Catalysis Letters 5 (1990) 13–16

SOLVOLYSIS AND ISOMERIZATION OF PHENYLOXIRANE CATALYZED WITH NIOBIC ACID

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Received 24 January 1990; accepted 8 March 1990

Niobic acid, hydrolysis, acid catalyst, phenyloxirane

Solvolysis and isomerization of phenyloxirane were studied with niobic acid ($Nb_2O_5.xH_2O$) as catalyst. In aqueous solution, niobic acid showed much higher hydrolysis performances in activity and selectivity than other solid acid catalysts. Selectivity of alcoholysis with methanol was much higher than that with other alcohols because of simultaneous isomerization and dehydration of alcohol.

The ring-opening reaction of 1,2-epoxide is one of key steps in organic syntheses. Sulfonic acid has been used as catalyst for this type reaction, however, it has many problems such as catalyst separation and post-treatment of acid. Although solid acid catalysts have been attempted by many workers, some problems remained [1].

Niobic acid ($Nb_2O_5.xH_2O$) have been focused as a new material of acid catalyst in recent years [2]. Because it shows strong acidity even in aqueous condition, it has been applied to some reactions with water as reagent such as olefin hydration, alcohol dehydration and esterification [3,4]. However, few studies have been reported in organic synthesis on catalytic utilization of niobic acid. In this report, we will describe the application of niobic acid for catalytic ring-opening reactions, solvolysis and isomerization of phenyloxirane.

Niobic acid that was supplied by CBMM int. ltda. (AD-438) and calcined in an air stream at various temperatures before use. Some solid acid catalysts, alumino-silicate and H-Nafion, were examined for comparison. Reactions were carried out in a flask under ordinary pressure and reflux condition. Phenyloxirane was injected by use of syringe to the solution containing catalyst. All products were identified by spectroscopic analyses and determined by gas chromatography (J&W DB-225, 20 m × 0.25 mm).

The results of phenyloxirane hydrolysis were shown in table 1. Niobic acid exhibited much better activity and selectivity than these of other solid acid

Table 1
Hydrolysis of phenyloxirane with some solid acid catalysts

Catalyst (calcination temp. /°C)	Solvent volume H_2O/dioxane [1] (ml/ml)	Yield (%)			Yield ratio (*H*/*I*)
		Phenyl-oxirane	Phenyl-acetaldehyde (*I*)	Phenyl-1,2-ethanediol (*H*)	
Niobic acid (300)	(10/90)	0.0	11.4	88.6	7.8
	(50/50)	0.0	0.5	99.0	>100
	(100/0)	0	0	100	>100
SiO_2-Al_2O_3 [2] (500)	(10/90)	3.9	34.8	61.2	1.8
SiO_2-Al_2O_3 [3] (500)	(10/90)	8.0	36.4	55.7	1.5
H-ZSM5 (500)	(10/90)	0.3	83.2	16.5	0.2
H-silicalite (500)	(10/90)	63.7	33.8	2.5	0.07
H-Nafion [4]	(10/90)	0.0	25.7	74.3	2.9

[1] Mixture of water and 1,4-dioxane was used as solvent.
[2] "High alumina" type ($SiO_2/Al_2O_3 \sim 3$), supplied by Catalysts & Chemicals Ind. Co., Ltd.
[3] "Low alumina" type ($SiO_2/Al_2O_3 \sim 6$), supplied by Catalysts & Chemicals Ind. Co., Ltd.
[4] Aldrich Chem. Co. Int., NR-50 (beads, 10–35 mesh).

Yields were determined by GC analysis after 3 hr reaction.
Reaction conditions: substrate volume 0.5 cm^3, catalyst amount 500 mg, total solvent volume 100 cm^3.

catalysts. The hydrolysis selectivity with niobic acid was sensitive to the solvent composition. Hydrolysis selectivities increased with increasing the water concentration. Even in water, niobic acid showed high activity and produced phenyl-1,2-ethanediol quantitatively.

Other solid acid catalysts were less active in hydrolysis than niobic acid. These catalysts produced concurrently phenylacetaldehyde in quantity by isomerization in addition to phenyl-1,2-ethanediol and showed small *H*/*I* values (products yield ratio of *h*ydrolysis to *i*somerization).

The surface hydrophilicity of alumino-silicate decreases with increasing of the ratio of SiO_2/Al_2O_3. In case of commercial amorphous SiO_2-Al_2O_3 catalysts which have different SiO_2/Al_2O_3 ratios, the high alumina type SiO_2-Al_2O_3 catalyst ($SiO_2/Al_2O_3 \sim 3$) showed slightly higher selectivity of hydrolysis that that of low alumina type SiO_2-Al_2O_3 catalyst ($SiO_2/Al_2O_3 \sim 6$) as shown in table 1. Very hydrophobic "high-silica zeolite", H-ZSM-5 ($SiO_2/Al_2O_3 = 43$), and silicalite ($SiO_2/Al_2O_3 = 2100$) exhibited low hydrolysis selectivities, phenyloxirane conversions and *H*/*I* ratios. These results suggested that there is a close relationship between surface hydrophilicity and rate of phenyloxirane hydrolysis (selectivity of hydrolysis) in aqueous condition. The differences of hydrolysis selectivities between niobic acid and others were recognized by the difference of catalyst surface hydrophilicity.

Table 2
Solvolysis and isomerization of phenyloxirane with niobic acid

Nucleophile *	Yield (%)			Yield ratio (*A*/*I*)
	Alcoholysis (*A*)	Isomerization (*I*)	Hydrolysis	
none	–	100	0	–
water	–	0.5	99.5	–
methanol	98.0	2.0	0.0	49
2-propanol	40.4	33.5	10.5	1.2
2,2-dymethylpropanol	26.6	63.3	4.6	0.42
2-methyl-2-propanol	16.3	66.7	8.8	0.25

* All alcohols were dried by distillation over CaH_2.

Yields were determined by GC analysis after 3 hr reaction.
Niobic acid was calcinated at 300 ° C.
Reaction conditions: substrate volume 0.5 cm^3, catalyst amount 500 mg.
total solvent volume 100 cm^3 (nucleophole and benzene 1 : 1).

H-Nafion, a hydrophilic organic solid acid catalyst, was also active for hydrolysis of phenyloxirane in aqueous condition, although it was less active than niobic acid.

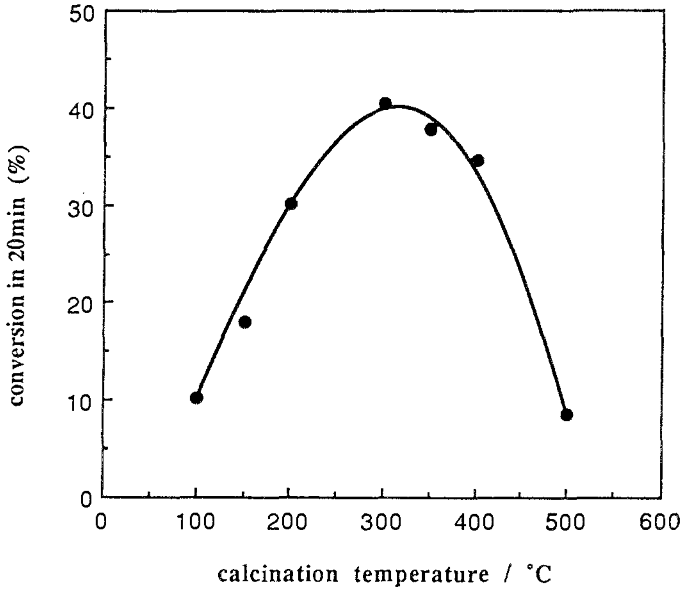

Fig. 1. The effect of calcination temperature on phenyloxirane isomerization activity in benzene.

Reaction condition: Catalyst weight 250 mg, reaction temperature 70 ° C, substrate volume 0.5 cm^3, solvent 100 cm^3 (benzene).

Table 2 showed the results of phenyloxirane solvolysis and isomerization carried out in a dry condition. Methanolysis of phenyloxirane occurred in high selectivity with niobic acid. However, selectivity of alcoholysis with other alcohols was much reduced because of accompanying isomerization and hydrolysis with alcoholysis. The selectivity of alcoholysis was decreased with decreasing alcohol nucleophilicity. The yield of alcoholysis with 2-propanol was much higher than that with 2-methyl-2-butanol. Nucleophilicity alcohol seemed to control the selectivities. Niobic acid catalyzed dehydration of alcohol during these experiments, and the produced water acted as the reactant for phenyloxirane hydrolysis. In an inert solvent, such as benzene, only isomerization of phenyloxirane occurred.

The catalytic activity of niobic acid was much affected by the calcination temperature. As shown in fig. 1, niobic acid calcined at 300 ° C had the maximum activity in isomerization. This behavior was almost similar to the results of propylene polymerization previously reported [4].

In summary, niobic acid showed high activities for ring-opening reactions of phenyloxirane, especially in hydrolysis. High hydrolysis activity and selectivity in aqueous condition was considered to explain by the high surface hydrophilicity of niobic acid.

Acknowledgments

This work was performed through Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

References

[1] G.A. Olah, A.P. Fung and D. Meider, Synthesis (1981) 280.
[2] S. Okazaki, Hyomen 27 (1989) 112.
[3] Z.-h. Chen, T. Iizuka and K. Tanabe, Chem. Lett. (1984) 645.
[4] T. Iizuka, K. Ogasawara and K. Tanabe, Bull. Chem. Soc. Jpn. 56 (1983) 2927.