Improvement of Catalyst Activity in the Ru-catalyzed Dimerization of Acrylonitrile by Using Diphenyl Ether as a Solvent

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For the catalyst system of ruthenium and carboxylic acid, which is useful for the efficient tail-to-tail dimerization of acrylonitrile, the TON increases as the ruthenium catalyst concentration is decreased. Furthermore, the addition of aromatic solvents of equal volume to that of acrylonitrile improves the catalyst activity. Especially, the use of diphenyl ether leads to a 1.7 time improvement of the TON.

The dimerization of acrylonitirile (AN) has provided an attractive alternative route to conventional industrial methods for the preparation of hexamethylenediamine, which is one of the monomers used in the production of Nylon-6,6.[1,2] Ruthenium-based catalysts have been important candidates for this reaction due to their high reactivity and selectivity for linear dimers 1–3.[3,4] In the Ru-catalytic system, the inevitable use of hydrogen as an extra agent to keep the reaction catalytic has resulted in the formation of a large amount of propionitrile (PN) (5) as an undesirable by-product.[3]

Recently, we have found that a new catalytic system [$RuCl_2(DMSO)_4$/CH_3CH_2COONa/DMSO/carboxylic acid] gives linear dimers of AN without the formation of PN (Scheme 1).[5] The reaction could be carried out neat, which would be an advantage in a large-scale operation.

In order to improve catalyst efficiency, we studied the effect of ruthenium catalyst concentration on the TON values for the dimerization of AN. Table 1 shows the effect of the molar ratio of Ru/AN on the dimerization of AN at 150 °C in the presence of o-benzoylbenzoic acid, which was the most suitable carboxylic acid for the catalytic system [$RuCl_2(DMSO)_4$/CH_3CH_2COONa/DMSO/carboxylic acid].[5,6] Products were analyzed by gas chromatography using anisole as an internal standard.

Decreasing the molar ratio of AN/Ru gave poorer yields of the dimers 1–3. Conversely, the TON for dimers 1–3 increased with the reduction of ruthenium catalyst concentration. The TON for dimers 1–3 rose up to 1240 when the molar ratio of
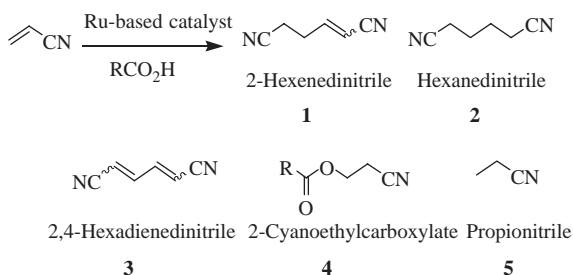
Table 1. Effect of the molar ratio of AN/Ru on the dimerization of AN using the combination of Ru-based catalyst and o-benzoylbenzoic acid[a]

AN/Ru	Conversion of AN/%	Combined yield[7] of dimers 1–3/%	TON[8]
3700[b]	28.8	21.4	792
	(0.430/0.479/0.014/0.041/0.021/0.015)[c]		
7400[b]	15.5	13.0	960
	(0.433/0.482/0.012/0.038/0.019/0.015)[c,9]		
10000[d]	13.1	10.3	1030
	(0.441/0.485/0.012/0.030/0.017/0.015)[c]		
15000[d]	9.0	7.2	1077
	(0.460/0.486/0.011/0.026/0.014/0.013)[c]		
20000[d]	7.2	6.2	1240
	(0.460/0.485/0.010/0.023/0.010/0.011)[c]		
25000[d]	4.9	4.0	997
	(0.462/0.483/0.010/0.023/0.011/0.011)[c]		

[a]Reaction conditions: (General procedure) AN 282.7 mmol, anisole 18.5 mmol, DMSO 6.4 mmol, $CH_3CH_2CO_2Na$ 0.306 mmol, $RuCl_2(DMSO)_4$ 0.0283 mmol, AN/Ru = 10000 (molar ratio), o-benzoylbenzoic acid 5.70 mmol, 150 °C, 9 h. See Supporting Information for details. See also Ref. 10. [b]Reaction time 6 h. [c]Molar ratio of dimers 1–3: cis-1/trans-1/cis,cis-3/cis,trans-3/trans,trans-3/2. [d]Reaction time 9 h.

AN/Ru was 20000. This result shows that lower catalyst concentration induces higher catalyst efficiency. However, contrary to our expectation, the TON for dimers 1–3 decreased when the molar ratio of AN/Ru was higher than 20000. Lower catalyst concentration induced slight increase of the production ratio of 2,4-hexadienedinitrile (DCBD 3). DCBD 3 may affect the catalyst activity. The TON for dimers 1–3 went down to under 1000 when the molar ratio of AN/Ru was 25000. In this case the dimerization reaction had poor reproducibility.

Thus, we examined the addition of a volume of solvent equal to that of AN to the reaction mixture in order to decrease catalyst concentration, while maintaining the molar ratio of AN/Ru (10000). Table 2 shows the additive effect of the solvents on the dimerization of AN. The dimerization of AN in saturated hydrocarbon solvents such as hexane and cyclohexane gave slightly reduced TONs compared to that without added solvent. Nevertheless, the addition of hydrocarbon solvents gave little adverse influence on the dimerization of AN. Unsaturated hydrocarbons such as cyclohexene, and toluene provided somewhat better results. Diphenyl ether turned out to be the most favorable solvent for the catalytic dimerization of AN in this experiment. The combined yield of dimers 1–3 became 18.1%

Scheme 1.

1 2-Hexenedinitrile
2 Hexanedinitrile
3 2,4-Hexadienedinitrile
4 2-Cyanoethylcarboxylate
5 Propionitrile

Table 2. Additive effect of solvents on the dimerization of AN using the combination of Ru-based catalyst and *o*-benzoylbenzoic acid[a]

Solvent	Conversion of AN/%	Combined yield[7] of dimers **1–3**/%	TON[8]
t-Butanol	8.7	6.7	675
	(0.441/0.506/0.010/0.025/0.014/0.004)[b]		
THF	10.8	8.9	890
	(0.472/0.475/0.009/0.024/0.014/0.007)[b]		
Hexane	11.5	9.7	972
	(0.473/0.475/0.009/0.024/0.012/0.007)[b]		
Cyclohexane	11.5	9.9	986
	(0.473/0.476/0.009/0.023/0.013/0.006)[b]		
Cyclohexene	12.9	10.8	1083
	(0.474/0.475/0.009/0.022/0.013/0.007)[b]		
Toluene	13.3	11.3	1125
	(0.473/0.477/0.008/0.023/0.013/0.006)[b]		
Diphenylether	20.3	18.1	1797
	(0.475/0.477/0.008/0.022/0.012/0.006)[b]		

[a]Reaction conditions: reaction mexture (AN/Ru = 10000, Table 1)/solvent = 1 (v/v), 150 °C, 9 h. See Supprting Information for details. See also Ref. 10. [b]Molar ratio of dimers **1–3**: *cis*-**1**/*trans*-**1**/*cis*,*cis*-**3**/*cis*,*trans*-**3**/*trans*,*trans*-**3**/**2**.

and the TON for dimers **1–3** rose up to 1797. It was 1.7 times higher than the TON in the solvent-free system. In addition, it was higher than when the TON was AN/Ru = 20000 under solvent-free condition. It seems that diphenyl ether has a favorable influence on the rate-determining step, in which the carboxylic acid allegedly cleaves the carbon–ruthenium bond of an intermediate ruthenium complex by means of protonolysis.[6,11] Aliphatic ether THF gave reduced TON. It contrasts with aromatic ether diphenyl ether. Alcoholic solvents, which have been often used in the catalytic dimerization of AN under hydrogen atomsplere, were not suitable for the catalytic dimerization of AN using the combination of the ruthenium-based catalyst and a carboxylic acid, as exemplified by *t*-butanol. No dimer was formed at all when *N*,*N*-dimethylformamide was used as the solvent. Judging from these results, it seems that the transition state of the protonolysis step is not very polar. This postulate is consistent with our previous results, which showed that the protonolysis step has a very early transition state.[6,11] Addition of solvents induced slight increase of the production ratio of DCBD **3**. It seems that the addition of solvents gives the formation of 2-hexenedinitrile (**1**), which is produced via protonolysis step, a slight advantage over the formation of DCBD **3**.

In conclusion, in the Ru-catalyzed dimerization reaction of AN, it was found that lower catalyst concentration gives higher TON for dimers **1–3** and the addition of a volume of diphenyl ether equal to that of AN to the reaction mixture increases the TON by 1.7 times (TON = 1797).

Further investigations on the additive effect of solvent are in progress.

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7 Combined yield of dimers **1–3** = 100 × [2 × (combined mols of dimers **1–3**)]/[mols of charged AN].

8 TON = [2 × (combined mols of dimers **1–3**)]/[mols of Ru]. The values are averages of three runs of which deviation was within 50.

9 The molar ratio of produced dimers **1–3** did not change largely even at a short reaction time of 0.5 h. See Supporting Information for details. See Ref. 10.

10 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chemlett/index.html.

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