Development of heterogeneous-homogeneous hybrid base catalyst

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Abstract: We demonstrate that CeO_2 modified with 2-cyanopyridine is effective for hydromethoxylation of acrylonitrile. The combination of CeO_2 and 2-cyanopyridine showed more than 2000-fold increase in reaction rate with high selectivity compared with CeO_2 or 2-cyanopyridine alone. The pK_a of the surface active sites on CeO_2 + 2-cyanopyridine was estimated to be 21, which is in superbase category. Therefore, it is suggested that a new strongly basic active site was established by the combination of heterogeneous CeO_2 and homogeneous 2-cyanopyridine.
Keywords: Cerium oxide, Base catalyst, Hybrid material.

1. Introduction

Hybridization of inorganic and organic components is one of the important methods for development of new catalysis concept. Among the hybrid materials, heterogeneous-homogeneous catalysts have attracted much attention because they show unique and exceptional properties derived from intimate interaction between the components. Base catalysts are important for organic synthesis because deprotonation is a key step in various organic reaction, and establishment of a new class of base catalysts is essential from academic and industrial viewpoints. To create a new base catalyst, hybridization of homogeneous and heterogeneous components is one of promising methods. Modification of metal oxides with organic compounds is known as a typical method for the hybridization technique. Recently, our group has reported that CeO_2 acts as a highly active catalyst at low temperatures (≤ 473 K) in liquid-phase organic reactions, which is derived from the unique acid-base property of CeO_2. As a target of heterogeneous component, CeO_2 is very attractive because of the unique property. In this study, we found that a combination catalyst of CeO_2 and 2-cyanopyridine formed by mixing these components acted as an efficient heterogeneous-homogeneous hybrid base for hydromethoxylation of acrylonitrile as a model base-catalyzed reaction.[1,2)]

2. Experimental

A typical procedure for nucleophilic addition of methanol to acrylonitrile was as follows: CeO_2 (Daiichi Kigenso Kogyo, calcined at 873 K for 3 h) 172 mg (1 mmol), 2-cyanopyridine (1 mmol) and methanol 0.64 g (20 mmol) were added to a reaction vessel capped by a rubber plug under air, and the mixture was vigorously stirred at 500 rpm at 323 K under air for 1 h. After the treatment, acrylonitrile 0.53 g (10 mmol) was added into the mixture, and the mixture was constantly stirred during the reaction at 323 K. The time when acrylonitrile was added into the reactor was defined as zero reaction time. The products were analysed by FID-GC. The surface of metal oxide was analyzed by BET and XRD analysis. Conversion ond yield were calculated on acrylonitrile basis.

3. Results and discussion

In order to develop the strategy, hydromethoxylation of acrylonitrile as a model base-catalyzed reaction was investigated using CeO_2 with various pyridine derivatives because it is known that pyridine can be adsorbed on the Lewis acid site of CeO_2 surface. Pyridine derivatives with OH, CH_3, OCH_3, $COCH_3$, CH_2OH, C_2H_5, $CONH_2$, CH_2OCH_3 or CN group were applied to the reaction. Only CeO_2 showed very low yield of 3-methoxypropionitrile (0.5%). In the case of CeO_2 with pyridine derivatives, the combination of CeO_2 and 2-cyanopyridine showed high yield of 3-methoxypropionitrile (20%), although the other pyridine derivatives showed low yield (<5%). The activity of the combination of CeO_2 and 2-cyanopyridine was more than 2000-fold reaction rate of that obtained with only CeO_2 or only 2-cyanopyridine. To confirm the necessity of CeO_2 in this system, we compared the reaction rates (V/mmolh^{-1}g$_{cat}^{-1}$) of various metal oxides modified with or without 2-cyanopyridine in the reaction. Figure 1 shows the reaction rates of only metal oxides and the hybrid system of metal oxides + 2-cyanopyridine. In the case of only metal oxides, almost no conversion was observed in this reaction. In the case of metal oxides with 2-cyanopyridine, rate enhancement was not observed over tested metal oxides except CeO_2 and La_2O_3, although the rate enhancement in the case of La_2O_3 was small (about two fold). These results indicate that the combination of CeO_2 and 2-cyanopyridine is essential for exhibiting high activity in this reaction system. Figure 2 shows the time course of the reaction over CeO_2 + 2-cyanopyridine. The reaction proceeded smoothly to reach almost 100% conversion in 12 h with >99% selectivity, affording 98% yield of the product. High selectivity was maintained at high conversion for prolonged reaction time (24 h). On the basis of the number of Ce cations on CeO_2 surface (1.13 mmolg^{-1}) calculated from the surface area of CeO_2 (86 m^{2}g^{-1}), the turnover number (TON) was calculated to be 50. Therefore, CeO_2 + 2-cyanopyridine catalytically promoted the reaction.

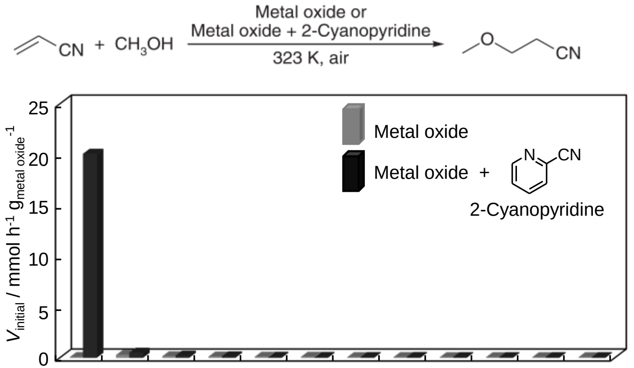

Figure 1. Comparison of hydromethoxylation of acrylonitrile over only metal oxides or the combination of metal oxides and 2-cyanopyridine. Conditions without 2-cyanopyridine: acrylonitrile (10 mmol), methanol (20 mmol), metal oxides (172 mg), 323 K, air, 12-48 h. Conditions with 2-cyanopyridine: acrylonitrile (10 mmol), methanol (20 mmol), metal oxides (172 mg), 2-cyanopyridine (2 mmol), 323 K, air, 0.5-48 h.

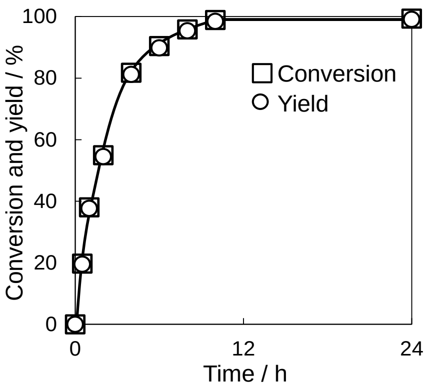

Figure 2. The time course of the reaction using the combination of CeO_2 + 2-cyanopyridine. Conditions: acrylonitrile (10 mmol), methanol (15 mmol), CeO_2 (1 mmol), 2-cyanopyridine (1 mmol), 323 K, air.

In order to determine the basicity of the active sites over CeO_2 + 2-cyanopyridine, hydromethoxylation of acrylonitrile was carried out using typical organic base compounds such as pyridine, 4-methoxypyridine, *N*,*N*-dimethylaminopyridine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The surface 2-cyanopyridine amount, which is the active site amount, was calculated from the job's plot of the reaction rate as a function of the molar ratio of the surface Ce amount to the sum of the surface Ce and 2-cyanopyridine amount. The value was estimated to be 0.28 mmol/g. The pK_a of CeO_2 + 2-cyanopyridine based on the active site was calculated to be about 21, which is in the category of superbases. This value was by far larger than those using only CeO_2 (estimated pK_a of the conjugated acid, 12) or only 2-cyanopyridine (estimated pK_a of the conjugated acid, 11), indicating that addition of 2-cyanopyridine to CeO_2 drastically increased the basicity by a factor of more than 10^9. Therefore, the strongly basic site was formed by hybridization of heterogeneous CeO_2 and homogeneous 2-cyanopyridine.

4. Conclusions

We developed a new hybrid base catalyst prepared by only mixing CeO_2 and 2-cyanopyridine and the hybrid catalyst was effective for hydromethoxylation of acrylonitrile. The combination of CeO_2 and 2-cyanopyridine has 2000-fold higher activity for the reaction than when only CeO_2 or 2-cyanopyridine is used. The pK_a of a new basic site composed of CeO_2 and 2-cyanopyridine was estimated to be 21, which is in the range of superbases.

References

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2. M. Tamura, R. Kishi, A. Nakayama, Y. Nakagawa, J. Hasegawa, K. Tomishige, J. Am. Chem. Soc., 139 (2017) 11857.