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NIOBIC ACID AS AN EFFICIENT CATALYST FOR VAPOR PHASE ESTERIFICATION OF ETHYL ALCOHOL WITH ACETIC ACID

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The niobic acids calcined at moderate temperatures of 120-300 °C showed high catalytic activities (52-75% conv. in 1 h) and selectivities (100%) for the esterification at reaction temperatures of 120-160 °C. No catalyst deactivation was observed even after the use for 60 h. The niobic acid catalysts were more effective than cation exchange resin, SiO_2-Al_2O_3, HZSM-5, and solid super acids such as ZrO_2-SO_4^{2-}, TiO_2-SO_4^{2-}, and Fe_2O_3-SO_4^{2-}.

Sulfuric acid is extensively used as a homogeneous catalyst for esterification reactions, but has disadvantages of corrosion of reactors, difficulties of catalyst recovery and waste disposal, etc. Cation exchange resin as a heterogeneous catalyst has some problems of low acid strength, restriction of reaction temperature, swelling, high cost, etc. Recently, Nafion$^{1)}$ (fluorinated sulfonic acid resin), heteropoly acids supported on carbon,$^{2)}$ ZrO_2-SO_4^{2-} $^{3)}$ and TiO_2-SO_4^{2-} $^{4)}$ were reported to be effective for esterification. However, the activity or selectivity of the catalysts is not necessarily sufficient and/or the catalyst cost is high.

We found recently that the surface of niobic acid ($Nb_2O_5 \cdot nH_2O$) calcined at moderate temperatures of 100-300 °C showed a very high acid strength ($H_0 \leq -5.6$),$^{5)}$ though it became almost neutral when calcined at 600 °C. This suggests that the niobic acid containing water activated at relatively lower temperatures would be effective as a catalyst for the reactions which liberate water molecule during the reaction. Thus, we have attempted to use it as a catalyst for esterification in the present work. For comparison, the catalytic activities of strong or super solid acids such as cation exchange resin, SiO_2-Al_2O_3, HZSM-5, ZrO_2-SO_4^{2-}, TiO_2-SO_4^{2-}, and Fe_2O_3-SO_4^{2-} were also examined. Since the acid amount of niobic acid has not been measured yet, we have determined the acid amount together with the acid strength.

The niobic acid catalysts were prepared by washing the niobic acid (purity; 99.8%) supplied by Companhia Brasileira de Metalurgia e Mineracao (CBMM) Ltd. with distilled water several times, drying at 100 °C for 40 h, and calcining in a nitrogen stream at various temperatures for 2 h before use. The ZrO_2-SO_4^{2-} was prepared by flowing 30 ml of 0.5 M H_2SO_4 through 2 g of $Zr(OH)_4$ placed on a filter

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paper, followed by calcining in air at 500 °C for 2 h. The $Zr(OH)_4$ was obtained by the hydrolysis of a solution of $ZrOCl_2 \cdot 8H_2O$ with ammonia water, followed by washing with distilled water, drying at 100 °C for 24 h. The $TiO_2-SO_4^{2-}$ and $Fe_2O_3-SO_4^{2-}$ were prepared by immersing $TiO_2 \cdot nH_2O$ and $Fe(OH)_3$ into solutions of ammonium sulfate, respectively, and evaporating to dryness, followed by drying and calcining at 500 °C for 2 h. The contents of sulfur were 6.4 and 5.0% as SO_3, respectively. The $TiO_2 \cdot nH_2O$ and $Fe(OH)_3$ were obtained by the hydrolyses of aqueous solutions of $TiCl_4$ and $Fe(NO_3)_3$ with ammonia water, followed by washing and drying similarly as in the case of $Zr(OH)_4$. The $SiO_2-Al_2O_3$ (Nikki N6314) was calcined at 500 °C for 2 h before use. The ion exchange resin used was Dow 50W-X2. The ZSM-5 zeolite was synthesized by the method described in an original patent.[6] The HZSM-5 zeolite was prepared by exchanging the cations with HCl and calcining at 500 °C. The X-ray patterns of the zeolites were identical to those reported for ZSM-5.[6]

The acid strength and acid amount of niobic acid were measured by the n-butylamine titration using Hammett indicators.[7] The reaction was carried out using a conventional flow reactor. The flow rate of the mixture of acetic acid and ethyl alcohol (volume ratio=1) was 2.2-2.3 ml/h. The products were analyzed by gas chromatography.

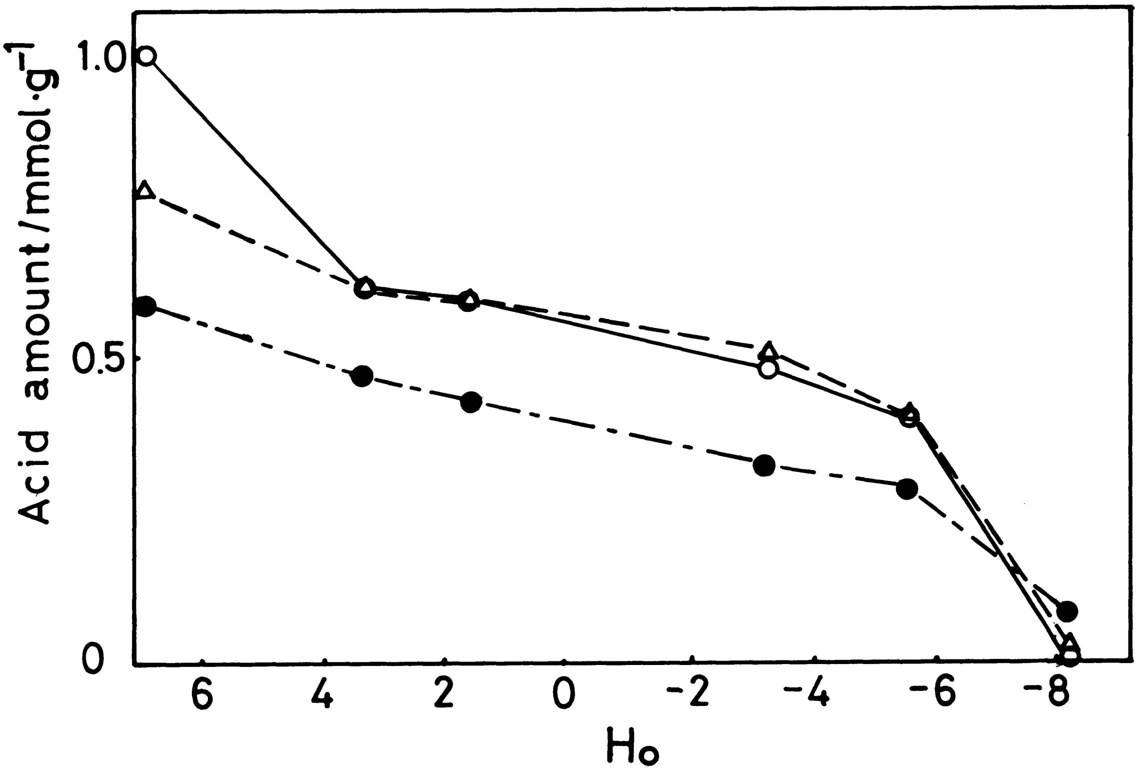

Fig. 1. Acid amount vs. acid strength of niobic acid.
○ ; Calcined at 120 °C, △ ; 200 °C, ● ; 300 °C

Figure 1 shows the acid amounts at different acid strengths on niobic acids pretreated at 120, 200, and 300 °C. The acidic property of niobic acid pretreated at 120 °C is the same as that pretreated at 200 °C except that the acid amount at $H_0 \leq +6.8$ is higher for the former than for the latter. In both cases, considerable acid amounts (>0.75 and >0.4 mmol/g, respectively, at $H_0 \leq +6.8$ and -5.6) were observed, though the acid amounts at $H_0 \leq -8.2$ were small. On the niobic acid pretreated at 300 °C, the acid amount at $H_0 \leq -8.2$ was larger.

Table 1 shows the catalytic activities and selectivities of niobic acids pretreated at different temperatures and a cation exchange resin for the esterification of acetic acid with ethyl alcohol at different reaction temperatures. The activities of niobic acids pretreated at 200-300 °C were a little better at 120 and 140 °C of reaction temperature than that pretreated at 120 °C. The same activity of the niobic acids pretreated at 200 and 300 °C is due to the compensation of smaller acid amounts at H_0 between -3 and -5.6 with larger acid amount at $H_0 \leq -8.2$ on the niobic acid pretreated at 300 °C. The higher activity of the niobic acid pretreated at 200 °C than that pretreated at 120 °C is considered due to a small amount of strong acid sites having $H_0 \leq -8.2$ on the former niobic acid. These discussion is based on our previous results⁸⁾ that water vapor hardly affects the acid strength provided that reaction temperature is above 100 °C. The selectivity for the formation of ethyl acetate was 100% in all cases. The ion exchange resin showed lower activities and selectivities than niobic acids. The resin became black after 1 h's reaction so that the repeated use was impossible under the reaction condition. On the other hand, the activities of niobic acid catalysts did not change even after use for 60 h.

Table 1. Activities and selectivities of $Nb_2O_5 \cdot nH_2O$ and ion exchange resin. Catalyst weight; 1 g, Volume ratio of acetic acid to ethyl alcohol=1, Reaction time; 1 h

Catalyst	Pretreatment temp /°C	Reaction temp /°C	C_2H_5OH basis Conversion/%	Ester selectivity/%
$Nb_2O_5 \cdot nH_2O$	120	120	57	100
		140	75	100
		160	79	100
	200	120	72	100
		140	86	100
		160	86	100
	300	120	73	100
		140	83	100
		160	84	100
Resin	120	120	38	99
		140	50	98
		160	53	98

The activities and selectivities of the other catalysts selected for comparison are shown in Table 2. The TiO_2-SO_4^{2-} showed a high activity, but the activity rapidly decreased and became much lower than that of niobic acid after 2 h's reaction. The HZSM-5 catalyst also exhibited a high activity but formed large amounts of diethylether and ethylene as by-products, the selectivity for the ester being less than 92%.

Table 2. Activities and selectivities of strong solid acids.
Catalyst weight; 1 g, Volume ratio of acetic acid to ethyl alcohol=1,
Reaction time; 1 h

	Reaction	From C_2H_5OH basis		
Catalyst[a)]	temp /°C	Conversion/%	Ester selectivity/%	By-products
ZrO_2-SO_4^{2-}	120	39	98	$(C_2H_5)_2O$
	140	56	90	
	160	68	90	
Fe_2O_3-SO_4^{2-}	120	8	98	$(C_2H_5)_2O$
	140	13	93	
	160	37	89	
TiO_2-SO_4^{2-}	120	95(54)[b)]	99(98)[b)]	$(C_2H_5)_2O$ C_2H_4
	140	100	95	
	160	63	94	
SiO_2-Al_2O_3	120	4	99	$(C_2H_5)_2O$ C_2H_4
	140	14	98	
	160	52	98	
HZSM-5	120	82	92	$(C_2H_5)_2O$ C_2H_4
	140	99	72	
	160	99	72	

a) Calcined at 500 °C. b) After 2 h.

It is concluded that niobic acids pretreated at 120-300 °C are highly active for the esterification with 100% selectivity and the catalyst life is very long.

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