Zeolites to catalyze dehydration of lactic acid to acrylic acid

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Introduction

Acrylic acid and its esters are primary building blocks of all acrylate polymers and plastics. Currently, 100% of acrylic acid (AA) is produced from fossil oil, mostly via direct oxidation of propene. Lactic acid (LA) can be produced by chemical synthesis or by fermentation of different carbohydrates such as glucose (from starch), and the production of lactic acid is around 350 000 t/year. Therefore, the production of acrylic acid via dehydration of lactic acids (LA) is an attractive method for creating new bio-based compounds.

The aim in this work was to study the dehydration of LA to produce AA with different solid acids.

The infrared spectra of adsorbed pyridine was used to determine the concentration of Lewis and Brønsted acid sites, and TPD of adsorbed NH_3 was performed to determine the density and strength of solid acids. The dehydration of lactic acid was carried out over a fixed bed reactor at 583K, using solid acids with different acid properties such as Na(Zn,H)Y, NaZSM5, KL and γ-Al_2O_3.

Allyl-lactates were detected inthe analysis of the condensate product sample from the lactic acid dehydration. These products

Fig. 1. Reaction scheme

Fig. 2. Pathway for the oligomerization of lactic acid.

were identified using a MS-GC.

The tentative pathways to form these species are shown in fig. 2. We summarized these oligomers (LA2, LA3 and LA4)of lactic acid as LAL. Incorporation of cations in NaY zeolites increased the total acidity, and changes the concentration of Lewis and Brønsted acid sites.

Results and discussion

Table I. Catalytic Results for different solid acids

Solid Acid	TPD NH_3		FTIR-Py	Conversion LA, %		Absolute yield, %at time = 0					
	weak[a]	Strong[b]	L/(L+B)	0min	240min	AA	AD	AP	PD	CO_x	LAL
NaY	280	---	1	87	76	33	12	2	3	16	21
Na(6.0)HY	390	490	0.4	78	20	4	17	2	1	20	35
Zn(2.4)NaY	676	200	1	98	0	2	45	2	0	45	4
NaZSM5	90	360	0.8	95	80	0	43	2	2	45	4
γ-Al_2O_3	180	20	-	80	70	6	18	6	0	18	32
KL	300	---	--	72	30	19	4	1	2	6	39

[a] T < 573K; [b] T > 573 K, Reaction 583K, 101.3 kPa(3kPa LA, 27kPa H_2O, 70.3 kPa of N_2) W/F_{AL}= 22.3g/mol.h

The dehydration reaction from the lactic acid presents a competition reaction to produce oligomers of lactic acid. Lactate was not detected in the condensated product for the pathway of dehydration to produce acrylic acid.

Strong Lewis and Brønsted sites promote the decarbonylation reaction. Weak acidity formed oligomers.

Results from the catalytic test show that NaY and KL zeolites are highly selective for the vapor-phase dehydration of lactic acid to acrylic acid, showing that weak acid sites promote formation of acrylic acid from the dehydration of lactic acid.