Calcium aluminate catalysts can be prepared by mixing the various components in aqueous 
NH₃ solution, a process leading not only to aluminate hydration but also to aluminate reac-
tion with any metal salts which may be present in the system. Calcium aluminate hydration 
and reaction with basic nickel carbonate leads to an alteration in the phase composition of 
the catalyst [2, 3]. The fact that [4, 5] calcium aluminate, and the products resulting from 
its hydration, have zeolite-type structures, may account for the properties of the aluminate 
based catalysts [3].

The present work was a study of the products resulting from the interaction of basic 
zinc carbonate with calcium monoaluminate and dialuminate.

EXPERIMENTAL

Study was made of the IR spectra of two series of catalysts, the first based on calcium 
monoaluminate CaO : Al₂O₃ (CA)† and basic zinc carbonate (BZC), and the second based on 
calcium dialuminate CaO · 2Al₂O₃ (CA₂) and BZC. Samples from each of the two series were 
prepared by introducing the components into a 25% aqueous NH₃ solution at 90°C and agitating 
the resulting mixture for 1 h. The BZC content was varied from 15 to 95%. Each sample was 
air dried at 18-20°C and then calcined for 5 h at either 400°C or 800°C. Preliminary ex-
periments showed that the maximum degree of aluminate hydration and interaction of the hy-
dration products with the BZC was attained by operating under these particular conditions. 
Both the air dried and the calcined samples were mixed with KBr (by weight, KBr : sample = 
500 : 6) and the mixture formed into disks under a pressure of 3-5 ton/cm². A UR-20 spec-
trometer was used to obtain spectra covering the range from 400 to 4000 cm⁻¹ for each sample.

DISCUSSION OF RESULTS

The IR spectrum of CA which had been treated with a 25% aqueous NH₃ solution showed ab-
sorption bands at 530, 800, 880, 920, 980, 1030, 1380, 1420, 1480, 3380, 3475, 3530, 3560, 3630, 
and 3660 cm⁻¹, none of which appeared in the spectrum of the untreated material (Fig. 1, 
curve 1).

The wide absorption bands at 530 and 800 cm⁻¹ have been assigned to Al-O vibrations in 
structures involving octahedral and tetrahedral Al coordination through oxygen [5]. The 
absorption at 800 cm⁻¹, and over the 1380-1600 cm⁻¹ interval, is associated with vibrations in 
carbonate structures resulting from Ca²⁺ interaction with the CO₂ of the atmosphere [5]. The 
series of absorption bands in the 900-1100 and the 3300-3700 cm⁻¹ intervals arises

*For Communication 23, cf. [1].
†Here, and in what follows, the notation is that commonly employed in the chemistry of the 
calcium aluminates and cements, namely: C = CaO, A = Al₂O₃, and H = H₂O.
Fig. 1. IR spectra of zinc-calcium aluminate catalysts which had been dried at 20°C: 1) Parent CA; 2) Ca + 50% BZC; 3) CA + 65% BZC; 4) CA + 90% BZC; 5) BZC.

from OH group stretching and deformation vibrations in the product aluminium hydroxide. The absorption bands at 920, 980, 1030, 3380, 3540 and 3630 cm\(^{-1}\) arise from a gibbsite phase contaminated with calcium hydroaluminate (3470, 3630 and 3660 cm\(^{-1}\)). The presence of the weak absorption at 1640 cm\(^{-1}\) is indication of the presence of water in the molecular form.

The introduction of 50% of BZC into the system led to the extinction of all of the discrete absorption in the OH group stretching and deformation vibration bands and gave rise to the appearance of new bands at 430, 560, 625, 1365, 1500, 3100 and 3470 cm\(^{-1}\) (curve 2). An increase in the amount of water in molecular form was indicated by an increase in the strength of the water molecule deformation vibration band at 1640 cm\(^{-1}\). Increasing the BZC content of the system to 65% brought about very little change in the band intensities (curve 3). Increasing the BZC content still further to 90% altered the spectrum appreciably, the intensities of the bands at 430, 560, 625 and 3080 cm\(^{-1}\) decreasing markedly and new bands appearing, at 470, 525, 690, 710, 740, 840, 960, 1050, 1390, 1510 and in the 3100-3600 cm\(^{-1}\) region, the latter characteristic of BZC in pure form (curves 4 and 5). Introduction of BZC at ~ 20°C led to component interaction with the formation zinc hydroxoaluminate (ZHA), a new compound with characteristic space lattice [6, 7] and absorption bands at 430, 560 and 625 cm\(^{-1}\). The appearance of an absorption band at 3100 cm\(^{-1}\) gave indication of strong OH group-H\(_2\)O molecule interaction with the formation of very short hydrogen bonds [8].

Maximum ZHA formation came at 50-60% BZC content; increasing the BCZ content to 90% led to the appearance of a free BZC phase and suppressed new phase formation. The intensities of the bands in the 1380-1480 cm\(^{-1}\) interval fell off markedly, and the band contours altered as well. The indication here was that the concentration of the CaCO\(_3\) phase resulting from CA interaction with BZC had increased.

The air-dried CA\(_2\) and CA based catalysts showed almost identical IR spectra. They did, however, differ in their degrees of hydration and in calcium hydroaluminate content.

Calcining the samples for 5 h at 400°C altered the form of the spectra (Fig. 2). Dehydration of the gibbsite and calcium hydroaluminate with the formation of both low and high basic calcium aluminates and Al\(_2\)O\(_3\), resulted in the disappearance of the OH group absorption bands in the 3300-3700 cm\(^{-1}\) interval. Water vapor from the atmosphere adsorbed on the surface of the newly formed phases and absorption bands, characteristic of absorbed water and polyassociates, appeared at 1640 and 3450 cm\(^{-1}\). There was also an increase in the relative intensity of the band at 850 cm\(^{-1}\) and a reduction in the intensities of the bands of the 530-570 cm\(^{-1}\) interval. The indication was that many of the Al\(^{3+}\) ions in the calcined sample were surrounded by O atom tetrahedra, just as in the case of C\(_{12}\)A\(_7\) [5, 7]. The absorption at 880 and 1380-1600 cm\(^{-1}\) remained essentially unchanged, the indication being that there was no carbonate breakdown during calcining of the hydrated calcium aluminate at 400°C.

The introduction of 50-65% ZnO into the system led to a redistribution of the intensities of the bands at 1420 and 1500 cm\(^{-1}\), with the former predominating at 90% ZnO content.