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A Ritter-Type Reaction over H–ZSM-5: Synthesis of *N*-Isopropylacrylamide from Acrylonitrile and Isopropyl Alcohol

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Catalytic synthesis of *N*-isopropylacrylamide from acrylonitrile and isopropyl alcohol has been studied using a variety of solid acids in a solid–liquid reaction system at 423 K. Among typical solid and liquid acids, H–ZSM-5 exhibited an exceptionally high catalytic activity. The activity (per gram) of H–ZSM-5 increased as the Al-content (100Al/(Si + Al)%) increased and then decreased through a maximum at an Al content of 2.63%. The specific activity per one acid site, which was estimated from the initial rate and the acid amount, increased greatly as the Al content decreased, which resembles those of the hydrophobicity and the acid strength. The superiority of H–ZSM-5 activity over other strong and hydrophobic solid acids suggests the importance of the unique pore structure. While H–ZSM-5 deactivated severely during the reaction, the catalytic activities were mostly recovered by calcination at 773 K in air. IR spectroscopy and adsorption measurements revealed that the deactivation of H–ZSM-5 was mainly caused by the formation of a polymer of acrylonitrile on the catalyst surface blocking the micropores, but not limiting desorption of the product from the micropores. © 2002 Elsevier Science (USA)

Key Words: **Ritter reaction; *N*-isopropylacryamide; acrylonitrile; isopropyl alcohol; zeolites.**

INTRODUCTION

N-isopropylacrylamide is an important monomer for water-soluble polymers which are applicable to water-soluble fibers, thickeners, and so forth (1). Ritter and Minieri (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. Although this monomer has commercially been produced by the so-called "Ritter reaction," this H_2SO_4 process contains problems of corrosion of the reactor and a large amount of catalyst waste.

$$CH_2{=}CH{-}CN + i\text{-}C_3H_7OH \rightarrow CH_2{=}CH{-}CONH{-}i\text{-}C_3H_7. \quad [1]$$

Besides H_2SO_4, BF_3 was reported to be effective for the reaction of benzyl alcohol with various nitriles (3). In addition, trifluoromethane sulfonic anhydride gave *N*-alkylamide from primary alcohols such as 1-pentanol and acetonitrile (4), while the sulfonic anhydride was added to alcohol at a 1 : 1 molar ratio. On the other hand, a metal complex, $Pd[(CH_3CN)_2(PPh_3)_2](BF_4)_2$, showed activities for Ritter- type reactions of acrylonitrile or acetonitrile with *tert*-butyl alcohol (5). These homogeneous systems have also the problems of separation and disposal. Thus solid catalysts in the place of H_2SO_4 are desirable for environmentally benign catalytic processes.

There are some reports on solid acids effective for Ritter-type reactions. A sulfonated polymer resin, Nafion–H, was active for the reaction of acrylonitrile and benzyl alcohol (6). An acidic Cs salt of $H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, showed a high activity and selectivity for the reaction of acrylonitrile and 1-adamantanol (7). In addition, some patents described Ritter reactions catalyzed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (8), $H_3PW_{12}O_{40}$ (9), or zeolites (10). However, solid acids effective for the reaction of acrylonitrile with isopropyl alcohol were not found, except for those mentioned in our recent preliminary report (11).

Here we wish to report on the catalytic reaction of acrylonitrile with isopropyl alcohol to *N*-isopropylacrylamide over a zeolite, H–ZSM-5, in a solid–liquid reaction system. The catalytic activity and selectivity of H–ZSM-5 have been compared with those of other typical solid acids. The influence of Al content in H–ZSM-5 on the activity was examined by using various H–ZSM-5s having different Al content. Furthermore, the origins for deactivation of H–ZSM-5 detected during the reaction have been investigated by IR spectroscopy and adsorption measurement of the product. The reusability of H–ZSM-5 by calcination has been examined.

EXPERIMENTAL

As solid acids, a variety of H–ZSM-5 having different Al content were used. Here the Al content is defined as $100 \times [Al]/([Al] + [Si])\%$, where [Al] and [Si] are the

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amounts of Al and Si atoms in the zeolite. A sample of H–ZSM-5 having an Al content of 2.63% (Tosoh, HSZ-860HOA) was mainly used. Other H–ZSM-5s—JRC-Z5-25H (Al content = 7.1%, Reference Catalysts of Catalysis Society of Japan (abbreviated as RC)), JRC-Z5-70H (Al content = 2.4%, RC), and HSZ (Tosoh, Al content = 2.70%)—were also used. In addition, HSZ870NHA (Al content = 1.0%, Tosoh), MFI-300 (Al content = 0.7%, UOP), MFI-40 (Al content = 4.8%, UOP), and CBV3024 (Al content = 3.3%, Zeolyst Int.) were also utilized. Besides H–ZSM-5, H–mordenite (HM-20, RC) and HY (HY4.8, RC) were tested. In addition, SiO_2–Al_2O_3 (SAL-2, Al_2O_3 = 13 wt%, RC), sulfated zirconia (denoted to SO_4^{2-}/ZrO_2) which was prepared according to the literature (12), and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ prepared by a titration method using aqueous solutions of $H_3PW_{12}O_{40}$ and Cs_2CO_3 (13) were also compared. Nafion–H (Du Pont, NR-50), Nafion–SiO_2 composite (14) (SAC 13, Nafion 13 wt%, Du Pont), Aciplex–SiO_2 (15) and Amberlyst 15 (Organo) were examined as polymer resin catalysts. H_2SO_4 (Wako Chemicals) and anhydrous $H_3PW_{12}O_{40}$ (Nippon Inorganic Color and Chemical Co.), which was obtained by evacuation (343 K) of $H_3PW_{12}O_{40}$ $13H_2O$ as received, were used as homogeneous acid catalysts.

Catalytic Reactions

The reaction was ordinarily performed in a glass autoclave at 423 K in an N_2 atmosphere using acrylonitrile, 10 cm^3 (150 mmol), isopropyl alcohol, 2.2 cm^3 (30 mmol), and 1 g of catalyst (11). Since acrylonitrile is a carcinogenic substance, scrupulous care should be taken in handling this. Hydroquinone (0.05 g) was added as an inhibitor of polymerization. As an internal standard, *n*-dodecane (0.25 cm^3) was added to the suspension. Prior to use, the catalyst was pretreated at elevated temperatures (the conditions are described in Table 1). Water as an impurity in acrylonitrile was removed with a Molecular Sieve 5A calcined at 573 K in air. The air in the reactor was replaced with nitrogen, and then the reaction was performed at 423 K for a certain time with vigorous stirring. Usually the pressure in the reactor increased to about 3 atm after the heating of the reactor. After the reaction, the reactant solution was cooled to room temperature, and then the products were analyzed by gas chromatography using an FID-GC (Shimadzu, GC 14B) equipped with a column of Carbowax 300M Chromosorb WAW (2 m).

Adsorption of Products

The adsorption of the product, *N*-isopropylacrylamide, was measured in a sealed glass tube (Pyrex glass, 20 cm^3) at room temperature. After H–ZSM-5 in the sealed tube was pretreated at 373 K for 3 h in a vacuum, solution of *N*-isopropylacrylamide in 1,3,5-trimethylbenzene was introduced into the reactor. The change in the concentration of *N*-isopropylacrylamide was followed at room temperature with the GC.

Other Measurements

The concentrations of acid site were measured by thermal desorption of NH_3 using a TPD apparatus (BEL Japan, Multi-task TPD) (16), where the TPD spectrum of NH_3 from H–ZSM-5 (JRC-Z5-25H) was used as a standard, assuming that the concentration of acid amount is 1.2 mmol g^{-1} (17). The surface area was measured by BET method using an N_2 adsorption system (BEL Japan 28SA). Infrared spectra of H–ZSM-5 before and after the reaction were taken with an IR spectrometer (Biorad, FTS-7) by KBr method at room temperature. As standard IR samples, polyacrylonitrile and poly-*N*-isopropylacrylamide, which were kindly supplied from Kohjin Co., were used. The amounts of carbon and nitrogen atoms remaining on the used catalysts were determined with an Elemental Analysis System (Yanaco CHN Corder MT-5). For the analysis, the solid catalysts were separated from the reaction suspension by centrifugation and then were dried in air at room temperature.

RESULTS

The surface areas, pretreatment conditions, and concentrations of acid sites are summarized in Table 1. In Table 2, the yield and selectivity for the reaction of acrylonitrile with isopropyl alcohol are summarized. The yield of *N*-isopropylacrylamide (abbreviated PAA) is expressed on the basis of isopropyl alcohol (abbreviated IPA). It is noted that H–ZSM-5 having an Al content of 2.63% gave PAA with a yield of 62.2% for 24 h of the reaction. This catalyst was far superior in yield to the other solid acids and liquid acids. Besides the zeolite, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Amberlyst gave PAA, but the yields were only 10%. $H_3PW_{12}O_{40}$ worked as the liquid acid and gave the yield of 15.5%. H_2SO_4 was not effective under these reaction conditions.

The percentage-conversion of acrylonitrile (abbreviated AN) and IPA are also provided in Table 2. The ratio in the conversion of IPA (or the yield of PAA) to that of AN should be 5, if the reaction took place without the side reactions, considering the molar ratio (=5) of AN to IPA in the reactant mixture. In addition, the yield of PAA should be equal to the conversion of IPA. However, the conversion of AN was higher than the value of the yield divided by 5, and the conversion of IPA was higher than the yield of PAA over H–ZSM-5. Side reactions such as dehydration of IPA to propene and/or diidopropyl ether (abbreviated as PE) took place. PE was formed, but the selectivity to PE was only 4% (Table 2). Propene was probably produced in the gas phase, while the gas phase was not quantitatively analyzed in the present study.

TABLE 1

The Amount of Acid, Pretreatment Conditions, and Surface Area

Catalyst	[Si]/[Al] ratio	Concentrations of acid sites (mmol · g^{-1})	Pretreatment conditions	Surface area ($m^2 \cdot g^{-1}$)
Solids				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$		0.15[a] (0.063)[b]	423 K, 3 h in He	130
HY		2.60[c]	673 K, 3 h in air	740
H–mordenite		1.40[c]	673 K, 3 h in air	371
SiO_2–Al_2O_3		0.35[c]	773 K, 3 h in air	560
SO_4^{2-}/ZrO_2		0.20[c]	773 K, 3 h in air	125
H–ZSM-5 (Al = 7.10%)	[13]	1.20[c]	773 K, 3 h in air	379
H–ZSM-5 (Al = 4.80%)	[20]	0.77[c]	773 K, 3 h in air	414
H–ZSM-5 (Al = 3.30%)	[30]	0.65[c]	773 K, 5 h in air	458
H–ZSM-5 (Al = 2.70%)	[36]	0.37[c]	773 K, 5 h in air	514
H–ZSM-5 (Al = 2.63%)	[37]	0.31[c]	773 K, 3 h in air	410
H–ZSM-5 (Al = 2.40%)	[40]	0.37[c]	773 K, 3 h in air	400
H–ZSM-5 (Al = 1.00%)	[95]	0.20[c]	773 K, 5 h in air	367
H–ZSM-5 (Al = 0.70%)	[150]	0.11[c]	773 K, 5 h in air	418
Organic resins				
Amberlyst 15		4.70[d]	as received	50
Nafion–H		0.80[d]	as received	0.02
Nafion–SiO_2		0.12[d]	as received	340
Aciplex–SiO_2		0.46[d]	as received	1.3
Liquids				
$H_3PW_{12}O_{40}$		1.0[a]	423 K, 3 h in He	—
H_2SO_4		20.4[a]	as received	—

[a] From chemical formula.

[b] Amount of surface.

[c] From TPD of NH_3.

[d] Ion exchange capacity.

TABLE 2

Yield and Selectivity of *N*-Isopropylacrylamide from Acrylonitrile and Isopropyl Alcohol over Acid Catalyst

Catalyst	Yield[a] (%)	TON[b]	Conversion[c] (%)		Selectivity[d] (mol %)		
			AN	IPA	PAA	AA	PE
Solid acids							
H–ZSM-5 (Al = 2.63%)	62.2	60.2	23.5	86.2	93.3	3.1	3.6
HY	7.4	0.8	9.7	37.0	52.6	7.9	39.5
H–mordenite	1.5	0.3	29.4	41.3	68.8	12.5	18.7
SiO_2–Al_2O_3	2.8	2.0	12.5	28.6	72.7	0.0	27.3
SO_4^{2-}/ZrO_2	7.7	11.5	6.7	40.0	54.8	4.7	40.5
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	10.0	47.6	21.5	50.0	74.7	5.1	20.1
Amberlyst 15	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
Nafion–H	6.0	2.1	20.5	57.5	46.9	16.7	36.4
Aciplex–SiO_2	6.5	4.2	17.6	48.3	34.4	12.4	53.2
Liquid acids							
$H_3PW_{12}O_{40}$	15.5	4.7	15.1	63.8	47.4	10.5	42.1
H_2SO_4[e]	4.8	0.4	29.4	65.5	27.5	39.2	33.3

Note. Reaction conditions: catalyst, 1.0 g; acrylonitrile, 150 mmol; isopropyl alcohol, 30 mmol; 423 K for 24 h.

[a] Yield = 100 × (mol of *N*-isopropylacrylamide)/(mol of isopropyl alcohol added initially).

[b] Number of *N*-isopropylacrylamide formed divided by the number of protons on the surface.

[c] The conversion is defined as (mol of acrylonitrile or isopropyl alcohol disappeared)/(mol of acrylonitrile or isopropyl alcohol present initially). Acrylonitrile and isopropyl alcohol are abbreviated AN and IPA.

[d] Selectivity to *N*-isopropylacrylamide is defined as 100 × (mol of *N*-isopropylacrylamide)/[(mol of *N*-isopropylacrylamide) + (mol of acrylamide) + (mol of diisopropyl ether)]. *N*-isopropylacrylamide, acrylamide, and diisopropyl ether are abbreviated PAA, AA, and PE, respectively.

[e] 0.18 g of the catalyst was used.

TABLE 3

Yield and Selectivity of *N*-Isopropylacrylamide from Acrylonitrile and Isopropyl Alcohol over H–ZSM-5

Al[a] (%)	Yield (%)	TON[b]	Conversion[b] (%)		Selectivity[b] (%)			Amount[c] $(\text{mmol} \cdot \text{g}^{-1})$	
			AN	IPA	PAA	AA	PE	C	N
7.10	18.0	4.5	23.5	70.3	82.5	15.8	1.7	—	—
4.80	32.9	12.8	25.0	76.9	86.8	9.0	4.2	23.6	4.8
3.30	33.3	15.4	23.5	70.0	88.5	7.1	4.4	10.8	2.2
2.70	43.3	35.1	20.0	78.6	89.0	5.5	5.5	11.8	2.3
2.63	52.2	50.5	11.1	71.0	92.0	4.6	3.4	10.9	1.7
2.40	42.5	34.5	6.5	68.8	87.9	5.3	6.8	—	—
1.00	38.3	57.5	7.8	65.0	90.9	4.7	4.4	—	—
0.70	23.6	64.4	6.2	33.3	88.3	4.8	6.9	11.5	1.8

Note. Reaction conditions: catalyst, 1.0 g; acrylonitrile, 150 mmol; isopropyl alcohol, 30 mmol; 423 K for 6 h.

[a] Al content.

[b] Yield, TON, conversion, and selectivity are the same as those in Table 2.

[c] Amounts of C and N atoms remaining on the surface measured by elemental analysis.

In addition, the conversions of AN higher than the value of the PAA yield divided by 5 might be brought about by the polymerization of AN, hydration of AN to acrylamide (abbreviated AA), and so forth. Since the selectivity to AA was 4%, the polymerization of AN might be appreciable. Similar trends were observed over the other solid acids, as shown in Table 2.

The conversion of AN over H–ZSM-5 (Al = 2.63%), 23.5%, can be divided into those to PAA (62.2/5 = 12.5%), AA (about 2%), and the polymer of AN (about 9%). In the cases of Amberlyst, Nafion, Nafion–SiO_2, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, the conversions of IPA were above 50%, while the yields were less than 10%, suggesting that dehydration of IPA to propene (including the polymers) is significant. While H–mordenite, Nafion–SiO_2, and H_2SO_4 gave the low yields, the conversions of AN were more than 29%, suggesting the preferential occurrence of the polymerization of AN. It should be emphasized that the selectivity to PAA was much higher (~94%) over H–ZSM-5 (Al = 2.63%) (Table 2). The TON, which is defined as the number of PAA molecules produced divided by the number of acid sites on the surface, reached 60 over H–ZSM-5 (Al = 2.63%) at 24 h. This shows that the reaction proceeded catalytically on H–ZSM-5. Furthermore, it is noted that H–ZSM-5 (Al content = 2.63%) gave the highest TON among these solid acids.

Table 3 gives the catalytic data on the reaction of AN with IPA over various H–ZSM-5s having different Al content. The data were collected at 6 h and 423 K. The yield of PAA depended greatly on the Al content of H–ZSM-5. The yield once increased as the Al content increased and then decreased through a maximum at 2.63% of the Al content. As shown in Table 3, the remaining amounts of nitrogen atoms after the reaction (6 h) became larger at higher Al contents. The largest amount of the N atom (4.8 mmol g^{-1}) corresponds to only about 3% of the amount AN presented initially. On the other hand, the remaining carbon atoms for all cases were about five times those of the N atoms.

Figure 1 shows the time courses of the reaction of AN with IPA at 423 K over H–ZSM-5s with different Al content. As shown in Fig. 1, the reaction took place rapidly at the initial stage over all these H–ZSM-5s, but the reaction rates became lower gradually. Figure 2 presents time courses of the accumulation of N atoms during the reaction. There are trends showing that the accumulated amount of N atom increased as the Al content increased.

Figure 3 shows the acid amount (Fig. 3A), the initial rates of the reaction, and N atom accumulation (Fig. 3B) as a function of the Al content. The acid amounts were estimated from the TPD spectra of NH_3. Both the initial rates were obtained from the slopes of the curves of Figs. 1 and 2. The acid amount increased nearly linearly with the Al content (Fig. 3A). As Fig. 3B shows, the rate of N atom accumulation correlates well with the Al content, that is, the

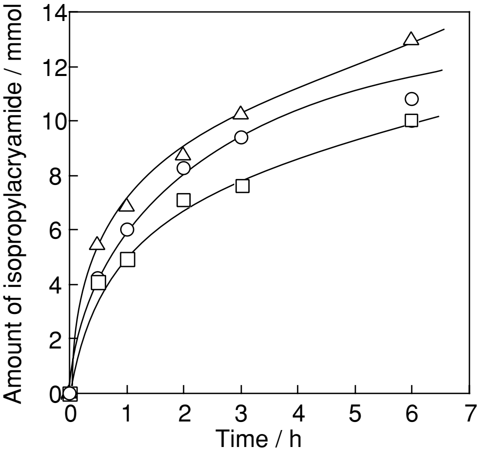

FIG. 1. Time courses of reaction of acrylonitrile and isopropyl alcohol over various H–ZSM-5s. Al content: (□) 3.30%, (○) 2.63%, and (△) 1.00%. Reaction conditions: catalyst, 1 g; temperature, 423 K. Acrylonitrile, 10 cm^3 (150 mmol), isopropyl alcohol, 2.2 cm^3 (30 mmol), and hydroquinone (0.05 g) as an inhibitor of polymerization and *n*-dodecane (0.25 cm^3) as an internal standard were mixed.

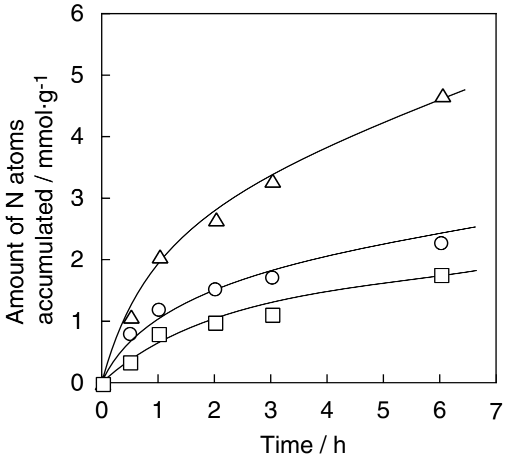

FIG. 2. Time courses of the accumulation of N atoms. The reaction conditions are the same as in Fig. 1. Al content: (□) 3.30%, (○) 2.63%, and (△) 1.00%.

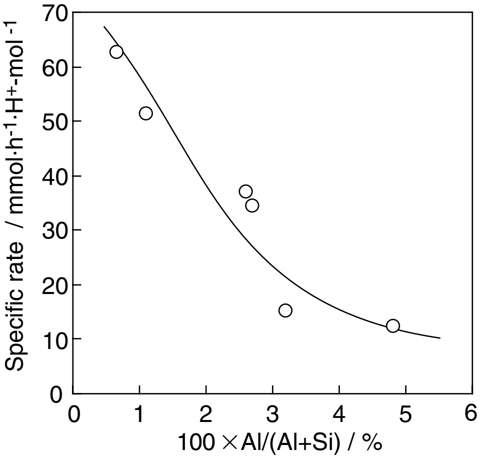

FIG. 4. Specific rate as a function of the Al content of H–ZSM-5.

acid amount. On the other hand, the initial rate for the formation of PAN became a near-saturated value or became lower with a further increase in the Al content.

Figure 4 provides the dependence of the specific rate on the Al content. It is clear that the specific activity decreased to about one-sixth as the Al content increased from 0.7 to 9.8%.

Reusability of H–ZSM-5 (Al content = 2.63%) is given in Fig. 5. When the reaction was repeated over the used catalyst without any treatment, the reaction hardly occurred; the yield was only 3% after 6 h. On the other hand, when the used catalyst was calcined at 773 K for 5 h in air, the catalyst became active again. The obtained yield and the selectivity to PAA are plotted against the number of repeated run. It should be emphasized that the decrease in the yield with the run number was slight and the selectivity gradually increased with the run number.

Changes in the surface area and pore volume of H–ZSM-5 (Al content = 2.63%) with the reaction and the calcination were measured. The total surface area of the H–ZSM-5 dropped greatly, from 410 to 16 m^2 g^{-1}, after the first reaction. By the calcination of the used catalyst at 773 K in air, the surface area almost recovered.

In Fig. 6, infrared spectra of used H–ZSM-5 (Al content = 2.63%) and the polymers of the product and reactant are given, together with the spectrum of H–ZSM-5 on which the product PAA was adsorbed. The used H–ZSM-5 which was dried at 373 K showed several peaks consisting of the

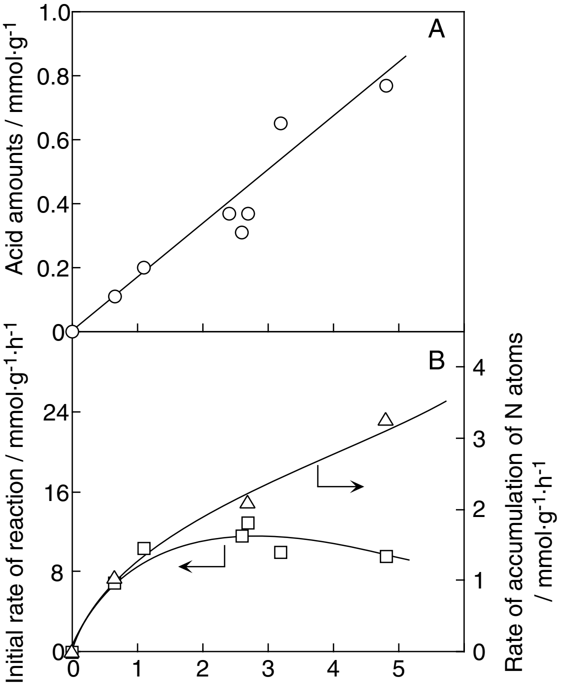

FIG. 3. Effects of Al content of H–ZSM-5 on the acid amount, the initial rate, and the rate of N atom accumulation. The reaction conditions are the same as in Fig. 1. The acid amounts were determined by NH$_3$ TPD.

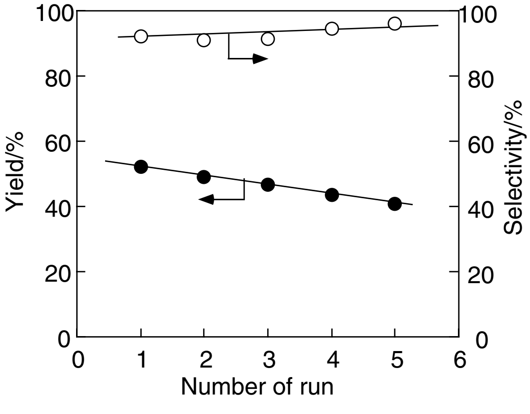

FIG. 5. Changes in yields and selectivities for the reaction of acrylonitrile and isopropyl alcohol as a function of the number of repeated runs. Between the runs, the catalyst was calcined at 773 K in air for 5 h. The reaction conditions are the same as those in the caption to Fig. 1.

first group (1460 cm^{-1}, 1544 cm^{-1} (NH), 1626 cm^{-1} (C=C), and 1657 cm^{-1} (C=O)), the second characteristic peak at 2244 cm^{-1} (CN), and the third group (2870 cm^{-1}, 2937 cm^{-1}, and 2970 cm^{-1}), together with the broad peak around 3400 cm^{-1} due to the OH region. Since the peak of the CN group in AN appears at 2230 cm^{-1}, the peak at 2244 cm^{-1} observed for PAN (Fig. 6d) can be distinguished from that of AN. The peak at 2244 cm^{-1} of the used H–ZSM-5 (Fig. 6a) is thus assigned to the PAN formed on the catalyst. On the other hand, the peaks of 1544 cm^{-1} and 2970 cm^{-1} were not detected for PAN but were found for poly-*N*-isopropylacrylamide (PPAA) or PAA adsorbed on H–ZSM-5 (Figs. 6b and 6c). This shows that PPAA and/or PAA were present on the surface of H–ZSM-5 after the reaction.

Adsorptions of product molecules were examined on H–ZSM-5 (Al content = 2.63%). Figure 7 shows the time courses of the adsorption of PAA at 298 K on H–ZSM-5 (Al content = 2.63%). When the solution of 1,3,5-trimethylbenzene containing PAA (0.41 mol dm^{-3}) was used, about 1.5 mmol g^{-1} of PAA was rapidly adsorbed on H–ZSM-5 (Fig. 7a). When AN (5 cm^3) was further added to the 1,3,5-trimethylbenzene solution, most of the PAA adsorbed in the micropores of H–ZSM-5 was desorbed rapidly at 298 K. It was confirmed that the adsorption amount was only 0.2 mmol g^{-1} on H–ZSM-5 (not shown), when AN was used as the solvent instead of 1,3,5-trimethylbenzene.

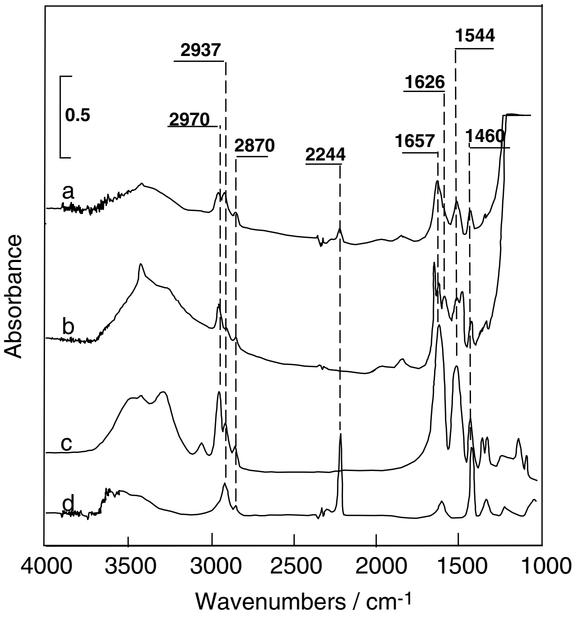

FIG. 6. Infrared spectra of used H–ZSM-5 catalysts. (a) The used H–ZSM-5 (Al content = 2.63%) for the reaction of acrylonitrile and isopropyl alcohol at 423 K, (b) H–ZSM-5 (Al content = 2.63%) on which *N*-isopropylacrylamide was adsorbed, (c) poly-*N*-isopropylacrylamide (PPAA), and (d) polyacrylonitrile (PAN). The adsorption of *N*-isopropylacrylamide was carried out at room temperature for 5 h in 1,3,5-trimethylbenzene.

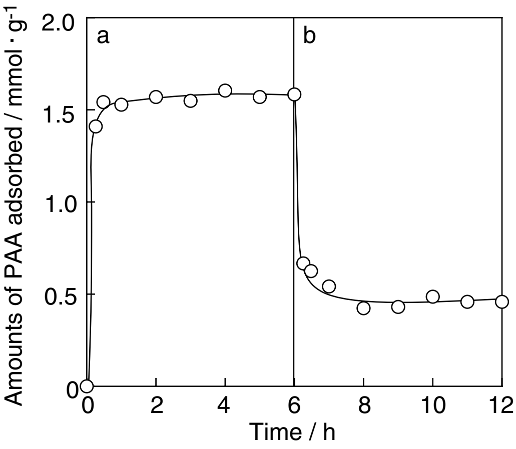

FIG. 7. Adsorption and desorption of *N*-isopropylacrylamide on and from H–ZSM-5 (Al content = 2.63%). (a) Fresh H–ZSM-5 (0.72 g) was added to a solution of *N*-isopropylacrylamide, 2.06 mmol (0.233 g), and 1,3,5-trimethylbenzene (5 cm^3) at room temperature. (b) Following (a), acrylonitrile (5 cm^3) was added to the solution.

Influence of the polymer of AN formed on H–ZSM-5 on the activity and selectivity was examined. After H–ZSM-5 (Al content = 2.63%, 1 g) was treated with AN (150 mmol) at 423 K for 6 h, the H–ZSM-5 was separated and then evacuated at 373 K for 3 h. The AN-treated H–ZSM-5 gave only a 7.1% yield at 6 h, which is one-sixth that of the fresh H–ZSM-5 (Table 3) under the same reaction conditions. When excess IPA (10 cm^3, 136 mmol) was added to the H–ZSM-5 (1 g) at 423 K for 6 h in the presence of dodecane (0.25 cm^3) and hydroquinone (0.05 g), the conversion of IPA was 62.4%, and the conversion to diisopropyl ether was 44%. After the used catalyst was separated by centrifugation and dried at 373 K, the elemental analysis of the used catalyst showed that the amount of remaining carbon atoms was 5.98 mmol g^{-1}. The IPA-tretated H–ZSM-5 gave a yield for PAA of 20%, which is about half that of the fresh catalyst. The surface area and the pore volume decreased to 40% that of the fresh catalyst.

DISCUSSION

Catalytic Property of H–ZSM-5

In a commercial process, *N*-isopropylacrylamide has been synthesized with excess H_2SO_4. As described in the Introduction, the synthetic process using a solid acid catalyst is desirable from the standpoint of it being an environmentally benign process. The data in Table 2 demonstrate that H–ZSM-5 exhibited an exceptionally high catalytic performance for the reaction of AN (acrylonitrile) with isopropyl alcohol (IPA). This reaction proceeded on acidic sites, while the reaction mechanism has not been fully elucidated. Luzgin and Stepanov (18) studied the reaction of acetonitrile with *tert*-butyl alcohol over H–ZSM-5 by means of solid-state NMR. They claimed that an *N*-alkylnitrilium cation is formed as an intermediate by the attack of a *tert*-butyl cation on the CN bond on the surface. Thus one can consider that the acid strength and amount of a catalyst are primarily important for the catalytic performance.

As shown in Table 3 and Fig. 1, the change in the activity of H–ZSM-5 with the change in Al content was intriguing. Since the acid amount increased monotonically as the Al content increased (Fig. 3A), the highest activity of H–ZSM-5 with an Al content of 2.63% is not due to the acid amount. The acid strength increases as Al content decreases for H–ZSM-5 zeolites (19), while Niwa and Katada (17) showed that the difference in acid strength was not significant for Al content between 4.80 and 2.63%. Indeed, the trend in the change in specific activity (Fig. 4) is consistent with that of acid strength, but the significant change in specific activity would not be only due to that of acid strength.

Ammonia TPD (20, 21) and microcalorimetry of NH_3 adsorption (13) revealed that H–ZSM-5 (Al content = 4.8%) was a weaker acid than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Also it was shown (17) that H–ZSM-5 with an Al content of 2.63% was a weaker acid than H–mordenite. Since the acid strength of H–ZSM-5 used in the present study is not higher than those of the above-mentioned solid acids, the exceptionally high activity of H–ZSM-5 (Table 2) suggests that the catalytic performance is not determined only by the acid strength.

As an important characteristic of H–ZSM-5, hydrophobicity should be considered. Some researchers inferred that the hydrophobicity of H–ZSM-5 becomes high as the Al content decreases (22, 23). Therefore the specific activity of H–ZSM-5 might be affected by the hydrophobic circumstance of the pores as well as by the acid strength (Fig. 4). Since isopropyl alcohol is more basic than acrylonitrile, isopropyl alcohol interacts more strongly with the acid sites of H–ZSM-5, which brings about the inhibition of the reaction. However, the adsorption of isopropyl alcohol would be effectively suppressed due to the increase in the hydrophobicity as the Al content decreased. By this the reaction may proceed smoothly due to the weakening of the inhibition effect of isopropyl alcohol. One can consider that water formed during the reaction poisons the catalyst. It is thus expected that the high hydrophobicity of the H–ZSM-5 with the low Al contents is also favorable to this water-participating reaction. As another possible factor influencing the activity and selectivity, the crystallite size should be considered. However, the effects of the crystallite size of H–ZSM-5 with the same Al content were not examined in the present study; these still remain to be solved.

It should be emphasized that the value of TON obtained for H–ZSM-5 (Al content = 2.63%) was higher than that of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Recently, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was reported to be highly hydrophobic (24). The density of water adsorbed on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at 298 K and 0.04 of the relative pressure of water was comparable to that of H–ZSM-5 (Al content = 2.63%), indicating similar hydrophobicity. It was already reported by us that for catalytic synthesis of *N*-adamantylacrylamide from acrylonitrile and 1-adamantanol, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was superior to various solid acids, such as H–ZSM-5, mordenite, HY, and so forth, and to liquid acids such as H_2SO_4 and $H_3PW_{12}O_{40}$ (7). Furthermore, as described above, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was more active than H–ZSM-5 for the synthesis of *N*-*tert*-butylacrylamide from *tert*-butyl alcohol. Since $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has mesopores (width, 40 nm) and at the same time micropores having widths larger than 0.75 nm (13), there is little restriction of diffusion of molecules (or products) into or out of the pores of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Thus it is reasonable that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has much higher activity for reactions concerning bulky reactants. The lower activities of H–ZSM-5 for the above reactions are due to the limitation of the diffusion of reactant or product molecules or the limitation of the formation of the intermediates in the pore.

In spite of the lower acid strength of H–ZSM-5 than of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and their similar hydrophobicity, as described above, H–ZSM-5 was more active than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Table 2) for the reaction with IPA. The microporous structure of H–ZSM-5 may be another critical factor governing specific activcity. At present, we speculate that the pore structure of H–ZSM-5 may be favorable for this reaction. For example, the reactant molecules are likely to be arranged in positions in the constrained pores of H–ZSM-5 (pore width, 0.54 × 0.56 nm) suitable for accelerating the reaction.

Catalyst Deactivation and Reusability

Although the reaction of AN and IPA proceeded catalytically on H–ZSM-5, the deactivation of H–ZSM-5 was severe. The reaction rate became lower at the latter stage of the reaction (Fig. 1). The extent of the deactivation seems to be nearly independent of the Al content. Plausible reasons for the deactivation are blockages of the pores by the polymers formed from the reactant AN or product PAA and/or by the irreversible adsorption method of product PAA. As described above, the considerable blockage of the pores was revealed by the adsorption of N_2.

As can be seen in Fig. 7, the product PAA can readily enter into the pores of H–ZSM-5 even at 298 K. Thus the possibility of the blockage by the adsorption of PAA can be excluded. Elemental analysis confirmed that the carbon and nitrogen atoms accumulated appreciably on H–ZSM-5s (Table 3). IR data indicated that PAN was present on the used H–ZSM-5 as well as the polymer of PAA (PPAA) (Fig. 6). Since the activity of H–ZSM-5 became about one-sixth after treatment with only AN, the main species responsible for the deactivation is probably PAN. The cross section of AN is estimated to be 2.5×10^{-19} m^2 from the molecular weight and the density in liquid state (25). Assuming that one nitrogen atom corresponds to one unit of AN monomer in the PAN on the surface, the surface area of the PAN formed corresponds to about 20 times that of the external surface area of H–ZSM-5. Thus the blockage of the pores of the PAN is plausible.

As described above, the carbon atom detected on the H–ZSM-5 was about five times that of the N atom (Table 3). The carbon deposition might be brought about from PAN (three times that of N atoms = about 5.1 mmol g^{-1}) and from IPA (6.0 mmol g^{-1}).

The reusability of deactivated H–ZSM-5 was confirmed (Fig. 5). By calcination at 773 K, the activity of used H–ZSM-5 was recovered mostly, and at the same time the pore volume was also restored. These results also support the idea that the deactivation of the catalyst would be caused by the blockage of the pores. However, this regeneration requires high temperature; in other words, this treatment is costly. An improved process for suppressing deactivation is necessary for this catalytic system.

CONCLUSION

We found that H–ZSM-5 was exceptionally effective for the *N*-alkylaltion of acrylonitrile with isopropyl alcohol to *N*-isopropylacrylamide in a solid–liquid reaction system. The microporous structure of H–ZSM-5 may be critical for this reaction. The Al content affected product yield and the catalyst having the Al content of 2.63% was most active among H–ZSM-5s. This unique activity pattern is due to the hydrophobicity as well as the acid strength. The catalyst deactivation might be caused mainly by the covering of the surface of the catalyst with polyacrylonitrile formed during the reaction and blockage of the pores. It should be emphasized that the catalytic activity was almost recovered by calcination of the catalyst in air.

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