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Direct Amination of 2-Methylpropene with Ammonia into t-Butylamine on Proton-exchanged ZSM-5 Zeolite Catalyst

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Proton-exchanged ZSM-5 zeolite with silica/alumina = 51 showed a pronounced catalytic activity for the title reaction and it was suggested that this reaction would proceed on Brønsted acid site.

Aliphatic amines are commercially important and have been industrially made by the reaction between the corresponding alcohols and ammonia.[1] Since the alcohols are usually obtained through the direct or indirect hydration of the olefin with the same carbon number, it would be more desirable to avoid the alcohol and synthesize the amine by a direct reaction between olefin and ammonia.[2] Direct amination of ethene to ethylamine has been achieved using alkali metal catalysts in a homogeneous system.[3-5] However, these system provide low yields of higher alkylamine except for patent literatures.[6] Here, we wish to demonstrate that proton-exchanged ZSM-5 zeolites efficiently catalyze formation of t-butylamine directly from 2-methylpropene and this reaction would be promoted by Brønsted acid site.

Parent zeolites, ZSM-5 (denoted as MFI), ferrierite (FER), L-type (LTL), offretite/erionite (OFF/ERI), mordenite (MOR), and Y-type (Y) zeolites were supplied by Tosoh Corporation and MgO was obtained from the Catalysis Society of Japan. SiO_2-Al_2O_3 and SiO_2-TiO_2 were commercially obtained from Catalysts & Chemicals Ind. Co., and Fuji-Davison Chemicals, respectively. $Cs_{3-x}H_xPW_{12}O_{40}$ (x = 0.15, 0.5) was prepared according to Ref. 7. Proton exchanged zeolite was prepared as described previously[8] and was abbreviated as H-MFI-51 (cation-zeolite structure-silica/alumina). The reaction between 2-methylpropene and ammonia in the presence or absence of water vapor was carried out in a conventional flow reactor at 423 - 673 K at an atmospheric pressure using 0.5 - 1.0 g

catalysts after the catalysts were treated in a N_2 stream at 773 K for 1 h except for $Cs_{3-x}H_xPW_{12}O_{40}$ (x = 0.15, 0.5), which was used without the treatment due to the thermal instability. The flow rates of 2-methylpropene, ammonia, and water vapor were 1.7 - 10.0, 5.0 - 16.0, and 0 - 0.68 $cm^3 \cdot min^{-1}$, respectively. Total flow rate was 7.5 - 20.0 $cm^3 \cdot min^{-1}$. The reactants and products were analyzed by gas chromatography. It was confirmed for H-MFI that the conversion was proportional to the contact time (weight of catalyst/total flow rate) and the carbon and nitrogen balances were good. The extent of conversion into t-butylamine over each catalyst was gradually increased with reaction time up to 1 - 2 h. Approximately steady formation of t-butylamine, which was the main product, was attained after 2 h in the reaction between 2-methylpropene and ammonia on each catalyst. No deterioration of each catalyst was observed at 473 K even after 6 h of continuous service and no change in XRD pattern between the fresh and used catalyst was observed for each zeolite catalyst. The total turnover number of H-MFI-51 (i.e., number of t-butylamine formed per number of Al content which reflects the number of Brønsted acid site) after a 30 h reaction was greater than 4, showing that the reaction is catalytic. The catalytic activity was evaluated by the conversion into t-butylamine after ca. 6 h.

The maximum yield of t-butylamine over each catalyst was obtained around 473 K and

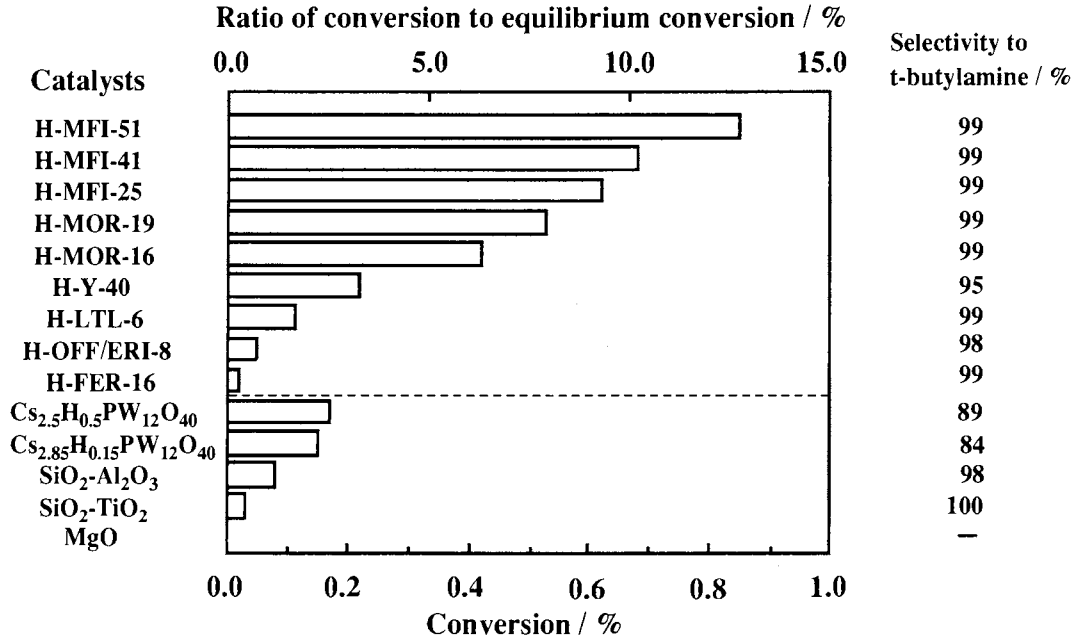

Fig. 1. Catalytic activities of various catalysts for the amination of 2-methylpropene into t-butylamine. 2-Methylpropene, 4.0 $cm^3 \cdot min^{-1}$; ammonia, 16.0 $cm^3 \cdot min^{-1}$; catalyst weight, 1.0 g; reaction temperature, 473 K.

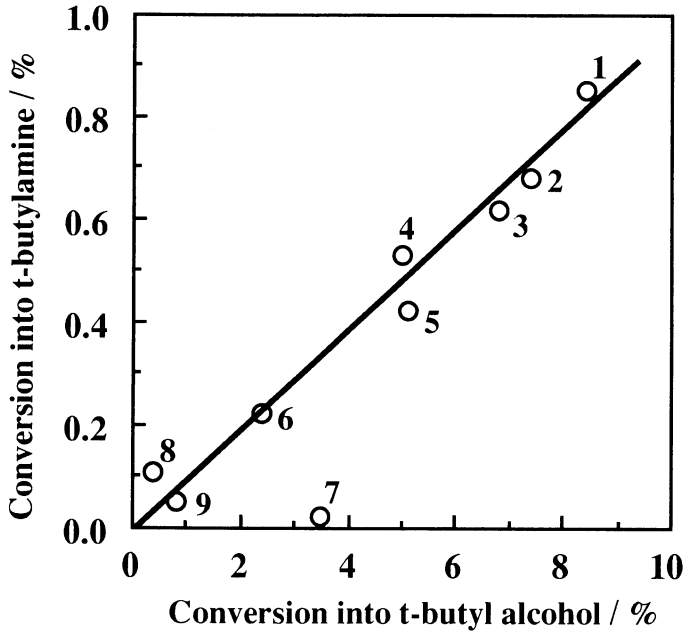

Fig. 2. Correlation between the activities of various proton-exchanged zeolite catalysts for amination and hydration of 2-methylpropene. Reaction conditions of the amination was the same as those of the note in Fig. 1. The activities for the hydration were cited from Ref. 9. Numbers 1 - 9 correspond to the conversions into t-butylamine or 2-methyl-2-propanol upon H-MFI-51, H-MFI-41, H-MFI-25, H-MOR-19, H-MOR-16, HY-40, H-FER-16, H-LTL-6, and H-OFF/ERI-8, respectively.

at the pretreatment temperature more than 523 K. Catalytic activities for the reaction between 2-methylpropene and ammonia at 473 K are summarized in Fig. 1. It is noted that the selectivity to t-butylamine is more than 95% for each zeolite. The low conversion of 2-methylpropene to t-butylamine is due to the limitation by equilibrium between starting materials (2-methylpropene and ammonia) and the product (t-butylamine). H-MFI-51, on which the conversion reached ca. 13% of the equilibrium conversion, showed the highest activity among the zeolite catalysts, solid acid catalysts ($Cs_{3-x}H_xPW_{12}O_{40}$ (x = 0.15, 0.5), SiO_2-Al_2O_3, SiO_2-TiO_2), and solid base MgO. The activity of the zeolites having ZSM-5 or mordenite structure increased with the increment in silica/alumina; H-MFI-51 > H-MFI-41 > H-MFI-25 or H-MOR-19 > H-MOR-16. The difference between activities of H-MFI-41 and H-Y-40 or between those of H-MOR-16 and H-FER-16 suggests that the activity of each zeolite depends not only on the silica/alumina ratio but also on the zeolite structure.

Addition of water vapor did not improve the catalytic properties; when the water vapor was added to the reactant gases (2-methylpropene and ammonia), the activity of each zeolite

little changed and the selectivity to t-butylamine slightly decreased to 87 - 97% from more than 95% due to the formation of 2-methyl-2-propanol.

The variation of the activity among the zeolite catalysts could be explained by the Brønsted acidity. Figure 2 shows the correlation between the activities of the respective zeolites for the amination and hydration[9] of 2-methylpropene. The latter reaction is well known to be catalyzed by the Brønsted acidity. The good correlation in Fig. 2 suggests that the direct amination of 2-methylpropene is catalyzed by the Brønsted acidity. It was indeed confirmed in a separate experiment that the activity was decreased by the Na^+ substitution for H^+ in H-MFI-25, supporting the above idea.

In conclusion, the novel route for the amination of 2-methylpropene was found and it was suggested that the controlling factor of the activity is Brønsted acidity of the catalyst.

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