An Infrared Study of Adsorption of Pyridine and n-Butylamine on Benzene Preadsorbed Zeolites Y and Mordenites

Ashim K. Ghosh and Geoffrey Curthoys*
Department of Chemistry, University of Newcastle, N.S.W. 2308, Australia

When pyridine or n-butylamine was adsorbed on benzene-preadsorbed HY zeolite the bases reacted with all acid sites by displacing benzene molecules but not in the case of mordenites when benzene molecules block the mordenite channels.

Nonaqueous titration using the Hammett indicators[1] or thermometry[2-4] are commonly used in the characterization of the acidity of solid surfaces. However, the reliability of results obtained by these methods has recently been criticised.[5-10] The methods consist of adding successive amounts of a suitable base (*e.g.* n-butylamine in benzene) to the

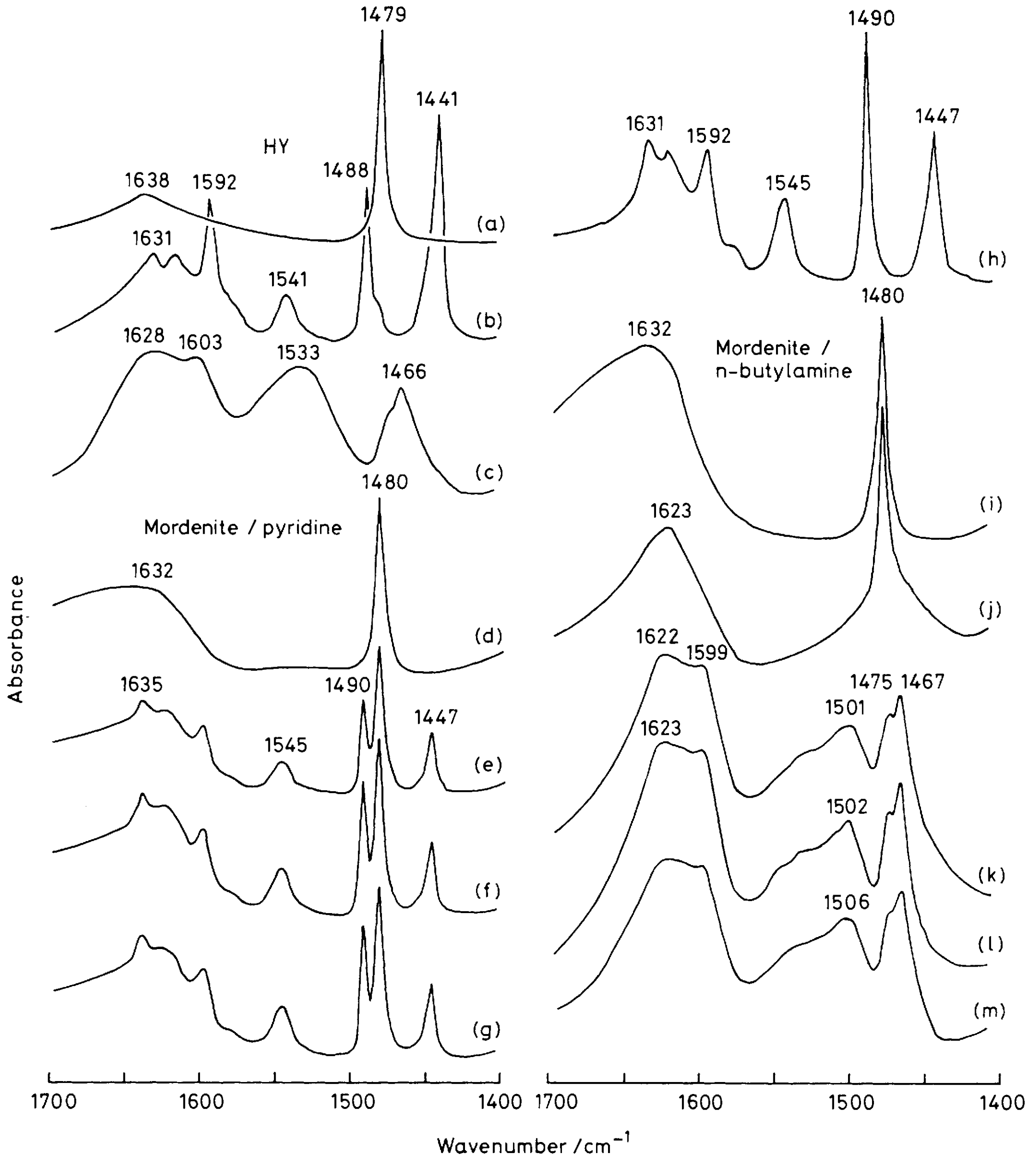

Figure 1. I.r. spectra of (a) benzene on HY zeolite; (b) pyridine and (c) n-butylamine on benzene preadsorbed HY; (d) benzene on dealuminated HM (mordenite); pyridine adsorbed for (e) 3, (f) 20, and (g) 40 h at room temperature and (h) 3 h at 423 K on benzene preadsorbed dealuminated HM; (i) benzene on dealuminated HM; n-butylamine adsorbed for (j) 40 h at room temperature, (k) 3 and (l) 16 h at 423 K, and (m) 3 h at 473 K on benzene preadsorbed dealuminated HM.

suspension of solid powder in an inert solvent, the end point of which is observed by colour change of indicator or by thermometry. It is considered that the nonaqueous solvent used in the titration methods does not affect the acid sites of the solid. However, it has been recently reported[11] that benzene which is commonly used as solvent in the titration methods interacts with the acidic hydroxy groups of HY, HZSM-5, and HZSM-11 zeolites. This interaction of benzene may be a source of error in the titration methods which showed a poor acidity for some zeolites.[7-10]

By means of infrared spectroscopy we have investigated the effect of benzene in the determination of zeolite acidity. Benzene was adsorbed for 1 h at room temperature on an activated HY wafer and excess of benzene was then pumped off. The spectrum showed that the OH stretching bands of the zeolite shifted to a lower frequency and a strong band appeared at 1479 cm^{-1} [Figure 1(a)] which is assigned to the valence vibration v_{13} of the C–C bond of the benzene molecule.[12] Pyridine or n-butylamine was then adsorbed at room temperature for 1 h and excess of base was finally pumped off. The spectra [Figure 1(b), (c)] showed the characteristic bands of pyridine (at 1541, 1488, and 1441 cm^{-1}) or n-butylamine ($\delta_{\mathrm{sym}}NH_3^+$ at 1533 cm^{-1} and $\delta_{\mathrm{asym}}NH_3^+$ at 1603 cm^{-1}) with the disappearance of the 1479 cm^{-1} band indicating that all the benzene molecules which were previously adsorbed on the zeolite acid sites had been replaced by the bases.

The above procedure was applied to a commercial HM (mordenite) and a dealuminated HM (SiO_2 : Al_2O_3 ratio 18 : 1). The hydroxy groups of mordenite behaved in the same way towards benzene as those of HY [Figure 1(d)/(i)] but the strong band at 1480 cm^{-1} attributed to the C–C bond of the benzene molecule did not disappear on adsorption of pyridine or n-butylamine in the case of the mordenites used. When pyridine (py) was the base a pyH$^+$ band at 1545 cm^{-1} and a common band for both pyH$^+$ and Lpy (Lpy = py adsorbed on Lewis sites) at 1490 cm^{-1} were observed [Figure 1(e)]. The Lpy band at 1454 cm^{-1} was masked by a hydrogen bonded pyridine band at 1447 cm^{-1}. No $\delta_{sym}NH_3^+$ band at 1500—1540 cm^{-1} characteristic of n-butylamine adsorbed on protonic sites[13] was observed but a band at 1623 cm^{-1} [Figure 1(j)] which may be attributed to n-butylamine physically adsorbed on the surface was observed.

The time dependence displacement of benzene by the bases was investigated by adsorbing the base (at its saturation pressure) for 1, 2, 3, 20, and 40 h at room temperature on the benzene pretreated mordenite samples. The pyridine bands [Figure 1(f), (g)] were found to increase with the decrease of the benzene band at 1480 cm^{-1} but the latter did not disappear completely, while the n-butylamine bands remained unchanged. When pyridine was adsorbed at 423 K for 3 h the v_{13} band of benzene completely disappeared and the characteristic bands of pyridine adsorbed on acidic sites were observed [Figure 1(h)]. n-Butylamine was also adsorbed on the benzene preadsorbed mordenites at 423 and 473 K and the $\delta_{sym}NH_3^+$ band at 1497—1506 cm^{-1}, a band at 1597—1616 cm^{-1} assigned to n-butylamine on Lewis sites, and $\delta_{asym}NH_3^+$ were observed [Figure 1(k), (l), (m)].

The present investigation shows that benzene interacts with the zeolitic hydroxy groups through its π-electrons forming a weak bond as evidenced by the frequency shift of hydroxy groups towards a lower frequency. Pyridine or n-butylamine undergo competitive interaction with benzene for the acidic hydroxy groups of the zeolite. HY has large pores and the channels are interconnected by large windows so that benzene and the bases pyridine or n-butylamine can move freely from one channel to another for interaction with the hydroxy groups. In the case of mordenite, which has a virtually one dimensional channel system having a free pore aperture of 0.67 nm, once benzene has reacted with the hydroxy groups it can only migrate with difficulty owing to its molecular size (width 0.66 nm, kinetic diameter 0.59 nm) and as a result it blocks the tubular channels of the mordenite. When base is added the competitive interaction for hydroxy groups is greatly affected owing to pore blockage/steric hindrance in the mordenite channels. A weak band for pyH$^+$ and a relatively strong band for both pyH$^+$ and Lpy indicate that a small number of pyridine molecules interacted with acidic sites. This interaction was found to be favoured when the adsorption time and temperature were increased. No competitive interaction for protonic sites in both the mordenites was observed when n-butylamine was the base until the base was adsorbed at 423 K. The adsorption of pyridine[14] and n-butylamine[15] was found to take place readily in the absence of benzene preadsorption. Our previous work[14,15] showed that ammonia or n-butylamine preadsorbed on mordenite was desorbed at lower temperatures than pyridine which is an indication that pyridine reacts more strongly with the catalyst active sites. Barthomeuf[16] stated that 'in contrast with the pK_b sequence it is well known that pyridine is more strongly linked to the acid sites than ammonia.' Pyridine on mordenite gives pyH$^+$ but $BuNH_2$ does not give $BuNH_3^+$ which may be because pyridine is more reactive. A relatively easy interaction was observed in the case of dealuminated mordenite which could be due to the widening of the zeolite pores and/or the increase in strength of acid sites on dealumination. Nonaqueous (benzene) n-butylamine titrations using Hammett indicators[8,9] or thermometry[9,10] which have been found to be satisfactory for HY but not for mordenite may be due to pore blockage by benzene.

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