Highly selective synthesis of 2-butoxy ethanol over Mg/Al/V mixed oxides catalysts derived from hydrotalcites

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The catalytic activity of a series of mixed oxides obtained by the thermal decomposition of hydrotalcite-like precursors was assessed for the alkoxylation of n-butanol with ethylene oxide. The calcination products of a decavanadate intercalated magnesium–aluminium layered double hydroxide were shown to possess extremely high activity for the alkoxylation reaction achieving up to 100% conversion in batch reaction. In all cases, the catalysts exhibit a much higher selectivity towards the monoglycol adduct than that obtained with the industrial catalyst.

Keywords: alkoxylation, hydrotalcites, polyoxometalates, mixed oxides, glycol ethers

1. Introduction

A large variety of products useful, for instance, as non-ionic surfactants, wetting and emulsifying agents, solvents and chemical reagents, are prepared by the addition reaction of epoxides (alkoxylation) with organic compounds having one or more active hydrogen. It is well known in the art that mineral acids, such as sulphuric acid and phosphomolybdic acid [1], and Lewis acids, such as boron trifluoride and aluminium perchlorate [2], can be effectively used as acid catalysts and alkali metal hydroxides, alkoxides and alkylamines are effective as base catalysts [3]. However, since these catalysts uniformly dissolve in the reaction system, they pose engineering problems such as separation of the catalyst from the reaction products, its post-treatment and its recycling, or the corrosion of the plant materials.

In the commercial production of alkylene glycol ethers by the alkoxylation of the lower alcohols, the product distribution, or ratio of mono-, di-, tri- and higher alkoxylates, is of considerable importance, the different alkoxylates being used in widely different end applications. From studies using the ethoxylation of ethanol as a model, Moody [4] showed that as a general rule the slower the reaction the higher the proportion of the monoethoxylate in the final product. The mono-alkoxylates are, in the main, the most important commercial products but their industrial production, using a homogeneous catalyst, is always accompanied by the production of the poly-alkoxylates. A survey of the literature relative to the development of proprietary catalysts for the synthesis of these ethoxylates reveals an increasing interest in clays, both cationic and anionic [5–10]. We have previously reported the use of some layered double hydroxides for glycol ethers synthesis [11,12], the materials then being used in the as-synthesized form, without prior thermal activation.

In this paper, we report on the use of calcined and calcined–rehydrated hydrotalcite-like materials as solid base catalysts for the selective synthesis of butoxy monoethylene glycol ether (BMGE). The results are compared to those provided by the conventional industrial catalyst and non-calcined LDHs.

2. Experimental

2.1. Materials

The decavanadate intercalated magnesium–aluminium LDH was prepared by structure reconstruction following a procedure similar to that described in the literature [13]. The parent [Mg–Al–CO_3] LDH, supplied by Süd-Chemie AG (Munich, Germany), was calcined for 16 h at 450 °C under inert nitrogen atmosphere. A typical batch of catalyst was prepared as follows: 40 g of calcined LDH material was slurried in deionised decarbonated water (DDW) for 1 h while the mixture is kept under nitrogen. A suspension of 61 g of $NaVO_3$ in 2 l of DDW (0.25 M) was degassed separately with nitrogen at 65 °C for 0.5 h. Then the pH of the solution was brought down to 4.5 by constant addition of a 2 M solution of HNO_3 until a clear red-orange solution was obtained. This solution was then mixed to the slurry and the pH was maintained at 4.5 ± 0.1 by controlled addition of nitric acid for about 1 h. The precipitate was left overnight at 65 °C, filtered out the following day, washed with 3 l of hot DDW and dried under dynamic vacuum.

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X-ray powder diffraction patterns of the catalysts were recorded in the range of $2\theta = 4°–76°$ using a Siemens D500 diffractometer with Cu Kα source. The scan step was 0.08° with a count time of 4 s at each point. BET surface areas were measured at liquid-nitrogen temperature using a Fison SP1920 instrument.

Starting from one single batch, the intercalated LDH [MAV] was calcined at 450 °C under nitrogen to generate three separate catalysts:

- mixed oxides used as such, $[\mathrm{MAV}]_{\mathrm{CAL}}$;
- mixed oxides rehydrated in deionised water, $[\mathrm{MAV}]_{\mathrm{HYD}}$;
- mixed oxides rehydrated in a 1 M solution of KOH, $[\mathrm{MAV}]_{\mathrm{KOH}}$.

The material rehydrated in potassium hydroxide was thoroughly washed with hot DDW to ensure complete elimination of the base.

2.2. Catalytic reactions

The screening tests were carried out in a 2 l batch autoclave, fitted with a mechanical stirrer. The catalyst (8 g), meshed to particle size <150 μm, was added to n-butanol (978.6 g) in the batch autoclave. After purging with nitrogen, approximately 116 g of ethylene oxide (n-BuOH/EO = 5.0 on a molar basis) was then added, and the sealed autoclave was pressured with nitrogen to 2 MPa to keep ethylene oxide in the liquid phase, while the temperature was raised to 120 °C. The pressure of the batch reactor was then stabilised at 3 MPa by applying a nitrogen top pressure, and reaction conditions maintained for 72 h.

The second part of the study involved the use of a fixed-bed, continuous-flow, stainless-steel tubular reactor (ID 10 mm). The powdered mixed oxides were pelleted using an infrared press and sieved to obtain a granulated material with particle size comprised between 0.850 and 1 mm. The catalyst charge was 5 cm^3 of sieved materials. Prior to starting the tests, the catalyst was activated overnight at 170 °C under continuous nitrogen flow (500 $\mathrm{ml\,min}^{-1}$). The feed consisted of n-butanol and ethylene oxide in a molar ratio of 5 : 1. The reactants were fed to the reactor at various flow rates to obtain liquid hourly space velocities (LHSV) between 1 and 10. The tests were carried at 120 °C and 3 MPa.

Collected samples were analysed off-line using a Pye Unicam 4500 gas chromatograph fitted with a WCOT fused silica capillary column (50 m, 0.25 mm ID, CP-Sil-5). The conversion in ethylene oxide is calculated as EO conversion (mol%) = 100 × ($\mathrm{EO}_{\mathrm{in}} - \mathrm{EO}_{\mathrm{consumed}}$ (based on ethoxylated products))/$\mathrm{EO}_{\mathrm{in}}$. Ethoxylated products were chosen to avoid errors in the determination of residual ethylene oxide due to its low boiling point (13 °C). The calculated mass balances were typically 97% or higher for any test period.

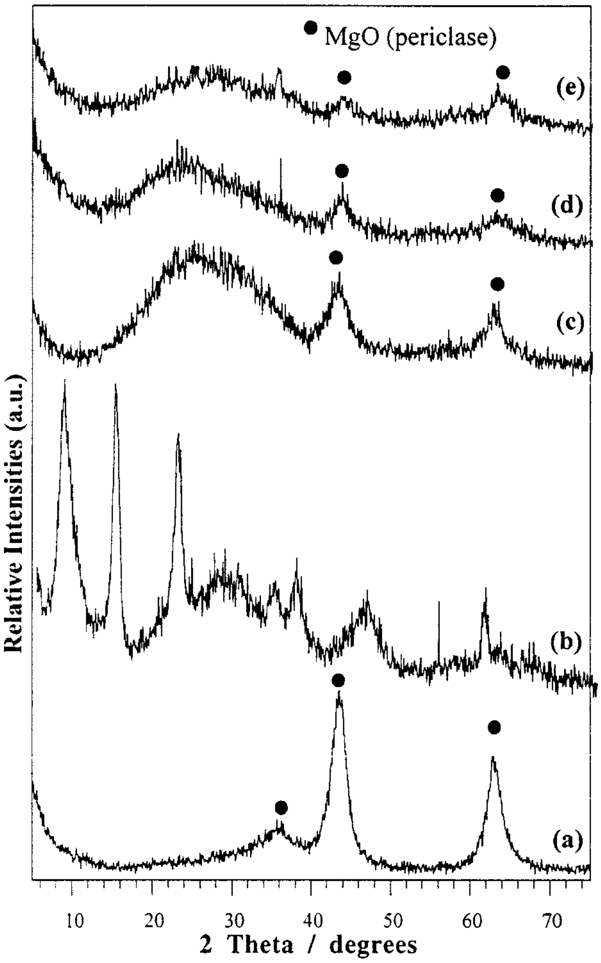


Figure 1. XRPD patterns of (a) starting material, (b) decavanadate LDH [MAV], (c) calcined [MAV], (d) calcined [MAV] rehydrated in water and (e) calcined [MAV] rehydrated in KOH.

3. Results and discussion

Catalyst characterisation

The X-ray powder diffraction pattern of the bright yellow powder resulting from structure regeneration revealed a typical hydrotalcite-like compound with a d_{003} spacing of 11.63 Å, which is in good agreement with literature values [13–15]. Figure 1 shows the XRD patterns of the three catalysts used in this study. As already reported by various authors [16–18], the calcination of hydrotalcite-like compounds at high temperature leads systematically to the collapse of the lamellar structure and the formation of oxide species. The starting material, a calcined hydrotalcite, shows the presence of a periclase MgO phase while aluminium oxide, although also present, is undetected being mainly amorphous.

According to Di Cosimo et al. [19] this is an indication that after thermal decomposition Al^{3+} cations remain closely related to the MgO structure and will confer to the catalyst its specificity. Following anion exchange and a further calcination step, the periclase phase is shown to decrease significantly. This suggests that part of the mag-

Table 1
Textural properties of HT-like compounds and derived mixed oxides.

Sample	Phase[a]	S_{BET} ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)
[Mg–Al–CO_3]	HT	75	0.490
[Mg–Al–CO_3]$_{CAL}$	MgO + Amorp.	193	0.652
[MAV]	HT	30	0.220
[MAV]$_{CAL}$	Amorp. + MgO	60	0.289
[MAV]$_{REH}$	Amorp. + MgO	45	0.295
[MAV]$_{KOH}$	Amorp. + MgO	42	0.291

[a] HT – hydrotalcite-like, Amorp. – amorphous.

nesium is most probably monopolised in the formation of a ternary oxide, (Mg–Al–V)–O. However, no definite compounds are shown to be formed and a predominantly amorphous material is obtained. The rehydration step appears to decrease even more the proportion of MgO in the final material and the XRPD patterns clearly indicate that the process is also affected by the pH of the rehydrating solution. The most likely explanation for this observation is that under such conditions most of the periclase phase will be transformed into an amorphous hydroxide form.

It is important to stress that in this work the calcination–rehydration procedure was not intended to induce structure reconstruction of the [MAV]. Such regeneration process is unique to hydrotalcite-like compounds containing anionic species like nitrates or carbonates [20]. Our main interest here was to evaluate how the reactivity of the mixed oxides could be modulated through rehydration.

As shown in table 1, all the solids studied as potential catalysts possess a rather low surface area, not exceeding 60 $m^2 g^{-1}$. No increase in the surface area is observed after the incorporation of the decavanadate anion. As distinct from materials such as [Mg–Al–CO_3], calcination of [MAV] does not increase the surface area. Furthermore, no important variation in the surface properties of the final mixed oxides is observed whether the material is rehydrated in water alone or in potassium hydroxide. There is, however, a significant decrease in the mean pore volume.

The catalytic performances of the various materials for the synthesis of 2-butoxy ethanol are represented in figure 2 as a function of time. The activity of the new catalysts, obtained after calcination or calcination–rehydration, is compared to that of the untreated [MAV]. On calcining the decavanadate magnesium–aluminium, to form [MAV]$_{CAL}$, a significant increase in activity is observed within the first 24 h. The maximum ethylene oxide conversion obtained was 74% as compared to a value of 47% with [MAV] after the same period. This difference in activity can be related to the more basic nature of the calcined material having MgO in the final phase. Calcined LDHs are known to be extremely basic materials, following the creation of O^{2-} basic centres, and their catalytic properties have been explored in a variety of chemical processes [21]. But in the search for solid base catalysts only the carbonate precursors were generally studied as the presence of other species, and more specifically transition elements, tend to reduce the basicity of the calcined phase. However, with regard to the ethoxylation of butanol, a previous study [11,12] demonstrated the beneficial role of the decavanadate species in both the activity and the selectivity.

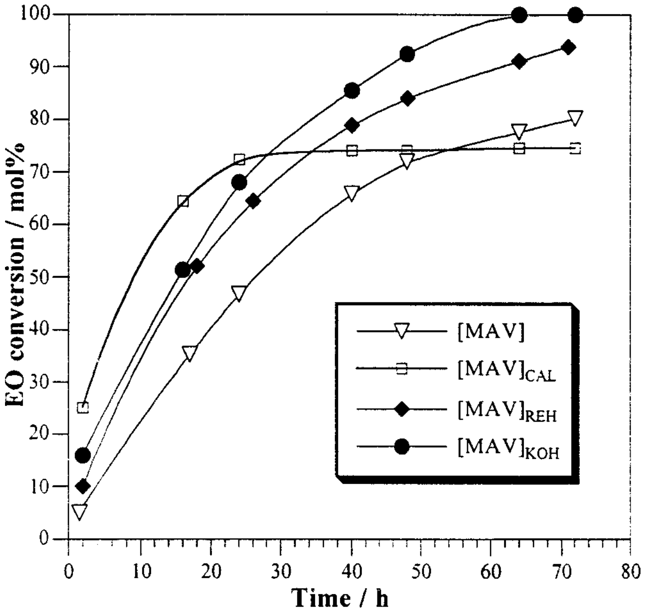
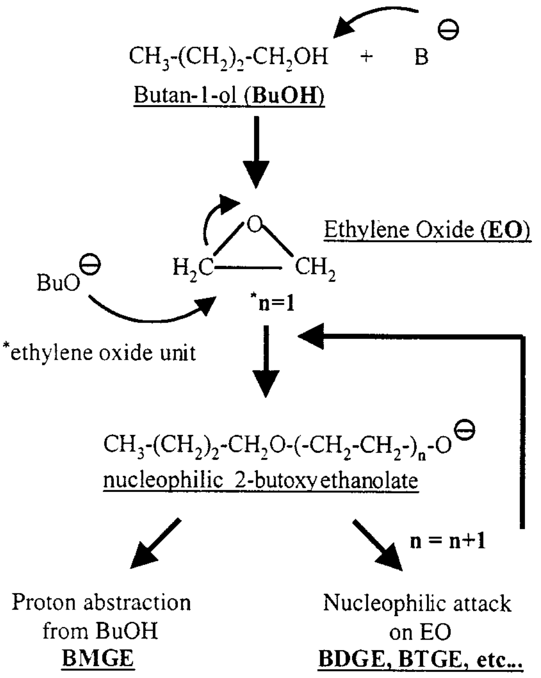


Figure 2. Overall conversion of ethylene oxide as a function of time using LDHs and derived mixed oxides.

However, the [MAV]$_{CAL}$ catalyst was completely deactivated after 24 h and no further conversion of ethylene oxide was observed. The behaviour of [MAV] clearly indicates that this deactivation is not a consequence of the temperature and pressure conditions prevailing during the tests. A likely cause of deactivation was revealed at the end of the run when a significant amount of a polymer type material was found to be present in the product. The gelatinous solid was attributed to polyethylene glycols (PEGs) and polyethoxylates. It is believed that these products would strongly adsorb on the surface of the catalyst and would be the most likely origin of the deactivation. The understanding of how these high molecular compounds are formed in this catalytic system is considered to be a key factor for the development of an adequate catalyst.

Scheme 1 describes the possible mechanism involved in the base-catalysed reaction, based on Chibwe's study of the propoxylation of butanol [22]. There is first abstraction of a proton from butanol giving the butoxide anion, which will in turn attack the ethylene oxide to yield the 2-butoxyethanolate species. The formation of the butoxide intermediate on the catalyst surface is most probably favoured by the existence of acid–strong base pair sites, which are, respectively, the cations (Al^{3+}, Mg^{2+}, V^{5+}) and surface O^{2-}. There are two possible reaction pathways for this anion: it either abstracts a proton from butanol to form BMGE and another butoxide molecule ($n = 1$) or it reacts with ethylene oxide to give the anion of the diglycol ether ($n = n + 1$). In the latter case the same scenario as before is reproduced, this time with $n = 2$, and so forth, thus leading to polyethoxylates. Also, the 2-butoxyethanol



Scheme 1. Possible mechanism for the base-catalysed ethoxylation of butanol showing the route for the formation of polyethoxylates.

newly formed being much more reactive than butanol is even more likely to be deprotonated, yielding the respective anion and reacting with ethylene oxide.

To minimise this polymerisation and the formation of PEG a high BuOH/EO molar ratio is normally used in the ethoxylation reaction. A BuOH/EO ratio of 5 was used to mimic as close as possible that of the commercial process.

Another possible cause for the formation of polyethoxylates is related to the intrinsic properties of the catalyst. Following calcination, [MAV] is transformed into a very unstable mixed oxide possessing a highly ionic surface. The glycol ethers formed during the reaction are much more polar than butanol and would be preferentially adsorbed on the surface of the catalyst. Being also more reactive they would readily react with ethylene oxide to form high molecular species causing a blockage of the active sites. A possible saturation of the surface with ethylene oxide is also plausible due to its polarity.

To modify the surface properties of the catalyst, it was then decided to rehydrate the calcined material prior to use. The material was found to be more active than the untreated [MAV], achieving a higher conversion in ethylene oxide at the end of the testing period (94 against 80%). These results seem to confirm the hypothesis that the high surface charge of the calcined material was detrimental to its catalytic performances. Rehydration most certainly converted the superficial O^{2-} sites into hydroxyl groups of lesser basicity but still catalytically active. Interestingly, it can be noted that the formation of hydroxide did not cause any deactivation of the catalyst, as opposed to what has been reported by Thomasson et al. [23] in the dehydrogenation of 2-butanol on modified MgO catalysts.

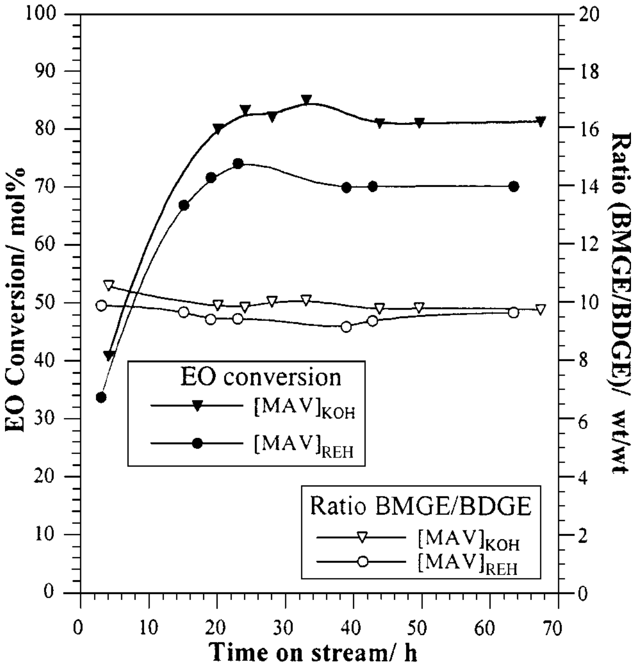


Figure 3. Conversion and selectivity of calcined–rehydrated hydrotalcites in the fixed-bed flow reactor.

Given the performance of $[MAV]_{REH}$, and in order to further increase the basicity of the rehydrated material, it was then decided to perform the rehydration process in a basic solution. The data presented in figure 2 show that even if the activity curves of $[MAV]_{REH}$ and $[MAV]_{KOH}$ are relatively similar, the advantage gained is that with the second catalyst all the EO is consumed after 64 h. Again, it is believed that this increase in the activity of the catalyst (100% conversion) is a result of the formation of surface hydroxyls. The use of potassium hydroxide seems either to increase the amount of OH groups or to form stronger ones.

Based on their high reactivity, the two rehydrated materials were further studied in a fixed-bed flow reactor to address the issues of selectivity and stable catalytic activity with time on stream. Figure 3 illustrates the behaviour of $[MAV]_{REH}$ and $[MAV]_{KOH}$ in the flow reactions performed under the same conditions of temperature and pressure: 120 °C and 3 MPa. The liquid flow rate was adjusted so as to have a LHSV of 1, the residence time of the reactant on the catalyst bed being then 60 min.

The two catalysts exhibit similar overall reaction profiles with an induction period of around 30 h during which the activity builds up. After reaching maximum activity (74% with $[MAV]_{REH}$ and 85% with $[MAV]_{KOH}$), a slight deactivation is observed and a more steady conversion rate is maintained until the test is terminated (70 and 81%). Initially, it was thought that this induction period was somehow related to the catalyst being chemically activated by the reactants. For example, a reduction of the surface vanadium species is not to be excluded. This possibility was ruled out following the observation of the same activity profile when a used catalyst was tested.

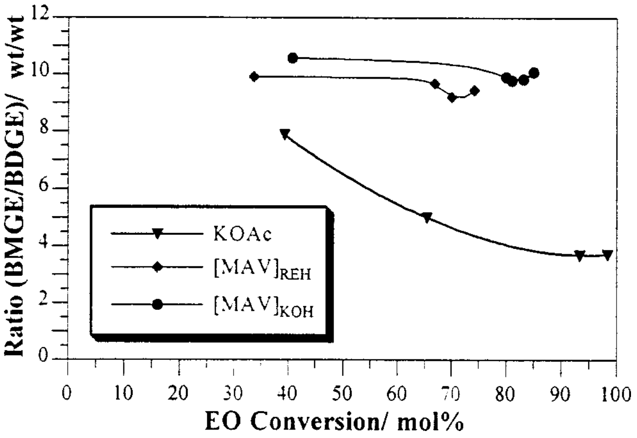


Figure 4. Comparing the ratio BMGE/BDGE between different catalysts.

Instead, it is believed that the induction period might be related to the formation of the intermediate reactive species, such as the butoxide anion. These species would remain adsorbed on the surface of the catalyst to further react with ethylene oxide. In which case it then appears that the induction period could be assigned to the time needed for the catalyst's surface to be saturated with these species. This "organic layer" on the surface of the catalyst, making it more hydrophobic, is suspected to facilitate the diffusion of the reactant to the active sites. The main reason for the observed difference in conversion rate between the two catalysts would be probably due to the strength of the superficial basic sites, normally expected to be higher in $[\mathrm{MAV}]_{\mathrm{KOH}}$ than $[\mathrm{MAV}]_{\mathrm{REH}}$. The profile of the activity curves of the two is very similar to that obtained in batch reactions: the material treated with KOH is again shown to be significantly more active than the one rehydrated in water alone. It is also worthwhile to note that they both exhibit almost the same selectivity in monoglycol ether, the ratio BMGE/BDGE being very close.

The evolution of the ratio monoglycol/diglycol as a function of conversion rate is illustrated by the examples in figure 4. When compared to the conventional potassium acetate catalyst it can be seen that either catalyst offers a much better selectivity in the monoglycol adduct.

This difference in selectivity is most certainly related to the catalytic system, heterogeneous against homogeneous catalysis. The continuous flow of the feed mixture over the catalyst bed will contribute to maintain a relatively constant concentration of the different species. The selectivity seems to be controlled by the adsorption properties of the intermediate species. Conversely, in the homogeneous system the catalyst is dissolved in the feed mixture and the different species are more likely to react with each other only on the basis of their reactivity. One particularity of the heterogeneous system, as indicated in figure 4, is that the selectivity remains roughly constant whatever the conversion rate.

In order to clarify the relationship between activity and selectivity in the heterogeneous system, the most active catalyst was further investigated by varying the contact time. Figure 5 shows the evolution in the conversion of ethylene oxide with increasing space velocities. As expected, the conversion rate is shown to decrease significantly with higher LHSV. For example, the conversion in ethylene oxide falls from 85% (LHSV = 1) to only 24% for a space velocity of 10. However, the selectivity in the monoglycol adduct is here again shown to be constant around 88%. The trend normally observed in catalytic systems involving step-wise reactions, i.e., decrease in selectivity with higher conversion is not respected in this reaction. This further suggests that the selectivity could be controlled by the adsorptive properties of the catalysts rather than by the kinetics of the reaction. As described in section 2, the formation of polyethoxylates (di-, tri- and tetra-glycol ethers) is suspected to be resulting mainly from successive reactions on the catalyst's surface. The secondary reactions occurring in the homogeneous phase seem to be negligible. In which case, the constant selectivity observed would depend on the rate of desorption of the primary product from the active site and be independent of the activity of the catalyst. With regard to the results obtained with $[\mathrm{MAV}]_{\mathrm{CAL}}$, it is believed that the main difference between the two catalysts lies in distribution of the surface charge: the calcined material possesses a highly ionic surface which will differ substantially during the rehydration process.

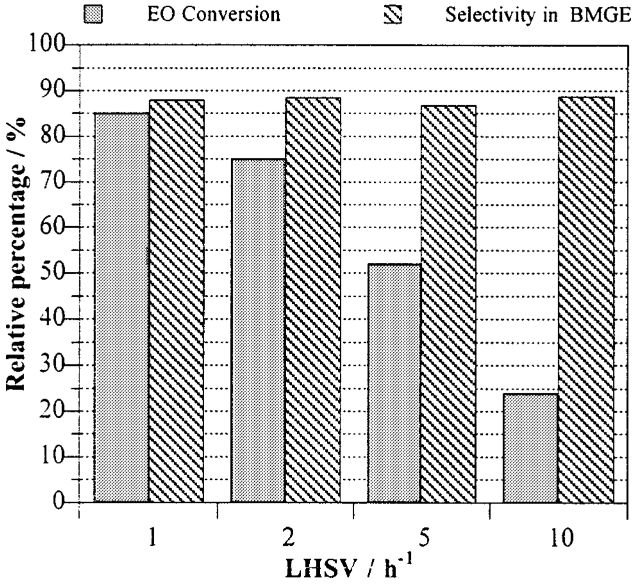


Figure 5. Conversion and selectivity as a function of space velocities (LHSV).

4. Conclusions

The use of these exchanged LDHs as precursors to mixed oxides catalysts represents a new approach in the study of the ethoxylation of n-butanol. The calcination products of a decavanadate intercalated magnesium–aluminium hydrotalcite exhibit high activity in this reaction. The most interesting catalysts were found to be the mixed oxides rehydrated in a potassium hydroxide solution. When the results were compared to those obtained with as-synthesised LDHs, the

Table 2
Performance of the mixed oxides catalysts compared to the industrial homogeneous catalyst.

	KOAc	$[MAV]_{KOH}$	$[MAV]_{REH}$
EO conversion (wt%)	100	84.95	74.12
Selectivity (wt%)			
BMGE	61	87.90	88.04
BDGE	26	8.71	8.68
BTGE	9	1.57	1.74
Dioxolanes		0	0
Aldehydes		0.55	0.36
Heavies	4	0.57	0.70
Unknowns		0.70	0.48
Ratio BMGE/BDGE	2.35	10.09	10.14
Mass balance		98.02	98.98

main conclusion was that the lamellar structure was not a crucial parameter in determining either the activity or the selectivity. It is believed that the LDH framework acts rather like a basic support for the oxo-vanadate species. In the case of the uncalcined LDHs, the activity observed was most probably due to anions on the edge of the interlamellar domain and adsorbed on the surface. On calcining the hydrotalcite-like compound, an extremely reactive material was obtained following the creation of highly basic active centres. Also a better dispersion of the catalytic sites is expected to be achieved. Besides, a subsequent rehydration of the calcined LDHs was found to be essential in limiting the side reactions yielding unwanted polyethoxylates. All catalysts tested in this study exhibit higher selectivity than the industrial homogeneous catalyst. Table 2 shows the products distribution of the ethoxylation reaction using $[MAV]_{REH}$, $[MAV]_{KOH}$ and potassium acetate. The data are for the highest conversion level observed for each catalyst.

These results indicate that the selectivity was the same independent of the final rehydration treatment. This suggests that the intrinsic characteristics inducing high selectivity in BMGE are the same in both materials. Accordingly, it is believed that this is related to the presence of vanadium species, which creates a synergistic effect with the basic support providing the activity.

The catalysts presented in this work are considered to be very promising candidates for the ethoxylation reaction and some improvements are necessary to achieve better activity, to make their use commercially viable.

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