

In order to analyze the type of acid sites (Lewis acid and Brønsted acid) in Cu-HMS, IR of pyridine adsorbed on acid sites in Cu-HMS with different Si/Cu ratio was shown in Fig. 1. The vibration bands in the 1400~1600 cm^{-1} regions of the IR spectrum of the chemisorbed pyridine could distinguish between the Brønsted and Lewis acid sites^{1, 2}. The bands at $\sim 1450 \text{ cm}^{-1}$ and $\sim 1540 \text{ cm}^{-1}$ are often used to determine the number of acid sites quantitatively, which attributed to the C-C stretching vibration of pyridine complex on Lewis sites and pyridinium ion on Brønsted sites. Adsorption of pyridine on a series of Cu-HMS materials shows that samples without Cu adding (Si/Cu = ∞) possess essentially Lewis sites, as observed on pure silica HMS. As far as the Cu content increased, Brønsted sites appear, whose relative concentration increases with the amount of copper in Cu-HMS. A similar trend was reported by *A. Tuel et al.*³ for Ti-HMS.

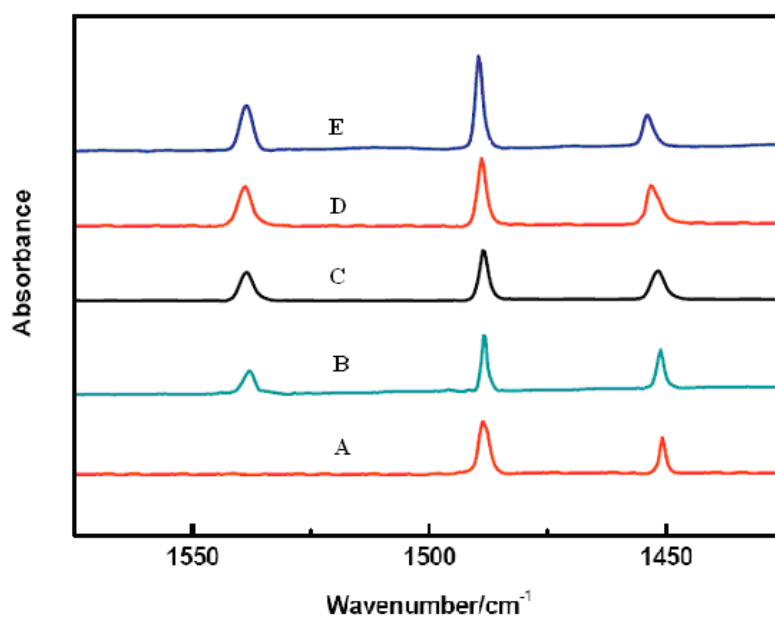


Fig. 1 IR of pyridine adsorbed on acid sites in Cu-HMS (A :Si/Cu = ∞ , B: Si/Cu = 100, C: Si/Cu = 75, D: Si/Cu = 50, E: Si/Cu = 20)

The presence of Brønsted sites in samples with Cu adding increasing suggests that

when Cu^{2+} substitutes for Si^{4+} in the framework, the framework possesses negative charges that can be compensated by protons. That was also explained in detail by the synthesis mechanism of Cu-HMS.⁴ The presence of Brønsted sites in Cu-HMS is beneficial to the catalytic performance for hydrolysis of diethyl ether. Thus, it shows a better catalytic performance using Cu-HMS (Si/Cu=50) as catalyst support for the coupling reaction.

[1] E. P. Parry, *J. Catal.*, 1963, 2, 371.

[2] T. R. Hughes, H. M. White, *J. Phys. Chem.*, 1967, 71, 2192.

[3] A. Tuel, *Micropor. Mesopor Mat.*, 1999, 27, 151.

[4] P. B. Zhang, Z. Zhang, S. P. Wang, X. B. Ma, *Catal. Commun.*, 2007, 8, 21.