

# Liquid-phase heterogeneous catalytic transfer hydrogenation of citral on basic catalysts

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## Abstract

The liquid-phase catalytic transfer hydrogenation of citral with 2-alkanols, 3-alkanols and cycloalkanols on basic catalysts obtained from  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  was studied. The catalysts were characterised by X-ray diffraction, and by adsorption of nitrogen and chemisorption of carbon dioxide. Both catalysts provided excellent results in terms of catalytic activity and selectivity in the reduction of citral with all the alcohols tested. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrogen transfer; Citral; Basic catalysts

## 1. Introduction

Catalytic hydrogenations by transfer with a variety of hydrogen donors [1,2] have been widely used in organic synthesis in the recent years, so much so that they have become major alternatives to conventional catalytic hydrogenations with gas hydrogen in many cases. For some time, our research group has examined the performance of  $\text{AlPO}_4$ ,  $\text{SiO}_2\text{-AlPO}_4$  and  $\text{Al}_2\text{O}_3\text{-AlPO}_4$  systems, and of sepiolites, as heterogeneous reduction catalysts. By supporting Pd on such systems, we have obtained excellent catalysts [3–6] that are suitable for transfer reduction processes involving various organic functions. The hydrogen-transfer reaction between carbonyl compounds and secondary alcohols, known as the Meerwein–Ponndorf–Verley (MPV) reaction, is highly sensitive and takes place under mild conditions; it is

usually activated by aluminium alkoxides [7,8]. Aluminium isopropoxide has proved the most suitable reagent for this process. This method, however, requires both the addition of at least 100–200% excess aluminium isopropoxide and neutralisation of the excess alkoxide salt with a strong acid.

Following findings in the 1970s [9,10] and recent experimental results, special attention has been given to MgO, a typical catalyst for gas-phase transfer hydrogenation processes [11–15]. Recently, other catalytic systems including zeolites [16,17], silica [18] and double layered hydroxides [19], have also been used in MPV reactions.

The wide range of applications and the high practical potential of MPV processes on basic catalysts led us to undertake a study of the reduction of liquid citral with various secondary alcohols on two MgO and CaO basic catalytic systems. The catalysts were structurally characterised by X-ray diffraction, and their textural properties and basicity determined

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by temperature-programmed desorption of carbon dioxide.

## 2. Experimental

### 2.1. Preparation of catalysts

The magnesium oxide solid was obtained by calcination of commercially available  $\text{Mg}(\text{OH})_2$  at  $600^\circ\text{C}$  in the air for 2 h. The solid thus obtained ( $\text{MgO}_\text{S}$ ) possessed a very low specific surface area, so it was rehydrated in refluxing water for 6 h. The resulting new solid,  $\text{MgO}_\text{W}$ , was air-dried and calcined at  $600^\circ\text{C}$  to obtain the catalyst named  $\text{MgO-600}$ .

The calcium oxide solid was obtained by calcining commercially available calcium hydroxide at  $900^\circ\text{C}$  in the air for 24 h. The catalyst thus obtained was designated  $\text{CaO-900}$ .

### 2.2. Characterisation of catalysts

The X-ray diffraction patterns (XRD) for the solids were recorded on a Siemens D-500 diffractometer using  $\text{Cu K}\alpha$  radiation. Scans were performed over the  $2\theta$  range  $5\text{--}75^\circ$ . The specific surface areas of the solids were determined by the BET method [20], which was implemented on a Micromeritics ASAP 2010 analyser.

The number of basic sites on the surface of the solids was determined by TPD of  $\text{CO}_2$ . A stream of argon containing 5%  $\text{CO}_2$  was passed at a flow-rate of  $50\text{ ml min}^{-1}$  over an amount of solid of 0.2 g until no further  $\text{CO}_2$  adsorption was observed. At that point, the argon stream was passed again and the desorption of physisorbed  $\text{CO}_2$  monitored. After the TCD baseline levelled off, TPD was conducted at a heating rate of  $15^\circ\text{C min}^{-1}$  from room temperature to  $600$  or  $900^\circ\text{C}$  on a Micromeritics TPD/TPR 2900 analyser.

### 2.3. Catalytic experiments

Catalytic hydrogen transfer runs were conducted under refluxing conditions in a two-mouthed flask containing 0.003 mol of citral (Aldrich ref. C8, 300-7, E/Z ratio = 0.6), 0.06 mol of alcohol — the donor-to-acceptor ratio was, thus, 20:1 — and 1 g of freshly calcined catalyst. One of the flask mouths was fitted with a reflux condenser and the other was

used for sampling at regular intervals. The system was shaken throughout the process. Products were identified on the basis of their retention times and by GC–MS analysis on an HP 5890 GC instrument furnished with a  $30\text{ m} \times 0.32\text{ mm}$  Supelcowax column and an HP 5971 A MSD instrument.

## 3. Results and discussion

### 3.1. XRD results

Fig. 1 shows the XRD patterns for the rehydrated product  $\text{MgO}_\text{W}$ , solid  $\text{MgO-600}$  and the  $\text{CaO-900}$  system. As can be seen from Fig. 1a, solid  $\text{MgO}_\text{W}$  possesses a brucite-like structure. On calcination at  $600^\circ\text{C}$  (Fig. 1b), the brucite layers are thoroughly dehydroxylated and periclase magnesium oxide is obtained. This is consistent with previous results of our research group [20]. Fig. 1c shows the XRD patterns for solid  $\text{CaO-900}$ , which is consistent with that for calcium oxide.

### 3.2. BET results

Table 1 gives the specific surface areas and mean pore diameters of the solids studied (determined by

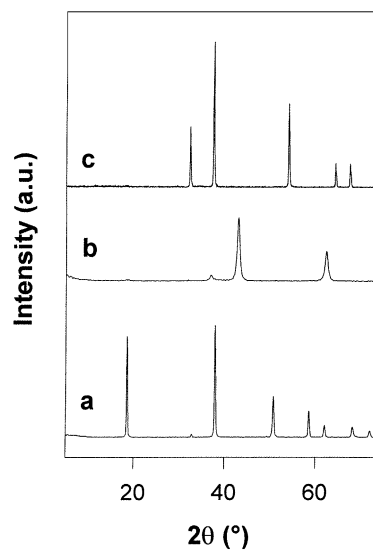


Fig. 1. XRD patterns for the rehydrated product  $\text{MgO}_\text{W}$  (a); solid  $\text{MgO-600}$  (b); and solid  $\text{CaO-900}$  (c).

Table 1  
Textural properties of the catalysts and their precursors

Solid	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$d_p$ (Å)
Mg(OH) <sub>2</sub>	14	204
MgO <sub>S</sub>	15	241
MgO <sub>W</sub>	11	232
MgO-600	116	77
Ca(OH) <sub>2</sub>	18	240
CaO-900	5	372

BDDH method). As can be seen, calcining Mg(OH)<sub>2</sub> at 600°C to obtain MgO<sub>S</sub> caused no significant change in specific surface area; nor did rehydration of MgO<sub>S</sub> to MgO<sub>W</sub>. On the other hand, calcination of the last solid at 600°C considerably increased its surface area. These results are consistent with previous findings (e.g. that rehydrating MgO and subsequently calcining it increases its specific surface area [21,22]). By contrast, calcining the calcium hydroxide solid at 900°C decreased its surface area.

### 3.3. Basic properties

Fig. 2 shows the TPD profiles for carbon dioxide adsorbed on the catalysts studied. In the profile for adsorbed CO<sub>2</sub>, the concentration of basic sites is reflected in the peak area and their strength in the temperature at which the CO<sub>2</sub> desorption peak appears. As can be seen from Fig. 2, the two solids exhibit three desorption peaks, so they contain three types of basic sites of differential strength. Table 2 gives the total number of basic sites obtained for each solid, as well as their proportion in relation to the desorption temperature, which is a measure of their strength. On the assumption that CO<sub>2</sub> is adsorbed with a 1:1 stoichiometry, a comparison of the deconvoluted plots with the response of a CO<sub>2</sub> standard dissolved in argon provided the number of surface basic sites

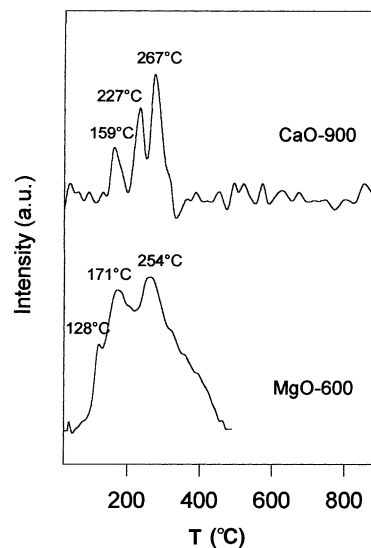


Fig. 2. TPD profiles for CO<sub>2</sub> adsorbed on the solids studied.

corresponding to the four desorption temperature ranges, viz.  $n_{120-140}$ ,  $n_{150-170}$ ,  $n_{225-240}$  and  $n_{250-270}$ . The total number of basic sites,  $n_b$ , was derived from the amount of CO<sub>2</sub> desorbed over the temperature ranges 100–600 and 100–900°C for MgO-600 and CaO-900, respectively.

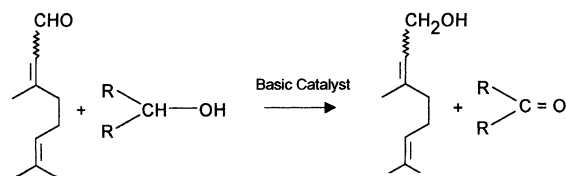
As can be seen from Table 2, the total number of basic sites in Mg-600 is almost three times greater than that in CaO-900; also, the basic sites in the magnesium oxide are weaker than those in the calcium oxide as part of the CO<sub>2</sub> is desorbed between 120 and 140°C in the former but not in the latter.

### 3.4. Catalytic activity

Scheme 1 depicts a typical catalytic transfer hydrogenation. During the reaction, the alcohol is oxidised to a ketone and citral, in its Z and E forms, is reduced to nerol and geraniol, with no change in olefin

Table 2  
Basic properties of the catalysts studied

Catalyst	$n_b$ ( $\mu\text{mol CO}_2 \text{g}^{-1}$ )	Proportion of basic sites (%)			
		$n_{120-140^\circ\text{C}}$	$n_{150-170^\circ\text{C}}$	$n_{220-240^\circ\text{C}}$	$n_{250-270^\circ\text{C}}$
MgO-600	257	14.6	38.6	–	46.8
CaO-900	89	–	18.1	29.5	52.4



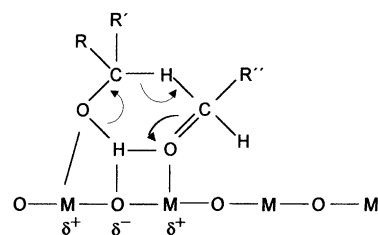
Scheme 1.

bonds. The reaction yield and selectivity exceeded 95 and 85%, respectively, in all experiments.

### 3.5. Hydrogen transfer in alcohols

Table 3 shows the catalytic activity results obtained in the MPV reaction, using the two catalysts tested and various alcohols. The figures in brackets are the selectivity values obtained at a conversion above 95%. From the results it follows that, for a given 2-alkanol, the catalytic activity of MgO-600 is greater than that of CaO-900; also, for a given catalyst, catalytic activity decreases in the following alkanol sequence: 2-hexanol > 2-pentanol > 2-butanol > 2-propanol. The selectivity, defined as ratio of the number of moles of alcohol formed (nerol + geraniol) to that of citral converted, always exceeds 85%.

Table 3 also gives the activity and selectivity results obtained in the reduction of citral with two different 3-alkanols. As can be seen, catalytic activity follows the same sequence as with the 2-alkanols, i.e. 3-hexanol exhibits better results than 3-pentanol, whichever the catalyst used, and MgO-600 is more active than CaO-900 in the process.



Scheme 2.

Finally, the MPV reduction process was also conducted by reducing citral with cycloalkanols. As can be seen from Table 3, catalytic activity was higher for cyclohexanol than for cyclopentanol. Also, the catalysts exhibit the same trend as with 2-alkanols and 3-alkanols.

Based on the results of Table 3, for a given alcohol family (2-alkanols, 3-alkanols or cycloalkanols), catalytic activity increases with increasing length of the molecular chain, which influences the refluxing temperature of the reaction mixture. Also, within a series of alcohol isomers, the cycloalkanol exhibits higher catalytic activity than the 2-alkanol, and this than the 3-alkanol.

A comparison of the catalytic activity exhibited by the two solids with the same alcohol reveals that MgO-600 always surpasses CaO-900 in this respect. These catalytic activity results can be explained on the basis of a mechanism similar to that proposed by Ivanov et al. [23] (see Scheme 2), where the hydrogen transfer takes place via a concerted process involving a six-link intermediate, with the alcohol and the carbonyl compounds adsorbed on a surface acid–base

Table 3

Catalytic activity (in μmol of alcohol formed per minute per grams) in the MPV reduction of citral with secondary alcohols

Alcohol	<i>T</i> (°C) <sup>a</sup>	MgO-600 <sup>b</sup>	CaO-900 <sup>b</sup>	TOFMgO <sup>c</sup>	TOFCaO <sup>c</sup>
2-Hexanol	136	106.0 (91.4)	40.0 (90.2)	0.41	0.45
2-Pentanol	118	82.0 (91.3)	27.7 (88.5)	0.32	0.31
2-Butanol	98	14.4 (94.2)	6.9 (86.5)	0.06	0.08
2-Propanol	82	11.4 (89.1)	2.7 (93.5)	0.04	0.03
3-Hexanol	135	100.9 (88.8)	37.1 (89.3)	0.39	0.42
3-Pentanol	115	74.2 (90.8)	23.2 (90.4)	0.29	0.26
Cyclohexanol	160	186.0 (90.3)	51.6 (85.8)	0.72	0.58
Cyclopentanol	140	165.2 (93.3)	43.0 (93.2)	0.64	0.48

<sup>a</sup> Reaction temperature.

<sup>b</sup> Selectivity in parentheses.

<sup>c</sup> Turnover frequency (μmol alcohol per min μmol CO<sub>2</sub>).

pair. The rate-determining step of the process must be related to the interaction of the alcohols with the acid–base site, which causes its dissociation to the corresponding alkoxide. Carbonyl compounds have been found to interact with acid and basic sites in a solid to give condensation reactions, as have alcohols with metal acid sites to yield olefins. In the proposed scheme, the surface-adsorbed alkoxide formed from the alcohol leads to the transfer of a hydride ion that attacks the carbonyl group. The synchronous process in Scheme 2 accounts for the fact that the hydrogen transfer yields a new alcohol and a new carbonyl compound. Ivanov et al. have also related the adsorption of the alcohol on weak Lewis acid–strong base pair sites, also, because the proportion of strong basic sites in the two catalysts studied is similar but the number of sites is much greater in MgO-600 than in CaO-900, the former will obviously exhibit higher catalytic activity than the latter.

Table 3 also shows the turnover frequency (TOF), defined as the ratio of the catalytic activity ( $r_a$ ) to the total number of basic sites ( $n_b$ ).

### 3.6. Recycling test

Figs. 3 and 4 show the catalytic activity and selectivity results obtained with MgO-600 and CaO-900 solids reused several times. Following filtering and washing

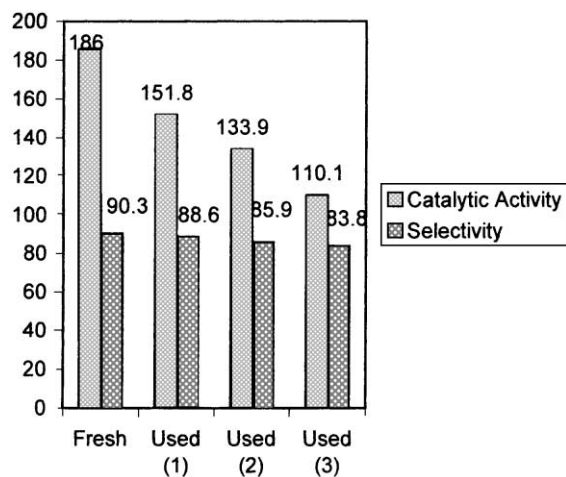


Fig. 3. Catalytic activity and selectivity results obtained with MgO-600 reused several times.

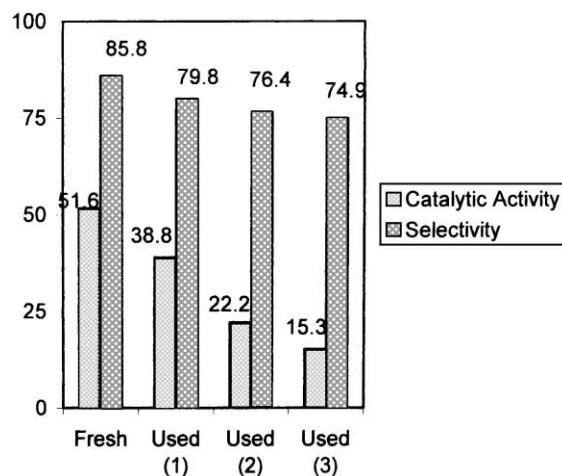


Fig. 4. Catalytic activity and selectivity results obtained with CaO-900 reused several times.

with methanol several times, the catalysts were recalined at 600 or 900°C, as applicable, and reused in a reaction similar to that described in Section 2.3, using cyclohexanol as hydrogen donor. Based on the results, even if the loss of some solid from one test to the next is highly probable, one must admit that some other deactivation process certainly takes place. It is also observed that while the selectivity of the MgO-600 catalyst remains unchanged even after the four experiences, the CaO-900 catalyst shows a small decay in both activity and selectivity toward nerol and geraniol.

## 4. Conclusions

The results obtained in this work allow us to conclude that the efficiency of the catalytic hydrogen transfer of citral on basic catalysts is directly related to the basic sites of the catalysts and their strength; thus, a comparison of the catalytic activity results reveals MgO to be the most active catalyst, even though the activity of the solids per active site (TOF) was quite similar with all the alcohols used. Also, the highest catalytic activity corresponds to cycloalkanol, which exhibit better results than 2-alkanols and these than 3-alkanols. Finally, the catalysts can be reused up to three times with no substantial loss of conversion or selectivity.

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