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Research Note

Group 5–7 transition metal oxides as efficient catalysts for oxidative functionalization of alkanes under mild conditions

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Abstract

Oxides of group 5–7 metals are convenient and efficient catalysts for the single-pot carboxylation of gaseous (methane, ethane, propane) and liquid alkanes to carboxylic acids, as well as for the aqueous peroxidative hydroxylation/oxygenation of liquid alkanes to alcohols and ketones. The reactions occur under mild conditions, and the carboxylations proceed with unprecedented remarkably high turnover numbers. The diagonal metals commonly provide the most active oxide catalysts in the order V > Re > Mo.

Keywords: Alkanes; C–H activation; Carboxylation; Peroxidative oxidation; Carboxylic acids; Homogeneous catalysis; Metal oxides; Vanadium; Methyltrioxorhenium

1. Introduction

The functionalization of alkanes (the most abundant and cheapest carbon raw materials, but usually unreactive for conventional syntheses) to more valuable products (e.g., carboxylic acids, alcohols, ketones) is a subject of much current attention [1–6]. Low-aliphatic *carboxylic acids* are products of wide use and novel preparative processes have been searched for, in some cases using single-component or multicomponent metal oxide catalytic systems, such as in oxidations of ethanol, 2-butanone, naphtha, C_1–C_4 alkanes, and alkenes, and in some carbonylation processes of alcohols, esters, and olefins [5,6]. However, a number of synthetic limitations have been encountered, including the common use of costly raw materials and catalysts, the need for several reaction stages, the usually drastic reaction conditions, low selectivity, and low yields, particularly when using alkanes as starting reagents [1–6].

Metal-catalyzed carboxylation of alkanes by CO is an alternative proposal in the type of system pioneered by Fujiwara [7–10], using a peroxodisulfate salt [11–15] in trifluoroacetic acid (TFA) at 80 °C. The most active catalysts in this system, before the current study, were the V-complexes that we have applied with various N,O-polydentate ligands of (hydroxyimino)dicarboxylate and aminoalcohol types, in particular synthetic amavadine and its models [11,12]. But the synthesis of these catalysts involves considerable work and generally provides only limited turnover numbers (TONs). Various metal oxides and salts also have been tested for CH_4 carboxylation by CO into acetic acid [7,8], but the observed activity was too low to merit further exploration. Stoichiometric and catalytic oxidations of alkanes to carboxylates and alcohols by OsO_4 (with $NaIO_4$ as the terminal oxidant) have been reported in an aqueous base at 85 °C, but also with very low TONs (up to ca. 4) [16]. An interesting Pd^{II}-catalyzed oxidative condensation of CH_4 to acetic acid at 180 °C in sulfuric acid has been achieved with TONs up to 18 and overall yields (acetic acid and methanol) of ca. 12% [17].

The catalytic oxidation of alkanes to the corresponding alcohols and ketones also has attracted much attention [18–21] in the development of efficient catalysts for the oxidation of cyclohexane to cyclohexanol and cyclohexanone (used in the production of Nylon-6,6′ and polyamide-6). Some metal oxide catalysts, with V, Cr, Mo, and Nb, have been reported

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[18,22–28], but most of these provide rather low conversions and/or are active only in the presence of additives [24,26,27], under photoirradiation [23–25], or at very high temperatures (up to 750 °C) [28], with low selectivity in the latter case. Amavadine and its models also catalyze the peroxidative conversion of cyclohexane and aromatics into alcohols, ketones, and aldehydes [29,30], but their use has the abovementioned limitations.

Consequently, in an attempt to overcome some of the above drawbacks, the current work was aimed at developing a catalytic system for direct (single-pot), efficient, and selective conversion of alkanes to the corresponding carboxylic acids, alcohols, and ketones under relatively mild conditions, based on the use of cheap, commercially available simple metal oxide catalysts. Here we report that (i) both gaseous (methane, ethane, propane) and liquid (cyclopentane, cyclohexane) alkanes can be catalytically carboxylated by CO and/or oxidized to carboxylic acids (in some cases with unprecedented high TONs) by a simple group 5−7 metal oxide (Tables 1 and 2) in TFA, at 80 °C and using $K_2S_2O_8$ as oxidizing agent, and (ii) these metal oxides also catalyze the peroxidative hydroxylation and oxygenation of the liquid alkanes into alcohols and ketones at room temperature, using aqueous H_2O_2 as an oxidant without the need for any additive.

2. Experimental

2.1. *Carboxylation of gaseous alkanes*

In a typical experiment, the reaction mixtures were prepared as follows. To a mixture of 20.0–0.05 µmol (typically 20.0 µmol) of the metal oxide catalyst with 4.00 mmol (1.08 g) $K_2S_2O_8$, contained in a 13.0-ml stainless steel autoclave was added 5.0 ml of CF_3COOH (TFA). The autoclave was closed and flushed with dinitrogen three times to replace the air inside, and then pressurized with CH_4 (5 atm; 1.53 mmol), C_2H_6 (1.5–10 atm [typically 10 atm; 3.06 mmol]) or C_3H_8 (5–10 atm [typically 8.5 atm; 2.60 mmol]) and CO (0–30 atm; 0.00–9.18 mmol). The reaction mixture was vigorously stirred for 20 h at 80 °C using a magnetic stirrer and an oil bath, after which it was cooled in an ice bath, degassed, and opened. The product analysis was undertaken as follows. To 1.0 ml of the reaction mixture were added 5.0 ml of diethyl ether and 90 µl of an internal standard (*n*-butyric acid for the carboxylation of CH_4 and C_2H_6; *n*-heptanoic acid for the carboxylation of C_3H_8). The obtained mixture was stirred, filtered, and then analyzed by gas chromatography (GC) using a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX fused silica capillary column (P/N 123-7032) and Jasco-Borwin v.1.50 software. In some cases, the products were also identified by GC-MS, ^1H and $^{13}C–\{^1H\}$ NMR techniques using a Trio 2000 Fisons spectrometer with a coupled Carlo Erba (Auto/HRGC/MS) gas chromatograph and a Varian UNITY 300 NMR spectrometer, respectively. Blank experiments performed for all tested alkanes in the presence of CO and $K_2S_2O_8$ confirmed that no carboxylic acid formation was detected unless the catalyst was used.

2.2. *Carboxylation of liquid alkanes*

In a typical experiment, the reaction mixtures were prepared as follows. To 21.0 µmol of metal oxide catalyst contained in a 13.0-ml stainless steel autoclave were added 4.18 mmol (1.13 g) $K_2S_2O_8$, 7.3 ml of TFA, and 3.06–3.20 mmol of cycloalkane. The autoclave was closed and flushed with dinitrogen three times to replace the air inside, and then pressurized with CO (5–30 atm). The reaction mixture was vigorously stirred for 20 h at 80 °C using a magnetic stirrer and an oil bath, after which the autoclave was cooled using an ice bath, degassed, and opened. The product analysis was undertaken as follows. To 2.5 ml of the reaction mixture were added 6.5 ml of diethyl ether and 90 µl of an internal standard (*n*-butyric acid). The resulting mixture was stirred, then filtered off and analyzed as discussed earlier. Blank experiments performed for both cycloalkanes in the presence of CO and $K_2S_2O_8$ confirmed that no carboxylic acid formation was detected unless the catalyst was used.

2.3. *Hydroxylation/oxygenation of liquid alkanes*

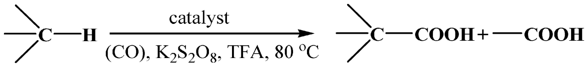
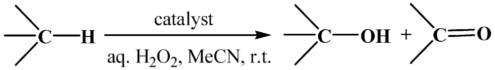
In a typical experiment, the reaction mixtures were prepared as follows. To 0.31–10.0 µmol of metal oxide catalyst, used either as a solid or in a 0.020 M MeCN solution, contained in the reaction flask, were added 2.5 (V-oxides) or 3.0 ml (Re, Cr oxides) of MeCN, 1.25–10.0 mmol (typically 5.00 mmol) of H_2O_2 (30% in H_2O), nitric acid (65% in H_2O) (2.90 mmol; used only for V-oxides, because increased catalytic activity was observed on the addition of nitric acid), and 0.63–5.00 mmol (typically 5.00 mmol) of cycloalkane, in that order. The reaction mixture was stirred for 6 h at room temperature and normal pressure. The product analysis was performed as follows. First, 90 µl of internal standard (cyclopentanone or cycloheptanone) and 6.5–10.0 ml diethyl ether (to extract the substrate and the organic products from the reaction mixture) were added. The resulting mixture was stirred for 10 min, after which a sample was obtained from the organic phase and analyzed by GC or GC-MS using the aforementioned equipment. Blank experiments performed for both cycloalkanes with H_2O_2 confirmed that no product of alkane oxidation was obtained unless the metal oxide catalyst was used. The amount of alkyl hydroperoxide (if formed) was estimated from the variations in the alcohol and ketone yields, determined by GC analyses, on addition of PPh_3 to the final reaction solution, according to a method reported by Shul'pin et al. [1,20,31].

3. Results and discussion

3.1. *Carboxylation and oxidation of alkanes to carboxylic acids*

The carboxylation reactions were typically performed under CO, in TFA at 80 °C for 20 h, using a slight excess of $K_2S_2O_8$ (typical $K_2S_2O_8$/alkane molar ratio of ca. 1.3–2.6) as the oxidizing agent in the presence of a metal–oxide catalyst. These conditions (i.e., temperature, time, and molar ratios

Table 1
Functionalization of alkanes catalyzed by metal oxides[a]

Reaction	Carboxylation 								Hydroxylation/oxygenation 			
Substrate	CH_4	C_2H_6		C_3H_8			C_5H_{10}	C_6H_{12}	C_5H_{10}		C_6H_{12}	
Product	MeCOOH	MeCOOH	EtCOOH	MeCOOH	*i*-PrCOOH	*n*-PrCOOH	C_5H_9COOH	$C_6H_{11}COOH$	C_5H_9OH	C_5H_8O	$C_6H_{11}OH$	$C_6H_{10}O$
Catalyst												
V_2O_5	19 (10)[c]	8 (12)[e]	52 (81)	3 (4)	19 (25)	17 (22)	10 (14)	17 (23)	1 (5)	2 (9)	9 (46)	1 (5)
V_2O_4	33 (17)[c]	8 (12)	59 (90)	3 (4)	22 (29)	25 (32)	16 (24)	6 (8)	1 (4)	2 (9)	9 (47)	1 (5)
$VOSO_4$	5 (2)[e,m]	5 (8)[f]	64 (98)	3 (4)	25 (33)	18 (23)	20 (29)	24 (36)	1 (4)[l]	2 (8)	7 (34)[l]	2 (10)
$K[ReO_4]$	16 (12)	5 (8)	39 (60)	8 (10)[d]	13 (16)	10 (12)	3 (5)	7 (10)[g]	1 (21)[l]	1 (43)	2 (74)[l]	2 (65)
Re_2O_7	4 (3)	8 (12)[g]	50 (77)	8 (10)[d]	8 (10)	13 (16)	5 (8)	5 (7)[g]	1 (30)[l]	1 (24)	2 (67)[l]	2 (62)
$[(Me)ReO_3]$	–	8 (12)	39 (60)	4 (5)[d]	31 (39)	18 (22)	6 (9)	7 (10)[g]	1 (27)	1 (54)	2 (68)	2 (53)
$Na_2[MoO_4]$	–	25 (63)[b,i]	–	12 (30)[b,j]	–	–	12 (18)	11 (15)[g]	–	–	–	–
$Na_2[WO_4]$	–	18 (17)[f,h]	–	12 (40)[d,i]	4 (13)	2 (7)	–	1 (1)	–	–	–	–
$K_2[Cr_2O_7]$	–	7 (10)	1 (1)	3 (4)	2 (3)	1 (1)	1 (2)	6 (8)[g]	1 (1)	4 (2)	7 (4)	7 (4)
Nb_2O_5	–	18 (10)[b,h]	–	4 (3)[b,j]	–	–	–	4 (6)	–	–	–	–
Ta_2O_5	–	1 (2)[f]	–	3 (2)[f,k]	–	–	–	–	–	–	–	–
$K[MnO_4]$	–	4 (7)	–	–	–	–	–	–	–	–	–	–

[a] Selected results; values of product yields (moles of product/100 mol of alkane) were determined by GC or GC-MS; turnover numbers (TON, moles of product/mol of catalyst) are given in brackets. Typical (unless otherwise stated) reaction conditions (i) for carboxylation: p(alkane) = 5, 10, and 8.5 atm (1.53, 3.06, and 2.60 mmol, respectively) or n(cycloalkane) = 3.20 and 3.06 mmol, pCO = 15, 15, 20, 30, and 15 atm for CH_4, C_2H_6, C_3H_8, C_5H_{10}, and C_6H_{12}, respectively, n(catalyst) = 20.0–21.0 µmol; (ii) for hydroxylation/oxygenation: n(cycloalkane) = 5.00 mmol, n(catalyst) = 10.0 µmol, $n(H_2O_2)$ = 5.00 mmol. See Section 2 for further reaction parameters. For typical reaction conditions, yields (%) based on $K_2S_2O_8$ can be estimated as the corresponding ones relative to the alkane divided by 2.61 (for CH_4), 1.31 (for C_2H_6 and C_6H_{12}), 1.53 (for C_3H_8), and 1.25 (for C_5H_{10}); yields based on H_2O_2 are equal to those relative to cycloalkane.

[b] p(CO) = 0 atm. [c] p(CO) = 7.5 atm. [d] p(CO) = 15 atm. [e] p(CO) = 20 atm. [f] p(CO) = 25 atm. [g] p(CO) = 30 atm.

[h] p(alkane) = 1.5 atm. [i] p(alkane) = 3 atm. [j] p(alkane) = 5 atm. [k] p(alkane) = 10 atm.

[l] n(catalyst) = 0.31 µmol, $n(H_2O_2)$ = 10.0 mmol.

[m] Included for comparative purposes [11].

Table 2
Carboxylation of alkanes with reduced amounts of catalysts ($\leqslant$0.10 μmol)[a]

Entry	Alkane	Catalyst (μmol)	Total yield (%)[b]	Total TON[c]	Total TOF[d] (h^{-1})
1	CH_4	V_2O_4, 0.10	42.1	4.21×10^3	211
2	CH_4	V_2O_4, 0.05	30.8	6.17×10^3	309
3	C_2H_6	V_2O_4, 0.10	33.0	1.01×10^4	505
4	C_2H_6	V_2O_5, 0.10	6.5	1.98×10^3	99
5	C_3H_8	V_2O_4, 0.10	7.8	1.92×10^3	96
6	C_3H_8	V_2O_5, 0.10	6.0	1.48×10^3	74

[a] Selected results; p(alkane) = 5, 10 and 8.5 atm (1.53, 3.06, and 2.60 mmol, respectively), pCO = 7.5, 25, and 20 atm (2.30, 7.65, and 6.12 mmol, respectively) for CH_4, C_2H_6, and C_3H_8, respectively. The carboxylic acids obtained from every alkane correspond to those of Table 1.

[b] Moles of carboxylic acid products/100 mol of alkane.

[c] Moles of carboxylic acid products/mol of catalyst.

[d] Moles of carboxylic acid products/mol of catalyst per hour.

of reactants) have been determined to be optimal for the carboxylation reactions of alkanes in TFA catalyzed by various transition metal coordination compounds [7–14]. The highest yields (based on the alkane) were obtained for V-oxides (particularly V_2O_4 and, usually less effectively, V_2O_5 and $VOSO_4$), in the following order (for alkane/catalyst molar ratios of ca. 50–150): ethane to propionic acid (ca. 64%), propane to n-butyric and i-butyric acids (ca. 50%), methane to acetic acid (33%), cyclohexane to cyclohexanoic acid (ca. 25%), and cyclopentane to cyclopentanoic acid (ca. 20%) (Table 1). The highest overall yields based on the oxidant were 53, 35, 13, 18, and 16%, respectively (Table 1). Remarkably high TONs (in the 1.5×10^3–1.0×10^4 range for the methane, ethane, or propane carboxylations catalyzed by V_2O_4 or V_2O_5; Table 2), not reported before for alkane functionalization, were achieved by using lower catalyst amounts (alkane/catalyst molar ratios of ca. 1.0×10^3–31×10^3), still with high yields of carboxylic acid products (e.g., 33–42% for CH_4 or C_2H_6 carboxylation catalyzed by V_2O_4).

The catalytic carboxylation of CH_4 to CH_3COOH was also achieved by Re-oxides, although less effectively (16% yield for $K[ReO_4]$). V_2O_5 and $VOSO_4$ were previously found to act as catalysts for this reaction, with CO [7,8,11], but they were less active (4–5% yields) than V_2O_4, V_2O_5, and $K[ReO_4]$ in the current work. These V-oxides previously had not been applied to any other alkane, and we also observed that the transformation of the gaseous alkanes to carboxylic acids can occur even in the absence of CO (particularly when using V-oxide catalysts), with the solvent TFA then behaving as the carboxylating agent. However, for the liquid alkanes, CO is always required for carboxylation.

The single-pot carboxylation of methane to acetic acid by metal oxides was more direct than the relevant industrial process involving three separate stages: high-temperature metal-catalyzed formation of synthesis gas, its conversion to methanol, and final carboxylation of the latter with CO and an expensive Rh or Ir catalyst (Monsanto or Cativa process, respectively). The activity of the V- and Re-oxides for the carboxylation of ethane to propionic acid was remarkable, achieving yields of 64% for $VOSO_4$, 59% for V_2O_4, 52% for V_2O_5, and 50% for Re_2O_7, with overall TONs ca. 10^2 for alkane/catalyst molar ratios of ca. 150 (Table 1) with much higher TONs (up to 1.0×10^4, corresponding to TOFs up to ca. 500 mol of products/mol catalyst per hour) obtained by increasing that ratio to 30.6×10^3 (Table 2). This activity is significantly greater than those reported in other studies of this still little-explored reaction [13,32–35]: 24% (TON = 37) for the picolinate complex $[ReOCl_2\{NC_5H_4(COO\text{-}2)\}(PPh_3)]$, the most active member of a series of Re^V compounds with N,O-ligands [13]; 18% (TON = 11) for $Pd(OAc)_2/Cu(OAc)_2$, only at a very low pressure of ethane (1 atm) [33]; and 0.4% (TON = 0.3) for $Co(OAc)_2$ [32].

The V- and Re-oxides of this work appear to be the most active catalysts for methane, ethane, and propane carboxylation reported to date. Within each metal group, the overall activity toward carboxylation commonly followed the orders V > Nb > Ta (group 5), Mo > W > Cr (group 6), and Re > Mn (group 7), which are suggestive of a diagonal-type (V, Mo, Re) relationship.

CO pressure had a significant effect; the highest yields of the main carboxylic acid products were achieved for ca. 15–25 atm or do not increase markedly above this pressure (Fig. S1 in Supplementary material). Compared with cyclohexane, cyclopentane requires higher CO pressures to reach the best yields, which are usually below those of cyclohexane, indicating the former alkane's greater difficulty in carboxylation. At pCO above these values, an inhibiting effect is commonly observed, presumably due to the formation of less-active carbonyl or derived complexes. Conversion of the gaseous alkanes to carboxylic acids can even occur without CO in some cases, namely for the reaction of CH_4 catalyzed by V-oxides and the reactions of C_2H_6, and C_3H_8 (although in low yields) catalyzed by some V- or Re-oxides. The optimal CH_4, C_2H_6, and C_3H_8 pressures for usual conditions are 5, 10, and 8.5 atm, respectively.

Acetic acid was also obtained under the conditions used for carboxylation from the oxidation of ethane and propane, in the latter case also involving C–C bond cleavage. This acid was a minor product when using the V- or the Re-oxide catalysts, where propionic and butyric acids were the main products, derived from the carboxylation of ethane and propane, respectively. But remarkable activity and selectivity toward the formation of CH_3COOH from C_2H_6 (25% yield, TON = 63) and from C_3H_8 (12% yield, TON = 30) was exhibited by $Na_2[MoO_4]$, even though it did not catalyze the carboxylation of the gaseous alkanes. Related behaviors, although with lower activities and selectivities, were shown by $Na_2[WO_4]$, $K_2[Cr_2O_7]$, and Nb_2O_5. Ta_2O_5 and $K[MnO_4]$ were much less active.

The oxidation of ethane to acetic acid in homogeneous systems has been reported only scantly and with low selectivities and yields by using some V-polyphosphomolybdates/H_2O_2 (possibly via hydroxyl radicals) [36], chromic acid/H_2O_2 or Bu^tOOH (via peroxocomplexes) [37], Co^{II}/N,N'-dihydroxypyromellitimide/O_2 [38], or Pd-C/H_2O_2 (generated in situ) [39]. Active heterogeneous systems include mixed metal oxides, such as $Mo_1V_{0.25}Nb_{0.12}Pd_{0.0005}O_x$, at high temperature (via formation of ethylene possibly at a V-center, followed by its Pd^{II}-catalyzed conversion into the acid) [40].

In view of the observed activity of the Re-oxides, we also evaluated methyltrioxorhenium [(Me)ReO_3] (MTO), which is also commercially available (although more expensive) and has been widely applied [41–43] in organometallic catalysis (e.g., epoxidation, hydroxylation, and metathesis of olefins, oxidation of alkynes and esters). Before the current work, MTO had been tested in alkane functionalization in only a different type of reaction, peroxidative oxidation [44,45] (see below). We observed that MTO also catalyzed the carboxylation of ethane and propane (mainly to propionic and butyric acids, respectively, with minor amounts of acetic acid, with overall TONs of ca. 70 for alkane/catalyst ratios of ca. 125–150) (Table 1). It was the most active catalyst for the carboxylation of propane (overall acids yield of 53%), but was inactive for CH_4 carboxylation, in contrast to K[ReO_4] and Re_2O_7.

3.2. Hydroxylation/oxygenation of cycloalkanes

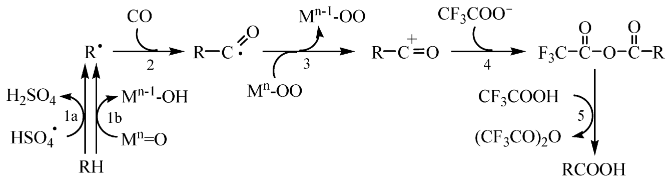
As was observed for carboxylation, the aqueous peroxidative hydroxylation/oxygenation of cyclohexane to cyclohexanol and cyclohexanone in our systems in aqueous H_2O_2/NCMe at room temperature was easier than that of cyclopentane. The highest TONs were obtained for the Re-oxides and MTO (ca. 140–120), followed by V-oxides (ca. 52–44) and $K_2[Cr_2O_7]$ (Table 1).

The Re-oxides and MTO displayed a considerably higher activity than Amavadine and its V-models (best TONs of ca. 50) [30], whereas the V-oxides had similar activity (maximum yield identical to that of the Amavadine models [10%]). A higher yield (14%) was displayed by $K_2[Cr_2O_7]$. Higher selectivity was shown by the V-oxides toward the formation of cyclohexanol, providing typical alcohol/ketone molar ratios of 9 for V_2O_5 and V_2O_4 and 4 for $VOSO_4$.

MTO also catalyzed the aqueous peroxidative hydroxylation/oxygenation of cyclohexane and cyclopentane at room temperature (overall TONs of 121 and 81, respectively). The activities of the Re-oxides, including MTO, were higher than those exhibited by the other known Re catalysts for the alkane peroxidative oxidation, namely some benzoyldiazenido phosphine complexes with N,O-type ligands, which, for the oxidation of cyclohexane and cyclopentane to the corresponding alcohols and ketones, display overall TONs up to ca. 45 [46] (compared with those of the Re-oxides of ca. 120–140 in the current work). MTO has previously been recognized [44,45] to catalyze the peroxidative oxidation, by anhydrous H_2O_2, of C_6–C_{10} alkanes either in the presence of an additive (pyrazine-2-carboxylic acid) in boiling acetonitrile at 80 °C (maximum TON of 126 for cyclohexane, with almost no cyclohexane oxidation if aqueous 30% H_2O_2 was used [44]) or in an alcohol at 40–60 °C (maximum TON of 6, although with good yields [45]).

3.3. Mechanistic considerations

The mechanisms of the above reactions conceivably involve both C-centered and O-centered radicals, since the reactions are essentially suppressed when carried out in the presence of either a C- or an O-centered radical trap [13], such as $CBrCl_3$, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), Ph_2NH, or 2,6-di-*tert*-butyl-4-methylphenol (BHT). Thus, the nonradical concerted (3 + 2) mechanism involving the addition of a C–H bond to two oxo-ligands, suggested for the alkane oxidation by OsO_4 [16] or RuO_4 [47,48], does not appear to be followed.



Scheme 1. Proposed mechanism for the carboxylation of alkanes catalyzed by a metal oxide.

$$M^n{=}O + H_2O_2 \longrightarrow M^{n-1}\text{-}OO^\bullet + H_2O \tag{1a}$$
$$M^{n-1}\text{-}OO^\bullet + H^+ \longrightarrow M^n{=}O + HO^\bullet \tag{1b}$$
$$M^{n-1}\text{-}OO^\bullet \xrightarrow{RH} M^{n-1}\text{-}OOH + R^\bullet \tag{2a}$$
$$HO^\bullet \xrightarrow{RH} H_2O + R^\bullet \tag{2b}$$
$$M^n{=}O \xrightarrow{RH} M^{n-1}\text{-}OH + R^\bullet \tag{2c}$$
$$R^\bullet + O_2 \longrightarrow ROO^\bullet \tag{3a}$$
$$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet \tag{3b}$$
$$R^\bullet + M^{n-1}\text{-}OOH \longrightarrow ROOH + M^{n-2} \tag{3c}$$
$$ROOH + M^{n-1}\text{-}OH \longrightarrow RO^\bullet + M^n(OH)_2 \tag{4a}$$
$$ROOH + M^n(OH)_2 \longrightarrow ROO^\bullet + H_2O + M^{n-1}\text{-}OH \tag{4b}$$
$$RO^\bullet + RH \longrightarrow ROH + R^\bullet \tag{5a}$$
$$2ROO^\bullet \longrightarrow ROH + R'{=}O + O_2 \tag{5b}$$
$$R^\bullet + M^{n-1}\text{-}OOH \longrightarrow ROH + M^n{=}O \tag{5c}$$

Scheme 2. Proposed mechanistic pathways for the peroxidative oxidation of alkanes catalyzed by a metal oxide.

For the carboxylation reactions (see Scheme 1 for proposed mechanistic pathways), $R^\bullet$ is expected to be formed by H-atom abstraction from the alkane (RH) (reaction 1) by the sulfate radical $SO_4^{\bullet-}$ (or its protonated $HSO_4^\bullet$ form) derived from thermolytic decomposition of $K_2S_2O_8$ [10,49], or by the metal oxide [44,50]. This is confirmed by radical trap experiments revealing the formation of various bromoalkanes and chloroalkanes (e.g., CH_3Br and CH_3Cl for methane carboxylation) in the presence of $CBrCl_3$ and $K_2S_2O_8$, in either the presence or absence of the catalyst. Carbonylation of $R^\bullet$ (reactions (2)) would form the acyl radical $RCO^\bullet$, which, on conceivable oxidation (reactions (3)) by a peroxo- or oxo-metal complex (the former derived from a metal oxide) and reaction with TFA (reactions (4)), would lead to the mixed anhydride $CF_3COOCOR$, which in turn, on further reactions (5) with TFA, would yield the acid RCOOH and $CF_3COOCOCF_3$ (trifluoroacetic anhydride), as has been proposed for the methyl radical [13,35].

Alkyltrifluoroacetates are also formed and experimentally detected as minor products in some cases (mainly at low CO pressures). CO_2 is detected in the gaseous phase, as expected from CO oxidation (up to 20%) or decomposition (thermal [51] or $K_2S_2O_8$-promoted [7,9,10]) of TFA. However, our carboxylation process does not appear to proceed via free CO_2, free alcohol, or free olefin, because CO_2 does not promote the carboxylation of alkanes, and the others (alcohol and olefin) are not converted into carboxylic acids in the presence of CO in our systems. Nevertheless, we cannot rule out the possible involvement of some free alcohols and aldehydes in the oxidation of alkanes, because they can be oxidized to the corresponding carboxylic acids (e.g., ethanol and acetaldehyde are converted to acetic acid). O_2 was not detected in the gaseous phase, and furthermore it inhibits the formation of carboxylic acids, conceivably acting as a $R^\bullet$ radical trap.

For the peroxidative oxidation reactions (see Scheme 2 for proposed mechanistic pathways), peroxo-metal M^{n-1}–$OO^\bullet$ and hydroxyl $HO^\bullet$ radicals can be derived from oxo-metal–promoted decomposition reactions of H_2O_2 (reactions (1)) [20,26,52], followed by the H-abstraction from alkane with formation of alkyl radicals $R^\bullet$ (reactions (2)) [26,44,50]. The process could then proceed via formation of the organo-peroxy radical $ROO^\bullet$ and the organo-hydroperoxide ROOH (reactions (3)) [2,44,53], which could undergo metal-assisted homolytic decomposition to the organooxy $RO^\bullet$ (reaction (4a)) and organoperoxy $ROO^\bullet$ (reaction (4b)) radicals [2], with the latter thus being regenerated. $RO^\bullet$ would form the alcohol ROH and $R^\bullet$ by H-abstraction from the alkane (reaction (5a)), whereas $ROO^\bullet$ would either decompose to the alcohol and the ketone (reaction (5b)) or regenerate ROOH and $R^\bullet$ on H-abstraction from the alkane (reaction (3b)), as has been proposed for some metal-catalyzed alkane oxidations by O_2 [20,44,53]. The alcohol also can be formed from $R^\bullet$ and a metal-hydroperoxide (reaction (5c)).

The involvement of the hydroperoxide ROOH in the V-oxide systems is corroborated by the significant increase in the amount of alcohol with a concomitant decrease in the amount of ketone when the final reaction solution, before GC analysis, is treated with an excess of PPh_3 following a method reported by Shul'pin et al. [1,20,31,52]. For the other metal catalysts, no ROOH was detected at the end of the experiments, probably due to its possible metal-promoted decomposition to the alcohol and ketone [54].

Peroxo- and hydroperoxo-metal species derived from peroxidation (by $K_2S_2O_8$ or H_2O_2) of the metal oxides are conceivably involved in some of the above reactions, supported by the recognition that peroxo-V complexes are key intermediates in the haloperoxidation of olefins by V-haloperoxidases [55] and that the peroxo complex $[(Me)ReO(O_2)_2]$ is an active species in the MTO/H_2O_2 catalytic system for olefin and aromatic peroxidative oxidations [41–43]. Alternatively, the alkane C–H bond can undergo heterolytic cleavage on electrophilic attack of the high-oxidation state metal to that bond [56], leading to an alkyl–metal species that can be involved in the carboxylation reactions (e.g., insertion of CO into the M–C bond to give an acyl derivative) and also in the C–C bond cleavage of propane to allow the formation of acetic acid possibly via a four-centered alkyl–alkane–metal species as has been proposed in the σ-bond metathesis of C_2–C_4 alkanes catalyzed by silica-supported Ta hydrides [57]. C–C bond cleavage also may occur via oxygen radical cation ($O^{+\bullet}$) transfer from a trioxo ligand (O_3^{2-}) to form a radical-cation pair, as has been suggested in a V^V/H_2O_2/CH_3COOH system [58].

4. Conclusions

The present study has shown that commercially available group 5−7 metal oxides, in association with suitable oxidants and solvents, can provide highly efficient, simple, and low- to moderate-cost catalytic systems for the single-pot oxidative functionalization of gaseous and liquid alkanes under mild conditions via radical reactions. TONs up to 10^4 were achieved, to the best of our knowledge by far the highest reported values in such reactions. V- and Re-oxides are usually the most active for the conversion of C_1–C_6 alkanes to the corresponding carboxylic acids, alcohols, and ketones, whereas a Mo-oxide is best for the production of acetic acid from ethane and propane, in the latter case also involving C–C bond cleavage.

The present study has provided the first catalytic applications of any Re-oxide in the functionalization of gaseous alkanes. The widely investigated MTO catalyst for olefin and aromatic oxidations has been shown to be active for all alkane reactions tested (and the most active catalyst for propane carboxylation) except CH_4 carboxylation. The diagonal metals V, Mo, and Re form, within the respective periodic groups, the most active oxides (V > Re > Mo) for the carboxylation reactions.

Although the effects of some electronic properties of metal oxides (i.e., electronegativity of the metal and/or Lewis acidity of the metal ion) on catalytic activity or selectivity have been recognized in a few heterogeneous systems [5,59], no general relationship was observed in the present study. Nevertheless, the activity of the most active metal oxides in the carboxylation reactions follows the trend V > Re > Mo > W, which parallels the Pauling electronegativity increase in the sequence V (1.63) < Re (1.9) < Mo (2.16) < W (2.36) [60]. A lower metal electronegativity (as in V-oxide) would correspond to a higher oxygen basicity, which eventually could promote H-abstraction from the alkane (reaction (2c), Scheme 2) as the most feasible pathway for alkane C–H bond activation by the metal oxide, as indicated by theoretical calculations on some molybdenum oxides [50]; alternative (2 + 2) or (5 + 2) pathways are less favorable.

The generality of these observations should be considered rather cautiously and tested further for other types of alkane reactions and metal oxides. The search, in the carboxylation reactions, for cheaper suitable solvent should proceed, and the favorable features of the oxide catalysts reported here should encourage further investigation into this challenging field of research.

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Supplementary material

The online version of this article contains additional supplementary material.

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