Synthesis of *N*-Isopropylacrylamide from Acrylonitrile and Isopropyl Alcohol over H-ZSM-5

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A solid acid, H-ZSM-5 (Si/Al = 37), exhibited exceptionally high catalytic performance for synthesis of *N*-isopropylacrylamide from acrylonitrile and isopropyl alcohol in a solid-liquid reaction system at 423 K.

N-Isopropylacrylamide is an important monomer for water-soluble polymers which are applicable to water-soluble fibers, thickeners, and so forth.[1] Ritter et al.[2] first reported five decades ago that N-alkylation of acrylonitrile with isopropyl alcohol to *N*-isopropylacrylamide (Eq. (1)) proceeded in the presence of excess H_2SO_4. This reaction is recognized as a highly difficult reaction. To avoid the polymerization of acrylonitrile, the reaction must be carried out at low temperatures. Practically, this amide has commercially been produced by this reaction with an excess amount of H_2SO_4.[1] Since this H_2SO_4-process contains disposal and toxicity problems, environmentally benign solid catalysts are desirable in the place of H_2SO_4.

$$CH_2{=}CH\text{-}CN + i\text{-}C_3H_7OH \rightarrow CH_2{=}CH\text{-}CONH\text{-}i\text{-}C_3H_7 \quad (1)$$

Solid catalysts have great advantages: the easy separation from the reactant suspension and the reusability. While other liquid catalysts such as BF_3,[3] $(CF_3SO_2)_2O$,[3] and $Pd[CH_3CN)_2(PPh_3)_2](BF_4)_2$[4] showed activities for "Ritter- type reactions" like acrylonitrile + benzyl alcohol, or acrylonitrile + *tert*-butyl alcohol, there are no reports about the catalytic reaction of acrylonitrile with isopropyl alcohol. Also solid acids effective for the reaction were not found, whereas there are some reports about acrylonitrile + benzyl alcohol over Nafion-H[5] and acrylonitrile + 1-adamantanol over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.[6]

Here we wish to report the first example of the catalytic reaction of acrylonitrile and isopropyl alcohol to form selectively *N*-isopropylacrylamide with a solid acid, H-ZSM-5 in the solid-liquid reaction system. Among a variety of solids and liquid acids, H-ZSM-5 was far superior in both the activity and selectivity. The reusability of this solid acid has been confirmed for this reaction.

The reaction was ordinarily performed in a glass-autoclave at 423 K for isopropyl alcohol in an N_2 atmosphere using acrylonitrile 10 cm^3 (150 mmol), isopropyl alcohol 2.2 cm^3 (30 mmol) (without solvent) and a solid catalyst 1.0 g. As an internal standard *n*-dodecane (0.25 cm^3) was added to the suspension. As reference reaction, the reaction between acrylonitrile and *tert*-butyl alcohol was performed at 373 K in the same reactor using acrylonitrile 10 cm^3 (150 mmol) and *tert*-butyl alcohol 2.9 cm^3 (30 mmol) in the N_2 atmosphere. These reactions were typically carried out for 24 h with stirring. The products were analyzed by gas chromatography using FID-GC (Shimadzu, GC 14B) equipped with a column of Carbowax 300M Chromosorb WAW (2 m).

As solid catalysts, the following were used after the pretreatment in air for 5 h: H-ZSM-5 (Tosoh, H-SZ-860 HOA, 410 m^2 g^{-1}, Si/Al = 37, the acid amount = 0.43 mmol g^{-1}, 773 K), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (130 m^2 g^{-1}, the acid amount = 0.063 mmol g^{-1} (on the surface), 473 K),[7] H-mordenite (HM-20, Reference Catalyst of the Catalysis Society of Japan, 371 m^2 g^{-1}, the acid amount = 1.40 mmol g^{-1}, 673 K), HY (HY4.8, Reference Catalyst of the Catalysis Society of Japan, 607 m^2 g^{-1}· the acid amount = 2.6 mmol g^{-1}, 673 K), SiO_2-Al_2O_3 (SAL-2, Reference Catalyst of the Catalysis Society of Japan, 546 m^2 g^{-1}, the acid amount = 0.35 mmol g^{-1}, 773 K), Nafion-H (Du Pont, NR-50, 0.02 m^2 g^{-1}, the acid amount = 0.8 mmol g^{-1}, without pretreatment), Nafion-SiO_2 composite[8] (SAC 13, Du Pont, 344 m^2 g^{-1}, the acid amount = 0.12 mmol g^{-1}, without pretreatment), and Amberlyst 15 (Organo, 50 m^2 g^{-1}, the acid amount = 4.7 mmol g^{-1}, without pretreatment). As liquid acid, H_2SO_4 (the acid amount = 20.4 mmol g^{-1}) and anhydrous $H_3PW_{12}O_{40}$ (Nippon Inorganic Color and Chemical Co., the acid amount = 1.0 mmol g^{-1}, 473 K (evacuation)) were used.

The results of the reaction with *tert*-butyl alcohol are summarized in Table 1. Polymer resin catalysts such as Nafion and Amberlyst gave higher yields more than 76%. On the other hand, solid oxide catalysts were not effective; the most active was $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5) which exhibits 32.2%-yield. H-ZSM-5 showed the activity similar to that of HY, while these were less active than Cs2.5. While the gas-phase by product, isobutylene, was not analyzed, the high values of the conversion of *tert*-butyl alcohol indicates that the dehydration took place readily.

Table 1. Yield and selectivity of *N*-*tert*-butylacrylamide from acrylonitrile and *tert*-butyl alcohol catalyst among solid oxides

Catalyst	Yield[a]/%	Conv./%		Selectivity[d]/mol%	
		AN[b]	TBA[c]	BAA[e]	AA[f]
H-ZSM-5	13.7 (9.6)	6.3	86.9	90.5	9.5
H-Y	14.3 (1.7)	12.5	89.3	96.2	3.8
H-M	0.6 (0.1)	6.3	40.4	77.7	32.2
Cs2.5[g]	32.2 (153)	13.3	96.0	94.1	5.9
SiO_2-Al_2O_3	6.1 (5.0)	12.3	72.4	95.3	4.7
Nafion-H	80.0 (30.0)	26.7	98.8	80.0	20.0
Amberlyst	76.0 (4.9)	31.3	97.4	91.8	8.2
Nafion-SiO_2	44.6 (112)	18.7	96.6	97.6	2.4

[a]Reaction conditions: acrylonitrile = 150 mmol, *tert*-butyl alcohol = 30 mmol, catalyst = 1.0 g, and 373 K. The yield is defined as 100 x (mol of BAA)/(mol of *tert*-butyl alcohol present initially). The figures in the parentheses are turnover numbers which are defined as the number of BAA molecules formed (at 8 h) divided by the number of protons on the surface. [b]Acrylonitrile. The conversion is defined as 100 x [mol of AN disappeared]/[mol of AN present initially]. [c]*tert*-butyl alcohol, [d]Selectivity of BAA is defined as 100 x (mol of BAA)/[(mol of BAA) + (mol of AA)], [e]*N*-*tert*-butylacrylamide, [f]Acrylamide, [g]$Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

In Table 2, the results of the reaction with isopropyl alcohol are provided. Contrary to the reaction with *tert*-butyl alcohol, HZSM-5 was far superior in the yield of *N*-isopropylacrylamide

(PAA) to the other solid acids and the liquid acids. In addition, the selectivity to PAA was the highest (93.3%) over H-ZSM-5; the formation of diisopropyl ether (PE) was greatly suppressed. The by-products from acrylonitrile were acrylamide and polymers, but these were small over H-ZSM-5. The TON, which is defined as the number of PAA molecules produced divided by the number of protons on the surface, reached 43 over H-ZSM-5 at 24 h, indicating that H-ZSM-5 worked actually as a catalyst for this reaction. Besides H-ZSM-5, Cs2.5, Nafion-SiO$_2$, Nafion-H, and SiO$_2$-Al$_2$O$_3$ accelerated the reaction, but these catalysts gave yields less than 10%. In the liquid acids, H$_3$PW$_{12}$O$_{40}$ produced PAA with the yield of 15.5%, but was less selective. In addition, H$_2$SO$_4$ brought about exclusively the polymerization of acrylonitrile under these reaction conditions. Further examination using H-ZSM-5 for this reaction revealed when the catalyst weight increased to 2.0 g (TON was about 31 at 24 h (Table 2)). In addition, the reusability of H-ZSM-5 was confirmed by repeating the reaction at least three times after the calcination at 773 K in air for 5 h. The obtained yields and selectivities in the repeated runs were very close to those of the first run. The effects of reaction temperature were examined. As the reaction temperature decreased to 393 K or 373 K over H-ZSM-5 (1 g), the yield decreased to 29.7% (TON = 20.7) or 8.3% (TON = 5.8), respectively, but it should be emphasized that the reaction proceeded still catalytically with high selectivities, more than 95%.

Table 2. Yield and selectivity of *N*-isopropylacrylamide from acrylonitrile and isopropyl alcohol

Catalyst	Yield[a]/%	Conv./%		Selectivity[d]/mol%		
		AN[b]	IPA[c]	PAA[e]	AA[f]	PE[g]
(Solid oxide)						
H-ZSM-5	62.2 (43.4)	23.5	86.2	93.3	3.1	3.6
H-ZSM-5[h]	89.3 (31.2)	22.2	90.3	93.8	3.5	2.7
HY	7.4 (0.8)	9.7	37.0	52.6	7.9	39.5
H-M	1.5 (0.3)	29.4	41.3	68.8	12.5	18.7
Cs2.5[i]	10.0 (47.6)	21.5	50.0	74.7	5.1	20.1
SiO$_2$-Al$_2$O$_3$	2.8 (2.0)	12.5	28.6	72.7	0.0	27.3
(Polymer resin)						
Nafion-H	6.0 (2.1)	20.5	57.5	46.9	16.7	36.4
Amberlyst	10.0 (0.6)	24.6	83.3	68.7	10.7	20.6
Nafion-SiO$_2$	3.0 (8.0)	33.3	60.0	59.4	12.5	28.1
(Liquid acid)						
H$_3$PW$_{12}$O$_{40}$	15.5 (4.7)	15.1	63.8	47.4	10.5	42.1
H$_2$SO$_4$[j]	4.8 (0.4)	29.4	65.5	27.5	39.2	33.3

[a]Reaction conditions; acrylonitrile = 150 mmol, isopropyl alcohol = 30 mmol, catalyst = 1.0 g, and 423 K. The figures in the parentheses are turnover numbers which are defined as the number of PAA molecules formed (at 24 h) divided by the number of protons on the surface. [b]Acrylonitrile. The conversion is defined as 100 x [mol of AN disappeared]/[mol of AN present initially]. [c]Isopropyl alcohol, [d]Selectivity of PAA is defined as 100 x (mol of PAA)/[(mol of PAA) + (mol of AA) + (mol of PE)], [e]*N*-isopropylacrylamide, [f]Acrylamide, [g]Diisopropyl ether. [h]2 g of the catalyst was used. [i]Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$. [j]0.18 g of the catalyst was used.

Since the acid strength of H-ZSM-5 is lower than that of Cs2.5[9] and the acid amount of H-ZSM-5 is smaller than H-M and H-Y, the higher catalytic performance of H-ZSM-5 for the reaction with isopropyl alcohol cannot be explained only by the acidic property. As was preliminarily reported, H-ZSM-5 was much less active for the *N*-alkylamide synthesis from acrylonitrile and 1-adamantanol than Cs2.5, probably due to the restricted diffusion of the bulky molecule into the constrained pore of H-ZSM-5 or the difficulty of the formation of the intermediates in the pore.[6] The lower catalytic performance of H-ZSM-5 for the reaction of *tert*-butyl alcohol is also probably due to the constrained pores. In the case of the reaction with isopropyl alcohol, the reaction would occur effectively in the pores of H-ZSM-5 because of the smaller reactants. The hydrophobic circumstances in the pore of H-ZSM-5 may be responsible for the high catalytic performance. It is necessary to elucidate the reasons for the unique catalysis of H-ZSM-5 for this reaction.

In conclusion, we found that the reusable solid acid catalyst, H-ZSM-5 was effective for the synthesis of *N*-isopropylacrylamide from acrylonitrile and isopropyl alcohol in the solid liquid reaction system.

Notes and References

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