.

XRD results showed that except pure ZrO_2 (tetragonal phase), the other samples are amorphous. The specific surface area and total pore volume gradually increased with the SiO_2 content increasing. In IPA-TPD experiments, the main desorption peak of IPA fragment was observed at the lowest temperature for Si-Zr oxide with the Si/(Si+Zr) of 0.7 (Table 1). The trend of IPA desorption temperature was well correlated with the per-gram quantity of Brönsted acid sites.

In the activity test of IPA dehydration at 180 ℃, the IPA conversion increased from zero for pure ZrO_2 to 95% for Si-Zr oxide with a Si/(Si+Zr) of 0.7 and then declined to 5% for a Si/(Si+Zr) of 0.9 (Fig. 1). The activity trend was in good agreement with the IPA-TPD result. Also, XPS results revealed that the core levels of Si 2p, Zr 3d and O 1s were shifted to higher binding energies with increasing the Si/(Si+Zr) ratio due to an increase of positive charge [4].

In conclusion, the catalytic activity of Si-Zr mixed oxides was maximized at Si/(Si+Zr) = 0.7 and well correlated with the results of IPA-TPD and Py-IR.

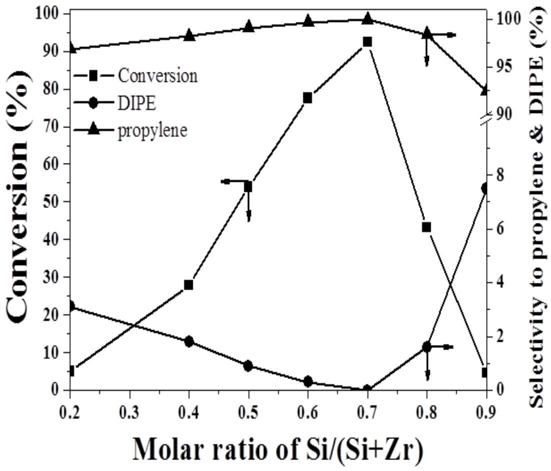

Fig. 1. IPA conversion and selectivity to propylene and DIPE over SiO_2-ZrO_2 with different Si/(Si+Zr) ratios in IPA dehydration.

Table 1. Physico-chemical properties of Si-Zr oxide catalysts prepared with various molar ratios of Si/(Si + Zr).

Si/(Si+Zr)		S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)	D_p (nm)	IPA-TPD Temp. (°C)	Quantity of acid (μmol g^{-1})	
Solution	EDX					B acid	L acid
ZrO_2	-	109	0.211	7.9	334	0	86.4
0.2	0.19	184	0.094	2.5	219	-	-
0.4	0.37	191	0.120	2.5	170	75.1	17.8
0.5	0.49	202	0.147	2.9	165	-	-
0.6	0.56	231	0.178	3.1	158	-	-
0.7	0.69	255	0.226	3.3	149	83.4	74.9
0.8	0.85	285	0.305	3.4	158	-	-
0.9	0.90	315	0.390	3.6	171	3.3	4.7

REFERENCES

[1] J.R. Sohn, H. J. Jang, J. Mol. Catal., 64 (1991) 349.
[2] J.B. Miller, S.E. Rankin, E.I. Ko, J. Catal., 148 (1994) 673.
[3] Y.N. Kochkin, N.V. Vlasenko, V.L. Struzhko, Theo. Exper. Chem., 50 (2014)318.
[4] H.J.M. Bosman, A.P. Pijpers, A.W.M.A. Jaspers, J. Catal., 161 (1996) 551.