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A – Catalysis and the Periodic Table

**Selected Metal Catalysts Spanned over the
Periodic Table Towards Alkane Functionalization**

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Selected Metal Catalysts Spanned over the Periodic Table Towards Alkane Functionalization

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He authored 1 book, edited 9 books, (co-)authored over 950 research publications (including *ca.* 145 book chapters and reviews) and *ca.* 40 patents, and presented *ca.* 120 invited plenary and keynote lectures at international conferences. His work has received *ca.* 11,300 citations (27,300 citing articles), h-index = 75 (Web of Science). Among his honors, he was awarded Honorary Professorship by the St. Petersburg State University (Institute of Chemistry), Invited Chair Professorship by the National Taiwan University of Science & Technology, the “Franco-Portugais Prix” of the French Chemical Society, the Madinabeitia-Lourenço Prize of the Spanish Royal Chemical Society, the Prizes of the Portuguese Chemical and Electrochemical Societies, and the Scientific Prizes of the Universidade Técnica de Lisboa and of the Universidade de Lisboa. <https://fenix.tecnico.ulisboa.pt/homepage/ist10897>

1. INTRODUCTION

Alkanes are the main components of natural gas and oil, constituting a huge reserve of carbon. They are often burnt as energy source or simply flared off (mainly methane) in oil fields, what **depletes the Earth from carbon** and boosts carbon dioxide emissions with harmful ecological effects, contributing also to the exhaust of those **non-renewable fossil fuels**.

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A sustainable use of alkanes can be envisioned by redirecting their application to **carbon feedstocks for synthesis** of valuable functionalized organic compounds (**alkane functionalization**) for which the alkanes provide the carbon frameworks to bear the desired functional groups, as a blooming tree branch with its blossoms [1] [Fig.1(a)]. This topic has been reviewed recently in a book we have edited [1,2] and constitutes one of the greatest challenges to modern Chemistry in view of alkane inertness which, however, can be overcome by the use of a **catalyst** [Fig.1(b)]. This presentation addresses approaches that have been pursued by the author's Group towards achieving direct and **sustainable routes of alkane functionalization** (Scheme 1) which would provide much easier synthetic methods for the derived organic products that are prepared industrially via multi-stage, complex and energy costly processes.

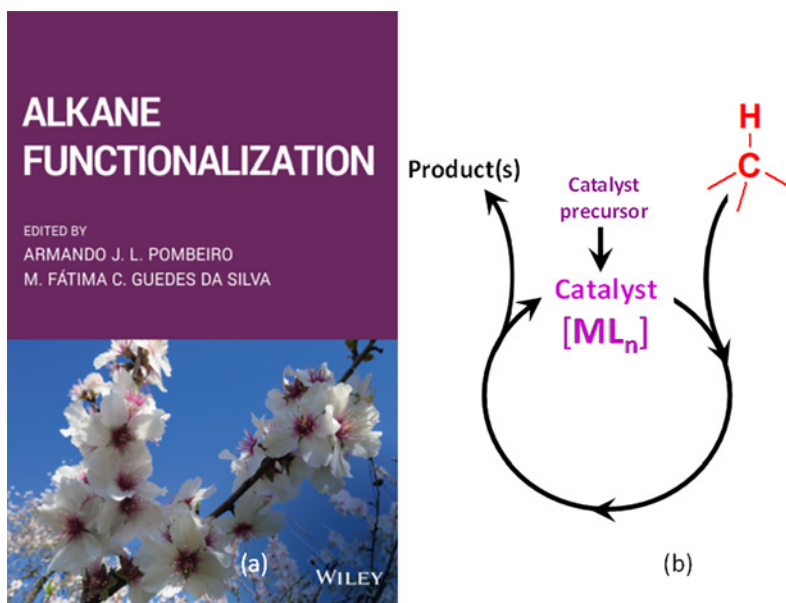
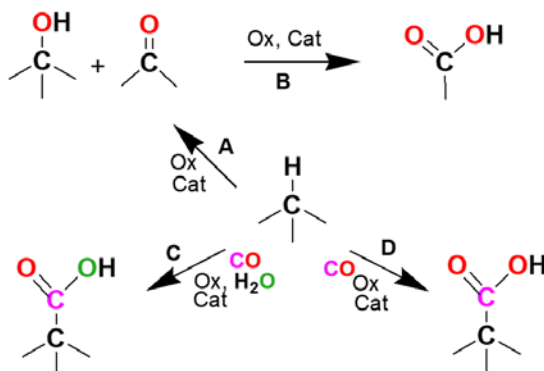


Figure 1. (a) "Alkane Functionalization" book cover [1]. (b) Overall catalytic cycle for the conversion of an alkane into a functionalized product. $[ML_n]$ = metal complex catalyst.



Scheme 1.

Alkane functionalizations to alcohols, ketones (A) and carboxylic acids (B, C, D). Ox = Oxidant: aqueous H_2O_2 or ROOH (A), O_3 (ozone) (B) or $K_2S_2O_7$ (C, D). Solvent: acetonitrile or ionic liquid (IL) (A), acetonitrile or IL/water mixture (C) or trifluoroacetic acid (TFA) (D). Cat = catalyst.

Almost all groups of the **Periodic Table** are represented (Fig. 2), accounting for the main roles played by their elements: groups 1 and 2 (mainly structural role); groups 13-17 (as ligands or their components); groups from 3 (including lanthanum) until 12 (except group 4) (active catalytic role).

Concerning the catalytically active elements, we have focused our interest mainly on 1st row transition metals (V, Cr, Mn, Fe, Co, Ni, Cu and Zn) which are abundant, cheap and usually without a negative environmental impact, although other metals have also been addressed (see below).

Structural role																Ligands or their constituents					18
1	2	Active catalytic role										13	14	15	16	17	He				
H	Li	Be											B	C	N	O	F	Ne			
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og				

Figure 2.

Elements (distributed along the Periodic Table) in catalysts for alkane functionalization which have been applied by the author's research Group ("Coordination Chemistry and Catalysis"), with assignment of their main roles. Red: active catalytic role; Blue: structural role; Violet: as ligands or their components.

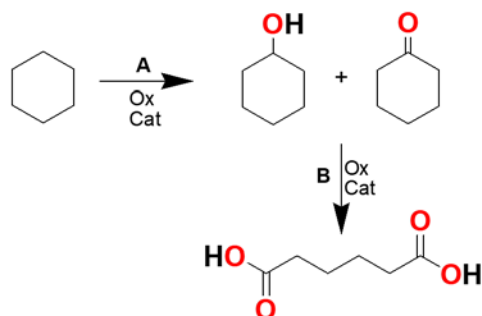
To promote sustainability, the use of **water** would be recommended, although it is challenging in view of the insolubility of the alkanes and usually of the catalysts. The latter difficulty can be surpassed by applying hydrosoluble ligands which would impart water solubility to their complexes (catalysts). They include aminopolyalcohols, N-hydroxyiminocarboxylates, benzene polycarboxylates, azo derivatives of β -diketones, tris(pyrazolyl)methane derivatives, etc. [2-8].

2. ALKANE OXIDATIONS TO ALCOHOLS AND KETONES

Model reaction and catalysts types

The alkane functionalization is mainly oxidative to form an alcohol and a ketone (Scheme 1, route A), typically the industrially significant conversion the cyclohexane into cyclohexanol and cyclohexanone, used as a model reaction (Scheme 2, route A). Further oxidation, *i.e.*, to adipic acid (Scheme 1, route B; Scheme 2, route B) is described in the next section. These products are intermediates for the industrial production of Nylon 6,6.

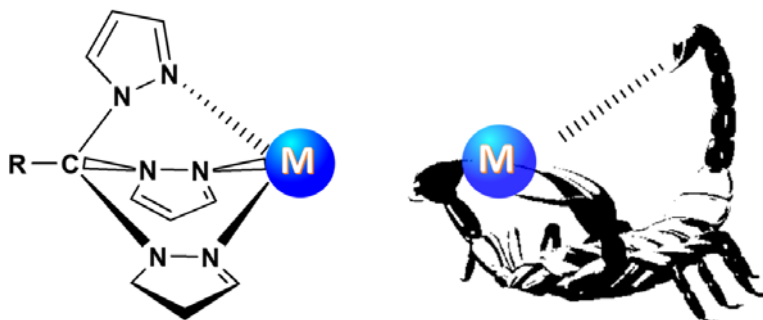
The reactions are usually performed in acetonitrile, with aqueous hydrogen peroxide as oxidant, at ambient temperature (or closeby), leading selectively to those products in good yields, in contrast to the industrial processes which operate under severe conditions and/or with noxious environmental effects.



Scheme 2.

Oxidation of cyclohexane to cyclohexanol and cyclohexanone (route A) as a model reaction for alkane oxidations, and further oxidation to adipic acid (route B). Ox = oxidant. Cat = catalyst.

The catalysts can be **mono- or dinuclear** complexes with the above types of ligands, and those with tris(pyrazolyl)methane derivatives (C-scorpions or C-scorpionates) are particularly active conceivably on account of the hemilabile character of these ligands which can coordinate the metal in a bi- or tridentate mode; their trivial name (“scorpionates” for the boron-based analogues), proposed by Trofiimenko, was inspired on the similarity to a scorpion grabbing its prey (Scheme 3). Vanadium, iron and copper are among the most active metals in these catalysts [7-9].



Scheme 3.

Hemilabile tri- or bidentate tris(pyrazolyl)methane (“C-scorpion” or “C-scorpionate”) ligand resembling a scorpion grabbing its prey. M = VO₂, VOCl₂, VCl₃, FeCl₂, NiCl₂, CuCl₂, AuCl₂, etc. (isolated with the tridentate coordination). R = H, CH₂OH, SO₃⁻, etc.

Self-assembled discrete polynuclear catalysts can also be quite effective, such as the tetracopper- μ -oxido-triethanolaminato complex [OCu₄(tea)₄(BOH)₄][BF₄]₂ [10] and other multi-copper compounds [10-12], and **heterometallic** complexes obtained by direct self-assembly from metal powder and aminoalcohols [3,4,13], *e.g.* the heterodimetallic hexanuclear salicylidene-2-ethanolamine complex [Co₄Fe₂O(Sae)₈] which, in the cyclohexane peroxidative oxidation, allows to achieve a high 46% products yield and a high turnover number (TON, number of moles of product per mole of catalyst) of 3.6×10^3 (corresponding to a turnover frequency, TOF, of $1.1 \times 10^4 \text{ h}^{-1}$) [13].

These multinuclear complexes are more effective, on a weight basis, than the multicopper enzyme particulate methanemooxygenase (pMMO) which catalyzes the oxidation of light alkanes to alcohols.

High nuclearity metallasilsesquioxanes can also provide good catalysts, such as that with the cluster cage Cu₉Na₆ (work in collaboration with G. Shul’pin and A. Bilyachenko, Moscow) [14].

Moreover, we discovered that **self-assembled metal-organic frameworks (MOFs)** or **coordination polymers** can also be quite active, as illustrated by water soluble heterometallic dioxido-vanadium(V)/alkali metal (Na, K, Cs) polymers with an azine fragment ligand (oxaloyldihydrazone). The catalytic activity (increasing from Na to Cs) parallels their complexity (1-, 2- or 3-dimensional, respectively), *i.e.*, a periodic trend appears to be followed [15].

Avoidance of an organic solvent, and catalyst recycling

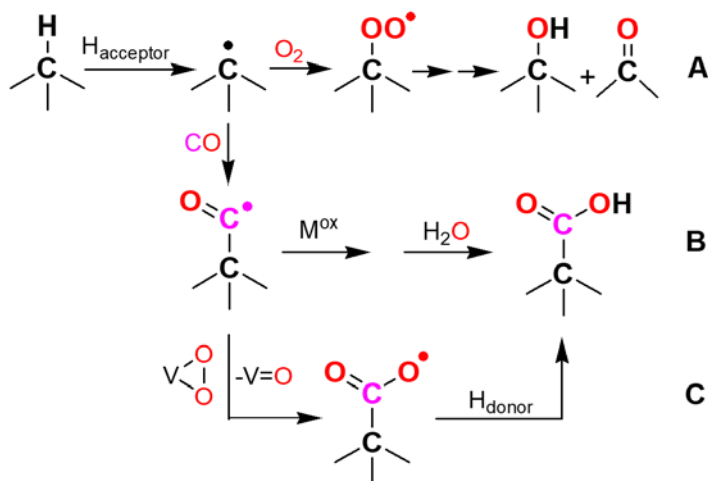
The volatile organic solvent (acetonitrile) can be avoided by replacing it with an **ionic liquid (IL)**, *e.g.*, 1-butyl-3-methylimidazolium dicyanamide ([bmim][N(CN)₂]) in the microwave-assisted neat oxidation of cyclohexane catalyzed by [FeCl₂{HC(pz)₃}] [16]. Another advantage of the use of the IL concerns the possibility of catalyst recovery and recycling without leaching, what is explained by theoretical DFT calculations that indicate the IL anion coordination to the metal catalyst [16].

Another way to achieve catalyst recycling consists in its **heterogenization** upon anchoring to a solid matrix. Carbon materials (with the collaboration of S. Carabineiro and J. Figueiredo, University of Porto), specially multiwalled carbon nanotubes (MWCNT) after adequate treatment, were disclosed to be appropriate ones, *e.g.* for [Cl₂Au{HC(pz)₃}]Cl [17] and related Fe, V and Cu catalysts in the peroxidative oxidation of cyclohexane.

The use as catalysts of recyclable **magnetic nanoparticles**, *i.e.*, first-row-transition-metal silica coated magnetite nanoparticles, Fe₃O₄@SiO₂-M²⁺ (M = Mn, Co, Cu or Zn), is also convenient in the same reaction assisted by microwave, without any added solvent, allowing an easy magnetic separation of the catalyst and its recycling [18].

Metal cooperation effects

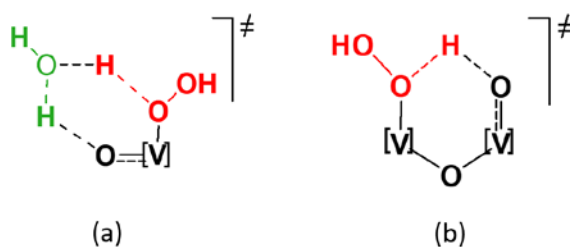
On the basis of radical trap experiments, selectivity and kinetic studies (with the collaboration of Prof. G. Shul'pin), as well as DFT calculations, the peroxidative alkane oxidation in our systems is believed to involve the metal-promoted formation of O- and C-based radicals, such as the hydroxyl radical HO• derived from H₂O₂, and the alkyl and peroxy radicals (R• and ROO•, respectively) from the alkane RH (Scheme 4, route A) [3-5].



Scheme 4. Overall metal-catalyzed radical mechanisms for the peroxidative oxidation (route A), hydrocarboxylation (route B) and carboxylation (route C) of an alkane. H_{acceptor} (hydrogen atom abstractor) = HO• or HSO₄*; H_{donor} (hydrogen atom donor) = RH or CF₃COOH; M^{ox} = metal catalyst as oxidant; V(OO) = peroxido-vanadium(V) catalyst.

The catalytic activity is often promoted by acid (generation of metal coordinative unsaturation upon protonation of an hemilabile basic N,O ligand) and, in some cases, by **water** and by the metal **dinuclear** character in oxido-divanadium catalysts. The latter unexpected behaviours are rationalized by DFT calculations which unveil various types of metal cooperation effects.

In the metal-assisted generation of the hydroxyl radical from H_2O_2 , **water** promotes proton-shift steps that are involved therein by forming stabilized 6-membered metal transition states [Scheme 5(a)] [19,20]. In the case of the **oxido-divanadium** catalysts, the bridging oxido ligand also cooperates with the metals, allowing the formation of a stabilized 6-membered di-vanadium transition state without requiring water [Scheme 5(b)] [21].



Scheme 5.
Stabilized 6-membered transition states in water-assisted (a) and oxido-divanadium-assisted (b) proton-shift steps towards the formation of hydroxyl radical from H_2O_2

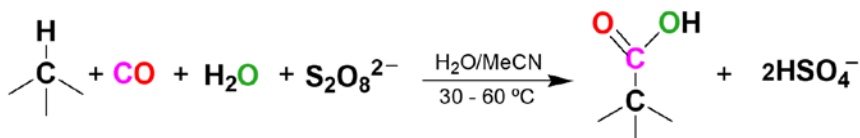
Another type of metal-ligand cooperation involves a non-innocent **redox active ligand** in the catalyst, which can perform the role typically assumed by the metal in the redox steps, allowing the latter to preserve its more favourable oxidation state under the reaction conditions.

We firstly proposed [22] this type of interpretation, based on DFT calculations, for the aluminium catalysed oxidation of cycloalkanes, and then extended it [23-25] to other metals of the same periodic group (13: gallium and indium) and of the periodic groups 2 (berillium), 3 (scandium, yttrium and lanthanum), 12 (zinc and cadmium) and 15 (bismuth). These elements form aqua complexes $[\text{M}(\text{H}_2\text{O})_n]^{m+}$ that act as catalysts for the alkane oxidation with H_2O_2 . The key step concerns the reduction of a H_2O_2 ligand by a deprotonated **hydrogen peroxide** co-ligand (HOO^-) to form the hydroxyl radical HO^\bullet without requiring the change of the stable metal oxidation state [25].

A quite different type of redox active ligand concerns **hydrazones** with the active azine moiety $\text{C}=\text{N}-\text{N}=\text{C}$. We recognized this effect in some highly active di(oxido-vanadium) catalysts which, in the presence of pyrazinecarboxylic acid additive, can lead to a TON of 4.4×10^4 , with an initial TOF of $3.3 \times 10^3 \text{ h}^{-1}$ in the oxidation of cyclohexane with H_2O_2 [26]. We disclosed other examples not only among vanadium catalysts [27-28], but also in other metal catalysts such as some octaazamacrocyclic (15- and 14-membered) nickel(II) complexes studied in collaboration with V. Arion (University of Vienna) [29]. Quinolinato ligands at vanadium complexes can also play a similar function [30].

3. ALKANE CARBOXYLATIONS AND OXIDATION TO CARBOXYLIC ACIDS

We discovered [31-33] that alkanes can undergo single-pot hydrocarboxylation with water and CO, peroxydisulfate acting as oxidant, in water/acetonitrile medium, to afford the corresponding carboxylic acids in high yields, at low temperature (30-60 °C), according to a radical mechanism in which (as proved by ^{18}O labeled water studies) water behaves as the hydroxide source (Scheme 1, route C; Scheme 6). The reaction proceeds via the acyl radical (RCO^\bullet formed upon reaction of CO with the alkyl radical R^\bullet) which, upon oxidation and nucleophilic attack of water, forms the carboxylic acid (Scheme 4, route B). The process can occur even in the absence of a metal catalyst, although less effectively.



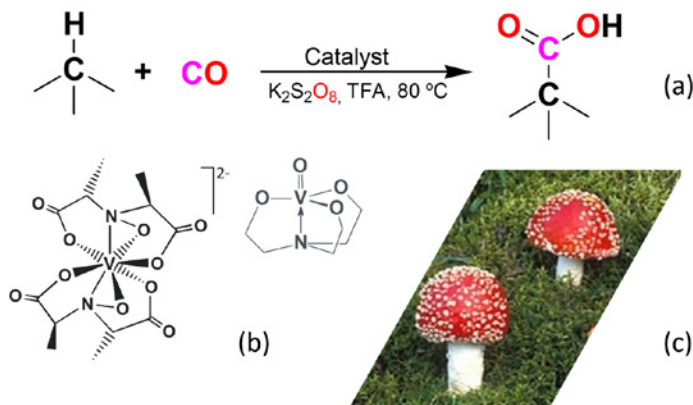
Scheme 6.
Alkane hydrocarboxylation in water/acetonitrile

The use of an organic solvent can be eliminated by replacing it (acetonitrile) by an ionic liquid, with the advantages of catalyst recycling and higher selectivity, features of “green” significance, as disclosed for a copper MOF with a bridging (terpyridinyl)benzyloxy benzoate linker [34].

This hydrocarboxylation reaction constitutes a development of a process of carboxylation of alkanes which we had developed earlier in trifluoroacetic acid (TFA), a less convenient solvent than water/acetonitrile, according to a method pioneered by Y. Fujiwara (Fukuoka, Japan).

In fact, we found [35-37] extremely active catalysts operating via a different mechanism (radical instead of electrophilic), namely *Amavadin*, an intriguing natural vanadium complex present in some *Amanita* toadstools, and its models or related vanadium species (Scheme 7). Yields above 90% and TONs over 10^4 could be achieved for methane or ethane carboxylation at the typical temperature of 80 °C.

Oxides of transition metals in the periodic groups 5-7 also act as carboxylation catalysts and the diagonal metals commonly provide the most active oxides in the order $\text{V} > \text{Re} > \text{Mo}$ [38].



Scheme 7.
Alkane carboxylation in trifluoroacetic acid: (a) general reaction; (b) typical catalysts (*Amavadin* and vanadatrane); (c) *Amanita* toadstools.

The reaction mechanism (Scheme 4, route C) involves the acyl radical (RCO•) as in the above hydrocarboxylation, but now the acyl is converted to the corresponding carboxylate radical (RCOO•) by a peroxide-vanadium catalyst [36, 37]. In the absence of CO gas, the reaction also occurs, although much less effectively, where the TFA solvent behaves as the carbonylating agent.

These single-pot alkane hydrocarboxylation and carboxylation reactions to yield carboxylic acids are much simpler and milder than the current industrial processes for the production of those products. However, they require peroxydisulfate as oxidizing agent and efforts to replace it by a “greener” oxidant have been pursued. We noticed [39] that ozone (a non-polluting oxidant), in the presence of the iron catalyst [FeCl₂{HC(pz)₃}], can oxidize, in a single-pot, cyclohexane to adipic acid, HOOC(CH₂)₄COOH (Scheme 1, route B; Scheme 2, route B), which is at a higher oxidation level than cyclohexanol or cyclohexanone (see above).

This one-pot oxidation of cyclohexane to adipic acid, a key intermediate for the production of Nylon-6,6, is also much simpler and sustainable than the industrial processes which usually require the oxidation of cyclohexanol/cyclohexanone with nitric acid leading to the emission of large amounts of the greenhouse nitrous oxide gas (N₂O) by-product.

4. FINAL COMMENTS

Following our first report (in 2000) on alkane functionalization (when we found that the natural vanadium complex *Amavadin* can act as a catalyst for alkane hydroxylation, oxygenation and halogenation [40]), our work has extended to the design and application in this field, under mild conditions, of a **diversity** of catalysts with metals playing a key catalytic role. They spread over most of the groups of the **Periodic Table** (12 in a total of 18 periodic groups). Elements of almost all the other periodic groups have also been used in the composition of the catalysts, namely with a structural role in their ligands.

The metal catalysts can be hydrosoluble, based on either a transition (almost all periodic groups from 3 to 12) or a non-transition redox inactive metal (in periodic groups 2, 13 and 15), and bioinspired. They can act as homogeneous catalysts in solution or supported on a matrix such as a suitable carbon material.

Routes towards **sustainable** alkane functionalization reactions (*e.g.*, simple, environmentally benign and with a low energy consumption) have already been followed, namely in terms of (i) metal catalysts design and mild operation conditions, (ii) “green” oxidants, (ii) avoidance of organic solvents, and (iii) use of water as solvent, reagent and catalyst. Moreover, applications of other unconventional conditions are growing, namely the use of supercritical carbon dioxide as solvent, of microwave heating or mechanochemical assistance [41].

The reaction **mechanisms** in our systems are of a radical nature and relevant **cooperative metal-ligand** effects have been disclosed.

Oxygenated and carboxylated products with an added value have already been obtained in good yields and under considerably mild conditions, thus demonstrating the potential use of inert alkanes as feedstocks. Can the onset of an Alkane Area for organic synthesis be foreseen?

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