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Catalysis Today 45 (1998) 13–22

CATALYSIS TODAY

# Simple chemical processes based on low molecular-mass alkanes as chemical feedstocks

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## Abstract

The present state of new developments in direct catalytic conversion of low-molecular-mass alkanes ($C_1$–$C_3$) to petrochemical feedstocks and petrochemicals is reviewed. Special attention is given to the following reactions: *methane* to methanol and formaldehyde by partial oxidation as well as to $C_2$ hydrocarbons by oxidative coupling, *ethane and propane* to their olefins by oxidative dehydrogenation and to their oxygenates, i.e., acetic acid, acrylic acid and acrolein by partial oxidation. Specific research results are presented on the oxidative dehydrogenation of ethane and propane. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Functionalization of light alkanes; Oxidative functionalization; Oxidative conversion of methane; Dehydrogenation of ethane and propane; Oxygen species in alkane dehydrogenation

## 1. Recent activities in the functionalization of light alkanes

During the last 10–15 years many research efforts have been devoted to the chemical conversion of light alkanes as a consequence of the tremendous amounts of natural gas available and presently exploited which contains appreciable amounts of ethane, propane and butane besides its major constituent, i.e., methane. Methane when converted to ethylene by its oxidative coupling and to methanol by its direct oxidation may be considered as $C_1$ building block. $C_{2+}$ alkanes might replace short-chain olefins for oxygenates production; if these raw materials are directly and easily as well as selectively converted to valuable chemicals such processes certainly would be economically and environmentally attractive. A more modest goal would be the catalytic oxidative dehydrogenation of $C_2$ to $C_4$ hydrocarbons to their respective olefins.

There are no industrial endeavours which have become known to transform these light alkanes by either coupling (methane to ethylene) or oxidative functionalization to valuable chemicals except for the industrially applied synthesis of maleic anhydride and acetic acid from butane. Production of maleic acid from butane replaced in particular benzene as feedstock; for this reaction vanadyl pyrophosphate has unique catalytic properties which are, unfortunately not transferable to oxidative functionalization steps for ethane and propane. Whether the oxidation of ethane to acetic acid and the ammoxidation of propane to acrylonitrile are close to industrial realization remains to be proven.

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PII: S0920-5861(98)00231-4

Table 1
Selected literature data on the oxidative transformation of low ($C_1$–$C_3$) alkanes

| Reaction | Temperature (°C) | Catalyst | Yield (mol%) | References |
|---|---|---|---|---|
| $CH_4 \rightarrow CH_3OH$ | 350 | $Cu/SiO_2$ | 5.7 | [6] |
| $CH_4 \rightarrow HCOH$ | 600 | V/Cab–O–Sil | 2.9 | [7] |
| $CH_4 \rightarrow C_2H_4$; $C_2H_6$ | 780 | $LiNiO_2$ | 27 | [8] |
|  | 700 | $LiCl/MnO_2$ | 30 | [9] |
| $CH_4 \rightarrow CO+H_2$ | 777 | $Ru/Al_2O_3$ | 91 (CO), 93 ($H_2$) | [10] |
| $C_2H_6 \rightarrow C_2H_4$; | 600 | Li/La/CaO | 44.5 | [11] |
|  | 920 | Pt Monolith | 57 | [12] |
| $C_2H_6 \rightarrow CH_3COOH$ | 200 | Mo–V–Nb–O | 2.3 | [13] |
|  | 277 | W–V–Re–Nb–Sb–Ca–O | 10.9 | [14] |
| $C_2H_6 \rightarrow CH_2CHCl$ | 400 | CuO/cement | 34.0 | [15] |
| $C_2H_6 \rightarrow CH_3CHO$ | 400 | $FePO_4$ | 2.5 | [16] |
| $C_3H_8 \rightarrow C_3H_6$ | 550 | $B_2O_3/Al_2O_3$ | 18.0 | [17] |
|  | 550 | V–Mg–O | 23.9 | [18] |
| $C_3H_8 \rightarrow CH_2CHCHO$ | 550 | $Ca_7Bi_5Mo_{12}O_x$ | 3.2 | [19] |
| $C_3H_8 \rightarrow CH_2CHCN$ | 420 | $V_{0.4}MoTe_{0.2}Nb_{0.1}O_x$ | 50.4 | [20] |
| $C_3H_8 \rightarrow CH_2CHCOOH$ | 380 | $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ | 13 | [21] |

The catalytic partial oxidation of methane to synthesis gas which has been extensively and successfully studied from a fundamental point of view (cf. for instance [1–5]) is not considered in the present context although it might replace steam reforming of methane in certain circumstances.

Against the described background there exists a challenging task to develop and understand new catalytic routes related to novel catalytic materials. An impressive spectrum of valuable products for petrochemical and chemical industry could be derived from $C_1$ to $C_3$ alkanes by their selective oxidation as summarized in Table 1.

The development of all the processes listed in Table 1 is still in the research stage although pilot or demonstration plants were reported to be built for the oxidative coupling of methane, the oxidation of methane to methanol, the oxychlorination of ethane and the ammoxidation of propane. In the following, results achieved for some of these reactions are briefly summarized.

### *1.1. Catalytic methane conversion to methanol and formaldehyde*

The overall outlook for these oxidation reactions looks still rather dim.

*Methanol.* The gas-phase homogeneous partial oxidation of methane to methanol in a high-pressure tubular reactor with methanol selectivities of 70–80% at methane conversions of 8–10% per pass has been reported by Gesser and coworkers (see e.g. [22]). The reaction was performed in a glass-lined reactor operated at about 65 bar, 450°C and a residence time of about 2 min. The results claimed still need validation in practice. Also the effect of solid catalysts ($SnO_2$, $MoO_3/SiO_2$, $Sm_2O_3$, $Bi_2O_3$, Li/ZnO, $Mn_2O_3/Mn_3O_4$) on the oxidation of natural gas to methanol was studied by Gesser's group at 30 bar and various temperatures [23]. No significant improvement of the methanol yield was achieved compared to homogeneous oxidation. Tin oxide showed some promising results ($Y$=3.3%) at a low reaction temperature of 247°C but it was easily deactivated. According to [23] the use of increased concentrations of oxygen, which is needed to increase the conversion, can be accomplished safely by lowering the pressure and temperature. To the authors' opinion higher yields of methanol can be only achieved by using a heterogeneous catalyst. To Gesser's opinion catalysts should generate methyl radicals at a high rate which then would further react in the oxygen-containing gas-phase to methanol [24]. An indirect route for the catalytic oxidation of methane to methanol has been suggested by Catalytica [25–27], which imply the selective, low-temperature, Hg(II) catalyzed homogeneous oxidation of methane to methanol via methyl bisulphate. Methane was oxidized by concentrated sulfuric acid to produce methyl bisulphate, water and sulfur dioxide. At a methane conversion of 50%, 85% selectivity to methyl bisulphate was obtained. Separate hydrolysis of methyl bisulphate and reoxidation of sulfur dioxide with air provides to the authors' opinion a potentially practical scheme for the oxidation of methane to methanol with $O_2$. [26,27]. Another novel approach for the catalytic oxidation of methane to methanol is the use of a $CH_4$–$O_2$–$H_2$ reaction mixture [28]. Among the catalysts tested, iron phosphate showed an enhancing effect of $H_2$ on both $CH_4$ conversion and $CH_3OH$ selectivity. The yields obtained were, however, below 0.2%. None of the processes of direct conversion of methane to methanol has come close to commercialization to the authors' knowledge. There seem to be no innovative concept for the development of catalysts which convert methane to methanol with yields of about 10% per pass. Presently homogeneous oxidation looks still most promising. The results achieved for homogeneous oxidation in pilot plant scale operation in Russia [29] (up to 60% selectivities towards methanol and formaldehyde at 3–4% methane conversion) were considered by the authors as sufficient for industrial use.

*Formaldehyde*. Partial oxidation of methane to formaldehyde has been studied applying oxygen [7,30–36] or nitrous oxide [30,37–39] as oxidants. In general oxide catalysts (e.g. $Mo/SiO_2$, $B_2O_3/BeO/SiO_2$, $V_2O_5/SiO_2$, Fe–Mo–O) were used. Methane-to-oxidant ratios varied in the range from 0.2 to 3.0, typical reaction temperatures were between 450°C and 700°C. At temperatures above 600°C the formation of $CO_x$ became dominant. Attempts to reach higher yields by increasing the methane conversion were not successful since the selectivity falls sharply under such conditions (see e.g. [31]). Also, the use of nitrous oxide did not result in any significant improvement. The yields did not exceed 3% in general. Only in references [35,36] higher yields were reported. Kastanas et al. [35] reported a yield of 22.5% ($S$=83%) per pass on $Fe_2O_3(MoO_3)_{2.25}$ catalyst at 700°C. In a Japanese patent [36], a yield of 7% at methane conversion of 10.5% was reported on a mixed-oxide catalyst consisting of Fe, Mo, Ni, Mg and Bi supported on silica.

Most of the mechanistic studies were carried out regarding the nature of the active surface structure of Mo-containing catalysts. In particular, the formation of silicomolybdates was proposed to cause an increase of selectivity [38]. A rather high amount of studies were published by Parmaliana and coworkers mainly concerning the elucidation of the reaction mechanism. In their recent work [40], the redox behavior of $SiO_2$, $MoO_3/SiO_2$, $V_2O_5/SiO_2$, $TiO_2$ and $V_2O_5/TiO_2$ were evaluated from temperature programmed reduction by $H_2$ and $CH_4$. The most effective mechanism leading to the primary formation of HCHO implies in the authors' opinion the direct participation of gas-phase oxygen, while the involvement of bulk-lattice oxygen leads to $CO_x$. Recent kinetic studies of Sexton and Hodnett [7] indicated that oxygen is adsorbed on silica-supported vanadia catalysts and takes part in the reaction in an Eley–Rideal or Mars–van Krevelen mechanism. The nature of the interaction depends whether methane rich or lean conditions are used. The results indicate only the sequential formation of $CO_x$ via HCHO; the formation of methanol as an intermediate was excluded [7]. For supported $MoO_3$, Spencer [41] has, however, pointed out that HCHO and $CO_2$ are the primary products while CO being the secondary product; no clear conclusion on the intermediate formation of $CH_3OH$ was made.

For improving selectivity and yield in the partial oxidation of methane to formaldehyde, systematic studies on the elucidation of the properties of solids determining HCHO formation are required.

### 1.2. Oxidative coupling of methane (OCM)

After more than 15 years of research activities on this very challenging reaction its catalysis is now mostly well understood. $C_2$ selectivities of partly more than 85% have been achieved. The main shortcoming of this reaction is, however, the low methane conversion required for these high selectivities in an one-pass operation through a catalytic reactor leading to significant recycle expenses as well as to expensive separation of $C_2$ hydrocarbons from methane. To reach high $C_2$ selectivities for methane conversions above 20%, the addition of chlorine-containing compounds to the catalyst or the reaction mixture was used. On $KBi_3O_4Cl_2$, a $C_2$ selectivity of 82% ($X_{CH4}$=24%) at 750°C was reported by Ueda and Thomas [42]. Yields of $C_2$ hydrocarbons of 30% ($S$=65%) were achieved by Otsuka et al. [9] using a $LiCl/MnO_2$ catalyst. The chlorine-containing catalysts showed, in general, a loss of activity within a few hours of operation. Moreover, the corrosion problems due to high reaction temperatures and chlorine contamination of the target product ethylene have to be considered.

Improvements in the OCM reaction can be only expected from innovative reaction engineering concepts taking into account the obstacles mentioned, i.e. relationship between $C_2$ selectivity and methane conversion as well as methane/$C_2$ separation. The extent of the non-selective reaction pathway is not only determined by the catalyst but also by the ratio of $CH_4$ to $O_2$. The higher this ratio the higher the selectivity. On the other hand, low oxygen partial pressures lead to low degrees of methane conversion and hence, low $C_2$ yields per pass. If cost reduction of $C_2$ separation from the reactor effluent can be achieved by an advanced technology being much less expensive than low-temperature distillation, single-pass operation with low methane conversion and feed recycle may be attractive leading to high overall yield at high $C_2$ selectivity. A respective process scheme applying a "separative chemical reactor" has been suggested by Tonkovich et al. [43] based on earlier studies on a countercurrent moving bed chromatographic reactor [44]. Also temperature- and pressure swing adsorption can be considered as alternative methods for separation of ethylene from the reaction mixture of low ethylene concentrations. Modified NaA zeolites and chlorides of Ag, Cu, and Al were reported as suitable adsorbents [45,46]. A gas-recycle reactor-separator consisting of an electrocatalytic or catalytic reactor unit, a molecular sieve trap unit and a recycle pump was reported by Yentekakis et al. [47] to improve $C_2$ selectivity and yield for both batch and continuous flow; overall $C_2H_4$ yields up to 53% were obtained.

Another solution might be distributed oxygen feed [48] in order to keep oxygen concentration low which might be also achieved by fluctuating feed concentrations at the reactor inlet. The effectiveness of the distributed oxygen feed approach is still controversial. Recent work of Wolf et al. [49] on kinetic simulations of surface processes showed that non-steady state operation could probably result in a significant increase of ethane yield if the operation would be started with an oxidized surface which is covered by monoatomic but not molecular adsorbed oxygen species. Experimental validation of these results is, however, still needed.

Although some promising solutions have been suggested regarding optimization of reactor operation, no final breakthrough appears to be near for the oxidative coupling of methane in practice.

### 1.3. Oxidative dehydrogenation of ethane

Oxidative dehydrogenation of ethane being the alternative of the highly endothermic thermal pyrolysis has been the subject of many studies in which different catalysts have been tested in the temperature range from 350°C to ca. 1000°C.

For $T<600°C$, high ethylene selectivities of 89% and 91% at ethane conversion of 19% and 15% were reported on $B_2O_3$ (30 wt%)/$Al_2O_3$ at 550°C and on $K_2P_{1.2}Mo_{10}W_1Sb_1–Fe_1Cr_{0.5}Ce_{0.75}O_n$ at 470°C, respectively [50,51]. Mo–V–Nb, Mo–V–Sb and Mo–V–Ta oxide systems showed high activity at low temperatures (350–400°C); an ethylene yield of 37.7% ($S=65\%$) was obtained on $Mo_{0.73}V_{0.18}Nb_{0.09}O_x$ catalyst at 350°C [52]. High selectivities and yields to ethylene can be achieved when chlorine-containing compounds are fed into the reactor or when the catalyst is doped with halides [53–55]. Conway et al. [54] obtained an ethylene yield of 57% ($S=76\%$) over a $Dy_2O_3/Li^+–MgO–Cl^-$ catalyst at 570°C after 25 h on stream.

Catalysts that show good selectivities at higher temperatures ($T>550°C$) generally do not contain easily reducible metal ions (such as V, Mo, Sb). At high temperatures the catalyst assisted homogeneous reactions play an important role [56]. As shown by Burch and Crabb [57], also significant non-catalytic oxidative dehydrogenation occurs already at 600°C; the authors obtained an ethylene yield of 33.2% ($S=73.7\%$) in an empty reactor ($D_{in}=5$ mm) at a flow rate of 40 ml/min. Thus, for high temperature catalytic measurements, the respective data in the absence of a catalyst are required for correct evaluation of catalyst performance. The oxidative dehydrogenation of ethane on perovskite-type catalysts with the general formula $SrCe_{1-x}Yb_xO_{3-0.5x}$ was studied by Velle et al. [58] in the temperature range from 500°C to 700°C. A maximum yield of approximately 49% ($S=70\%$) was obtained at 700°C on $SrCe_{0.5}Yb_{0.5}O_{2.75}$ using a feed composition of 21.0% $C_2H_6$, 16.3% $O_2$, 62.7% $N_2$.

Although a high reaction temperature of 700°C was used, the authors did not report on results in the absence of a catalyst. Recently lithium doped lanthanum–calcium oxide (Li:La:Ca=1:1:2.5) was described as an effective catalyst resulting in $C_2H_4$ yields of 48.2% ($S$=89.2%) at 620°C and GHSV=1000 $h^{-1}$ [11]. The dehydrogenation of ethane at $T$=650–850°C was studied by Choudhary et al. [59] under fuel rich condition ($C_2H_6/O_2$=5–10) using a diluted $SrO/La_2O_3$ catalyst to avoid temperature gradients. Ethane conversions of approximately 20% ($S_{C_2H_4}$=75%) and 68% ($S_{C_2H_4}$=82%) were obtained at 700°C and 850°C, respectively. Although the authors proposed that the reaction is initiated on the catalyst surface no results on ethane oxidation without a catalyst under the same conditions are given. This is a very important issue, especially concerning this particular study since high ethylene yields were achieved only at very high temperature of 850°C at which non-catalytic reactions might be prevailing.

Another route of olefin synthesis is the so-called autothermal oxidative dehydrogenation. Huff and Schmidt [12,60] reported on the conversion of ethane in the presence of oxygen over Pt- and Rh-coated ceramic foam monoliths in an autothermal reactor at contact times in the order of milliseconds. The catalysts were operated autothermally, the heat generated by the reaction was sufficient to sustain reactions after ignition. A $C_2H_4$ yield of 52.3% ($S$=69%) was obtained over a Pt–Sn (7:1) catalyst at 920°C using $C_2H_6/O_2$ of 1.9 and a feed flow rate of five standard liters per minute. The authors believe that heterogeneous reactions dominate under these conditions.

The oxidative dehydrogenation of ethane on Pt in a fluidized bed reactor at contact times from 0.05 to 0.2 s was studied by Bharadwaj et al. [61,62]. Contrary to monolith reactor nearly isothermal conditions were maintained due to efficient solids circulation. For ethane conversion on $Pt/\alpha\text{-}Al_2O_3$, an ethylene selectivity of 70% at a conversion of 86% ($Y$=60%) was achieved at 850°C and $C_2H_6/O_2$=2. Pure $\alpha\text{-}Al_2O_3$ gave, however, an ethylene yield of 56% ($S$=67%) at 825°C and $C_2H_6/O_2$=2. As follows from latter result the careful evaluation of the role of the catalyst in the oxidative conversion of ethane at high temperatures is required in order to draw conclusions on the improvement of the process parameters by using a catalyst.

Our own results on the oxidative dehydrogenation of ethane on rare-earth oxide based catalysts under non-isothermal conditions are described in Section 2 "Specific research results" of the present contribution.

### 1.4. *Oxidative functionalization of ethane*

Research activities on the partial oxidation of ethane to acetic acid increased during last seven years. BP Chemicals [14,63], The Standard Oil [64,65], Rhone-Poulenc [66,67] claimed catalysts and processes for the production of acetic acid from ethane. The oxidation of ethane to acetic acid requires significantly lower temperatures than the oxidative dehydrogenation of ethane. The reaction was generally performed at elevated pressures up to 30 bar in the temperature range between 200°C and 350°C. The addition of water to the feed gas resulted in an increase of selectivity towards acetic acid and in a decrease of ethylene selectivity [14,68]. A fluidized-bed process with gas recycle was claimed by Benkalowycz et al. [64]. An acetic acid yield of 2.3% ($S$=100%) at 200°C was reported by Merzouki et al. [13]. A rather high yield of 10.9% was reported by Kitson [14] on a catalyst consisting of the oxides of W, V, Re, Nb, Sb and Ca at 277°C at 28 bar when adding water to the reaction mixture. Other types of catalysts such as $V/TiO_2$, $V\text{–}P/TiO_2$, $V\text{–}PMo/TiO_2$ [66–69] showed rather poor selectivity performance compared to the above mentioned results on Mo–V–Nb and doped W–V catalysts. On $MoVPO/TiO_2$, selectivity to acetic acid amounted to 21% at ethane conversion of 3.2% at 275°C and 7 bar [69].

### 1.5. *Oxidative dehydrogenation of propane*

Catalysts based on vanadia, especially V–Mg–O were most intensively studied. For the latter system, the pure phases (e.g. $Mg_2V_2O_8$, $Mg_2V_2O_7$, $MgV_2O_6$) as well as their mixtures are formed depending on the ratio of V-to-Mg applied. On $Mg_2V_2O_8$, a selectivity of 63% was obtained at propane conversion of 7% [70]. A propene yield of 23.9% was achieved over Mg–V–O catalyst at selectivity of 38% [18]. Phosphates and molybdates of various transition metals have been tested (see e. g. [71,72]). The yields obtained were generally not higher than 15%.

Recently a boria–alumina catalyst was used resulting in propene yields of 16–18% [17]. The surface oxidation was found to be significantly suppressed for boria loadings of about 30 wt%. No significant decrease of selectivity was observed at high degrees of propane conversions. Besides propene, ethylene and oxygenates were formed. Propyl radicals are assumed to be reactive intermediates; olefines and oxygenates are formed with high selectivities by secondary reactions of these propyl radicals after their release into the gas phase due to diminished surface oxidation.

The development of a stable catalysts leading to propene yields higher than 20% at high propene selectivities is still a challenging task.

### 1.6. Oxidative functionalization of propane

Direct oxidation of propane to acrolein could be an interesting alternative to propene oxidation. The data published indicate, however, that the reaction still leads to significantly lower selectivities and yields, respectively. Maximal yields of 13% as reported by Kim et al. [73] were achieved under conditions where, however, primary gas-phase dehydrogenation of propane occurred [74]. When considering literature data on selectivities of acrolein as a function of propane conversion it can be seen that maximal acrolein selectivities did not exceed 60% even at low propane conversions. Total oxidation as a non-selective side reaction of propane as well as the consecutive oxidation of acrolein contributes to a loss in acrolein selectivity. Yields reported are generally below 3–5% [75–77].

In our own work [19], the catalyst selection for the partial oxidation of propane to acrolein was based on the widely accepted assumption that propene is an intermediate product in the overall process. According to this fact a suitable catalyst composition should consist of two different active sites for propane dehydrogenation and for oxygen insertion in propene. $Me_xO_y$-supported $Ag_{0.01}Bi_{0.85}V_{0.54}Mo_{0.45}O_x$ ($Me_xO_y$=$\gamma$-$Al_2O_3$, $TiO_2$, $SiO_2$) and $Me_7Bi_5Mo_{12}O_x$ (Me=Mg, Ca, Zn) catalysts were tested and characterized using XPS, XRD, ESR, IR and transient experiments. It was concluded that different types of lattice oxygen are involved in propane dehydrogenation to propene and in consecutive reactions towards acrolein and $CO_x$. The catalyst design approach by combining two active phases had severe shortcomings since the two active phases did not act co-operatively to any large extent. Moreover, under conditions of effective propane dehydrogenation to propene a competitive reaction between an allylic intermediate and propane forming propene and a propyl radical can be assumed as the reason for low acrolein formation over the catalysts used. A two layer fixed-bed reactor was required to obtain an acrolein yield of 7.4% ($S$=20%) [19].

Selective oxidation of propane to acrylic acid is more successful compared to its oxidation to acrolein. The earliest studies on this reaction were performed using a V–P–O system [78]. More recently heteropoly compounds were studied; a yield of 9% was obtained by Centi and Trifiro on $H_5PV_2Mo_{10}O_{40}$ [79]. Oxidation of propane over heteropolymolybdophosphoric acids which were treated in pyridine during catalyst preparation was investigated by Ueda and Suzuki [80]; an acrylic acid selectivity of 24% at propane conversion of 12% was achieved. Recently, Mizuno et al. reported a yield of 13% when using $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$ as a catalyst at 380°C [21]. The maintenance of the Keggin structure during the reaction in the range of 300–400°C was derived from IR and XRD measurements.

## 2. Specific research results

### 2.1. Oxidative dehydrogenation of ethane and propane

Catalyst selection was based on assumptions about possible mechanisms prevailing in the oxidative dehydrogenation of alkanes on metal-oxide catalysts. Three types of mechanisms were considered which are based on the type of oxygen species involved in alkane activation (cf. Fig. 1).

In the redox mechanism (case A) oxygen of the metal oxide takes part in the reaction by abstracting and oxidizing the hydrogen from the hydrocarbon. The OH groups being formed in this way are then removed from the surface by dehydration. The catalyst is subsequently reoxidized by oxygen from the gas phase. In case B oxygen participates via its adsorbed state; hydrogen is abstracted forming OH-groups on the catalytic surface which are removed by dehydra-

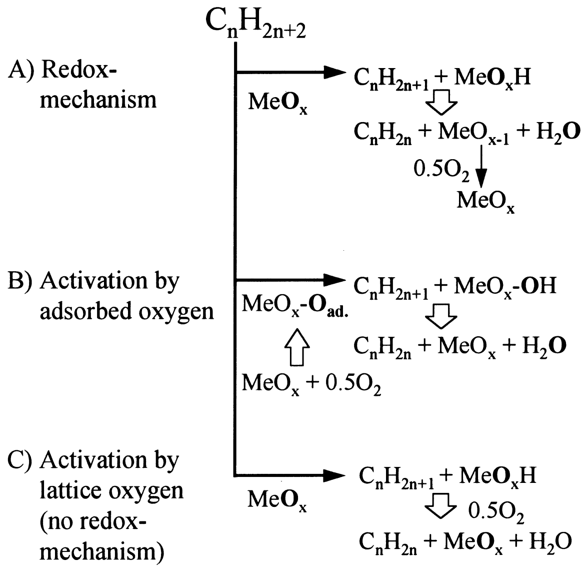

Fig. 1. Primary reaction steps of the oxidative dehydrogenation of alkanes on metal oxide catalysts for three different assumptions A, B and C.

tion. The active surface oxygen is then restored by oxygen adsorption from the gas phase. In case C it is assumed that strongly bound lattice oxygen abstracts hydrogen which is removed from the surface by interaction with gas-phase oxygen. For these different hypotheses on initial surface processes of alkane activation, different types of materials are needed as catalysts for the oxidative dehydrogenation of short-chain alkanes.

In the current contribution, the oxidative dehydrogenation of ethane and propane on rare-earth oxide (REO) based catalysts is described (for details of this work see [81,82]). On this type of catalyst, the alkane molecule is activated by adsorbed oxygen as has been confirmed by transient experiments. Continuous flow experiments on Na–P/$Sm_2O_3$, Sm–Sr(Ca)–O, La–Sr–O and Nd–Sr–O catalysts at 1 bar showed that the reaction mixture is ignited resulting in enhanced heat generation at the reactor inlet. The heat produced by the oxidative reactions was sufficient for the endothermic thermal pyrolysis which most probably takes place preferentially in the gas phase.

Results of catalytic experiments on rare oxide based catalysts using a non-isothermal mode of operation for the oxidative dehydrogenation of propane and ethane are given in Tables 2 and 3, respectively. To sustain the reaction after ignition at the desired temperature ($T_{max}$), the feed gas was preheated up to a certain temperature $T_0$.

From the results obtained the following conclusions can be derived:

- Rare-earth oxide-based catalysts were found be very active towards ethane and propane oxidation. Due to high activity ignition of the reaction mixture takes place. The heat produced by the oxidative reactions was sufficient for subsequent thermal pyrolysis which most probably takes place in the gas phase.
- Oxygen adsorption determining catalyst activity and ignition temperature on rare-earth oxide-based catalysts was significantly suppressed by high alkali doping.
- The addition of strontium or small amounts of alkali metals resulted in catalyst compositions showing low ignition temperatures of 440–485°C.

Table 2
Results on propane conversion in the presence of oxygen on various REO-based catalysts under non-isothermal conditions

| Catalyst | $S_{BET}$ ($m^2/g$) | $T_0$ (°C) | $T_{max}$ (°C) | Conversion (%) | | Selectivity (%) | | | $Y$(Olefins) (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $C_3H_8$ | $O_2$ | $C_3H_6$ | $C_2H_4$ | $CH_4$ | |
| Na–P/$Sm_2O_3$ (Na:P:Sm=2:1:700) | 4.6 | 397 | 660 | 40.6 | 96.2 | 20.9 | 33.6 | 5.1 | 22.1 |
| $Sm_2O_3$/SrO (Sm:Sr=5:1) | 8.0 | 530 | 710 | 49.7 | 99.4 | 20.4 | 36.0 | 10.9 | 28.0 |
| $La_2O_3$/SrO (La:Sr=50:1) | 4.1 | 419 | 560 | 39.7 | 94.7 | 19.3 | 34.0 | 8.3 | 21.1 |
| $La_2O_3$/SrO (La:Sr=5:1) | 4.1 | 555 | 680 | 53.5 | 99.7 | 20.3 | 36.7 | 11.0 | 30.5 |
| $Nd_2O_3$/SrO (Nd:Sr=5:1) | 7.2 | 420 | 676 | 45.1 | 100 | 19.9 | 35.5 | 8.4 | 25.0 |
| Quartz | | 603 | 600 | 0.1 | <0.1 | 87.0 | 13.0 | 0.0 | 0.1 |
| | | 705 | 700 | 21.7 | 22.5 | 48.9 | 31.6 | 12.6 | 17.5 |

$C_3H_8/O_2/N_2$=2/1/2; $m_{cat}$=0.2 g, total flow rate 200 ml/min (STP), quartz reactor ($\phi_{in}$=6 mm).

Table 3
Results on ethane conversion in the presence of oxygen on various REO-based catalysts under non-isothermal conditions

| Catalyst | $S_{BET}$ ($m^2$/g) | $T_o$ (°C) | $T_R$ (°C) | Conversion (%) | | Selectivity (%) | | | $Y(C_2H_4)$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $C_2H_6$ | $O_2$ | $C_2H_4$ | $CH_4$ | $C_{3+}$ | |
| $Sm_2O_3$/SrO (Sm:Sr =5:1) | 8.0 | 560 | 855 | 51.9 | 100 | 65.7 | 6.4 | 2.6 | 34.1 |
| $Nd_2O_3$/SrO (Nd:Sr =5:1) | 7.2 | 529 | 800 | 45.6 | 100 | 63.0 | 6.7 | 2.9 | 28.7 |
| $La_2O_3$/SrO (La:Sr =50:1) | 4.1 | 484 | 800 | 46.3 | 100 | 63.6 | 4.8 | 2.3 | 29.5 |
| $Sm_2O_3$/CaO (Sm:Ca =1:5) | 1.6 | 548 | 829 | 45.4 | 99.2 | 66.8 | 3.7 | 2.4 | 30.3 |
| Na-P/$Sm_2O_3$ (P:Na:Sm =1:2:700) | 4.6 | 330 | 750 | 42.5 | 99.3 | 65.9 | 3.3 | 2.3 | 28.0 |
| Na-P/$Sm_2O_3$ (P:Na:Sm =1:2:70) | 3.3 | 693 | 867 | 67.0 | 98.9 | 68.3 | 11.1 | 2.9 | 45.8 |
| Quartz | | 720 | 698 | 2.9 | 4.6 | 98.7 | 0.0 | 0.0 | 2.9 |
| | | 803 | 796 | 67.7 | 89.5 | 66.0 | 6.9 | 4.8 | 44.7 |

$C_2H_6/O_2/N_2$=2.5/1/2; $m_{cat}$=0.2 g, total flow rate 330 ml/min (STP), quartz reactor ($\phi_{in}$=6 mm).

- Contrary to non-catalytic oxidative dehydrogenation, reaction temperatures above 600°C could be achieved without significant additional external heat input.
- A catalyst layer of 1 mm was sufficient to ignite the reaction mixture at gas velocities of 6 cm/s (STP) and to sustain the reactions when the reaction mixture was preheated.

In the oxidative dehydrogenation of ethane, ethylene yields amounted to 34–45% ($S$=66–73%) under non-isothermal conditions ($T_{max}$=810–865°C) at contact times in the order of 30–40 ms. For the oxidative dehydrogenation of propane, olefins yields of 21–30.5% ($S$=53.3–56.8%) were obtained at contact time of 40 ms and $T_{max}$=560–710°C; higher selectivities to $C_2H_4$ (ca. 30%) compared to $C_3H_6$ (ca. 20%) were observed in the whole range of the reaction conditions indicating that C–C splitting is prevailing when adsorbed oxygen participates in the reaction.

## 3. Conclusions

Successful realization of simple chemical processes based on low molecular-mass alkanes as chemical feedstocks would result in attractive processes. For the direct formation of oxygenates from $C_1$ to $C_3$ alkanes, the partial oxidation of methane to methanol and ethane to acetic acid appears to have a future potential for being put into practice. Potential improvement in the OCM reaction by reaction engineering means and separation technology might lead to an increased interest to this reaction regarding its commercialization. Oxidative dehydrogenation of ethane may become a viable process. Selectivities and yields for the oxidative dehydrogenation of ethane in the presence of catalysts are in the range of present technology applying non-oxidative thermal dehydrogenation. Small reactor volume due to contact times in the millisecond range and autothermal operation are the advantages of the oxidative conversion. Explosion limits have, however, to be considered by the realization of this process. Among $C_1$–$C_3$ alkanes, especially the selective oxidative conversion of propane suffers from low selectivities and yields and needs innovative concepts in the development of catalysts to improve their performance. As a final conclusion, further improvements of catalytic performance in all the reactions mentioned may be expected in the near future.

## Acknowledgements

This work was supported by the German Federal Ministry for Education, Science, Research and Technology (Contract no. 03C30120) and by the Department for Science, Research and Culture of the State of Berlin.

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