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Catalytic synthesis of N-alkylacrylamide from acrylonitrile and 1-adamantanol with a novel solid heteropoly compound

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Catalytic synthesis of N-adamantylacrylamide from acrylonitrile and 1-adamantanol has been studied over various solid and liquid acids. Solid acids such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, Amberlyst 15, Nafion, and Nafion–SiO_2 composite gave yields higher than 97% at 373 K, and were superior in yield to liquid acids like *p*-toluenesulfonic acid, $H_3PW_{12}O_{40}$, and H_2SO_4. It was further demonstrated that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ exhibited the highest catalytic performance for this reaction in the presence of excess water.

Keywords: heteropoly compound, acidic Cs salt of heteropoly acid, N-alkylacrylamide, acrylonitrile, adamantanol, solid acids, liquid acids

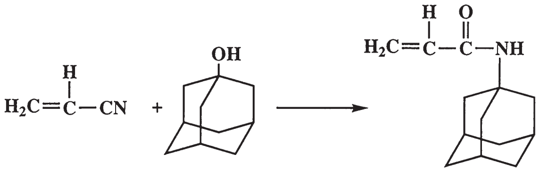
1. Introduction

N-alkylacrylamides such as N-*sec*-propyl- and N-*tert*-butylacrylamide are important monomers for water-soluble polymers which are potentially valuable as sizing agents, thickeners, water-soluble fibers and so forth [1]. At present, these amides are commercially produced from acrylonitrile and 2-propanol or *tert*-butanol with excess H_2SO_4 as Ritter et al. [2] first reported five decades ago. However, since these processes contain disposal and toxicity problems, environmentally benign solid catalysts in the place of H_2SO_4 are desirable.

Besides H_2SO_4, BF_3 and $(CF_3SO_2)_2O$ showed activities for the reaction of acrylonitrile and benzyl alcohol [3], but these catalysts are also toxic. It was reported that a Pd compound, $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$, was effective for the reaction between acetonitrile and *tert*-butanol in a homogeneous system [4], while this system has a difficulty in product separation. Nafion-H, which is a commercial catalyst for various acid-catalyzed reactions [5], was reported to be active for this reaction with acetonitrile and benzyl alcohol [6].

Heteropoly acids have been recognized as excellent acid catalysts and have been actually utilized in some industrial processes [7–11]. Owing to their strong acidities [12,13], they showed very high catalytic activities for various kind of reactions [7–11]. Among the heteropoly compounds, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an intriguing solid acid especially in solid–liquid reaction systems, because of the high surface acidity (large quantity of acid sites on the surface), insolubility in water or polar solvents, mesoporous structure, etc. [7,14]. Recently, some results as for the catalysis by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ have been reported [14–18]. However, to our knowledge, there is no report about the N-alkylation of nitrile by heteropoly compounds.

Here we wish to report results of a study on N-alkylamide synthesis from acrylonitrile and 1-adamantanol (Ritter-type reactions [2]) (equation (1)) catalyzed by prominent solid acids including $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. We found that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was catalytically active for the reaction to give the correponding N-alkylamide with a high yield, especially even in the presence of excess water.



(1)

2. Experimental

2.1. Materials

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5) was prepared by a titration method using aqueous solutions of $H_3PW_{12}O_{40}$ (Nippon Inorganic Color and Chemicals Co.) and Cs_2CO_3 (Merck) as described previously [12]. As reference, HY (reference catalyst of the Catalysis Society of Japan, JRC-Z-HY 4.8), H-ZSM-5 (Tosoh, HSZ-860HOA), H-mordenite (reference catalyst of the Catalysis Society of Japan, JRC-Z-HM20(3)), SiO_2–Al_2O_3 (reference catalyst of the Catalysis Society of Japan, JRC-SAL (Al = 13.6%)), and sulfated ZrO_2 which was prepared according to the literature [19] were used. These solid acids were pretreated in a flow of He at elevated temperatures (473 K for Cs2.5 and 573 K for the other solid catalysts) prior to use for the reaction. As organic resins, Amberlyst 15

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(Organo Co.), Nafion (NR-50, Du Pont), Nafion–SiO_2 composite (SAC 13, Nafion 13 wt%, Du Pont) [20], Amberlite 200C (Organo Co.) were used as received. *Para*-toluenesulfonic acid monohydrate (abbreviated PTS, Wako Pure Chemicals Co.), H_2SO_4 (Wako Chemicals Co.) and $H_3PW_{12}O_{40}\cdot 6H_2O$ were used as liquid acids.

2.2. Catalytic reaction

The reaction was carried out at 373 K in a pressure batch reactor (Pyrex, about 25 cm^3) with acrylonitrile (4 cm^3 (60 mmol)), 1-adamantanol (0.2 g (1.3 mmol)), and dodecane (0.1 cm^3) as an internal standard. In addition, hydroquinone (10 mg) was added to the reactant solution as an inhibitor for polymerization. Water present as an impurity in acrylonitrile was removed with Molecular Sieve 5A which was calcined at 573 K in air. After the air of the reactor was replaced by nitrogen, the catalyst (0.2 g) was added to the solution. The reactor was heated at 373 K with an oil bath and the reaction was performed with vigorous stirring by using a magnetic stirrer. In some cases, water (0.24 cm^3 (13 mmol)) was added to the reactant solution to examine the influence of water on activity and selectivity. The reactants and products were analyzed with an FID gas chromatograph (Shimadzu GC14B) with a column of Carbowax 300 M Chromosorb WAW (2 m).

3. Results and discussion

The yield and selectivity of N-adamantylacrylamide (abbreviated as NAA) at 373 K are summarized in table 1. Among solid oxide catalysts, Cs2.5 was found to be most active; the yield of NAA reached 97% at 373 K for 6 h. The selectivity to NAA, which is defined as $100 \times (\mathrm{NAA})/[(\mathrm{NAA}) + (\mathrm{AA})]$ (%), was about 93% over Cs2.5, where AA denotes acrylamide which is a by-product by the reaction between acrylonitrile and water contained in the reactant and/or catalyst. The formation of dehydration products (olefin and ether) from 1-adamantanol was confirmed to be negligibly small over all catalysts.

As shown in table 1, turnover number (designated as TON) for the formation of NAA reached 42 over Cs2.5, where TON is defined as the number of NAA formed divided by the number of acid sites in the catalyst. When the TON was calculated on the basis of the surface acidity of Cs2.5 (60 $\mu\mathrm{mol\,g^{-1}}$) [12], it became higher than 100. These results clearly indicate that the reaction proceeded catalytically over Cs2.5. While HY zeolite showed an activity, the yield and selectivity were less than those over Cs2.5. H-ZSM-5 showed a low yield, which is probably due to limitation of the diffusion of the bulky alcohol into the constrained pores. H-mordenite, SiO_2–Al_2O_3, and SO_4^{2-}/ZrO_2 gave poor activities.

Table 1
Yield and selectivity for N-adamantylacrylamide synthesis from acrylonitrile and 1-adamantanol at 373 K.[a]

Catalyst[b]	SA[c] ($m^2\,g^{-1}$)	Acidity[d] (μmol g^{-1})	Yield[e] (%)	Selectivity[f] (%)	TON[g]
Oxides					
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	130	150	97	92.6	42
HY	740	2600	79	89.3	2
H-ZSM-5	400	390	17	100	3
SO_4^{2-}/ZrO_2	125	200	9	100	3
H-mordenite	371	700	6	100	0.6
SiO_2–Al_2O_3	560	350	6	100	1
Organic resins					
Amberlyst 15	50	4700	100	80.6	1
Nafion	0.02	800	98	91.7	8
Nafion–SiO_2[h]	340	120	97	93.5	53
Amberlite 200C	39	4300	2	–	0
Liquid acids					
$H_3PW_{12}O_{40}$[i]	–	1000	95	72.5	6
PTS[j]	–	5741	89	55.6	1
H_2SO_4	–	1980	0[k]	–	–

[a] Reaction conditions: acrylonitrile 60 mmol, 1-adamantanol 1.3 mmol, 373 K for 6 h.

[b] Catalyst weight 0.2 g.

[c] Surface area.

[d] The amount of acid sites in the catalyst.

[e] $100 \times$ [N-adamantylacrylamide]/[1-adamantanol added initially].

[f] $100 \times$ [N-adamantylacrylamide]/([N-adamantylacrylamide] + [acrylamide]).

[g] Turnover number; the number of N-adamantylacrylamide formed divided by the number of acid sites in the catalyst.

[h] Nafion–SiO_2 composite (SAC 13, Nafion 13 wt%, Du Pont).

[i] Hexahydrate.

[j] *p*-toluenesulfonic acid (monohydrate).

[k] Acrylonitrile was polymerized.

Table 2
Yield and selectivity for N-adamantylacrylamide synthesis from acrylonitrile and 1-adamantanol in the presence of excess water at 373 K.[a]

Catalyst	Yield[b] (%)	Selectivity[c] (%)	TON[d]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	84	92.6	36
HY	8	82.0	0.2
Amberlyst 15	68	82.0	1
Nafion	77	84.0	6
Nafion–SiO_2	40	93.5	22

[a] Reaction conditions: acrylonitrile 60 mmol, 1-adamantanol 1.3 mmol, water 13 mmol, catalyst 0.2 g, 373 K for 6 h.

[b] 100 × [N-adamantylacrylamide]/[1-adamantanol added initially].

[c] 100 × [N-adamantylacrylamide]/([N-adamantylacrylamide] + [acrylamide]).

[d] Turnover number; the number of N-adamantylacrylamide formed divided by the number of acid sites in the catalyst.

Among organic resins, Amberlyst, Nafion-H, and Nafion–SiO_2 composite exhibited high activities. The TON and selectivity over Nafion–SiO_2 composite were comparable to those over Cs2.5. The liquid acids, PTS and $H_3PW_{12}O_{40}\cdot 6H_2O$, also gave considerably high yields, while the selectivities were low. Under these conditions, $H_3PW_{12}O_{40}\cdot 6H_2O$ was present as homogeneous catalyst, while at temperature lower than 353 K, it was insoluble in the reactant solution. The lower selectivities over PTS and $H_3PW_{12}O_{40}\cdot 6H_2O$ are probably due to the large quantities of water in these catalysts; PTS and $H_3PW_{12}O_{40}\cdot 6H_2O$ (0.2 g) contain 1.05 and 0.52 mmol of water, respectively. H_2SO_4 brought about mainly the polymerization of acrylonitrile under these reaction conditions, while it was confirmed that, when the reaction was carried out at 323 K with excess amounts of H_2SO_4, NAA was produced with a high yield.

Table 2 provides the yields and selectivity in the presence of excess water (molar ratio of water to 1-adamantanol = 10) in the reactant solution. The yield declined by the addition of water over all the solid catalysts. However, it should be emphasized that the yield of NAA was still high (84%) over Cs2.5. Further, it is noted that the selectivity to NAA was almost retained over Cs2.5 even in the presence of water, in contrast to the results over the other solid acids such as HY, Amberlyst, and Nafion (table 2).

This water-tolerant property of Cs2.5 pointed out in the present study is understood by the hydrophobic nature of the surface. We already reported that the adsorption of water on the surface of Cs salts like $Cs_3PW_{12}O_{40}$ (Cs3) and Cs2.5 was greatly suppressed [21], similarly to the case of H-ZSM-5. By comparison of the H_2O isotherms between Cs2.5 and Cs3, the average number of water molecules adsorbed on the H^+ of Cs2.5 was estimated to be 2.9 molecules at the relative pressure of 0.5 and room temperature [21]. This is in contrast with the case of the acid form, $H_3PW_{12}O_{40}$; $H_3PW_{12}O_{40}$ forms $H_3PW_{12}O_{40}\cdot 29H_2O$ [22]. Thus the water adsorption indicates that H^+ on Cs2.5 is present in a circumstance in which water molecules are rather excluded.

As a matter of fact, among solid oxide catalysts, Cs2.5 was reported to be especially active for hydrolysis of esters and hydration of olefins in a solid–water reaction system [23,24]. Together with the hydrophobicity, the strong acidity of Cs2.5 [12] is responsible for the high catalytic performance for the Ritter-type reaction in the presence of excess water. In conclusion, Cs2.5 catalyst is a promising solid acid for this useful reaction and a candidate as a solid acid for environmentally friendly catalytic processes.

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