

Styrene partial oxidation over oxidized and reduced Co-ZSM-5

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Introduction

Many studies on the styrene oxidation over different catalysts, such as meso and microporous materials substituted with metal ions have been reported: Co, Ti, V and Fe-MCM-41[1-2], Ti-ZSM-5 [3], and Co-VSB-5 [4]. With hydrogen peroxide as oxidant agent it is possible to perform the oxidation of olefins to epoxides, the hydroxylation of aromatic compounds, and the oxidation of primary and secondary alcohols with high selectivity [5].

Materials and Methods

ZSM-5 zeolite (Si/Al=17) with MFI structure was prepared by hydrothermal method. The NH₄-zeolite was prepared by ion-exchange with 1 M NH₄Cl solution at 80°C for 40 h and the Co-HZSM-5 was prepared from NH₄-MFI by ion-exchange with CoCl₂ 0.05 M aqueous solution at 80°C for 24 h, to yield the 0.64 wt % of Co. Finally, the samples were dried at 110°C and desorbed at 500°C under N₂ flow (10 ml/min) and an oxidizing atmosphere for 12 h. These samples were called oxidized zeolites. In order to carry out a complete study, calcined cobalt samples were reduced from room temperature to 500°C at 5°C/min and holding at 500°C for 5 h, in H₂ flow (5 ml/min). These samples were called reduced zeolites. The samples were characterized by AA, XRD and FTIR.

Catalytic oxidation of styrene with H₂O₂ (aqueous solution 30 wt%) as oxidant agent was carried out in a glass batch reactor with a magnetic stirring immersed in a thermostated bath, and a reflux condenser, with acetonitrile as solvent, at 60°C and 0.2 g of the catalyst. Different styrene/hydrogen peroxide molar ratios (R) were studied. The reactions were monitored at different reaction times. Organic compounds were analyzed by gas chromatography and mass spectrometry. The substrate conversion was measured as a function of reaction time and the values observed are reported as mol %.

Results and Discussion

The Figures 1 and 2 show an increment of styrene conversion when increased reaction time. The major styrene conversion was observed at R: 1.7 over reduced and oxidized zeolites.

The results reported in Table 1 show an increment on styrene oxide selectivity and a diminution of benzaldehyde selectivity when styrene/H₂O₂ molar ratio decrease from 3 to 0.9 over oxidized zeolites. The same effect appeared when Brønsted/Lewis ratio is increased on cobalt samples at constant R. Benzoic acid (other products, Table 1), is from the benzaldehyde oxidation and the amount of this by-product was very low. An adequate combination of R and Brønsted/Lewis sites allow us to find good conditions to improve conversion levels and products selectivity.

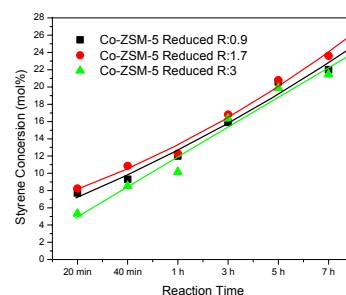


Figure 1 Effect of the styrene/H₂O₂ molar ratio(R) in the conversion of styrene over ion-exchanged reduced Co-ZSM-5

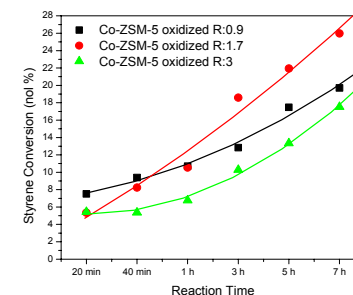


Figure 2 Effect of the styrene/H₂O₂ molar ratio(R) in the conversion of styrene over ion-exchanged oxidized Co-ZSM-5

Table 1. Styrene/H₂O₂ molar ratio effect on products selectivity at 7 h of reaction time.

Catalysts ^a	Benzaldehyde Selectivity (mol %)	Styrene Oxide Selectivity (mol %)	Other Selectivity (mol %)	Acidity FTIR ^b B/L
Co-HZSM-5 Oxidized R: 3	88.69	8.76	2.55	0.6286
Co-HZSM-5 Oxidized R:1.7	83.47	11.98	4.55	0.6286
Co-HZSM-5 Oxidized R: 0.9	81.79	16.89	1.32	0.6286
Co-HZSM-5 Reduced R: 3	70.16	24.92	4.92	0.9961
Co-HZSM-5 Reduced R: 1.7	79.25	16.01	4.74	0.9961
Co-HZSM-5 Reduced R: 0.9	79.92	16.94	3.14	0.9961

^a > 98 % crystallinity by XRD and FTIR

^b B/L: Brønsted/Lewis ratio calculated by FTIR of pyridine (mmol/g) retained at 400°C; 10⁻⁴ Torr

Significance

As known, the scope of partial oxidation catalysis is wide, ranging from the large-scale production of commodities to the synthesis of pharmaceuticals products and fine chemicals. The selective catalytic oxidation is an active field of research. In this context the selective styrene oxidation gives benzaldehyde and styrene oxide as main products which are important organic intermediates for the chemical industry. The use of H₂O₂ has environmental implications, being water the only chemical by-product of oxidation reactions.

References

- Tang Q., Zhang Q., Wu H. and Wang Y., *J. Catal.* 230, 384 (2005).
- Wang Y., Zhang Q., Shishido T. and Takehira K., *J. Catal.* 209, 186 (2002).
- Xu C., Jim T., Jung S., Hwang J., Chang J., Qiu F., and Park S, *Korean Chem. Soc.* 25-5, 681 (2004).
- Gao D. and Gao Q., *Micropor. Mesopor. Mater.* 85, 365 (2005).
- Clerici M., Bellussi G. and Romano U., *J. Catal.* 129, 159 (1991).