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Non-conventional oxidation catalysis

Leon Lefferts*, K. Seshan, Barbara Mojet, Jan van Ommen

Catalytic Processes and Materials, Faculty of Science and Technology,
IMPACT University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Abstract

This short review provides an overview as well as background of ongoing work in our laboratory on unconventional catalysts in selective oxidation reactions with remarkable selectivity. The three cases reviewed here have in common that the catalysts are oxides that do not posses any formal redox capacity.

The use of doped defective oxides gives rise to surface-redox chemistry in the case of partial oxidation of methane over yttrium-modified zirconia, where actual removal of oxygen from the surface sites indeed takes place. Surprisingly, this oxygen species is not able to activate hydrogen to a significant extent. In contrast, Li-modified MgO catalyst does not allow removal of oxygen; O^- sites generated by Li are now able to abstract a H-radical from, e.g., propane. Radical gas-phase chemistry of the propyl radicals is then responsible for selective formation of olefins. The significant fact in this case is that olefins are activated to a lesser extent then alkanes.

The remarkable selectivity obtained in propane oxygenation on earth-alkali-modified zeolite Y at unusually low temperatures is due to the confinement of radicals in the cages of the zeolite, turning radical chemistry into stoichiometric chemistry. The second significant effect is the very effective stabilization of the resulting oxygenate, acetone, in the cage. However, the stabilization thus also implies extremely strong adsorption of the acetone, thus preventing desorption of the product. Our work indicates that desorption can be assisted by offering water as a competitive adsorbing species, thus opening the possibility to close the catalytic cycle.

Keywords: Oxidation; Catalysis; Unconventional catalysts

1. Introduction

Catalytic selective oxidation processes account for about a quarter of the industrial production of monomers and chemical intermediates. The total turnover of this business is in the order of 50 billion dollars per year (1998), evenly distributed over America, Europe and Asia [1]. Efficient operation of these processes therefore has a major commercial and environmental impact and the catalysts used are key to obtain sufficient efficiency.

Most catalysts used in these industrial processes are based on mixed metal oxides. Typically, direct oxidation of hydrocarbons by O_2 gives poor selectivity at high conversion, which limits conversion to a few percent in most practical situations. The inefficiency associated with low conversion has motivated the search for solid catalysts with higher activity in selective oxidation of hydrocarbons [2]. Driving forces for new breakthroughs are:

- Selectivity control; lack of selectivity is severe if conversion is pushed due to over-oxidation of partially oxidized products [3]. This is caused by the general phenomenon that the product molecules are more reactive than the reactants to be activated [1].
- Use of cheaper and easily available raw materials, e.g., lower alkanes such as methane, ethane and propane. This is very challenging because alkanes are difficult to activate, and thus the severe conditions required make the quest for selectivity even more urgent. The underlying motivation is the better use of natural gas and volatile petroleum fractions [4–6].
- Environmental constraints; development of processes that produce less waste and have greater safety is essential.

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* Corresponding author. Fax: +31 53 4894683.
E-mail address: l.lefferts@utwente.nl (L. Lefferts).

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Several concepts to improve selectivity have been proposed, especially for alkanes, e.g., the use of alternative oxidants (N_2O, peroxides, ozone e.g.), site isolation, multi-staged dosing of oxygen, spatial separation of the reduction and oxidation steps for redox catalysts and integration of reaction and product-separation in membrane reactors. In many cases it seems difficult to prevent the unacceptably high cost of these new approaches.

This short review describes work over the last decade in our laboratory on an alternative approach: i.e., the use of oxides that formally do not have any redox properties as oxidation catalysts. On the one hand we will discuss the application of defect oxides at relatively high temperatures, i.e., Li–MgO for oxidative dehydrogenation (ODH) and cracking of light alkanes and yttria-stabilized ZrO_2 for catalytic partial oxidation of methane to synthesis gas. On the other hand we will discuss the use of zeolite-Y modified with alkaline earth metals in the selective oxygenation of alkanes at unusually low temperatures, i.e., room temperature.

2. ODH-cracking on Li–MgO

The present industrial capacity for lower olefins such as propene, butenes is expected to be insufficient as the demand for these important building blocks in the modern petrochemical industry grows [7]. These light olefins (along with methane and aromatics) are, e.g., obtained from catalytic or steam cracking of naphtha and from FCC in oil refining. While these two routes are very well developed, increasing the capacity of these processes is limited.

Dehydrogenation of alkanes, an alternative route to light olefins, shows some major disadvantages, i.e., the reaction yields are equilibrium limited, a high tendency to coking and consequently short catalyst lifetime. Oxidative dehydrogenation is conceptually an interesting route as limitations by the chemical equilibrium are removed by the coupling of dehydrogenation and hydrogen oxidation; moreover, the presence of oxygen limits coking and extends therefore catalyst lifetimes. Conventional transition metal oxides with pronounced redox properties such as supported vanadia catalysts have been explored [8]. Results have not been promising, as re-adsorption of olefins (leading to sequential/total oxidation) appears to limit the olefin yields to below 35% [9].

In contrast, recent reports [10,11] show that magnesia-based catalysts containing rare-earth oxides, promoted with alkali halide (mainly chlorides) show high activity and selectivity in comparison to other mixed oxides for forming olefins. For LPG range hydrocarbons, these catalysts yielded up to 50% of total olefins at 600 °C at 62% conversion. While the catalysts showed only a minor tendency to form carbon oxides, catalyst stability was still not satisfactory.

Our own results [12] with propane show that presence of Cl is not essential for the high olefin yields obtained, and in the absence of chlorine the stability of the catalyst is further improved. High olefin selectivity is maintained even at high conversions over Li–MgO catalyst, very little secondary conversion of olefins formed to CO_x occurs [13] (Fig. 1).

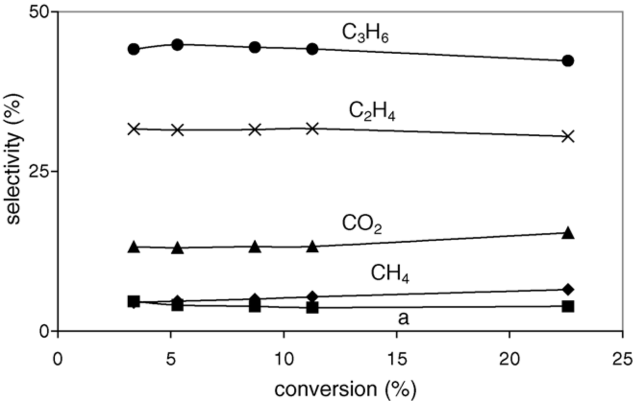


Fig. 1. Selectivities vs. propane conversion; at 600 °C, Li–MgO catalyst.

2.1. Active site

The activity and selectivity increase with Li addition, as shown in Fig. 2. Addition of up to 3 wt.% Li_2O onto magnesia increases the rate of propane conversion normalized to catalyst surface area. Based on observations on the inhibition of the reaction by CO_2 and from the interaction of the catalyst with CO_2 in TPD experiments at reaction

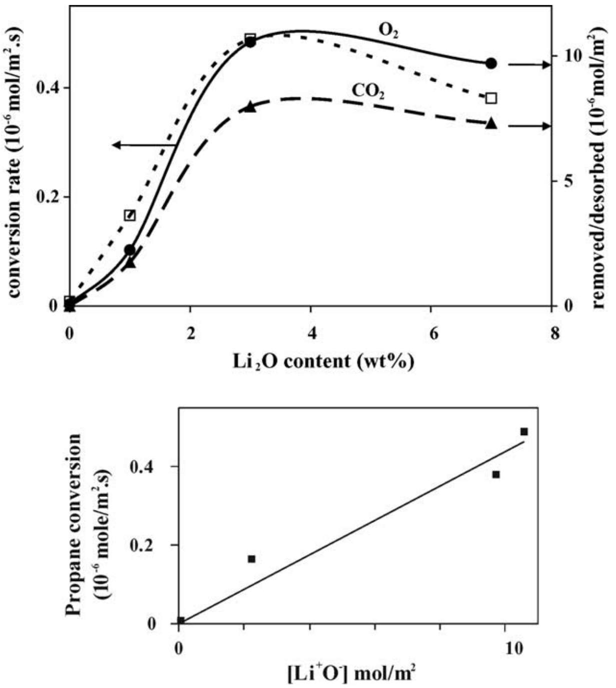


Fig. 2. (a) Dependence of rate of propane conversion (□), amount of removable oxygen (●) and the amount of CO_2 that can be desorbed at 600 °C (▲). (b) Dependence of the rate of propane conversion on the concentration of the [Li^+O^-] sites.

temperatures, it was concluded that Li is part of the active site. It was proposed that $[Li^{+}O^{-}]$-type active sites, as defects on the MgO surface, are responsible for catalytic activity, similar to the active site in methane oxidative coupling [10]. Furthermore, in the kinetic analysis of propane conversion, a strong correlation between catalytic activity and CO_2 concentration was found. It was proposed that $[Li^{+}CO_3^{-}]$ is formed on the $[Li^{+}O^{-}]$ active site based on the observation that CO_2 showed a minus one order in the conversion rate of propane [13].

Quantification of the amount of $[Li^{+}O^{-}]$ active sites in the catalysts was achieved by two methods. The first consisted of the removal of the oxygen from the active site by reduction with hydrogen and subsequent re-oxidation. The second method involved the decomposition of the $[Li^{+}CO_3^{-}]$ species, which is formed and is stable at 600 °C only when CO_2 is present. Bulk Li_2CO_3 phase is, in contrast, thermally stable at 600 °C. Adsorption–desorption studies at 600 °C therefore allow quantification of $[Li^{+}CO_3^{-}]$ through differentiation from bulk Li_2CO_3.

Catalytic activity is thus attributed to the oxygen present in the $[Li^{+}O^{-}]$ site. This is demonstrated by the linear correlation of the reaction rates with the density of $[Li^{+}O^{-}]$ sites (Fig. 2b). However, the question regarding the location of the $[Li^{+}O^{-}]$ active site remains.

2.2. Reaction mechanism

Activation of propane on the $[Li^{+}O^{-}]$ active site takes place by splitting one C–H bond in propane while forming $[Li^{+}OH^{-}]$ and a propyl radical, that is released into the gas phase where it undergoes radical-chain propagation reactions. It appears that the rate-determining step in the reaction pathways to propene, ethene and methane involves activation of propane on the catalyst surface [12].

Oxygen present increases the number and the concentration of the chain carrier radicals. When oxygen is not present $H^{\bullet}$ and $^{\bullet}CH_3$ radicals are the main chain propagators. In the presence of oxygen the *i*-propyl radical reacts fast with the oxygen molecule forming a hydroperoxyl ($HO_2^{\bullet}$) radical and propene. The hydroperoxy radical further reacts with a new propane molecule forming H_2O_2, which by decomposition gives two hydroxyl radicals ($^{\bullet}OH$). Hydroxyl radicals become the main chain propagator and it forms water by reacting with a propane molecule.

Regeneration of the $[Li^{+}OH^{-}]$ sites occurs in the presence of oxygen without the removal of the O^{-} of the active site [13,14], which would be typical in a conventional redox catalyst.

Importantly, the amount of propane converted over a pre-oxidized catalyst, oxygen in the gas phase being absent, is 70 times higher than the number of removable oxygen sites. This fact supports a radical-chain mechanism in which one propane molecule is activated on the active site resulting in propyl radical which undergoes chain-propagation reactions in the gas phase. The number 70 is a typical chain-propagation length in homogeneous chemistry [15].

To summarize, Li–MgO catalyst does not posses the conventional redox type nature of oxidic selective oxidation catalysts. The alkane oxidative dehydrogenation follows an initial activation on the catalyst, resulting in radicals which undergo chain reactions in the gas phase. This route minimizes combustion and enhances olefin yields as olefins are activated to much lesser extent then alkanes. Defect chemistry, i.e., presence of $[Li^{+}O^{-}]$-type sites on MgO, is the key to the functioning of these new, highly efficient catalysts for the oxidative dehydrogenation of alkanes to olefins. The extent of CO_x formation is however still too high for commercial application as the separation of CO_x from olefins is costly. Current activities in our lab aim on further suppressing the CO_x formation based on a better understanding of the structure–performance relationship and improved control in the preparation of the catalysts. One approach is to maximize the concentration of $[Li^{+}O^{-}]$ active sites, e.g., by varying the morphology of the catalyst; another approach is to minimize CO_2 formation after the reaction pathway to CO_2 has been identified.

3. CPO on Y–ZrO_2

The large amount of natural gas found worldwide has recently led to extensive research in the area of methane conversion. None of the catalytic processes proposed for methane utilization in one single step, e.g., oxidative coupling, partial oxidation to methanol or formaldehyde, is yet mature for industrial exploitation [16] due to the limited yields. Therefore, indirect utilization of natural gas has attracted more attention. Catalytic partial oxidation of methane to synthesis gas (CPOM) is an attractive option among these indirect transformation routes, because of its mild exothermic heat of reaction and suitable H_2/CO ratio for downstream processes such as methanol synthesis and Fischer–Tropsch synthesis. A considerable amount of work concerning the reaction mechanism of CPOM over metallic catalysts has been carried out. Two general mechanisms for the partial oxidation of methane to synthesis gas have been proposed. The so-called ‘‘indirect mechanism’’ claims that methane is combusted to CO_2 and H_2O, followed by both steam and carbon dioxide reforming [17,18] as consecutive reactions. The ‘‘direct mechanism’’ proposed by Schmidt and co-workers [19–21] assumes that methane is directly converted to CO and H_2, without initial deep oxidation. This issue is important because the indirect mechanism will cause huge temperature gradients in the reactor.

Metallic catalysts suffer from deactivation by sintering of metal and/or support and from evaporation of the metal in the form of volatile metal oxide formed at very high temperatures, especially in the present of oxygen [22,23]. The same problem occurs in the ammonia oxidation process over Pt–Rh gauzes operated at similar conditions as CPOM

[24]. Furthermore, precious metal-based catalysts are more sensitive for poisoning with, e.g., sulfur and halogens then zirconia, as illustrated by a recent patent on the oxidative removal of ammonia and tar from gasified biomass and waste with zirconia as the preferred catalyst [25].

Steghuis [26] and Stobbe [27] investigated oxidation of methane over some oxide catalysts, such as ZrO_2, Y_2O_3, La_2O_3/ZrO_2, yttrium-stabilized zirconia (YSZ) and TiO_2. Among these irreducible oxides, YSZ was the most active catalyst for CPOM. These catalysts show lower activity and selectivity compared to metal catalysts. However, catalyst stability is superior and the issue of lower selectivity can be dealt with by introducing a second metal-based reforming catalyst that can be kept stable because contact with oxygen at high temperatures is avoided [28].

Stobbe [27] concluded, based on the relation between methane conversion and selectivities over ZrO_2, that CO and H_2 are primary products of CPOM over ZrO_2, whereas CO_2 was formed by water-gas shift and oxidation of CO. Steghuis [26] proposed a reaction mechanism of CPOM over YSZ, including homolitic dissociation of methane over $O^-_{(S)}$ sites followed by conversion to CO, H_2 and H_2O via the formation and decomposition of formaldehyde as an intermediate. CO_2 was produced by further oxidation of the reaction intermediate, but not via oxidation of CO.

The linear relationship between yields and conversion (Fig. 3) shows that the four major products, CO, H_2, CO_2 and H_2O over yttrium-stabilized zirconia are all primary products. Surprisingly, methane is more effectively activated than H_2 on this catalyst.

Besides these major products, traces of hydrocarbons, formaldehyde and formic acid were also observed in the product mixture, especially at high reaction temperatures [29]. In situ IR studies showed that formate was formed by activation of methane on the surface of YSZ catalyst at temperatures between 400 and 475 °C, i.e., under conditions that do not allow a significant steady-state reaction rate. Adsorbed formaldehyde was not observed, probably due to rapid conversion to formate. Temperature-programmed desorption/decomposition (TPD/TPDE) of formate resulted in an essentially identical mixture of CO, CO_2, H_2 and H_2O as compared to the product mixture in steady-state CPOM. Addition of formaldehyde to the CPOM reaction mixture caused the yields of CO, CO_2 and H_2 to increase without influencing the product distribution. These observations are strong indications that CH_2O and formate are indeed intermediate products. Activation of methane appears to be the rate-determining step at 600 °C and higher temperatures. When temperature is decreased the rate-determining step shifts to the decomposition of formate.

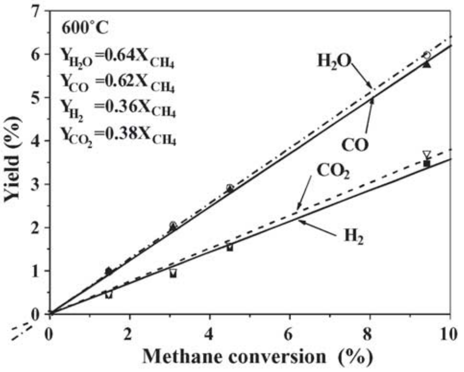


Fig. 3. Yield as a function of methane conversion over YSZ at 600 °C.

Characterization of the catalysts by X-ray fluorescence (XRF) and low-energy ion scattering (LEIS) revealed the influence of calcination temperature (500–1100 °C) on the enrichment of the YSZ surface with Y_2O_3 and impurities such as CaO, TiO_2, Na_2O, which have profound influence on the catalytic performance [30]. Creation of active sites by doping with Y_2O_3 improved the catalytic performance of ZrO_2 significantly. The surface composition rather than the bulk composition determined the catalytic performance of the catalysts in CPOM. As long as YSZ catalyst was not contaminated, the composition of the outermost surface of calcined YSZ was independent of both the concentration of Y_2O_3 in the bulk and calcination temperature; the surface always contained 12 ± 2 mol% Y_2O_3 due to segregation of Y_2O_3. Calcination at higher temperatures created more active sites per m^2, while the catalyst lost surface area via sintering. The same sintering treatment caused the activity of YSZ containing trace of (earth) alkali oxides to collapse. The effect is due to segregation of the impurities to the surface, which either blocks active surface of YSZ catalyst or forms new phases with different catalytic properties.

Heterogeneous reactions occurred concurrently with homogeneous reactions at temperatures above 950 °C. At such high temperatures, CPOM, steam/CO_2 reforming, as well as reverse water-gas shift, occurred in competition, although the catalyst activity is still too low for the reforming reactions to reach thermodynamic equilibrium. Therefore, a second bed of metal catalyst is needed.

Summarizing, zirconia-based catalysts act as redox catalysts due to defect chemistry. Their extremely low redox capacity is responsible for low activity as well as remarkable selectivity as compared to conventional redox catalysts. Current research in our lab aims at a detailed description of the surface oxygen species that are responsible for the activation of methane. At the same time the sites for activation of O_2 will be identified. A combined study based on temperature programmed experiments, transient experiments as well as isotopic exchange experiments will allow us to decide on the role of adsorbed oxygen species, lattice oxygen species as well as oxygen vacancies in the catalytic cycle.

4. Oxygenation earth-alkali–zeolite-Y

Recently, a new approach for selective oxidation of alkanes (ethane, propane, isobutane and cyclohexane) on cation exchanged Y zeolite was presented by Frei and co-workers [31–34], Grassian and co-workers [35], Vanoppen et al. [36] and our group [37,38]. The proposed explanation for the selective oxidation, either thermally or photochemically activated, is the confinement of the reactants in a restricted environment (super cage) that exhibits a strong electrostatic field. Complete selectivity to oxygenates was reported due to: (1) the diffusional constraints to avoid radical coupling reactions and (2) strong adsorption of partially oxidized products to avoid over-oxidation [35,38–40]. Activity was reported to increase in the order $\mathrm{NaY} < \mathrm{BaY} < \mathrm{SrY} < \mathrm{CaY}$ caused by the increasing cation electrostatic field [36,37]. Note that the catalytic cycle has not yet been closed because the oxygenates formed are left adsorbed strongly in the zeolite.

To turn this type of selective oxidation into a practical process, the barrier for product desorption has to be overcome. Release of small oxygenated hydrocarbons from zeolite Y is normally only achieved by extraction with polar organic solvents [41]. A solvent free method would be environmentally and economically preferable. Thus, the critical problem is to achieve continuous desorption of products from the zeolite. Use of a carrier gas at modestly elevated temperature has been proposed to give polar products chance to desorb at acceptable rates [40]. However, desorption data are still absent for those reactions. Moreover, selectivity will face a challenge due to over-oxidation of oxygenates by increasing temperature.

In our laboratory, in situ FTIR spectroscopy was used to study the partial oxidation of propane to acetone by oxygen on exchanged Y zeolites. Systematic variation of cation size, Brönsted acidity, cation location and kinetic isotope effects have been investigated in order to understand the real mechanism of this reaction.

With changing type of cation, it was found at room temperature and low propane and oxygen partial pressure, that acetone and water are formed exclusively from the reaction intermediate isopropylhydroperoxide (IHP). The reaction rate decreased in the order $\mathrm{CaY} > \mathrm{SrY} > \mathrm{MgY} > \mathrm{BaY}$. Surprisingly, MgY was less active than CaY and SrY despite its smaller ionic radius. We suggested that this is due to the higher hydrolysis level of

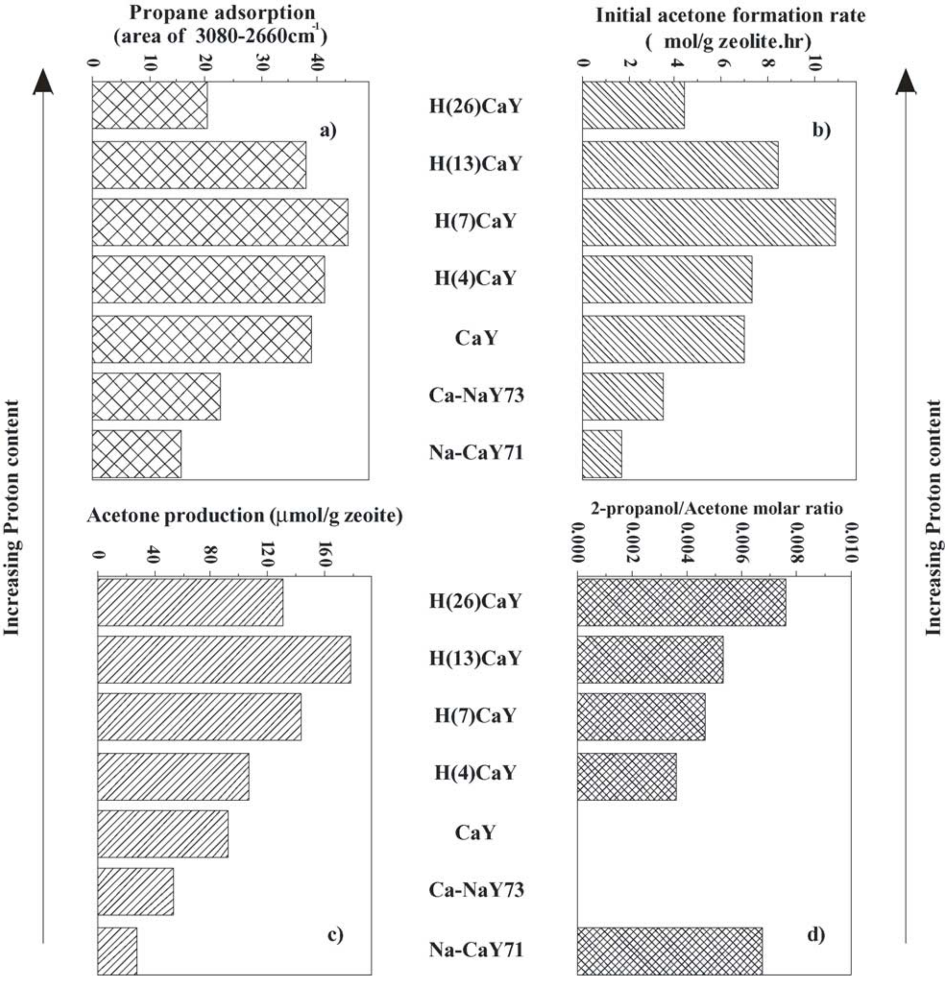
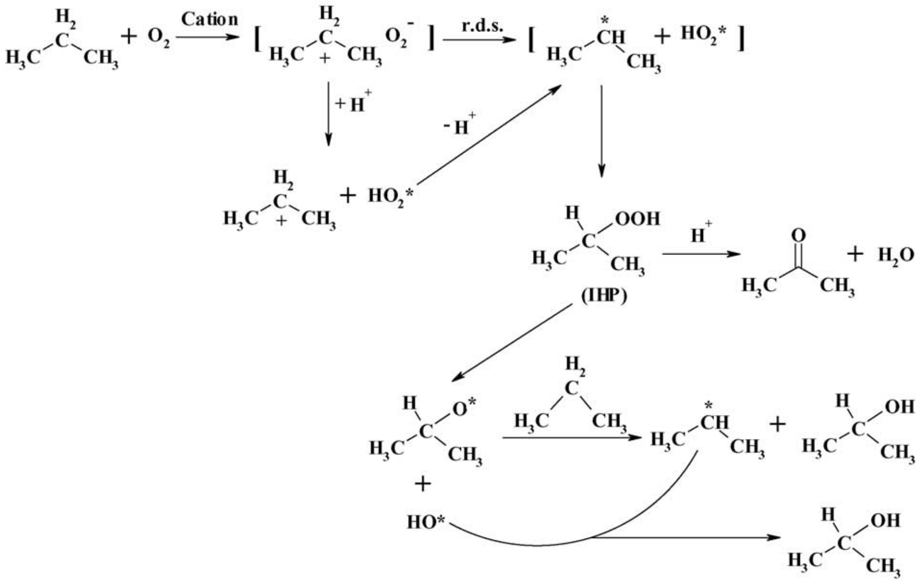


Fig. 4. (a) Propane adsorption; (b) initial acetone formation rate; (c) acetone formation after 20 h reaction; (d) 2-propanol to acetone ratio on series calcium exchange Y zeolite.



Scheme 1. Reaction pathway for oxidation of propane in alkaline earth zeolite Y, depicting the catalytic function of M^{2+} and Brönsted acid sites.

Mg^{2+} resulting $Mg(OH)^+$ and Brönsted acid sites, thus decreasing the concentration of bare Mg^{2+} ions. Studies on Ca^{2+}-exchanged zeolites with different exchange level revealed that only super cage Ca^{2+} contribute significantly to the selective oxidation of propane [38]. Brönsted acid sites were also found to be important for propane partial oxidation activity over H–CaY zeolites. With increasing number of protons in calcium exchanged Y zeolite, Volcano plots were observed for: (1) amount of adsorbed propane; (2) initial acetone formation rate; (3) total amount of acetone produced after 20 h of reaction; and (4) acetone selectivity (Fig. 4). Moreover, both IHP formation rate and decomposition rate increased with increasing number of Brönsted acid sites. Both observations mark the importance of Brönsted acid sites for this reaction, in addition to (earth) alkali cations.

A reaction mechanism with two different active sites is proposed (Scheme 1): conversion of propane into IHP takes place on cations, eventually assisted by the presence of protons (steps 2–5), while IHP decomposition into acetone occurs by Brönsted acid sites. Under specific experimental conditions, in addition, 2-propanol can be formed through cation activation of IHP to form radicals (steps 6–8).

Finally, TPD results (Fig. 5) on CaY zeolites point to two acetone adsorption sites, which we assign to Brönsted acid sites and $Ca(OH)_x$ species. Acetone mainly desorbs at higher temperatures (>250 °C) under dry conditions, only a minor amount is observed around 120 °C. Addition of water, however, results in gas phase acetone already at room temperature. Moreover, upon addition of water, both desorption peaks are shifted to lower temperatures and show increased intensities. It can be concluded that water clearly facilitates acetone desorption either via shielding of the electrostatic field or creation of additional sites.

The activity of alkaline earth cations in zeolite cages is a prominent example of oxidation catalysis over non-redox oxidic materials. To reach practical application of this type of catalysts for partial oxidation of small alkanes, a balance has to be found between cations, acid sites and the amount of water in the zeolites or reactants. The results show that the super cages in alkaline earth-modified zeolite Y can be regarded as unique selective nano-reactors for oxygenation of alkanes. The performance of such a nano-reactor is determined by its detailed structure, including the properties and location of alkaline earth cations, Brönsted acid sites as well as lattice oxygen that comprise the wall of the nano-reactor.

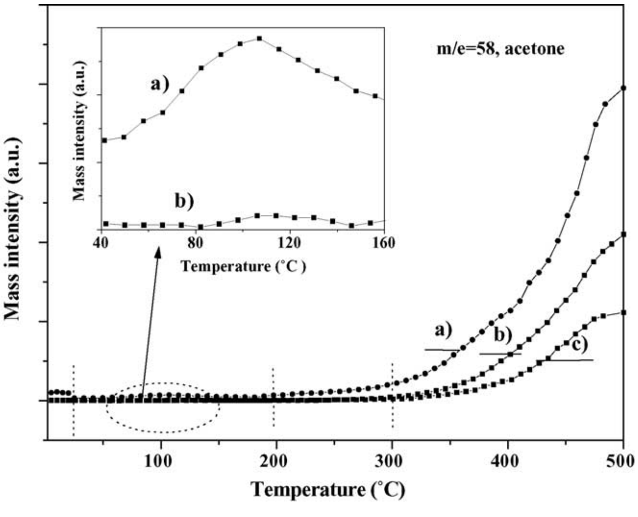


Fig. 5. TPD acetone desorption on CaY at conditions: (a) after 25 h reaction, evacuated 10 min, followed adding 0.5 mbar water; (b) after 35 h reaction; (c) after 20 h reaction.

5. Conclusion

The work summarized here stresses that the use of unconventional catalysts in selective oxidation reactions indeed gives rise to remarkable selectivity, though the mechanistic reasons may be very diverse.

The use of doped defective oxides gives rise to surface-redox chemistry in the case of partial oxidation of methane over yttrium-modified zirconia, where actual removal of oxygen from the surface sites indeed takes place. Surprisingly, this oxygen species is not able to activate hydrogen to a significant extent. In contrast, Li-modified MgO catalyst does not allow removal of oxygen; O^- sites generated by Li are now able to abstract a H-radical from, e.g., propane. Radical gas-phase chemistry of the propyl radicals is then responsible for selective formation of olefins. The significant fact in this case is that olefins are activated to a lesser extent then alkanes.

The remarkable selectivity obtained in propane oxygenation on earth-alkali-modified zeolite Y at unusually low temperatures is due to the confinement of radicals in the cages of the zeolite, turning radical chemistry into stoichiometric chemistry. The second significant effect is the very effective stabilization of the resulting oxygenate, acetone, in the cage. However, the stabilization thus also implies extremely strong adsorption of the acetone, thus preventing desorption of the product. Our work indicates that desorption can be assisted by offering water as a competitive adsorbing species, thus opening the possibility to close the catalytic cycle.

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