Analysis of active site for methylation of benzene with methane on Co/MFI catalyst with ammonia IRMS-TPD method

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Abstract: The acidic properties of cobalt loaded on MFI zeolite (Co/MFI) and the samples with second metals (Co+M/MFI) were measured by ammonia IRMS-TPD method. The cobalt species on ion exchange site of MFI had Lewis acidity. The deformation band (1300 cm^{-1}) of NH_3 coordinated on Lewis acid site was shifted to higher wavenumber with increasing the cobalt loading or addition of Mg and Pb. The strong Lewis acidic cobalt species giving the high wavenumber band is attributed to the active site for methylation of benzene with methane.

Keywords: IRMS-TPD, cobalt, MFI

1. Introduction

Supply of natural gas and shale gas has increasing, and their main component, methane, has attracted much attention as a chemical resource alternative to petroleum. However, the utilization of methane has been believed to be very difficult due to the high chemical stability. We previously found that the cobalt loaded on MFI zeolite (Co/MFI) showed high catalytic activity for direct methylation of benzene with methane ($CH_4 + C_6H_6 \rightarrow C_6H_5\text{-}CH_3 + H_2$) . The catalytic activity was strongly dependent on the amount of cobalt. The toluene yield was small at > 20% of the Co/Al ratio, indicating that inactive cobalt species were formed at Co/Al < 20%. Then, the activity was generated by loading of Co in the region of >20 % of Co/Al ratio, showing that the active cobalt species were formed at Co/Al > 20%. On the other hand, the activity was found to be strongly dependent on the second additives. Active cobalt species were generated selectively by the addition of typical elements such as Mg, Zn, Pb and Ca, while transition metals brought inactive species[1]. Ammonia infrared mass spectrometry/temperature-programmed desorption (IRMS-TPD)[2] and XAFS (XANES and EXAFS) showed that a part of Lewis acidic divalent cobalt species mono-atomically dispersed on the ion exchange site of MFI were the active species. On these backgrounds, we further investigated on the Lewis acidic nature of cobalt species on Co/MFI and Co+M/MFI (second metal added Co/MFI) in the present study to identify the active species.

2. Experimental

Co/MFI were prepared by cobalt ion exchange of NH_4-MFI zeolite (Si/Al = 11) with a solution of cobalt nitrate (Co/Al = 20, 30, 40, 200%) at 343 K for 4 h followed by filtration and drying. Co+M/MFI were prepared by ion exchange on NH_4-MFI zeolite with a mixed solution of cobalt nitrate (Co/Al = 200%) and second metal nitrate or chloride (M/Al = 200%) at 343 K for 4 h followed by filtration and drying. The amounts of cobalt and second metal containing in the final solids were measured by an inductively coupled plasma - atomic emission spectrometer (ICP-AES). The acidic property was evaluated by the ammonia IRMS-TPD method[2] using Microtrac BEL IRMS-TPD analyzer. After the pretreatment in N_2 at 823 K, 13 kPa of NH_3 was adsorbed on the solid sample at 343 K. Then the temperature was increased at a rate of 2 K min^{-1} up to 823 K in a flow of He. On this step, IR spectra were recorded and NH_3 concentration at the outlet was measured by a mass spectrometer. The catalytic activity was evaluated by a fixed bed flow method at 773 K[1].

3. Results and discussion

With several other bands, IR spectra of NH_3 adsorbed on the Co/MFI showed that the deformation bands of NH_3 coordinated to Lewis acid site (ca. 1300 cm^{-1}) of NH_4^+ bounded to Brønsted acid site (ca. 1450 cm^{-1}) which will be used for quantitative analysis as follows. The absorbance of 1300 cm^{-1}-band increased (Fig. 1) and that of 1450 cm^{-1}-band decreased (not shown) with the cobalt loading, indicating that the ion exchange site was covered by Lewis acidic cobalt species. The peak top of 1300 cm^{-1}-band shifted to higher wavenumber side with increasing cobalt. The addition of Mg and Pb was found to result in the shift of this band to the higher wavenumber from the position observed on the Co/MFI with the equivalent Co content, while the addition of Cu shifted it to lower wavenumber. We have found that the activity was generated in the high cobalt content region or in the co-presence of Mg and Pb[1]. Therefore it is speculated that the active species had a nature showing the peak at high wavenumber.

The quantitative analysis was attempted. The 1300 cm^{-1}-band peak was deconvoluted into L1 (1305 cm^{-1}) and L2 (1287 cm^{-1}) components. From the temperature dependence of the intensities (peak areas) of L1 and L2, the NH_3 species was further classified into the weakly-held species desorbed at 350-500 K and strongly-held ones desorbed at 500-870 K. Thus, the Lewis acid sites (Lewis acidic cobalt species) can be classified into L1S, L1W, L2S and L2W species; here S means the strong Lewis acid, whereas W means the weak one. On the assumption that the sum of ammonia desorbed from Brønsted acid sites and these four types of Lewis acid sites was equal to the ammonia detected in the outlet gas over the experimental temperature range, the amounts of all these species were calculated using curve fitting technique.

As shown in Fig.2., on Co/MFI, the amount of L1S was low at Co/Al < 20 % and increased significantly by the loading at Co/Al > 20%. The L2 (L2S+L2W) and L1W species were found also in the low Co/Al region. The addition of Pb and Mg increased all the Lewis acidic species including L1S, while the addition of Cu increased mainly L1W and L2. The activity for direct methylation of benzene with methane is overlapped in Fig. 2. The dependence of activity on the Co/Al ratio was similar to that of L1S amount, and the nature of the activity increased by the addition of Pb and Mg but not by Cu was again similar to the behavior of L1S. Based on these findings, we propose that the Co species with Lewis acidity classified into L1S was the active site for methylation of benzene with methane.

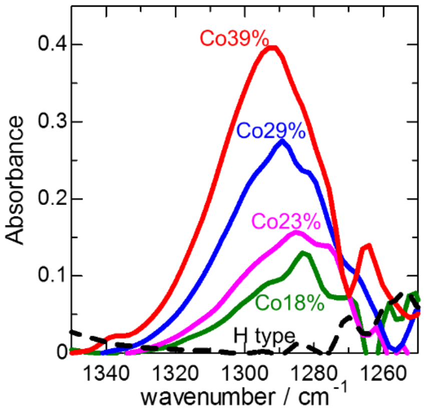

Fig. 1. IR spectra at nearby 1300 cm^{-1} of NH_3 adsorption onto Co/MFI (Co*X*%, *X*% is measured value by ICP-AES.) and H type MFI at 573 K.

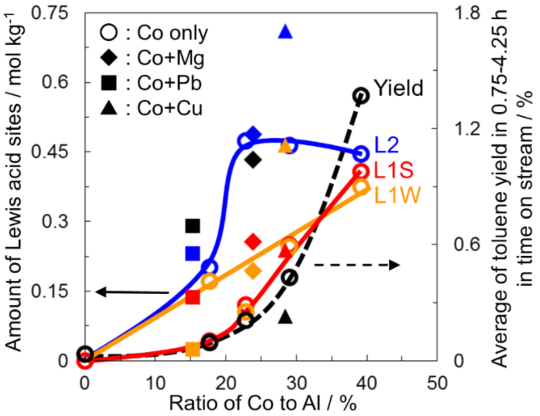

Fig. 2. Amount of Lewis acid sites and catalytic activity for methylation of benzene with methane plotted against Co loading in Co/MFI and Co+M (Mg, Pb, Cu) /MFI

4. Conclusions

The deformation band (ca. 1300 cm^{-1}) of NH_3 coordinated to Lewis acidic cobalt on MFI was shifted to higher wavenumber by increasing the cobalt loading or addition of Mg and Pb. The Lewis acid sites were classified based on the strength and wavenumber of this band. The quantitative analysis suggest that the L1S species was the active site for methylation of benzene with methane.

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References

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