DIMETHYL CARBONATE PRODUCTION FOR FUEL ADDITIVES

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INTRODUCTION

Dimethyl carbonate is very attractive as for use as an oxygenate for fuel additives. A feasible method of mass production at a low cost is needed for producing dimethyl carbonate for fuel additives.

The transesterification process is one of the dimethyl carbonate production processes(1). In this process, ethylene carbonate with methanol is transesterificated to dimethyl carbonate.

ethylene carbonate methanol dimethyl carbonate ethylene glycol

In the transesterification process, ethylene glycol is co-generated with dimethyl carbonate. The ethylene glycol is considered to correspond economically with the conventional product from hydration of ethylene oxide, because the quality of the ethylene glycol produced by transesterification is equal to the quality of the conventional product and the demand for ethylene glycol is growing year by year. Therefore, development of the dimethyl carbonate process through the transesterification is indicated.

Oxidative carbonylation processes in both the liquid-phase and vapor-phase are known as the other dimethyl carbonate processes. Liquid-phase oxidative carbonylation is the oxidation of carbon monoxide with oxygen in methanol in the presence of copper chloride(2). A catalyst is used in a slurry mixture. In the vapor-phase oxidative carbonylation, the reaction of carbon monoxide and methyl nitrite by the oxidation of methanol and nitric oxide in the presence of both palladium chloride and copper chloride is used(3). These processes are based on oxidation due to the presence of both oxygen and chloride.

Transesterification is a mild reaction with small exotherm, and is carried out in the liquid phase without toxic chemicals and corrosiveness. These features will be the merit of scale up with a low fixed capital.

We started transesterification process development for dimethyl carbonate production from the above considerations. Zeolites were studied as catalysts for this transesterification, due to their properties of resistance to heat and organic solvents. Zeolite catalysts can be used in fixed bed reactors without a catalyst separation unit. Chiyoda has developed processes using zeolites, for example, the Z-forming process to produce BTX from light hydrocarbons, the 2,6-DIPN production process using zeolite adsorbent, etc.

EXPERIMENTAL

Catalysts

Almost all of the popular industrial zeolites, for example the A, X, Y, L, Mordenite, ZSM-5 type, etc., were used in the catalysts screening. Several types of zeolites with adjusted cation species were screened next. Those catalysts were provided to reaction tests after calcination.

Test units

Reaction tests were performed in batch reactors and fixed bed reactors. Stainless steel was used for the reactors. Fixed-bed flow reactors were operated automatically under good material balance and well controlled of catalysts bed temperature.

RESULTS

The catalysts screening were performed from the points of activity, selectivity and sustainability. The reaction condition, the regenerating method, etc., were studied in order to develop the process for dimethyl carbonate production through transesterification. We will discuss some results of the catalysts screening and catalytic performance tests. The details of catalysts design will be discussed in the future.

Catalysts screening

Various structure types of zeolites were examined during the first step of the catalysts screening based on activity, selectivity and sustainability. The influence of the cation species of zeolite on catalytic ability was studied next in several types of zeolites. A part of the results for the catalysts screening of commercially available zeolites is as follows.

Zeolite types

Na form zeolites with Al_2O_3/SiO_2 molar ratios varying from 0.04 to 0.5 were used.

The activity is varied according to the types of zeolites as shown in Fig.1. it is considered that the order of activity depends on Al_2O_3/SiO_2 which represents the quantity of active site of the zeolites. Zeolite A with the largest Al_2O_3/SiO_2 ratio of 0.5 shows the highest activity, and ZSM-5 with the small Al_2O_3/SiO_2 of 0.04 has a very low activity. It seems that the activity depends on the quantity of active sites of the zeolites. Zeolite A has the most active sites, because the maximum value of Al_2O_3/SiO_2 in the zeolites is at 0.5. After that, the catalysts with the same Al_2O_3/SiO_2 of different structures were examined.

Cation species

The influence of the cation species including proton on catalytic ability was studied for several types of zeolites. We will discuss a part of the results for commercially available zeolites having different cation species.

The H form zeolites shows no activity. Fig.2 shows a comparison of the activity with 3 A(KA), 4 A(NaA) and 5 A(CaA) zeolites which have same Al_2O_3/SiO_2. The 3 A (KA) zeolite shows the highest activity. The order of the activity in zeolites A is as follows; 3 A>4 A>5 A. As for A type of zeolites which have the same crystalline structure, the activity depends on the cation species.

Several types of K form zeolites were studied. Fig.3 gives a comparison of the activity of the industrially popular 3 A and L types of the zeolites, and the activity of the K form X type which is in adjusted cation species. The order of the activity for these zeolite types is A > X > L. The activity depends on the Al_2O_3/SiO_2 and here zeolite A also shows the highest activity of the K form zeolites.

From the results of catalysts screening, the activity of the zeolite catalysts depends on the Al_2O_3/SiO_2 which represents the quantity of active sites, and the activity level of the site depends on the cation species.

Catalytic performance tests

Catalytic performance tests were achieved in order to study the zeolite catalysts for use in fixed bed reactors. The content of the cation species, the temperature for calcination, the material for binder, etc., were studied in addition to the catalysts screening.

Table 1 shows an example of catalytic performance tests. A 46% of one pass dimethyl carbonate yield was obtained at 120 (°C) and 10 (kg/cm^2).

CONCLUSION

The catalytic activity of zeolites for the production of dimethyl carbonate for use an oxygenate for fuel additives was studied.

We studied the activity of some of the industrially popular zeolites by the catalysts screening based on activity, selectivity and sustainability. We found that the order of zeolite catalyst activity depends on the Al_2O_3/SiO_2 which represents the quantity of active sites. Zeolite A with a maximum value of Al_2O_3/SiO_2 at 0.5 in the various zeolite types shows the highest activity.

The influence of the cation species of the zeolites was studied using several types of zeolites. The order of the activity for industrially popular zeolites A is; 3A (KA) > 4A (NaA) > 5A (CaA). It is believed that the activity level of the site depends on the cation species. In the case of zeolite A, the order of activity for cation species is as follows; $K^+ > Na^+ > Ca^{2+}$.

Catalytic performance tests were achieved to study zeolite catalysts for use in fixed bed reactors. A 46% of one pass dimethyl carbonate yield was obtained at 120 (℃) and 10 (kg/cm^2). Zeolite catalysts can be used in fixed bed reactors with significant properties of resistance to heat and organic solvents in comparison with ion exchange resin. The zeolite catalysts for dimethyl carbonate production by transesterification were prepared using commercially available zeolites by a simple ion exchange treatment.

REFERENCES

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Table 1 Fixed- bed flow reaction test

Temp. (℃)	Press. (kg/cm^2)	DMC Yield (%)
120	10	46

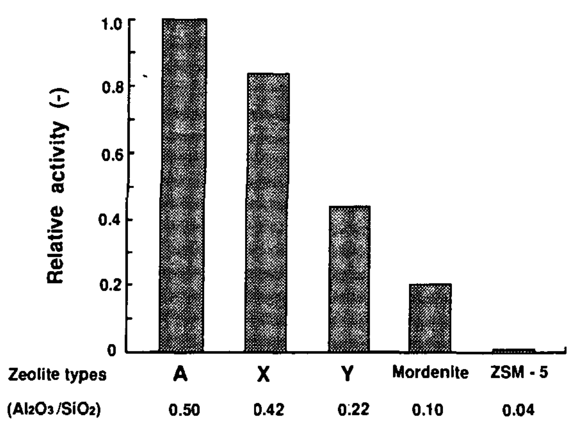

Fig.1 Activity of various types of zeolites

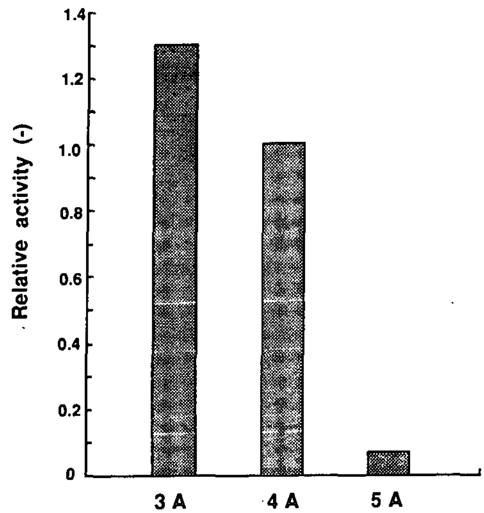

Fig.2 Activity of A type zeolites

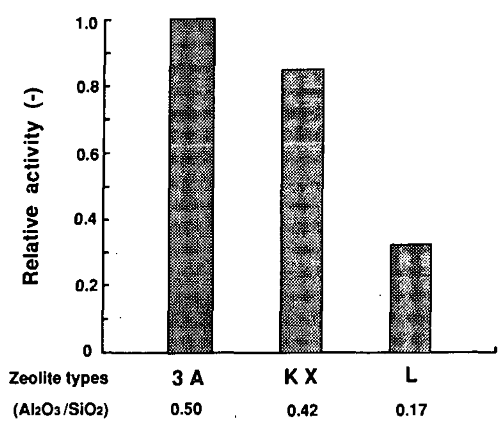

Fig.3 Activity of K form zeolites