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Comparison of microwave and mechanochemical energy inputs in the catalytic oxidation of cyclohexane†

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The effect of microwave and mechanochemical ball milling energy inputs was studied for the peroxidative oxidation (with aqueous H_2O_2) of cyclohexane to cyclohexanol and cyclohexanone, over $CoCl_2$ and/or V_2O_5 dispersed (µm scale) catalysts. A maximum total yield of cyclohexanol and cyclohexanone of 43% after 1 h of reaction at 30 °C, in acetonitrile and under microwave irradiation (5 W), was achieved over the $CoCl_2$–V_2O_5 (3 : 1) catalyst prepared by ball milling. Cyclohexanol is the main final product with a selectivity of up to 93% over cyclohexanone. Conducting the oxidation reaction under microwave irradiation under the same conditions but without any mechanochemical treatment of the catalyst prior to use resulted in a lower total yield of 30% with a lower selectivity (69%) towards cyclohexanol over cyclohexanone. The sole application of mechanochemical treatment for the catalyst preparation and the catalytic oxidation of cyclohexane allowed to reach yields of 29% after 1 h of reaction, at room temperature, without microwave irradiation and any additive and in the absence of any organic solvent. Ball milling is shown to provide a convenient, solvent-free method to disperse these solid catalysts and to promote the above cyclohexane oxidation, although, in the latter case, not so effectively as microwave irradiation.

1. Introduction

The application of alternative energy inputs, such as microwave or ultrasonic irradiation, is one of the ways to perform effective chemical transformations under mild reaction conditions.[1] As a result, a number of existing synthetic protocols can be significantly improved in comparison with those performed under con-

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ventional heating. For instance, electromagnetic microwaves (MW) with wavelengths of 1 mm–1 m can directly transfer energy to polar intermediates or catalysts, thus improving the efficiency and decreasing the reaction time. However, the utilization of MW irradiation is not always advantageous due to its rather complicated relationship to the composition of the reaction mixture, the reaction mechanism and a number of other factors.[2]

Reactions can also be promoted by applying mechanical energy, for example, by ball milling (BM). If mechanical grinding is under consideration, the elevated rates of the performed reactions are related to high concentrations of the starting materials, interaction over large areas, formation of point defects and dislocations in the crystal lattices, breaking the order of the crystalline structure, production of new surfaces and cracks, ionic exchange, *etc.*[1b] At the point of collision of edges, the solids deform and melt, forming hot points where the molecules reach high excitation states.[1b] However, the energy accumulated in the defects of the crystalline structure can also lead to slower chemical transformations. Hence, mechanochemical processes can significantly differ from those performed under other energy inputs. For example, conventional heating of solid HgCl and AgCl leads to their melting and subliming, while their milling results in metal recovery with Cl_2 gas evolution.[1b]

Although the advantageous effects of alternative energy inputs have been well recognized and reviewed during the last decade,[1] an experimental comparison of microwave and mechanochemical treatments has not yet been intentionally performed for the same catalytic reaction. Hence, we decided to fill this blank and compare microwave and mechanochemical energy inputs in the catalytic oxidation of cyclohexane. We choose this reaction due to our longstanding interest in such a transformation[3] and its importance in industry.[4]

2. Experimental

2.1. Materials

Vanadium oxide (V_2O_5, Sigma Aldrich), cobalt chloride ($CoCl_2$, Sigma Aldrich), multiwalled carbon nanotubes (MWCNT-HP

150, Bayer Material Science), acetonitrile (MeCN, Fisher Chemical), cyclohexane (C_6H_6, Sigma Aldrich), and 30% aqueous solution of hydrogen peroxide (H_2O_2, Sigma Aldrich) were handled under normal ambient conditions without any purification prior to use.

2.2. Preparation and characterization of dispersed catalysts

V_2O_5 and/or $CoCl_2$ with different molar ratios (total mass: 200 mg) were directly placed in a PM100/200 Retsch GmbH planetary ball mill equipped with a 50 mL bowl and mechanically ground with 10 stainless steel balls of 10 mm diameter for 1 h similar to the procedures described before.[5] Multiwalled carbon nanotube (CNT) additives (loadings from 0.1 to 5 wt% or ca. 100–1000 metal-per-carbon molar ratios) were also added in some cases to prepare catalytic composites.[5a,c] The milling frequency was 450 rpm, with rotational inversions every 5 minutes. All the dispersed mixtures were prepared by dry milling. The dispersed materials were characterized by scanning electron microscopy (SEM) using JEOL 7001F equipment. The composition of the (1 : 1) $CoCl_2$–V_2O_5 ball milled mixture was studied by X-ray Photoelectron Spectroscopy (XPS) using a XSAM800 spectrometer from Kratos. The characterization of each individual salt was reported previously.[5a] The operating and recording conditions as well as the details of data treatment were as described in ref. 5a. The sensitivity factors used for the mixture analysis were those of the software library when the radiation source is an aluminum anode.

2.3. Catalytic studies

100 μmol of catalyst (dispersed with or without ball milling treatment), 3 mL MeCN (solvent) and 5 mmol (540 μL) cyclohexane (substrate) were introduced into a pyrex tube. Subsequently, 10 mmol of a 30% aqueous hydrogen peroxide solution (oxidant) was added. For the experiments under microwave radiation, the tube was sealed and placed in a microwave reactor and the system was stirred under 5 W at 30 °C for 1 or 2 h. CAUTION: Mixtures of H_2O_2 with organic compounds are potentially explosive! At the end of the reaction, 10 mL of diethyl ether (for the substrate and organic product extraction) and 90 μL of cycloheptanone (internal standard) were added. The final mixture was stirred for 10 min and finally a sample (1 μl) was taken from the organic phase and analyzed by GC. Following a method developed by Shul'pin,[6] an excess of triphenylphosphine (PPh_3) was added prior to the GC analysis, to reduce the cyclohexyl hydroperoxide formed to the corresponding alcohol and the hydrogen peroxide to water. The reported and below-discussed cyclohexanone/cyclohexanol (ONE/OL) ratio corresponds to the cyclohexanone/(cyclohexanol + cyclohexyl peroxide) [ONE/(OL + ROOH)] ratio. Blank experiments were performed using different amounts of H_2O_2 and confirmed that no cyclohexane oxidation product was obtained in the absence of a metal catalyst.

For performing the oxidation of cyclohexane exclusively under mechanochemical (ball-milling) treatment, the calcu-

lated amount of the catalytic material was directly added to the grinding bowl of the ball mill, whereafter the substrate (cyclohexane) and the oxidant (H_2O_2, 30% aq. solution) were added and the reaction was performed as described above, but without the addition of the NCMe solvent.

Gas chromatographic measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) (He as the carrier gas) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature of the column was maintained at 100 °C for 1 min, then increased at a rate of 10 °C min⁻¹ up to 180 °C and the column was maintained at this temperature for 1 min. The attribution of the peaks was made by comparison with the chromatograms of genuine samples.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

The dispersed catalytic materials were prepared by the mechanical treatment of V_2O_5 and/or $CoCl_2$ in a planetary ball reactor[7] as indicated above. The choice of these systems was made based on our previous studies[3,5] and the literature data.[2,4] According to SEM images (Fig. 1), the produced materials consist of non-uniform microcrystallites with different shapes and particle sizes above 1 μm for the ball milled $CoCl_2$ (Fig. 1a), V_2O_5 (Fig. 1b), and the $CoCl_2$–V_2O_5 (3 : 1)‡ mixture (Fig. 1c and d). More details of the morphology and structure of the prepared catalysts can be found in our previous papers devoted to the preparation and study of related dispersed materials.[5]
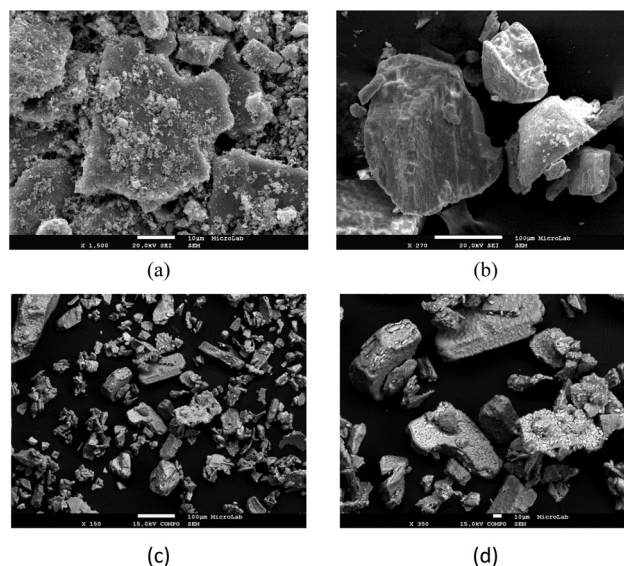
Fig. 1 SEM images: (a) ball-milled $CoCl_2$, scale, 10 μm; (b) ball-milled V_2O_5, scale, 100 μm; (c) $CoCl_2$–V_2O_5 (3 : 1), scale, 100 μm; (d) $CoCl_2$–V_2O_5 (3 : 1), scale, 10 μm.

XPS shows that after ball milling the composition of each salt is nearly the same as that before mixing.

Fig. 2 shows the relevant XPS regions of the ball milled mixture $CoCl_2$–V_2O_5 (1:1). In Table 1, the atomic ratio Co/Cl > 0.5 suggests that the mixture is composed not only of cobalt chloride, but also of some cobalt hydroxides and/or oxyhydroxides, as in $CoCl_2$.[5a] Actually, the main peaks in Co $2p_{3/2}$, centred at 782.2 ± 0.2 eV and 783.9 ± 0.2 eV (Fig. 2a), are both assigned to Co^{2+} in $CoCl_2$ and in $Co(OH)_2$ but, most probably, included in powder phases with different resistivities.[5a] Such an effect, which was also observed for a $CoCl_2$–Fe_2O_3 mixture studied previously,[5a] is also detected in the Cl 2p region: Cl 2p was fitted with two doublets (the main Cl $2p_{3/2}$ component being centred at ~200.3 eV) revealing the presence of some differential charge resulting from mixed phases with different conductivities and/or important contact potential between powder particles. V 2p, detected next to O 1s, with V $2p_{3/2}$ centred at 517.6 eV ± 0.1 eV, confirms that the vanadium oxide is quite stable, maintaining the stoichiometry of the starting material (V_2O_5 [5a]) even after ball milling (Table 1). O 1s was fitted with three peaks: the main peak, centred at 530.6 eV, is assigned to oxygen in V_2O_5 (it is not detected in $CoCl_2$ [5a]), and the other two peaks, at the high binding energy side, with low relative intensities, centred at 532.4 and 534 eV, are assigned to oxygen bound to cobalt (as showed by the quantitative analysis) and to some oxidized carbonaceous contamination.[8]

3.2. Catalytic studies

To choose the most appropriate catalytic material for further comparative studies, several ball-milled $CoCl_2$–V_2O_5 mixtures with different metal ratios (1:1, 3:1 and 1:3) and starting V_2O_5 and $CoCl_2$ samples (also dispersed in the ball mill under the same conditions) were screened for the peroxidative microwave-assisted oxidation of cyclohexane with H_2O_2 (30% aq. solution) (Table 2). CNTs were also added in several cases since our previous studies[5] demonstrated that their addition can provide a significant promoting effect. In all cases, the formation of a mixture of cyclohexyl hydroperoxide (CyOOH,

Table 1 XPS quantitative results for the precursor salts (studied in ref. 5a) and the mixed material $CoCl_2$–V_2O_5 (1:1)

	Co/Cl	$O_{530.6}$/V
$CoCl_2$	0.8	
V_2O_5		2.5
$CoCl_2$–V_2O_5	0.9	2.4

primary product), cyclohexanol (CyOH) and cyclohexanone (CyO) (Scheme 1a and Fig. S1†) was observed. The alcohol and ketone are the major products upon the metal-assisted decomposition of CyOOH, the formation of the alcohol being promoted by the reduction of CyOOH with triphenylphosphine (PPh_3) (Scheme 1b).[6]

The $CoCl_2$–V_2O_5 (3:1) ball-milled mixture showed a remarkable activity under the established experimental conditions, resulting in a 43% (in relation to the substrate) overall yield of cyclohexanol and cyclohexanone with a total turnover number (TON) of 22 (22 moles of products per mole of metal compound) (entry 2, Table 2) and a selectivity of up to 93% for (cyclohexanol + cyclohexyl peroxide), after 1 h of reaction at 30 °C and under microwave irradiation (5 W). In the tested catalytic systems, the cyclohexanone/cyclohexanol ratio is in the range of 0.07–0.7 (Table 2), whereas in the industrial processes,[4,9] the ratio generally falls in the 0.5–0.7 range. The common high predominance of cyclohexanol over cyclohexanone in our systems suggests the presence of cyclohexyl hydroperoxide in the reaction mixture as a primary oxidation product of cyclohexane which, after treatment with PPh_3 (see the Experimental part), gives the corresponding alcohol in a relatively large quantity[6] (Scheme 1b).

The use of a ball milled $CoCl_2$–V_2O_5 mixture (3:1) resulted in a marked yield increase relative to the use of any starting component, from 1.3% for $CoCl_2$ or 13.5% for V_2O_5 to 43.3% for $CoCl_2$–V_2O_5 (3:1) (entries 11, 10 and 2, respectively, Table 2). The achieved yield for the $CoCl_2$–V_2O_5 (3:1) mixture (43.3% overall yield), with a concomitant high selectivity, is much higher than that (ca. 4–6%) of the industrial process[4,9]
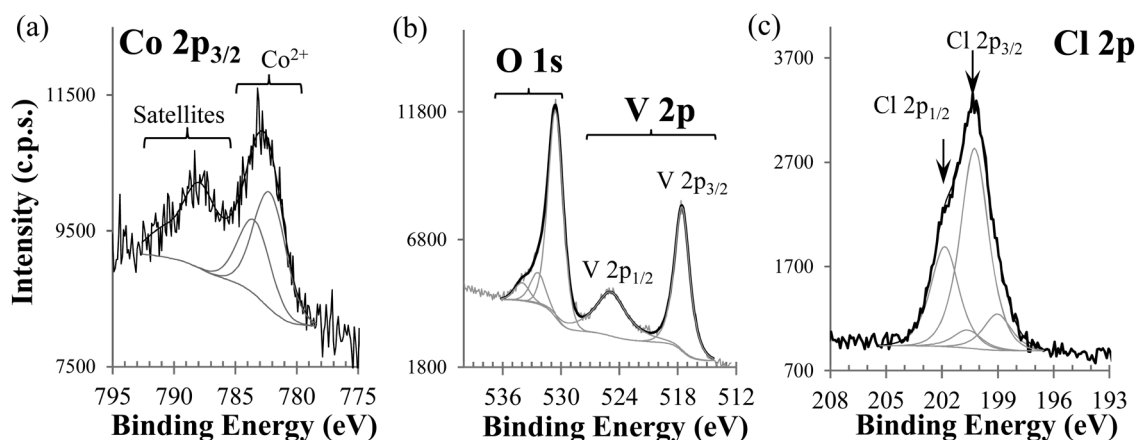
**Fig. 2** $CoCl_2$–V_2O_5 (1:1) XPS regions: (a) Co $2p_{3/2}$; (b) O 1s and V 2p; and (c) Cl 2p.

Table 2 MW-assisted peroxidative oxidation of cyclohexane, over ball milled $CoCl_2$–V_2O_5 mixtures, V_2O_5 or $CoCl_2$ as catalysts[a]

			Yield[c] (%)			
Entry	Catalyst	Ratio[b]	OL + ROOH	ONE	Tot[d]	ONE/(OL + ROOH)
1	$CoCl_2$–V_2O_5	1 : 1	6.5	4.5	11.0	0.7
2		3 : 1	40.3	3.0	43.3	0.07
3		1 : 3	3.4	1.5	4.9	0.4
4	$CoCl_2$–0.1% CNTs	—	0.7	0.3	1.0	0.4
5	$CoCl_2$–1% CNTs	—	7.0	0.8	7.8	0.1
6	$CoCl_2$–5% CNTs	—	6.0	0.6	6.6	0.1
7	($CoCl_2$–V_2O_5)–0.1% CNTs	3 : 1	8.5	6.0	14.5	0.7
8	($CoCl_2$–V_2O_5)–1% CNTs	3 : 1	9.9	6.8	16.7	0.7
9	($CoCl_2$–V_2O_5)–5% CNTs	3 : 1	23.6	2.2	25.8	0.09
10	V_2O_5	—	8.9	4.6	13.5	0.5
11	$CoCl_2$	—	1.1	0.2	1.3	0.2
12	CNTs	—	0.4	1.2	1.6	3.0

[a] Reaction conditions (BM + MW): Cyclohexane (5.0 mmol), 100 μmol of catalyst (2 mol% *vs.* substrate, after ball mill treatment, BM), NCMe (3 mL), 30% aq. H_2O_2 solution (10 mmol), 1 h, 30 °C, microwave (MW) irradiation (5 W); yield and TON determined by gas chromatography upon treatment with PPh_3 (see the text). [b] Molar ratio between the components of the prepared catalyst mixture. [c] Molar yield (%) based on the substrate, *i.e.* moles of products [cyclohexanol (OL) and cyclohexanone (ONE)] per 100 moles of cyclohexane. [d] Total yield = moles of products [OL + ONE]/100 moles of C_6H_{12}. CNTs = multiwalled carbon nanotubes.
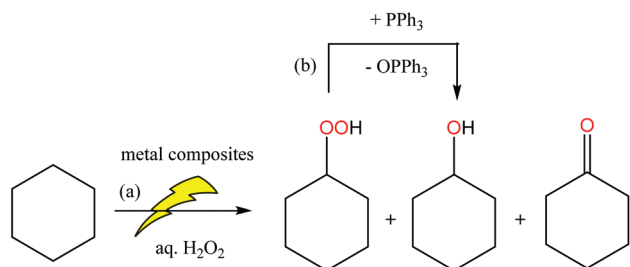
Scheme 1 Microwave-assisted peroxidative (with H_2O_2) oxidation of cyclohexane.

Scheme 2 Comparison of microwave and mechanochemical energy inputs.

in spite of the mild reaction conditions used and is comparable to those obtained[3h] in the presence of Fe(III)–Cr(III) hydroxides (up to 45%). However, the latter catalytic system requires the use of a strong acid (HNO_3).[3h] The combination of such a considerable yield achieved in a short reaction time (1 h) under mild conditions (30 °C, 5 W) and without any additive is a rare example which points out an outstanding activity of the catalytic system based on the $CoCl_2$–V_2O_5 (3 : 1) binary mixture prepared by ball milling treatment.

The presence of CNT additives affects differently the catalytic activity of the studied systems (Table 2). Thus, for $CoCl_2$, a yield improvement is observed when 1 and 5 wt% of CNTs have been used, namely from 1.3% in the absence of CNTs (entry 11, Table 2) to 7.8 and 6.6%, (entries 5 and 6, Table 2, respectively). However, for the $CoCl_2$–V_2O_5 systems, the yield decreases in the presence of CNTs (entries 7–9, Table 2). This hampering effect of the CNTs contrasts with a few other cases where the presence of such additives can result in a significant improvement in the catalytic performance.[5]

In order to compare the influence of MW and mechanochemical BM energy inputs, we have chosen the most active catalytic material, *i.e.* the $CoCl_2$–V_2O_5 (3 : 1) mixture. With this catalytic material, some tests were carried out using the following combinations (Scheme 2): (i) preparation of the catalyst by ball milling (1 h) and its subsequent application in the peroxidative oxidation of cyclohexane under MW irradiation (1 h, 30 °C) (BM + MW); (ii) conducting the oxidation reaction under MW irradiation without any BM treatment of the catalyst before use (MW) and (iii) conducting the catalyst preparation and the oxidation reaction by ball milling in one pot without MW irradiation (BM + BM). The results are presented in Table 3.

The first method (BM + MW), which is the one in which the catalyst is prepared by ball milling and then used in the peroxidative oxidation of cyclohexane under MW irradiation, results in the highest overall product yield (43%, entry 1, Table 3) with the maximum 93% selectivity towards cyclohexanol over cyclo-

Table 3 Peroxidative oxidation of cyclohexane over the CoCl$_2$–V$_2$O$_5$ (3 : 1) catalyst using MW and BM treatments[a]

Entry	Method	Reaction time (h)	Yield[b] (%)		
			OL	ONE	Total[c]
1[d]	BM + MW	1	40.3	3.0	43.3
2[e]	MW	1	20.9	9.5	30.4
3[e]	MW	2	29.1	10.8	39.9
4[f]	BM + BM	1	22.4	6.2	28.6
5[f]	BM + BM	2	26.6	5.5	32.1
6[g]	BM	1	0.2	0.1	0.3
7[h]	BM	1	5.9	0.7	6.6
8[i]	—	1	0.7	0.4	1.1

[a] Reaction conditions: 5 mmol of substrate, 100 μmol metal composite (2 mol% *vs.* substrate), NCMe (3 mL) (only for the BM + MW and MW methods, entries 1–3), 10 mmol of H$_2$O$_2$ (aq. 30%), 30 °C, microwave irradiation (5 W). [b] Molar yield (%) based on the substrate, *i.e.* moles of product per 100 mol of substrate determined by GC. [c] Total yield = moles of products [cyclohexanol (OL) + cyclohexanone (ONE)]/100 mol of C$_6$H$_{12}$, determined by GC after treatment with PPh$_3$. [d] BM + MW = preparation of the catalyst with ball milling treatment (BM) and catalysis under MW irradiation. [e] MW = preparation of the catalyst without ball milling treatment, by manual grinding, and used directly in peroxidative oxidation under MW irradiation. [f] BM + BM = catalyst preparation and catalytic reaction exclusively by ball milling treatment, without MW irradiation and without the NCMe solvent. [g] Oxidation reaction performed by ball milling without any catalyst. [h] Catalytic reaction performed with a ball milled catalyst and without microwave irradiation. [i] Catalytic reaction performed with a catalyst mixture used without previous ball milling treatment (mixed manually) and without microwave irradiation.

hexanone. Conducting the oxidation reaction under MW irradiation under the same conditions but without any ball milling treatment of the catalyst before use (MW method) gives a lower total yield of 30.4% with a 69% selectivity towards cyclohexanol over cyclohexanone (entry 2, Table 3).

The results obtained in the third procedure (BM + BM) (entries 4 and 5, Table 3) are rather interesting, since the catalyst preparation and the catalytic reaction were assisted only by ball milling, without any additive and in the absence of any organic solvent, leading to high overall yields of 28.6 and 32.1% after 1 or 2 h of reaction, respectively, at room temperature.

Additionally, the oxidation reactions were performed in the absence of microwave irradiation (entries 6–8, Table 3) using catalytic mixtures with (entry 6, Table 3) and without (entry 8, Table 3) previous ball milling treatment. In both cases, the yields were quite low (6.6 and 1.1%, respectively), demonstrating once again the importance of MW irradiation in the catalytic reaction and the advantage of using ball milled catalytic mixtures as catalysts. The oxidation of cyclohexane was also performed exclusively by ball milling without the addition of metal composites and residual amounts of the product were detected (entry 7, Table 3).

Among the reported vanadium or cobalt metal catalysts applied for alkane oxidations with H$_2$O$_2$, the product yields achieved herein are remarkable.[3,10] Besides this, the catalytic systems under study involve greener reaction conditions, since they do not involve any additive or organic solvent (in the case of the sole use of mechanochemical treatment, BM + BM

method) and perform well at room temperature in a short reaction time (1 h). Compared to our catalysts, the binuclear oxidovanadium(v) complex bearing an NO$_2$-donor Schiff base ligand [{VO(EtO)(EtOH)}$_2$(1κ^{2}O,κN:2κ^{2}O,κN-L)]·2H$_2$O (H$_4$L = bis(2-hydroxybenzylidene)oxalohydrazonic acid), a homogeneous catalyst for the oxidation of gaseous and liquid alkanes by aqueous H$_2$O$_2$ under mild conditions, leads to 27.6% yield of oxygenates (cyclohexanol + cyclohexanone) in the presence of the acid co-catalyst 2-pyrazinecarboxylic acid (PCA), using H$_2$O$_2$ (50% aqueous solution) as an oxidant, in acetonitrile, at 50 °C and after 4 h of reaction.[11]

4.   Conclusions

Cobalt and/or vanadium dispersed catalytic materials were prepared by a simple and solvent-free mechanochemical method, *i.e.*, ball-milling. The prepared heterometallic systems act as efficient catalysts for the peroxidative oxidation (with aq. H$_2$O$_2$) of cyclohexane to cyclohexanol and cyclohexanone, under mild conditions. The microwave and mechanochemical energy inputs were compared and it was shown that the most effective combination comprises the catalytic reaction performed under microwave irradiation and using the CoCl$_2$–V$_2$O$_5$ (3 : 1) catalyst prepared mechanochemically. However, the catalyst preparation and the catalytic reaction can be achieved in one-pot at room temperature and by using exclusively the mechanochemical BM energy input with considerable yields of 29 and 32% after 1 and 2 h, respectively. Hence, mechanochemical methods appear to be quite promising in the field of alkane functionalization and deserve to be further explored for a variety of catalytic systems and reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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‡ Here and further molar ratios are indicated.

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