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Studies on the structural characterization of sodium-promoted calcium oxide systems used as catalysts for the oxidative coupling of methane

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Abstract

Calcium hydroxide, $Ca(OH)_2$, was impregnated with different sodium compounds, namely, NaOH, Na_2O, Na_2O_2, $NaNH_2$, Na_2CO_3, Na_2SO_4, $NaBH_4$, and dried and calcined (650–800°C). The nature of structural changes in the different mixed composites during the course of calcination was studied using different analytical techniques, i.e. DSC, IR, and XRD. The results indicate that a solid–solid interaction develops between NaOH, which was also formed as an intermediate from the other sodium compounds employed, and the $Ca(OH)_2$ matrix, even after oven-drying at 120°C. The measured lattice parameters indicate that the inclusion of Na^+ ions in the CaO matrix remains very limited on calcining the samples at 650°C. It may be presumed that most of sodium oxide/hydroxide remains in a well-dispersed state over the CaO matrix. The use of different sodium compounds does not show any significant differences in C_{2+} selectivity and activity for the oxidative coupling of methane.

Keywords: Sodium-calcium oxide catalyst; Solid state interaction; Structural transformation

1. Introduction

According to various investigations [1–6], a high surface basicity helps to improve the activity and selectivity of catalysts for the oxidative coupling of CH_4 to higher hydrocarbons. In this regard, alkali metal oxides are strong bases. However, the use of an alkali metal oxide as a catalyst is not feasible due to the formation of a liquid

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hydroxide phase in the presence of water vapour formed under reaction conditions. Alkali metal hydroxides, except LiOH, do not dehydrate readily due to their strong electrovalent metal–hydroxide bonding character. Thus, the alternative source for preparation of strong basic oxides is the use of alkaline earth metal oxides doped with low concentrations of alkali oxides. Although alkaline earth metal oxides are as basic as alkali metal oxides, their hydroxides are readily dehydrated under reaction conditions because they possess mobile protons [7]. A favourable dehydration is necessary for the preparation of a stable catalyst, which is related to the surface regeneration process under reaction conditions. The high surface basicity required for the selective oxidation reaction is obtained by incorporating a suitable concentration of alkali hydroxide on the surface of the alkaline earth oxide, such as CaO or MgO, which acts as a stable carrier for alkali hydroxides under reaction conditions. Activity measurements show that alkali–alkaline-earth mixed oxide systems are more active and selective than the individual component oxides [1–5, 8–10]. The role of alkali ions and the state of the alkali ions in alkali–alkaline-earth mixed oxide systems is still not well-defined. It is generally presumed that the incorporation of an appreciable amount of Na^+ ions into the CaO matrix is necessary to produce an active catalyst, as well as to stabilize the alkali ions under the reaction conditions (>750°C) [2–5].

Not much work has been reported on the structural assignment of alkali-doped CaO or MgO catalytic systems [1–5]. From earlier works, it seems that the incorporation of alkali ions into the CaO or MgO lattice is not quite favourable, particularly below 800°C which is normally used for the preparation of mixed oxide catalysts. Abraham and coworkers [11, 12] reported that it is only possible to produce an Li^+O^- centre in single crystals of lithium-doped MgO by heating the samples to temperatures up to 1000–1300°C in the presence of O_2 and then rapidly quenching to -204°C.

For the above reasons, it seemed to be essential to perform a systematic study of the structural characterization of alkali-doped CaO systems in order to identify the state of the alkali ions in the CaO matrix. In general, sodium carbonate, sodium hydroxide and sodium oxalate have been used in the preparation of Na^+-doped CaO catalysts. In addition to some of these compounds, the suitability of the application of some other more easily decomposable sodium compounds, namely, $NaNH_2$, $NaBH_4$, and Na_2O_2, was examined as possible ingredients in the preparation of alkali-doped CaO catalysts. In the present communication, the nature of the structural changes of these different sodium compounds in the presence of $Ca(OH)_2$ during the course of calcination has been studied with the aid of DSC, XRD and IR spectroscopic measurements.

2. Experimental procedure

2.1. Catalyst preparation

Three samples were prepared by the incipient wetness method, i.e. impregnating the pore volume of calcium hydroxide with an aqueous solution of NaOH for 1 h, with different concentrations of NaOH, namely 10, 20 and 50 mol%. The preparation technique has been discussed in detail elsewhere [2]. The samples were oven-dried at

120 ± 5°C under vacuum for 15 h; they were designated as A-1, A-2 and A-3. Another four samples were prepared by dry mechanical mixing of $Ca(OH)_2$ with Na_2O, Na_2O_2, $NaNH_2$, and $NaBH_4$, separately. The concentration of sodium compounds was kept to 10 mol% in all the samples, which were designated B, C, D and E, respectively. Two other samples, namely F and G, were prepared by the incipient wetness method using Na_2CO_3 and Na_2SO_4; the concentration of the sodium compounds was kept at 10 mol%. The samples were oven-dried at 120°C ± 5°C for 15 h and calcined at different temperatures for 10 h, as summarized in Table 2, see below. The structural changes in the calcination process were determined. All the chemicals used were analytical grade reagents.

2.2. DSC studies

DSC measurements with various solid samples were performed using a controlled-atmosphere differential thermal analyser (DuPont DTA-900). α-Al_2O_3 was used as a reference material. During calcination under nitrogen atmosphere, the temperature was increased at a rate of 5°C min^{-1}. A sample of about 10 mg was introduced into the DSC cell, using gold crucibles as sample holders.

2.3. IR studies

IR spectra were recorded on a Perkin-Elmer FTIR-1710 spectrometer using a 2 mg sample, admixed with 200 mg KBr in an agate mortar and then pelletized in the usual way. The samples were dried for 1 h at 110°C prior to preparing the pellets.

2.4. XRD studies

X-ray diffraction patterns of the samples were recorded on a Philips instrument using a Guinier camera, applying crystal-reflected monochromatic Cu Kα radiation (operating conditions, 45 kV and 25 mA). Silicon was used as an internal standard for correction of the 2θ values. The crystal phase compositions were determined by comparing the measured *d*-spacings with standard ASTM values. The lattice parameter values were determined from corrected θ values using a suitable computer program.

3. Results and discussion

3.1. Thermoanalytical studies

The influence of different sodium compounds on the dehydration of $Ca(OH)_2$ was derived from thermoanalytical experiments. The results obtained from DSC studies are shown in Table 1 and Figs. 1–3.

The thermoanalytical studies indicate that the dehydration of $Ca(OH)_2$ occurs at around 450°C under air atmosphere and is completed below 480°C. In the DSC curves,

Table 1
DSC results of the samples under nitrogen atmosphere

Sample	Peak maximum/°C	
	Endo	Exo
A-1	430 sh	
	455 s	
A-2	430 sh	
	450 s	
A-3	410 sh	
	430 s	
	445 s	
B	395 s	
	415 m	
	430 w	
C	370 m	
	395 s	
	415 sh	
D	405 s	
	420 m	
	445 w	
E	420 m	370 w
		445 m
		490 w
F	455 s	310 vw
G	445 s	310 vw

Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder.

a strong endothermic peak at approx. 450°C is apparent in all the samples. The presence of different atmospheres, CH_4, H_2 or N_2, does not have any significant influence on the dehydration of $Ca(OH)_2$. An endothermic peak maximum has been reported at ≈ 510°C in two separate earlier studies [13,14]. The observed endothermic peak at ≈ 450°C in the present study is lower compared to the value reported earlier; this may be due to the small amount of sample of low crystallite size used in the DSC cell (< 10 mg).

The DSC curve shows a sharp endothermic peak at 310°C during heating of pure NaOH, which can be ascribed to melting of Na(OH); this is confirmed by the appearance of an exothermic peak in the DSC curve during cooling at nearly the same temperature. The details were reported in our earlier work [15].

The endothermic peak assigned to the dehydration of the $Ca(OH)_2$ phase is affected by the presence of different sodium compounds (Figs. 1 and 2). On addition of 10 and 20 mol% of NaOH, the endothermic peak in the DSC curve splits into two with a maximum at 450°C and a shoulder peak at 430°C. In the case of sample A-3, the endothermic peak shows two shoulder peaks at 410 and 445°C along with a maximum at 430°C. In the case of the mixed $Ca(OH)_2$–NaOH system, the DSC curves of samples A-1, A-2 and A-3 do not show the sharp endothermic peak below 400°C indicative of

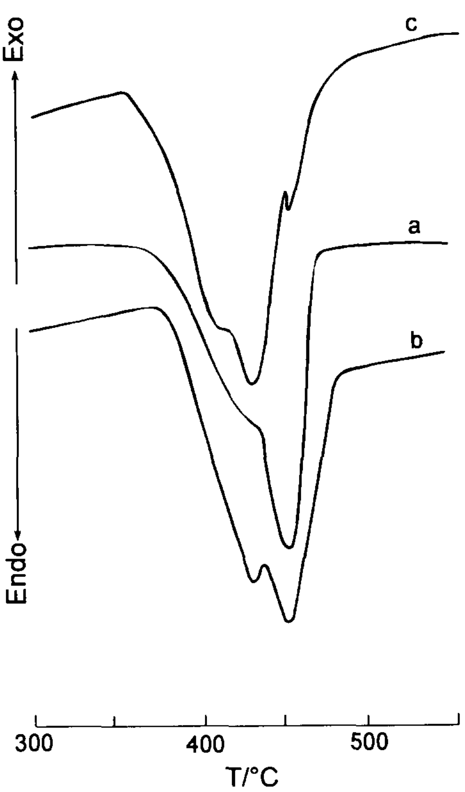

Fig. 1. DSC curves (nitrogen): a, sample A-1; b, sample A-2; c, sample A-3.

the melting of NaOH [15]. The results may be interpreted as the absence of free sodium hydroxide phase; it may be that it has interacted with $Ca(OH)_2$. The endothermic peak for the dehydration of the $Ca(OH)_2$ phase has also been similarly affected in the case of samples B, C and D, where Na_2O, Na_2O_2 and $NaNH_2$ were mixed with $Ca(OH)_2$ (Fig. 2). In the case of sample D consisting of a mixture of $NaNH_2$ and $Ca(OH)_2$, the endothermic peak also shows three maxima at 405, 420 and 445°C.

It should be mentioned that all the sodium compounds used have a strong tendency to transform into NaOH after being mixed with $Ca(OH)_2$ under ambient conditions, as observed from XRD studies. The presence of different shoulder peaks in the dehydration of $Ca(OH)_2$ may be ascribed to an interaction of NaOH with $Ca(OH)_2$, possibly through the formation of hydrogen bonds, or to the presence of NaOH causing a distortion in the $Ca(OH)_2$ lattice. Similar shoulder peaks to those observed in the present work were also noticed by Paterson and Swaffield [16] in the dehydration of α-Fe–O–OH phase; the authors suggested that the presence of lattice defects can influence the dehydration process.

The DSC curve for sample E ($NaBH_4/Ca(OH)_2$) shows an endothermic peak at 420°C along with three exothermic maxima at 370, 445 and 490°C, respectively. The

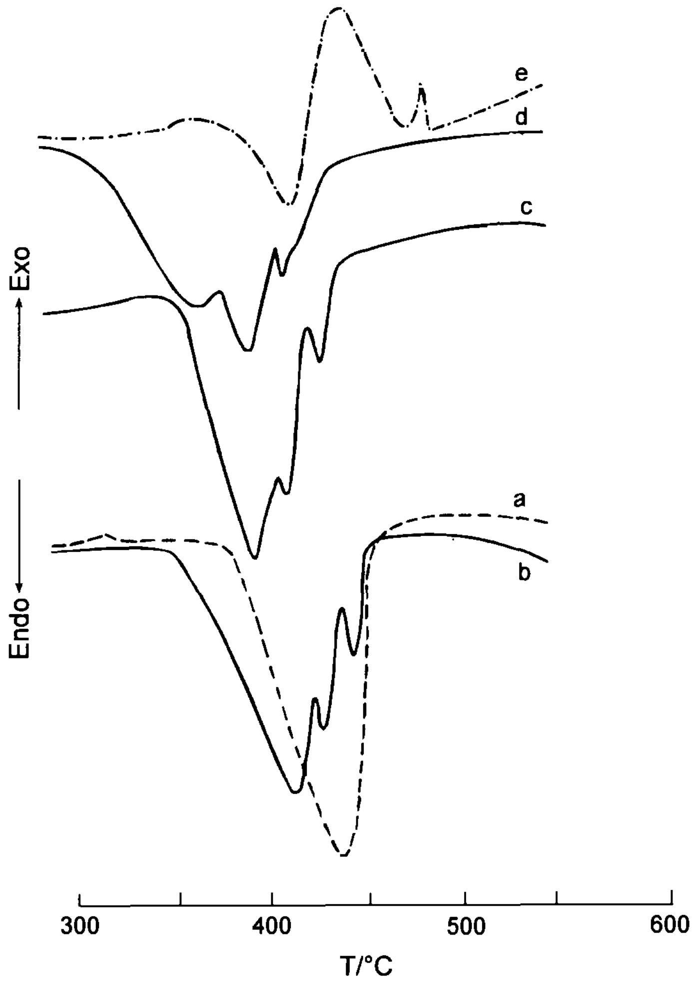

Fig. 2. DSC curves (nitrogen): a, $Ca(OH)_2$; b, sample D; c, sample B; d, sample C; e, sample E.

exothermic peaks can be assigned to the decomposition of an $NaBH_4$ phase, which was observed in the DSC curve at 350, 430 and 490°C for pure $NaBH_4$ under N_2 atmosphere; the endothermic peak at 430°C can be assigned to the dehydration of $Ca(OH)_2$.

In the case of samples F and G, where Na_2CO_3 and Na_2SO_4 are mixed with $Ca(OH)_2$, the shape of the endothermic peak remains unaffected. The DSC curves show a single endothermic maximum at 455 and 445°C respectively (Fig. 3). A weak exothermic peak is also observed at 320°C in both samples F and G; this peak is difficult to assign correctly. It has also been observed in some other samples, with even lower intensity. One possibility is the interaction of adsorbed CO_2 with $Ca(OH)_2$. Ther-

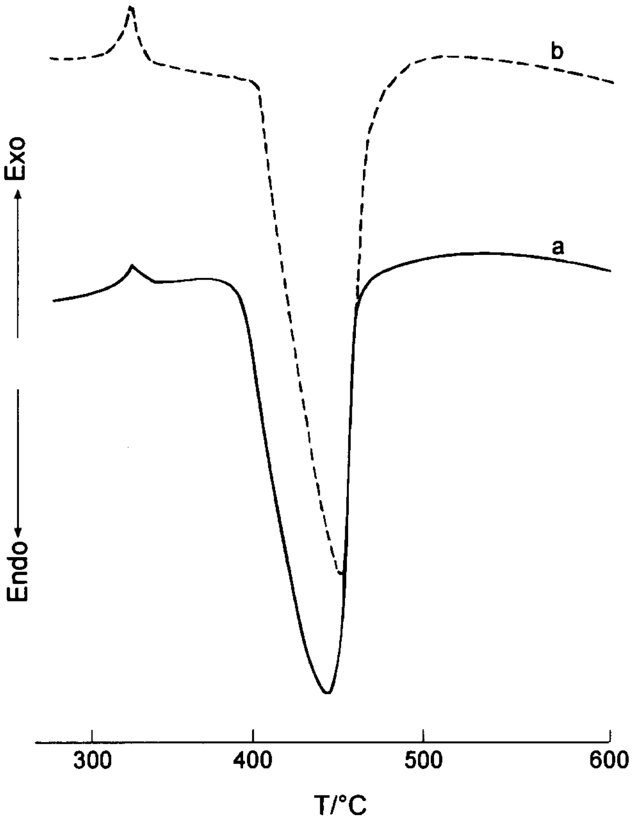

Fig. 3. DSC curves (nitrogen): a, sample G; b, sample F.

moanalytical results show that the interaction of Na_2CO_3 and Na_2SO_4 with $Ca(OH)_2$ is not distinct as in the case of samples A to D.

3.2. *IR spectroscopic studies*

The influence of different sodium compounds on the $Ca(OH)_2$ lattice was examined by infrared spectroscopic studies. IR spectra were recorded for the samples after oven-drying at 120°C and after calcining at 650°C. IR spectral bands of oven-dried and calcined samples are shown in Table 2 and Figs. 4 and 5.

The IR spectra show a strong absorption band at 3640 cm^{-1}, both for pure $Ca(OH)_2$ and Na(OH), together with a broad band in the 3000–3600 cm^{-1} region. Similarly, a strong absorption band at 3640 cm^{-1} has been observed for samples A-1, A-2 and A-3. This strong band can be assigned to the (OH) mode of vibration of OH^- ions and the broad band can be assigned to hydrogen-bonded hydroxyl ions as well as to adsorbed water molecules. In the broad region, another absorption band at 3521 cm^{-1} can be assigned in the IR spectra. As well as the (OH) absorption band, other bands are

Table 2
Infrared spectral bands of the samples at 120 and 650°C

Sample	Calcined at °C	Absorption band position/cm^{-1}								
A-1	120	3640 s	3540 w	3440 w		1640 w	1490 m	1440 m	881 w	
	650	3640 m		3440 w				1450 m	880 w	
A-2	120	3640 s	3520 w	3450 w		1640 w		1440 m	880 w	
	650	3640 m		3477 w				1443 m	880 w	
A-3	120	3640 s	3520 w	3450 w		1640 ew		1438 s	880 w	
D	120	3648 s		3440 w		1640 w		1447 m	880 w	
	650	3640 m		3435 w		1640 w		1445 m	880 w	
E	120	3648 s	3560 w		2387 w	1640 w	1460 w	1129 s	876 w	
			3480		2292 s					
			3417 s		2224 m	1618 m				
			3240 m							
	650	3640 m	3614 w				1468 m	1275 s	880 w	756 w
			3442 w				1451 m	941 w		730 w
			3374 w							
			3262 w							
F	120	3640 s	3540 w	3435 w			1455 s		870 m	
G	120	3640 s	3540 w	3440 w			1455 m	1129 w	876 w	
	800	3640 m		3420 w			1524 m		876 w	
							1413 m			

Key: see Table 1.

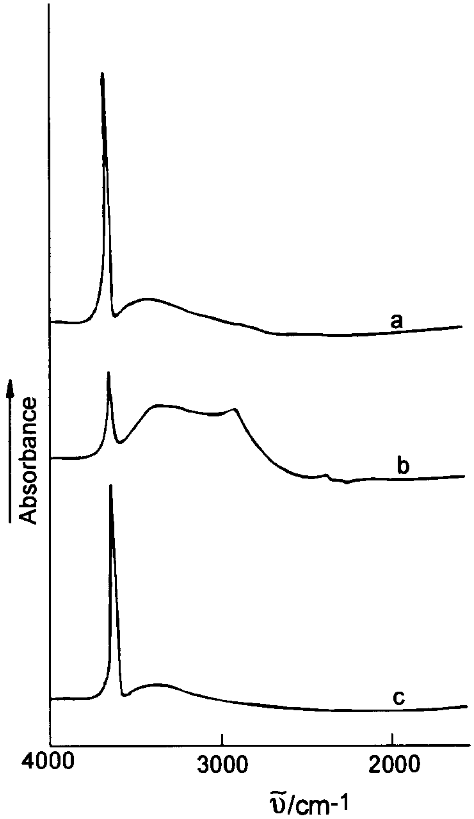

Fig. 4. IR spectra of samples air-dried at 120°C: a, $Ca(OH)_2$; b, NaOH; c, sample A-1 ($Ca(OH)_2$)–10% (NaOH).

observed at 1480, 1420 and 880 cm^{-1}, attributable to CO_3^{2-} ion impurities, which are due to contamination during preparation and handling of the samples. Similar absorption bands are also observed in the case of sample D, where $NaNH_2$ has interacted with $Ca(OH)_2$. IR spectra indicate that most of the $NaNH_2$ has interacted with $Ca(OH)_2$, even on oven drying at 120°C, and most likely transformed into NaOH. In the case of sample E, $NaBH_4$ has also interacted within $Ca(OH)_2$ at 120°C. The IR spectrum shows a number of new bands in the stretching region from 3500 to 3200 cm^{-1} as well as the main (OH) band at 3640 cm^{-1} (Table 3). Two sharp absorption bands in the bending mode region at 1640 and 1618 cm^{-1} were also apparent. However, $NaBH_4$ does not decompose on interaction (oven-dried at 120°C), as the IR spectrum also shows bands at 2387, 2292, 2240 and 1129 cm^{-1} which are characteristic for BH_4 tetrahedral modes [17]. In the case of sample F, a broad band occurs at 1130 cm^{-1} for SO_4^{2-} ions in addition to the stretching bands at 3640 and 3540 cm^{-1}.

On calcination of samples A–D at 650°C, the presence of an absorption band at 3640 cm^{-1} can be assigned to the partial rehydration of CaO particles under ambient

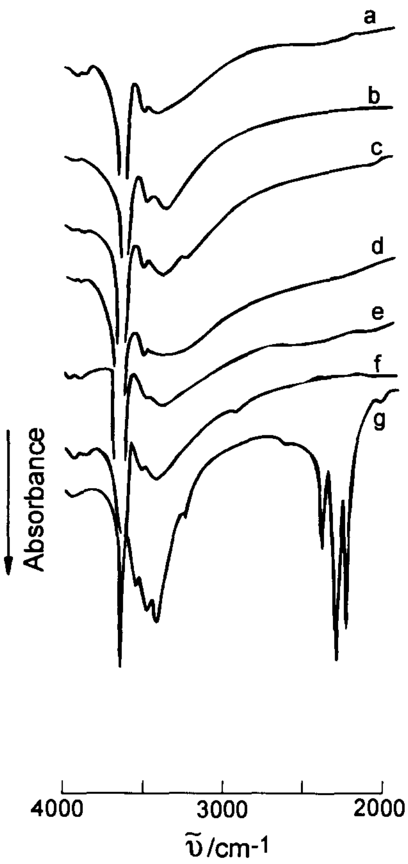

Fig. 5. IR spectra of the samples air-dried at 120°C: a, sample A-1; b, sample A-2; c, sample A-3; d, sample D; e, sample G; f, sample F; g, sample E.

conditions (Table 2). In the case of sample E, on calcining at 650°C, no band for free $NaBH_4$ is observed. However, in the stretching region, a number of extra bands as well as the band at 3640 cm^{-1} still exist; these may be assigned to the hydroxyl groups hydrogen-bonded with newly formed $Ca_3B_2O_6$ phase. This compound is also indicated from the XRD pattern. The IR spectrum also shows bands at 1275, 941, 756, 730 and 606 cm^{-1}, which can be assigned to $Ca_3B_2O_6$ phase [17]. No band is located at 1130 cm^{-1} for SO_4^{2-} ions in the case of sample G, calcined at 800°C. For sample F, it is difficult to assign the conversion of Na_2CO_3 into $CaCO_3$ on interaction with $Ca(OH)_2$, because the IR bands for CO_3^{2-} ions occur in all calcined samples and because the bands are also broad.

Summarizing, it can be stated that IR spectroscopic studies indicate, in the appearance of new bands in the stretching regions, that surface OH^- ions have interacted on admixing $Ca(OH)_2$ with different sodium compounds. However, it is not possible to

Table 3
Crystal phase composition of the samples at different temperatures

Sample	Calcination temperature/°C				Lattice parameter of CaO a_0 nm
	120	350	650	800	
A-1	$Ca(OH)_2$ NaOH	$Ca(OH)_2$	CaO $Ca(OH)_2$ trace		0.4815
A-2	$Ca(OH)_2$ NaOH	$Ca(OH)_2$ NaOH	CaO $CaOH_2$ trace Na_2O, NaOH Na_2CO_3 trace		0.4807
A-3	$Ca(OH)_2$ NaOH	$Ca(OH)_2$ NaOH	CaO $Ca(OH)_2$ trace Na_2O, NaOH Na_2CO_3 trace		0.4805
B	$Ca(OH)_2$ NaOH	$Ca(OH)_2$	CaO $Ca(OH)_2$ trace		–
C	$Ca(OH)_2$ NaOH	$Ca(OH)_2$	CaO $Ca(OH)_2$ trace		–
D	$Ca(OH)_2$ NaOH	$Ca(OH)_2$	CaO $Ca(OH)_2$ trace		0.4816
E	$Ca(OH)_2$ $NaBH_4$	CaO[a] $Ca_2B_5O_8(OH)_3$ $Ca(OH)_2$	CaO $Ca_3B_2O_6$		0.4808
F	$Ca(OH)_2$ Na_2CO_3	$Ca(OH)_2$ $CaCO_3$	CaO $CaCO_3$ $Ca(OH)_2$ trace	CaO $Ca(OH)_2$ trace	0.4804
G	$Ca(OH)_2$ Na_2SO_4	$Ca(OH)_2$ Na_2SO_4	CaO $Ca(OH)_2$ trace	CaO $Ca(OH)_2$ trace	0.4808

[a] Poorly crystalline

confirm the existence of free NaOH in the samples from the IR spectroscopic studies, as both $Ca(OH)_2$ and NaOH show an (OH) band at almost the same value (3640 cm^{-1}, Fig. 4). But the nature of the dehydration process (sample A-1) has also been followed from in situ recording of IR spectra at different temperatures. The results show that the dehydration starts above 350°C and is complete at 450°C. The IR spectrum at 450°C shows only a very weak indication of the (OH) band at 3640 cm^{-1}, which can be assigned to the residual OH^- ions. IR spectroscopic studies indicate that the dehydration of NaOH occurs along with the dehydration of $Ca(OH)_2$ phase; the details of this have been discussed elsewhere [15].

3.3. *X-ray diffraction study*

The change in the crystal phase composition of the prepared samples after different heat treatments was examined by XRD technique (Table 3). The results indicate that the samples A-1, A-2 and A-3, oven-dried at 110°C, consist of free NaOH and $Ca(OH)_2$ phases. XRD lines for NaOH were very weak; only the strongest line, with $d_{hkl} = 0.2353$

nm was clear, while the other lines were diffuse and weak. On calcining the samples at 350°C, the XRD patterns were nearly unchanged, except that the XRD lines for NaOH phase became more diffuse. On calcining the sample at 650°C, CaO was detected along with traces of $Ca(OH)_2$. But no further free Na_2O or Na(OH) was detected for sample A-1; however, it was present for samples A-2 and A-3 (samples A-2 and A-3 consist of 20 and 50 mol% of NaOH respectively). Formation of a trace of an Na_2CO_3 phase was also identified in the XRD patterns of A-2 and A-3. XRD studies indicated that on mechanical mixing of Na_2O, Na_2O_2 and $NaNH_2$ with $Ca(OH)_2$, all of them transformed into NaOH, even on oven drying at 120°C. In the case of samples B, C and D, it was not possible to detect any crystalline sodium-containing phase after calcination at 650°C, although they showed the presence of NaOH in the oven-dried samples. In the case of sample E, the XRD pattern indicated the presence of both $Ca(OH)_2$ and $NaBH_4$ phase at 120°C. On calcining the sample at 650°C, XRD patterns indicated the formation of a $Ca_3B_2O_6$ phase along with the main CaO phase. In earlier work it was reported that the decomposition of $NaBH_4$ leads to the formation of $NaBO_2$ above 400°C [18]. It may be assumed that $NaBH_4$ has been transformed into $NaBO_2$ during dehydration and concomitantly interacted with newly formed CaO to build a $Ca_3B_2O_6$ phase, in the case of sample E. In the case of sample F, Na_2CO_3 also interacted with $Ca(OH)_2$ before dehydration and $CaCO_3$ was formed. However, the reaction proceeded slowly and it took more than 10 h for the complete conversion of Na_2CO_3 into NaOH in the case of sample F. On calcining sample F at 800°C, the XRD pattern indicated CaO as the major phase along with $Ca(OH)_2$ as a minor phase. For sample G, Na_2SO_4 interacted during heat treatment because no Na_2SO_4 phase was detected at 800°C. All the samples indicated the presence of trace amounts of $CaCO_3$ (not shown in Table 3) as impurities.

The XRD results indicate that a solid–solid interaction develops between NaOH and $Ca(OH)_2$ lattice, even on oven-drying the samples at 120°C. However, it is difficult to confirm the formation of mixed hydroxides or any other compound formation. It is also indicated that most of the other sodium salts interact with $Ca(OH)_2$ and transform into NaOH, except $NaBH_4$. In the case of Na_2SO_4, further study is needed to identify the products in the intermediate stages.

The experimental results indicate that NaOH undergoes at least partial dehydration during calcination, along with $Ca(OH)_2$. In the case of pure sodium hydroxide, the dehydration does not proceed due to the strong ionic bonding [19]. But the experimental data suggest that dehydration of NaOH can occur in the presence of a CaO matrix. Details of this have been discussed in an earlier communication [15]. Thermoanalytical studies also show that some sort of solid–solid interaction takes place between mechanically admixed NaOH and $Ca(OH)_2$ matrix, as evidenced from the appearance of shoulder peaks on the main endothermic peak, assigned to the dehydration of $Ca(OH)_2$ phase. IR spectroscopic studies also indicate the presence of an extra weak band at 3521 cm^{-1} as well as a broad absorption band at 3450 cm^{-1} in the stretching vibration regions; these can be assigned to the hydrogen-bonded OH^- ions on the surface of the $Ca(OH)_2$ matrix. XRD studies indicate an extra line-broadening in the diffracted peaks in the case of both the $Ca(OH)_2$ phase in oven-dried samples and the CaO phase in the calcined state, in the presence of NaOH in the samples [15]. The extra line-broadening may be ascribed to the distortion of the $Ca(OH)_2$ or CaO lattice in the presence of NaOH or Na_2O. A similar extra line-broadening in the case of MgO system doped with Rb^+ and Na^+ ions has been suggested by Iwamatsu et al. [20] for the lattice distortion in the MgO lattice. No appreciable change in the lattice parameter values of CaO is noticed (Table 3). The lattice parameter value diminishes only slightly which makes it difficult to assign correctly for the amount of substitution of Na^+ ions in the CaO matrix. On heat treatment of sample A-1 at 650°C, the XRD pattern does not indicate the presence of any crystalline phase for the sodium component. On considering the decrease in the lattice parameter value, a partial substitution of Na^+ ions in the CaO matrix may be deduced. Another possibility is that the Na_2O phase exists in a poorly crystalline state due to its being well-dispersed over the CaO and that it tends to transform again into NaOH under ambient conditions. However, XRD patterns indicate the presence of free Na_2O and Na(OH) phase in the case of samples A-2 and A-3. XRD patterns also indicate the formation of traces of Na_2CO_3 phase due to possible interaction with contaminating CO_2 molecules from the ambient atmosphere. The results show that the incorporation of NaOH above 10 mol% causes a segregation of Na_2O/NaOH phases over the CaO matrix. The amount of sodium on the surface depends on the compounds used for impregnation and the surface becomes enriched in sodium during the calcination process. Higher bulk amounts of sodium in the sample cause a build-up of several overlayers of sodium compounds [21].

The experimental results indicate that the wet mixing of NaOH, Na_2O_2, Na_2O, Na_2CO_3 and $NaNH_2$ with $Ca(OH)_2$ resulted in Na_2O, NaOH and $Ca(OH)_2$ phases after drying at 120°C and calcination at 650°C. When $NaBH_4$ was used for impregnation, $Ca_3B_2O_6$ was observed as an extra phase. In all the samples, the incorporation of Na^+ ions in the CaO matrix was limited. It should be mentioned that all the samples exhibited similar catalytic performances: no significant differences in C_{2+} selectivity which amounted to approx. 70% were observed [3, 22]. The results obtained from thermoanalytical, XRD and IR studies are in good agreement with the observed catalytic activity and selectivity for the different samples, because all the samples possess nearly similar structural properties.

4. Conclusions

The results indicate that the sodium compounds interact with $Ca(OH)_2$ in all the mixed composites, except $NaBH_4$, and tend to transform into NaOH. A solid–solid interaction develops between NaOH and the $Ca(OH)_2$ lattice, even after oven-drying at 120°C. Calcium hydroxide which is transformed into CaO on calcination seems to be a suitable matrix for only limited inclusion of Na^+ ions. Attempts to increase the concentration of Na^+ ions in the CaO matrix were not effective because they mostly remain on the CaO surface. The amounts of sodium on the surface also depend on the nature of the compounds used for impregnation. The use of higher bulk amounts of sodium compounds causes a build-up of several overlayers of sodium on the surface.

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