

論文の内容の要旨

論文題目 Investigation on base catalytic properties of nitrogen sites in nitrogen-containing porous materials (窒素含有多孔質材料における窒素種の塩基触媒特性に関する研究)

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Base catalysts are widely used in various industries such as fine chemicals, cosmetics, and pharmaceutical. There is a need from the viewpoint of green and sustainable chemistry to shift to an environmentally benign heterogeneous catalytic system because the homogeneous system has disadvantages associated with the separation and recycling of the catalysts. Nitrogen-containing materials such as nitrated silica, carbon nitride, and amine-functionalized silica have been reported as solid base catalysts. In these materials, various nitrogen sites have been reported to work as base sites.

In this dissertation, by comparing the properties of various nitrogen sites, effects of nitrogen sites on base catalytic properties were investigated. Based on the results, design guidelines for a novel solid base catalyst would be developed.

In Chapter 2, nitrogen sites in nitrated silica were studied. By comparing the catalytic properties of nitrated zeolite and nitrated delaminated zeolite, the effect of the type and location of nitrogen sites on the catalytic properties was discussed.

MCM-22 (Si/Al=15) was synthesized according to the previous works. Delaminated samples (MCM-22-Del) were prepared by swelling and dispersing the lamellar precursor, MCM-22(P). The swelling temperature and time were changed from 313 to 373 K and from 16 to 46 hours, respectively. Nitration of the samples was performed at 973 K in NH_3 flow. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was conducted as a model base reaction. The reactants (10 mmol each) and a catalyst (50 mg) were put in a flask with toluene (40 mL) and heated at 353 K for 24 h. The product was analysed by gas

chromatography.

The results of catalytic test showed that product yield increased monotonously with increase in reaction time over all the samples. The apparent initial product formation rates were calculated from the slope of initial 1 hour with a linear approximation. In order to figure out the key parameter affecting the catalysis, the formation rates were plotted as a function of textual properties (total surface area, total nitrogen content, external surface area, and external nitrogen content). A proportional relationship was observed only between the formation rate and the external surface area of the catalyst with the correlation coefficient of 0.74. This suggests that the reaction mainly proceeds on the external surface. However, this contradicts with the non-linear correlation with the external nitrogen content. Thus, these experimental results suggest that the number of major active site is correlated with external surface (i.e. structurally unique) but not with the number of total surface nitrogen atoms. The most plausible active site would be Si-NH₂ because the number of surface silanols on MCM-22 type zeolite is unique per unit external surface area. It should be noted that the nitrogen content is much larger than the theoretical amount of silanol groups on MCM-22 type zeolite, indicating all the surface silanols would be turned into Si-NH₂. Although another discussion or analysis is required to determine the shape and the number of active sites, here, I concluded that Si-NH₂ is the most plausible active site on the NMCM-22 type catalyst, and that delamination of lamellar zeolite precursor is an effective approach to increase the number of Si-NH₂.

In Chapter 3, nitrogen sites of nitrated silica were compared with those of carbon nitride. The effect of the functional groups attached to the nitrogen sites on the catalytic properties was investigated.

Nitrated SBA-15 with nitridation temperature of X K, NSBA-15- X , was obtained by heating SBA-15 at 973-1173 K in NH₃ flow. Porous carbon nitride obtained by carbonization at Y K, PCN- Y , was obtained by a hard-template method. Knoevenagel condensation of benzaldehyde with malononitrile or ethyl cyanoacetate was conducted at 333 K for 3 h to evaluate the base catalytic properties.

The nitrogen contents of NSBA-15-973, NSBA-15-1073, and NSBA-15-1173 were 7.86 wt%, 13.1 wt%, and 18.2 wt%, respectively, and those of PCN-773, PCN-873, PCN-1073, and PCN-1273 were 31.7, 19.7, 10.6, and 6.72 wt%, respectively. The nitrogen contents of PCN samples were maintained after the catalytic tests and even after 3 months of storage, whereas those of NSBA-15 decreased in three-quarters of the initial amount after the catalytic tests probably due to the Si-N bond cleavage by hydrolysis with atmospheric H₂O. Thus, PCN-type N site could be a more durable catalyst under ambient conditions. Figure 1 shows the relationship between the nitrogen content of each catalyst and the product yield by the Knoevenagel condensation. In the case of malononitrile (pK_a of 11.1) as a reactant, both NSBA-15 and PCN showed high product yields (Figure 1(a)). On the other hand, in the case of ethyl cyanoacetate (pK_a of 13.1), only NSBA-15 catalyzed the reaction (Figure 1(b)). This is probably due to the difference of active nitrogen structures. In NSBA-15, a nitrogen atom bond with silicon atoms, which is a quasi-aliphatic amine. On the other hand, nitrogen atoms in PCN are on or in aromatic rings, i.e., they are aromatic amines. Aliphatic amines generally exhibit a stronger property for proton abstraction than aromatic ones. Therefore,

NSBA-15 can catalyze a basic reaction involving a higher pK_a reactant than PCN.

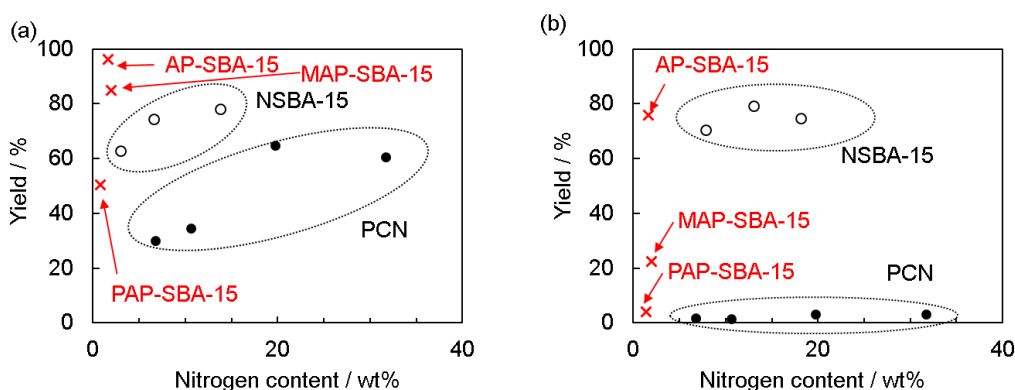


Figure 1. The relationship between product yields at 3 hours of the reaction and the nitrogen content of the catalysts in Knoevenagel condensation between benzaldehyde and (a) malononitrile or (b) ethyl cyanoacetate.

In Chapter 4, nitrogen sites of nitrated silica were compared with those of amine-functionalized silica. A variety of nitrogen sites were modified on the silica surface by a grafting method, and the properties of each nitrogen site were investigated by comparing them. AP-SBA-15, MAP-SBA-15, and PAP-SBA-15 were prepared by functionalizing SBA-15 with aminopropyl, methyl aminopropyl, and phenyl aminopropyl groups, respectively, using the corresponding silane coupling agents. FT-IR measurements confirmed that the desired amine groups were attached on each surface of SBA-15. The properties of the synthesized catalysts were evaluated by Knoevenagel condensation as in Chapter 3.

Figure 1 also involves the relationship between the yields and the nitrogen content of the amine-functionalized SBA-15. At every data point, the selectivity towards the desired product was over 99%. Therefore, amine-functionalized SBA-15 showed a good selectivity for Knoevenagel condensation. In addition, no peak derived from desorbed aminopropyl group was observed in GC, indicating that amine-functionalized SBA-15 showed a good stability. AP-SBA-15 showed the high catalytic activity in both reactions. This trend of AP-SBA-15 was similar to that of NSBA-15. On the other hand, PAP-SBA-15 showed high catalytic activity only in the reaction using malononitrile. This trend of PAP-SBA-15 was similar to that of PCN. In AP-SBA-15, the nitrogen atom bonded with the alkyl group which donates electrons. On the other hand, the nitrogen atom in PAP-SBA-15 bonded with the phenyl group, which show an electron-withdrawing property. Therefore, AP-SBA-15 can catalyze a basic reaction involving a higher pK_a reactant than PAP-SBA-15.

Comparing the catalytic activity of AP-SBA-15 with that of NSBA-15, AP-SBA-15 showed a higher catalytic activity than NSBA-15, even though the nitrogen content was lower. One possible reason for the high activity of AP-SBA-15 could be that AP-SBA-15 is hydrophobic. The hydrophobicity of catalysts provides two advantages: 1) The water produced by the condensation reaction is released rapidly. 2)

Reactants (such as benzaldehyde and ethyl cyanoacetate) can easily access the catalyst surface. Furthermore, AP-SBA-15 showed a higher activity than MAP-SBA-15. This would be explained by the formation of imine intermediate via dehydration of benzaldehyde and primary amine. In summary, the alkyl amine sites are more active than the aromatic amine sites, which might derive from electron movement. Also, high hydrophobicity is given to the former catalyst with alkyl groups, leading to a more successful catalyst design.

In Chapter 5, the basicity of nitrogen-containing catalysts was evaluated by CO₂ adsorption. Adsorption of acidic molecules such as CO₂, benzoic acid and phenol is one of the typical tools for evaluating basicity. The amine functionalized SBA-15 prepared in Chapter 4 was evaluated by CO₂ probe FT-IR at ambient temperature.

Figure 2 shows typical FT-IR difference spectra of each amine functionalized SBA-15 for CO₂ adsorption. A broad peak derived from gas phase CO₂ was observed at around 2345 cm⁻¹ in all samples. Furthermore, in the case of AP-SBA-15 and MAP-SBA-15, peaks derived from carbamate species were observed in the range of 1380-1620 cm⁻¹, indicating the formation of strong bond between amine sites and CO₂ molecules. This result indicates that alkylamine sites possess a stronger basicity than aromatic amine sites. The result is consistent with the results of the Knoevenagel condensation in Chapter 4.

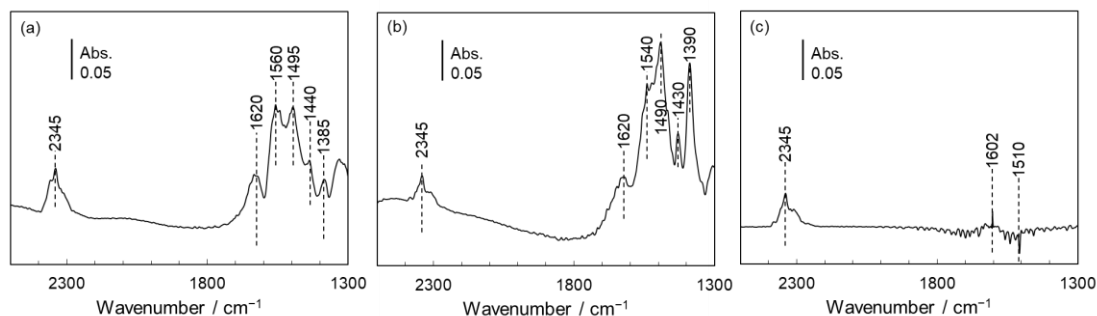


Figure 2. CO₂ probe FT-IR spectra of (a) AP-SBA-15, (b) MAP-SBA-15, and (c) PAP-SBA-15 measured at ambient temperature. 6.0 torr CO₂ was introduced.

Through the studies in the dissertation, the relationship between the type of nitrogen site and the catalytic properties was clarified. All of the nitrogen sites investigated in this study are highly selective for Knoevenagel condensation. Nitrogen sites bonded to an electron-donating group (such as an alkyl group), i.e., nitrogen sites with a high pK_a, can promote reactions using substrates with low reactivity. In addition, a catalyst with high hydrophobicity can make the reaction proceed faster. Nitrogen sites bonded to silicon atoms are not durable because they are easily hydrolyzed in atmosphere or water produced in catalytic reactions.

As a grand design for a better base catalyst, a nitrogen site surrounded by a periodic hydrophobic structure, attached with an electron-donating group is proposed to be created on a porous solid surface.