Hydrophilic solid acid Sn-Nb_2O_5/α-Al_2O_3 for Epoxides Hydration

Yingcheng Li*, Weimin Yang, Zaiku Xie, Qingling Chen

Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, China
* lyc@sript.com.cn

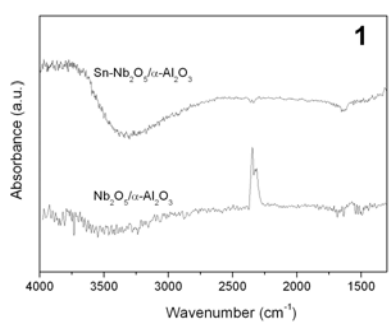
Introduction

Hydration of epoxides is important industrial processes to produce corresponding glycols. However, the low product selectivity and use of large excess amount of water are economically unattractive [1]. Therefore, development of alternative effective solid acids to solve the problems, is desirable in the chemical industry. However, for reactions in which water participates, only a few solid acids are acceptable in terms of their activity and stability, among those niobic acid ($Nb_2O_5 \cdot nH_2O$) has been paid much attention for years for its affinity for both water and organic substrate [2, 3]. As SnO_2 also showed excellent hydrophilic properties [4], we therefore prepare Sn-promoted Nb_2O_5/α-Al_2O_3 for epoxides hydration to produce glycols. High epoxide conversion and glycol selectivity, good stability, as well as lower water-to-epoxide mole ratios were obtained.

Experimental

The α-Al_2O_3 was impregnated with niobic acid and $SnCl_4$ in sequence, dried at 150 °C for 2 h, calcined at 400 °C under a flow of N_2/H_2 (5 v/v% of H_2) for 2 h, then under N_2 for another 2 h to obtain Sn-10wt%Nb_2O_5/α-Al_2O_3（Sn/Nb=0.8）catalyst. The catalyst was examined for reactivity in ethylene oxide (EO), propylene oxide (PO) and styrene oxide (SO) hydration reactions. For the water adsorption experiment, the catalyst was immersed in water for 24 h, then centrifuged and pressed into a disc. The sample disc was evacuated under 3 Pa for 4 h, then raised to 250 °C, and the spectra were recorded after 15 minutes equilibration.

Results and Discussion



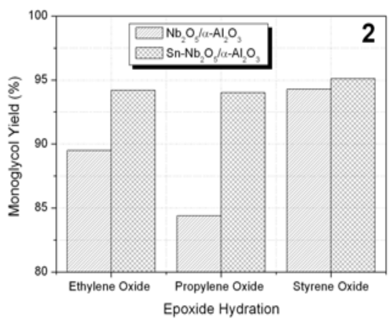


Figure 1. IR spectra recorded at 250°C, 3 Pa for catalyst after immersion in water.
Figure 2. Catalytic performances of epoxides hydration.

Adsorption behavior of water on the surface of the catalyst. The broad band around 3400 cm^{-1} in IR spectra (Fig. 1), was assigned to H-bonded surface OH stretching modes (or strongly held water-related species) [5]. For Nb_2O_5/α-Al_2O_3 catalyst, it was hardly observed, indicating that the adsorbed H_2O species were removed from surface after evacuation. For Sn-promoted catalyst, the absorption band was much stronger than that of non-promoted one. The amount of chemsisorbed water on the surface of catalyst was measured by TGA [5]，and was 0.76 wt% and 0.44wt% based on the weight of the catalyst with or without Sn promoter respectively, indicating that addition of tin enhanced the water adsorption capacity.

Catalytic performances. The reaction test in Fig.2 showed that monoglycol selectivity was significantly improved in epoxides hydration by introduction of hydrophilic promoter tin compared with that of the unpromoted Nb_2O_5/α-Al_2O_3 catalyst. By comparing with the results of other catalysts reported in the literature in Table 1 [1], The Sn-Nb_2O_5/α-Al_2O_3 catalyst exhibited much better selectivity and lower water-to-epoxide mole ratios among solid acids listed.

Stability test. It was found that the catalyst demonstrated excellent stability in 1000 h durability test, no obvious decline in epoxides conversion and monoglycol selectivity was observed. The XRD patterns showed that the fresh catalyst and the used one gave similar XRD patterns, indicated that no structural change occurred during epoxides hydration reactions.

Table1 Catalytic performances for epoxide hydration over solid acid catalyst

Reactions	Catalyst	temp. (°C)	H_2O/epoxide ratio (mol.)	Conv. (%)	Sel. (%)
EO hydration to ethylene glycol	—	140-230	22	100	88
	Nafion XR (6%)/SiO_2	50-110	10	94	94
	HZSM-5 (Si/Al=612)	150	22	98	76
	$AlPO_4$-$Cu(NO_3)_2$	266	—	90.4	57.4
	Sn-Nb_2O_5/α-Al_2O_3	150	22	99.7	94.0
		150	10	99.7	88.0
PO hydration to propylene glycol	Nafion-H	r.t.	2.8	Yield=73	
	Sn-Nb_2O_5/α-Al_2O_3	180	2.8	99.8	91.0
SO hydration to phenyl-1,2-ethanediol	SiO_2-Al_2O_3 (Si/Al=3)	100	~223	Yield=61.2	
	Sn-Nb_2O_5/α-Al_2O_3	180	22	95.1	100

Significance

The results indicate that modifying the water adsorption property of the catalyst by introducing water-insoluble hydrophilic species such as tin oxide so as to influence the surface H_2O/Epoxide ratio may be a effective way to improve monoglycol selectivity in epoxides hydration.

References

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