

RECENT PROGRESS IN OXIDATION OF *n*-ALKANES BY HETEROGENEOUS CATALYSIS

AKELLA SIVARAMAKRISHNA^{1*}, POTHINI SUMAN¹,
E. VEERASHEKHAR GOUD¹, SANNAPANENI JANARDAN¹,
CHINDULURI SRAVANI¹, C. SURESH YADAV¹
and HADLEY S. CLAYTON²

¹Chemistry Division
School of Advanced Sciences
VIT University
Vellore 632014
Tamil Nadu
India
*e-mail: asrkrishna@vit.ac.in

²Department of Chemistry
UNISA, Pretoria
South Africa

Abstract

Many heterogeneous catalysts are known to convert alkanes at high temperatures to a variety of products, but unfortunately most of these systems are not amenable to catalytic transformations since the reactive intermediate species are converted to different products in low yields. It is also observed that the product distribution in these reactions strongly depends on the parametric conditions. The commercial interest as the industrially applicable process for the selective oxidation of *n*-alkanes to give alcohols and carbonyl compounds is

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gaining a lot of significance in modern catalytic chemistry. Also, the production of hydrogen gas from saturated hydrocarbons is one of the focus areas in the present scenario. This review article mainly focuses on important methodologies adopted to activate C–H bonds of *n*-alkanes by various heterogeneous catalysts by highlighting their strengths as well as drawbacks. As there is a demand in searching for the new techniques and modifications to the existing methodologies for the functionalization of *n*-alkanes, the factors that can influence the efficiency and selectivity of desired products will be highlighted.

1. Introduction

Metal-mediated C–H bond activation has been studied since the 70's after the direct interaction of metal centers with C–H was proved. Much recent research in C–H activation has focused [1-10] on the selective transformation of inert carbon-hydrogen bonds into other useful functional groups. Due to the need of conversion of these highly accessible hydrocarbons, direct and catalytic transformation of alkanes to higher value chemicals via C–H activation is of considerable interest to chemical industries globally, and remains a challenge to chemists, biochemists, and chemical engineers [10].

If conversion of alkanes into useful products, such as alkenes, alcohols, aldehydes, and carboxylic acids can occur under milder and better controlled catalytic conditions, then this can offer large economic benefits. The selectivity between different C–H bonds also depends on the bond strength trends. The order of reactivity for C–H bonds decreases as follows: $3^\circ\text{CH} > 2^\circ\text{CH} > 1^\circ\text{CH} > \text{CH}_4$. However, it is very difficult to achieve selective transformations under the usual experimental conditions. Methane is the most abundant and a very useful raw material for the synthesis of valuable oxygenated products, such as methanol and formaldehyde. The partial oxidation of methane is a very economically attractive process in the petroleum industry. However, known homogeneous catalysts for this process suffer from various drawbacks, such as difficulty of catalyst recovery, expense, decomposition at moderate temperatures, and the highly reactive nature of some of the catalysts leading to a wide range of products. Research efforts of the past five years on hydrocarbon activation reactions indicate the significance of

this topic (Figure 1). A review of the literature reveals the domination of soluble metal complexes for C–H activation over other catalytic systems.

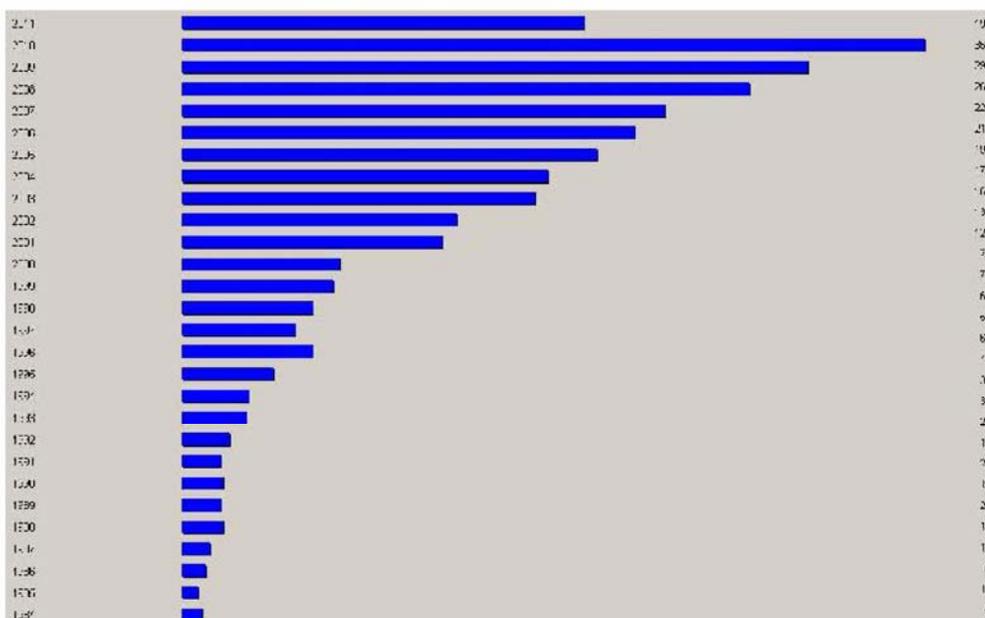


Figure 1. A histogram of research articles on C–H activation reactions, which show the popularity of this research area and the exponential growth in publications over the past decade.

Out of three different broad approaches available (Figure 1), namely, homogeneous, heterogeneous, and bio catalysis [1, 2, 9]. The potential of soluble metal complexes there in useful C–H bond activation strategies and thus indicate that the many modes of C–H bond activation are possible. However, a general problem with organometallic complexes is to achieve the required selectivity from different C–H bonds in the same molecule as well as making the reaction catalytic. One of the major drawbacks of using homogeneous catalysts is the difficulty in separating the relatively expensive catalysts from the reaction mixture at the end of the process. The possible contamination of catalyst in the product also restricts their use in industry [10].

In general, various heterogeneous catalysts can yield only carbon dioxide and water, but no higher value products as potential starting materials. The conversion of *n*-alkanes to valuable olefins is possible through controlled cracking and thermal dehydrogenation processes. In addition, *n*-alkanes can be induced to react by highly reactive free radical species, but these methods suffer from the poor product selectivity and the difficulty in generating the reactive species. Cavani and co-workers [11] have summarized the properties of heterogeneous catalysts required to promote the oxy-functionalization of light paraffins to valuable chemicals via (i) the oxidation of *n*-butane to maleic anhydride by vanadium/phosphorus [VPO] mixed oxide; (ii) Keggin-type heteropoly-compounds for oxidation of propane to olefins or oxygenated compounds; and (iii) ammoxidation by rutile-based mixed oxides, promoting the different role of the various elements in the formation of acrylonitrile from propane. Moreover, these authors have shown that the selective oxidation of light alkanes to bulk chemicals depends on several factors, such as the role of redox properties of transition metal oxide-based systems, the contribution of radical-type, homogeneous and heterogeneously-initiated homogeneous reactions over non-reducible metal oxide and noble metal catalysts, bulk and surface properties of catalysts, and control of oxygen supply to the catalyst [11].

A series of heterogeneous iridium containing SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , and MCM-41 (mobile crystalline material-41, a silicate molecular sieve) catalysts were able to dehydrogenate alkanes to give alkenes and hydrogen without a sacrificing olefin [12]. The heterogeneous dehydrogenation reactions showed high temperature dependence with a temperature maximum depending on the catalyst combination used. The iridium containing catalysts also activated the linear alkanes (e.g., *n*-pentane and *n*-octane) in catalytic C-H activation reactions. The applications of single-site nonporous catalysts have been reported in the aerobic, shape-selective oxidation of cyclohexane to adipic acid, and regiospecific oxidation of linear alkanes [13]. An extensive review on various properties and structural aspects of heterogeneous catalysts has been written by Misono and Mizuno [14].

A variety of enzymes [15] have been used as efficient and selective catalysts for *n*-alkane oxidation reactions under physiological conditions. In practice, these approaches seem to be applicable only to the small scale conversions, and not for the large scale bioprocesses for *n*-alkane transformations. Recent research on *n*-alkane transformations by biocatalysts have been focused on understanding the reaction mechanisms, so as to guide the design of synthetic catalysts mimicking their function, efficiency, and selectivity [15].

A number of key reviews on this topic have been published over the past few years including a critical review emphasizing the choice of the metal catalyst (Pt, Rh, Pd, and Ni surfaces) for each kind of reaction and the effect of reaction conditions. Also included is a discussion on the role of low-coordination sites and possible intermediate species [16]. In this context, this review article focuses mainly on recent advances in the oxidation of C–H bonds in *n*-alkanes by heterogeneous catalysts.

2. Heterogeneous Catalysts

Heterogeneous materials including the homogenized heterogeneous substances have played an important role in various catalytic transformations in petrochemical, fertilizers, and food industries [17]. Various methodologies have been developed for the immobilization of homogeneous transition metal complexes over organic polymers or inorganic solids like zeolites/molecular sieves, silica, alumina, other metal oxides, and carbon have been used as supports for the heterogenization of homogeneous catalysts. In addition, these catalysts exhibit enhanced stability and improved selectivity, which is ascribed to contributions of site-isolation and confinement effects, as well as cooperation effects from the support. In these systems, the catalytic action occurs at specific or active sites on the solid surface. It is highly desirable to have a uniform dispersion of metal catalysts on the support as this significantly improves catalytic activity. The main advantage of heterogeneous catalytic systems in the liquid phase over their homogeneous counterparts lies in their ease of separation from products and recyclability.

Various biological catalytic processes involving vanadate based enzymes [18, 19] have inspired extensive research on the catalytic aspects of vanadium complexes. The vanadium complexes showed catalytic activity towards various organic transformations including paraffin activation reactions [20, 21]. This class of catalyst has been reviewed with focus on the catalytic applications of polystyrene-supported [22], zeolite and ordered mesoporous molecular sieve supports [21, 23], and immobilized catalysts containing various ligands and metal complexes [24].

There are four main distinct methodologies developed for the heterogenization of homogeneous catalysts, through adsorption, encapsulation, covalent tethering, and electrostatic interaction. Catalysts immobilized by adsorption rely only on weak van der Waals interaction between the catalyst and the support with good stability. This can be improved by modifying the catalyst and support to allow hydrogen bonding to occur. Encapsulation is a process that does not require interactions between the catalyst and the support, and thus this method mimics the homogeneously catalyzed reactions. The other methods listed above lead to changes in the catalyst. In general, the mechanism involved in heterogeneous catalytic processes is presumed to entail diffusion of reactants (gases and liquids) on the catalyst surface (solids) followed by adsorption onto the surface, *via* the formation of chemical bonds. After reaction, the products desorb from the surface and diffuse away. The rich literature indicated the possible important C-H activation reactions of *n*-alkanes through heterogeneous processes. This review article mainly focuses on C-H bond activation and subsequent oxidation reactions of paraffins by using heterogeneous catalysts to yield valuable oxidation products.

2.1. Partial oxidation

In heterogeneous catalysis, C-H bond activation through homolytic cleavage of one C-H bond is a crucial first step. Once the first bond is broken, the other sequential reactions to oxidized products are relatively facile. As the exact mechanism of C-H bond activation reactions by

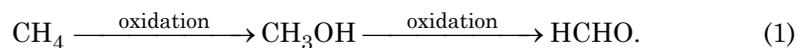
heterogeneous catalysts is still unknown, it is very important to understand how C–H bonds in hydrocarbons are activated, as well as assess the influence of catalytic and process parameters on the rate and efficiency of catalytic combustion [25]. Recent studies have shown direct proton exchange between the zeolite surface and the methyl groups of alkane [25]. Most of the heterogeneous catalysts are either non-reducible or reducible metal oxides [26-28] and metals [29], which are capable of oxidizing hydrocarbons with different efficiencies.

It was reported that ethane is oxidatively dehydrogenated to ethylene with high selectivity using mixed metal oxide catalysts containing Mo, V, and Nb [30a]. As depicted in Table 1, various heterogeneous metal oxide catalysts exhibit the activity and selectivity towards the dehydrogenation of ethane to ethylene. For example, the catalysts Mo_{16}V_4 , $\text{Mo}_{16}\text{V}_4\text{Mn}_4$, and $\text{Mo}_{16}\text{V}_4\text{Nb}_2$ showed the quantitative dehydrogenation of ethane under the mentioned experimental conditions. The effect of promoter (e.g., Nb_2O_5) as an additive to an $\text{MoO}_3 - \text{V}_2\text{O}_5$ catalyst for the same reaction was studied [30b].

Table 1. Catalytic activity and selectivity for oxidative dehydrogenation of ethane to ethylene

Metal oxide catalyst (composition)	Temperature (K) for 10% conversion of C_2H_6	Selectivity to C_2H_4 (%)
Mo	500	88
$\text{Mo}_{16}\text{Mn}_{16}$	550	35
$\text{Mo}_{16}\text{Nb}_4$	634	74
$\text{Mo}_{16}\text{Ti}_4$	600	65
Mo_{16}V_4	540	100
$\text{Mo}_{16}\text{V}_4\text{Fe}_1$	435	87
$\text{Mo}_{16}\text{V}_4\text{Mn}_4$	505	100
$\text{Mo}_{16}\text{V}_4\text{Nb}_2$	286	100

The reaction pathway followed by oxide based metal catalysts in the activation of methane proposed [31] that both the acidic (a metal cation) and basic (an oxide anion) sites are important in the deprotonation of methane to form a CH_3^- ion attached to a metal cation. The influence of various factors, such as the nature of hydrocarbon substrate, metal system and reaction conditions, poisoning effects, and promotion effects on the activation of C-H bonds with metal-based heterogeneous catalysts have been extensively studied by various research groups [32, 33]. In recent years, much research has been focused on the partial oxidation of alkanes to their respective alcohols and aldehydes [34, Equation (1)], effected by a variety of transition metal substituted MCM-41 catalysts.

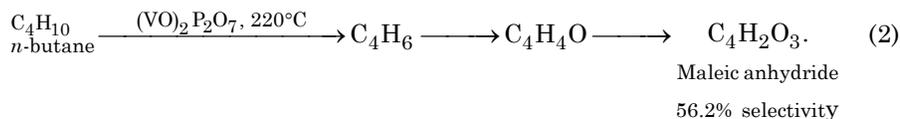


The direct conversion of methane to methanol has proven to be an extremely difficult reaction, due to the harsh conditions required to activate the methane molecule. However, several oxides [35], such as MoO_3 , Nb_2O_5 , Ta_2O_5 , and WO_3 have been shown to successfully catalyze this reaction to yield formaldehyde and dimethylether as the major products. The oxidation of higher hydrocarbons was also studied using other metal oxides [36], such as vanadium-phosphorous oxide (Equation (2)) and magnesium orthovanadate ($\text{Mg}_3\text{V}_2\text{O}_8$). Studies on the oxidation of *n*-butane were carried out to obtain maleic anhydride using supported vanadium oxides as catalysts (Table 2) [37].

Table 2. The effect of the metal oxide support on *n*-butane oxidation on supported vanadia catalysts at 494K in vol% *n*-butane in air

Catalyst	Weight (g)	Flow (cm ³ /min)	Butane conversion (mol%)	Maleic anhydride selectivity (mol%)
7%V ₂ O ₅ /SiO ₂	0.577	7.4	2.8	91.8
17.5%VO ₅ /Al ₂ O ₃	0.625	17.8	7.2	44.5
6%V ₂ O ₅ /Nb ₂ O ₅	0.885	13.9	17.3	36.7
4%V ₂ O ₅	0.794	11.3	16.0	9.3
3%V ₂ O ₅	0.622	14.2	10.6	12.6
5%V ₂ O ₅	0.566	25.5	27.8	30.5

As the strong M–O interactions in a metal oxide catalyst are usually responsible for effecting C–H cleavage, direct functionalization of inactivated C–H bonds using these catalysts usually requires severe reaction conditions, such as high pressure and high temperature. These extreme conditions yield complete oxidation to carbon dioxide and water as the thermodynamically favoured products of an alkane oxidation. The ideal catalysts should be selective for the first stages of oxidation, stopping at the desired product, and not continue further with subsequent reactions [38].



The oxidation of alkanes catalyzed [26] by chromium silicate with *t*-butyl hydroperoxide as the oxidant can be carried out under mild reaction conditions. Similarly, the ferrisilicate analogues of ferrierite type zeolites were found to exhibit catalytic activity for methane oxidation reactions with hydrogen peroxide as the oxidant as shown in Equation (3) [39].



Otsuka et al. [40] have shown that FePO_4 is an interesting model catalyst for the methane mono-oxygenase (MMO) enzyme. The iron based catalyst is able to activate methane to give CH_3OH and HCHO through the formation of a surface peroxide species as shown in Figure 2. The direct oxidation of ethane to ethanol and methanol at high pressures (34atms) has also been reported [41]. With this catalyst system, a total alcohol selectivity of 57% at an ethane conversion of 6.2% was obtained. It was also established that selectivity for ethanol was particularly sensitive to reaction conditions. At high temperatures, a transition to oxidative coupling of ethane with *n*-butane as the major product (33% selectivity) was observed.

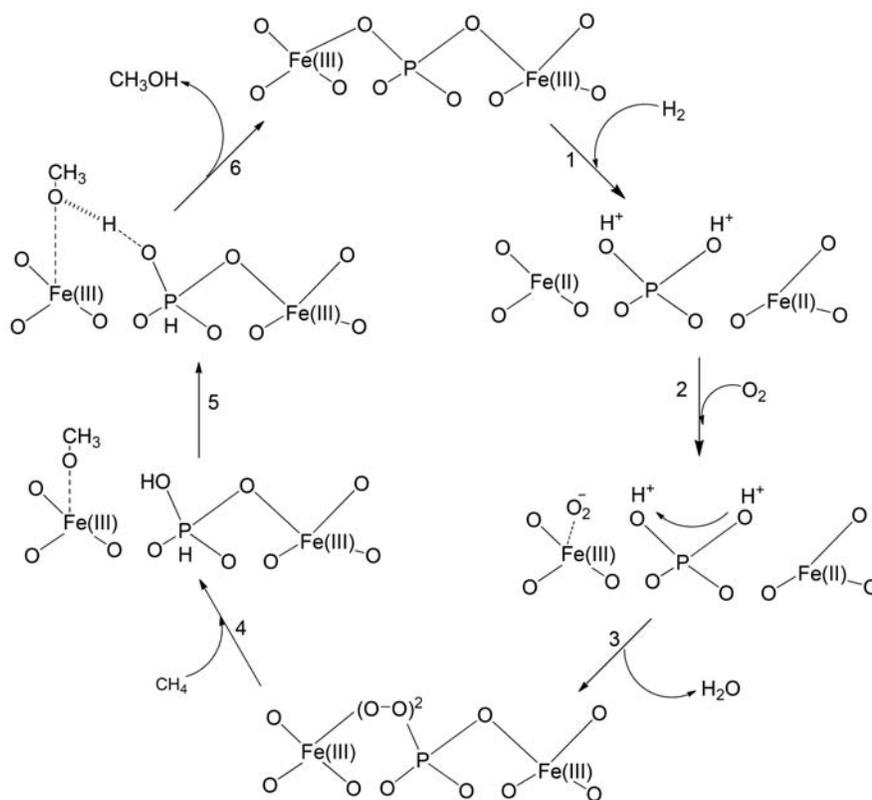
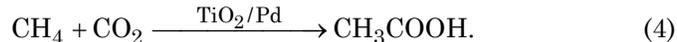
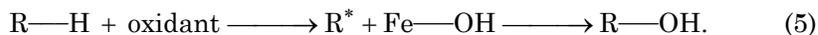


Figure 2. Proposed catalytic cycle for the conversion of CH_4 to CH_3OH .

Late transition metals as well as main group metals have been shown to activate C–H bonds. The carboxylation of saturated hydrocarbons with carbon monoxide in the presence of various catalysts (Pd, Cu or Mg) in trifluoroacetic acid at moderate temperatures was achieved (Equation (4)) [42]. However, catalytic activity is not restricted to any particular region of *d*-block metals. A study on the oxidation of alkanes with molecular oxygen using *N*-hydroxyphthalimide in the presence of Co or Mn was shown to give oxygenates, such as alcohols, ketones, and dicarboxylic acids [43]. Selective carbonylation reactions of alkanes were also reported [44] in the presence of carbon monoxide using diverse catalysts, such as sulphated zirconia and polyoxotungstates [45]. Dicationic Mn(III)-salen, containing phosphonium groups supported on Dowex MSC1 an ion-exchange resin by electrostatic interaction, has been used as catalyst in alkane hydroxylation with sodium periodate [46].



The heterogeneous catalytic hydroxylation of alkanes with the supported iron (III) and manganese (III) catalysts [47] in the presence of an oxidant has been reported (Equation (5)).



While oxidation of alkanes to carbon dioxide and water is thermodynamically favourable, metal complexes are capable of inhibiting complete oxidation. The reaction of methane with oxygen over a lanthanum oxide catalyst at elevated temperatures yields C₂H₆ as a primary product and C₂H₄ as a secondary product. The selectivity of these products can be increased by the better catalysts, such as SrO/La₂O₃ [48], Mn/Na₂WO₄/SiO₂, and Ru³⁺-substituted silicotungstate [49]. However, there are many limitations with these catalyst systems [50]. Several bifunctional catalysts, such as Mo/H-ZSM-5 zeolite [51] are known to promote the conversion of methane to benzene, toluene, and naphthalene, which have been highlighted by various review articles and the conversion of methane to methanol by following catalytic cycle

[52]. Zhang and co-workers [53] reported a catalyst (W, Zn/H-ZSM-5) for the 23% conversion of methane to benzene with high selectivity at 850°C. Using uranyl anchored/loaded microporous zeolite catalysts (silica or zeolite-Y (Na-Y) or ZSM-5) and ozone as an oxidant, higher normal alkanes, such as hexadecane, tetradecane or dodecane have been oxidized to ketones as major products, but with the moderate selectivity [54].

The industrial preparation of maleic anhydride through oxidation of butane is carried out over a VPO catalyst or other similar materials. Even though higher alkanes are oxidized to maleic anhydride over VPO catalysts, smaller alkanes, such as ethane (to ethylene and/or acetic acid) and propane (to acrylic acid) cannot be oxidized [55]. It has been revealed that selective butane oxidation is generated by the formation of VPO-butane combination that conforms to geometric-fit model as well as certain bond-strength considerations. However, Labinger and co-workers reported a selective oxidation catalyst based on the PMo11V Keggin ion, exchanged with Nb and reduced with pyridine, which can catalyze both the butane to maleic acid, propane to acrylic acid, and ethane to a mixture of ethylene and acetic acid [56].

Alkane hydroxylation has been extensively studied with transition metal complexes of porphyrins, phthalocyanines, and Schiff bases as the oxidation catalysts [58]. Also, the metallo derivatives of corroles [59], tetrapyrrolic macrocycles have evoked keen interest in their catalytic properties towards hydroxylation of alkanes [60]. Iron (IV) corrole-catalyzed oxygenation of ethyl benzene to 1-phenylethanol (6.6%) and acetophenone (4.2%) is the first example of metallocorrole-catalyzed hydroxylation of a hydrocarbon [30]. A significantly high catalytic activity of iron (IV)-corrole complex in the oxidation of alkanes at ambient temperature with *m*-CPBA has been achieved [61]. As the chemical transformation of C-H \rightarrow C-OH is an energy intensive process due to the inertness of alkanes toward chemical conversion, the biological world has evolved several enzymes (e.g., cytochromes P-450) to accomplish this transformation selectively and under very mild conditions [57].

Supported Fe catalysts and in particular, Fe-substituted MFI zeolites have attracted industrial and academic attention due to their ability to promote selective partial oxidation of hydrocarbons [62, 63]. It is generally accepted that atomically isolated Fe^{3+} species are involved in the selective processes catalyzed by these materials [64]. A straightforward method has been developed for isolated Fe sites towards *n*-alkane oxidation by H_2O_2 via IWI (incipient wetness impregnation) of SiO_2 with aqueous Fe-EDTA complexes [65].

It has been demonstrated that the catalytic oxidation of alkanes with 30% H_2O_2 under mild reaction conditions using polymer anchored Cu(II) Schiff base complex is possible. The heterogeneous catalyst system showed high catalytic activity in oxidation of various saturated hydrocarbon species. Surprisingly, the results also revealed that the immobilized catalyst is slightly more active than its homogeneous analogue [66]. Vanadyl pyrophosphate (VPO) catalysts derived from the vanadyl hydrogen phosphate hemihydrate ($\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$) precursor are known to selectively oxidize light alkanes [67]. The dispersed VPO phase on lignocellulosic-based activated carbon gives a catalyst that is selective for the partial oxidation of propane, and stable under oxidizing conditions [68]. The selective catalytic oxidation of short chain alkanes (C_2 to C_4) with MoVTaNbO and vanadium phosphorous mixed oxides catalysts yielded ethylene from ethane, acrylic acid from propane, and maleic anhydride from *n*-butane as the major products [69]. A further vanadium based catalyst oxovanadium (IV)-cucurbit [6], uril $[\text{VO}(\text{CB}[6])]\text{SO}_4 \cdot 9\text{H}_2\text{O}$ has been reported to act as a size-selective heterogeneous catalyst to oxidize linear alkanes like *n*-pentane at room temperature, but not styrene and cyclohexane due to cavity size restrictions [70].

Methane can be converted to methanol selectively by alkaline treated templated Na-ZSM-5 zeolites through the creation of intercrystalline mesopores within the zeolite agglomerates [71a]. Supported Fe catalysts containing substituted MFI zeolites have attracted industrial and academic attention due to their selective partial oxidation of saturated hydrocarbons [63, 71]. Several studies have sought to reproduce the

structures and reactivity of these substituted zeolites on different supports [72]. The selective oxidation of saturated hydrocarbons by highly dispersed and supported Fe^{3+} catalysts is also known. The catalyst is prepared via incipient wetness impregnation of SiO_2 with aqueous Fe complexes of ethylenediaminetetraacetic acid (FeEDTA), followed by calcinations [72]. The results indicated that σ -bond protolysis of alkanes by strong acid sites containing either H-zeolites or D-zeolites is the first step for alkane activation to H_2 and methane or HD and CH_3D , respectively. These transformations occur under mild conditions, which is in agreement with the activation path occurring in liquid super acid media [73].

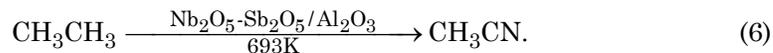
Catalytic total oxidation is a promising valuable technology for the destruction of volatile organic compounds (VOCs) at temperatures much lower than those of incineration [74]. In this context, transition metal oxides have been used as oxidation catalysts as they possess high thermal stability, resistance to poisoning and are low cost. This makes these complexes very attractive to oxidize paraffins, in particular, *n*-propane [75]. It has been reported that the most active catalysts for total oxidation of propane are those based on platinum [76] and palladium [77]. Other catalysts have also been reported for the oxidation of methane [78]. The complete oxidation of propane under oxygen rich-conditions has been studied by alumina supported ruthenium nanoparticles [79].

The adsorption of alkanes on solid surfaces has been investigated extensively, with most studies focusing on clean transition metal (TM) surfaces [80]. A number of research groups have contributed to this field and greatly advanced the fundamental understanding of alkane activation on metallic surfaces. It is interesting to note that several applications of oxidation catalysis occur under conditions that cause TM surfaces to oxidize and the resulting surfaces modifies the catalytic properties. It is reported that methane undergoes oxidation with Pd catalysts, where the PdO phase has a high activity for methane oxidation [81]. The immobilization strategies, product characterization procedures,

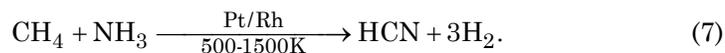
and their catalytic applications of various vanadium based catalysts for the oxidation of alkanes have been very well reviewed [82]. Studies on oxidation of alkanes in the presence of oxygen have been reported using various solid catalysts, Pt/Eu₂O₃/TiO₂/SiO₂ and the analogues. This study also showed the radical mechanism for oxidation of alkanes and that cleavage of C–H bond was the rate determining step [83]. Tabushi and co-workers first reported application of the reductive activation of hydrocarbons, which was soon followed by further reports from several other research groups on oxidation of alkanes under mild conditions [84]. Apart from the redox properties of active sites, acid-base properties and the role of water in the oxidation of paraffins have been comprehensively investigated [85].

2.2. Ammoxidation

Ammoxidation is another important process, where the unsaturated nitriles are prepared from hydrocarbons (Equation (6)). Propane can be converted to acrylonitrile with 63% selectivity in the presence of ammonia and oxygen by various mixed metal oxide catalysts [86, 87] such as Mo-VNb-Te [88, 89].



C–H activation of methane in the presence of ammonia using gas phase reactions of the cluster ions Rh₂⁺ and Pt/Rh⁺ is reported through dehydrogenation reactions [20]. This procedure employs heterogeneous Pt/Rh catalysts for the generation of hydrogen cyanide from methane and ammonia at elevated temperatures as shown in Equation (7).



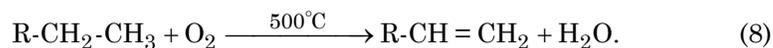
The ammoxidation of propane to acrylonitrile using substituted SbVO₄ with Fe³⁺ and Ga³⁺ replacing V³⁺, and Nb⁵⁺ replacing Sb⁵⁺ has been reported. It has been demonstrated that isolation in the structure of the propane activating V–O sites in a surrounding of nitrogen

inserting Sb-sites results in improved selectivity for acrylonitrile formation [90]. There is a great interest in developing heterogeneous catalysts for producing useful chemicals from alkanes [91], and the production of acrylonitrile was reported earlier by ammoxidation of propane over either iron antimonate or multicomponent bismuth molybdate catalysts [92]. The development of a heterogeneous catalyst for the one-step ammoxidation process of propane towards the formation of acrylonitrile has been paid attention recently as propane is substantially cheaper than propene, rendering a lower production cost of acrylonitrile [93]. The best known catalyst systems for propane ammoxidation are the MoV(Nb, Ta)(Te, Sb)O system [94] and modified Sb-V-O system [95]. Interestingly, the presence of excess antimony oxide (Sb : V > 1) in the catalyst results in improved performance [96, 97]. It has been shown that the substitution of V by small amounts of Fe has been reported to increase the activity and decrease the selectivity to acrylonitrile [98]. Other additions including Cr [99, 100], Mo and Nb [101] has been reported to have some positive effect on both the activity and the selectivity in the presence of V-Sb-Nb [97e], Cr-V-Sb-Nb- [102] and Sn-V-Sb-Nb- [103] mixed oxide systems. Moreover, both alumina and niobia have been investigated as supports for Sb-V-oxide [104] and it has been shown that the niobia supported material is more active and selective compared to that on alumina [104]. Studies related to catalytic behaviour of surface planes in layered mixed metal oxides including vanadium based aluminum oxynitrides catalysts for the ammoxidation of propane to acrylonitrile have been reported [105].

2.3. Oxidative dehydrogenation

The oxidative dehydrogenation of light paraffins to their olefins is still of great practical interest [Equation (3)]. For this reaction, two types of catalytic materials exist, which differ in the nature of surface-oxygen species taking part in the hydrocarbon activation: (1) redox-type metal oxides make lattice oxygen available, which is responsible for the formation of selective and nonselective reaction pathways leading to the olefins and carbon oxides; (2) adsorbed oxygen species are active species over non-redox-type materials including rare-earth and alkali-earth

metal oxides. The oxidative dehydrogenation of alkanes offers an energetically attractive route to the production of alkenes using various mixed metal oxides containing Mo, V, and Nb as catalyst [106]. The oxidative dehydrogenation reaction of hydrocarbons particularly butane was comprehensively studied over a large range of doped molybdate catalysts [106]. The results indicated that 1-butene and 2-butene are formed as primary reaction products, while butadiene and CO_x are secondary products. The dehydrogenation of propane yielded 33% of propene and 62.3% of C₁–C₂ products (Equation (8)).



Vanadium oxides supported on various metal oxides (e.g., MgO, TiO₂, Al₂O₃, ZrO₂, SiO₂) are an important group of catalysts for a variety of reactions, including selective oxidation of hydrocarbons [107]. Their surface properties have been analyzed in detail and many studies have investigated the relationship between their surface structure and catalytic properties [107, 108]. In particular, ZrO₂ supported vanadium oxide samples have been investigated as catalysts for the oxidative dehydrogenation (ODH) reaction of alkanes, one of the most feasible processes to obtain light olefins [109]. Numerous studies have focused on propane ODH reaction [110].

The structural properties and reactivity of zirconia-supported vanadium oxide catalysts have also been tested for the *n*-butane oxidative dehydrogenation (ODH) reaction. These results suggested that the active sites for the ODH reaction are associated with the V–O–V bonds of the polymeric exposed structures, whereas the Zr–O–V sites favour alkane combustion [111]. Heterogeneous acid catalysis of saturated hydrocarbons by heteropolyacids has also been focused much because of its potential of great economic rewards and green benefits [112]. Iron/calcium-hydroxyapatite catalysts have been used in propane oxidative dehydrogenation (ODH) and they exhibit good propene selectivity (35-90%) but with limited conversion [113].

MgAlO mixed oxide catalysts (M= Mn, Fe, Co, Ni, Cu, Zn, Ag, and Pd) obtained from layered double hydroxide (LDH) precursors calcined at 750°C have been used in the complete oxidation of methane and the oxidative dehydrogenation of propane. Other mixed oxides containing transition metals have been tested and their catalytic activity followed the order: MgAlO - FeMgAlO < NiMgAlO < ZnMgAlO < MnMgAlO < Co MgAlO < AgMgAlO < CuMgAlO. It has been shown that highly reducible metal oxide species play an important role in the catalytic combustion of methane [114a]. Nitrogen containing catalyst CoNx/Al₂O₃ yielded high performance in the oxidative dehydrogenation of propane and *n*-butane at 82% butane and 76.7% propane conversion rate. It is interesting to note that ethylene and propylene were the main products at > 400°C in the oxidative cracking of paraffins [114b]. Ni-Nb-O catalysts with various Nb contents (0-19%) have been studied as catalysts for the oxidative dehydrogenation of ethane. It has been shown that optimum ethane conversion of 33% with 78% of selectivity to ethylene was obtained for an Ni-Nb-O catalyst containing at 350°C [115].

2.4. Oxidative coupling

A large number of heterogeneous *M*-zeolite catalytic systems have been found [116] to activate alkanes by oxidative coupling. The reactions of several hydrocarbons in the presence of a microwave-activated charcoal catalyst and the oxidative coupling of methane using microwave activated carbon catalyst have been reported for the catalytic conversion of C₁ - C_{*n*} (where *n* = 1 - 4) hydrocarbons to olefins and hydrogen [117].

Recently, methane oxidative coupling reactions have been mainly focusing on the formation and reaction of methyl radicals [118]. The oxidative coupling of methane to higher hydrocarbons was also investigated by using niobium oxide semiconductor catalysts [119]. It has been demonstrated that the conversion of *n*-hexane yielded [120] a variety of products including propane, propene, butane, benzene, carbon oxides over magnesium orthovanadate (Mg₃V₂O₈) catalyst, depending on the experimental conditions.

3. Future Prospects

Many metal complexes undergo oxidation reactions with alkanes at high temperatures under heterogeneous conditions, but unfortunately most of these systems are not amenable to catalytic transformations, since the reactive intermediate species are converted to different products in low yields. It is also observed that the product distribution in these reactions strongly depends on the parametric conditions. The commercial interest as the industrially applicable process for the selective oxidation of *n*-alkanes to give alcohols and carbonyl compounds is gaining a lot of significance in modern catalytic chemistry. Also, the production of hydrogen gas from saturated hydrocarbons is one of the focus areas in the present scenario. The main challenge still remains for the heterogeneous catalytic approaches to produce a cheaper and highly active catalyst for the selective and high yield functionalized paraffins. There will be rapid growth in searching for the new techniques and modifications to the existing methodologies for the functionalization of hydrocarbons as many research groups trying to intensify their efforts.

4. Conclusion

The direct methods for the conversion of paraffins to the desired products by heterogeneous catalysis have a distinct economic advantage, but to date, no direct processes have progressed to a commercial stage. Product yields are generally low, which makes separations very difficult and expensive. New approaches to obtain a fine control over the industrial transformation of saturated hydrocarbons through catalytic reactions will provide new ways to improve selectivity of the desired products.

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