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Selective Oxidations of Linear Alkanes with Molecular Oxygen on Molecular Sieve Catalysts—A Breakthrough?

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Hydrocarbons that are oxidized at the terminal, that is, in the α- or 1-, position are important feedstocks for the chemical and pharmaceutical industry. Nevertheless, the selective oxidation of alkanes at their terminal methyl groups is still a challenge in modern catalysis research. It is well known that some enzymes are capable of performing selective terminal oxidations, however, without the necessary stability for use in the conditions employed for pure inorganic catalysts. In principle, selective partial oxidations are easier to control when hydrogen peroxide or organic hydroperoxides (for example, *tert*-butylhydroperoxide) are used as oxygen donors, although from an economic point of view, the use of molecular oxygen, that is, air or O_2, is preferred.

Recently, Thomas and co-workers [1, 2] succeeded in the preparation of a pure inorganic catalyst that allows for the oxidation of *n*-alkanes at the terminal carbon atoms with high selectivity using molecular oxygen in a liquid-phase reaction. These catalysts belong to the group of zeolite-like, crystalline and microporous aluminophosphates, in which small amounts of manganese or cobalt ions are introduced as redox centers into the zeolite framework.[3, 4] Essential for this group of catalysts is the fine tuning of the pore diameter, which enables the terminal C atom of the *n*-alkane to approach the catalytically active site. The especially selective catalysts have the $AlPO_4$-18 (AEI) topology. These are eight-ring molecular sieves with pore openings formed by eight TO_4 tetrahedra (T = Al, P, Co, Mn) and a pore diameter of about 0.38 nm. With such catalysts it seems feasible that the terminal carbon atom of the reactants approach the active site (that is, the transition metal ions in tetrahedral positions) and are oxidized at the end of the hydrocarbon chain to give the respective alcohols, ketones, and carboxylic acids. The catalytic results are explained by an oxidation mechanism involving radical intermediates, whose selectivities are superimposed by shape selectivity, that is, certain products or intermediates are not formed as a result of the restricted space in the zeolite channels or cages.

From mechanistic considerations, oxidation reactions can be divided into three categories: 1) autoxidation via a free-radical chain reaction; 2) oxidation of the substrate coordinated to the metal ion followed by reoxidation of the reduced metal, and 3) catalytic oxygen transfer.[5] The dominance of one of these mechanisms depends on the reaction conditions (gas or liquid phase, reaction temperature, pressure) and especially on the nature of the metal and the oxidizing agent used. Cobalt- and manganese-containing compounds are known to be highly efficient catalysts for the liquid-phase autoxidation via free radicals (mechanism 1) with oxygen as the oxidizing agent. Intermediates along this reaction path are alkoxy and alkylperoxy radicals [Eq. (1–6)]:

$$\mathrm{RH} + \mathrm{O_2} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{HOO^{\bullet}} \tag{1}$$

$$\mathrm{R^{\bullet}} + \mathrm{O_2} \longrightarrow \mathrm{ROO^{\bullet}} \tag{2}$$

$$\mathrm{ROO^{\bullet}} + \mathrm{RH} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{ROOH} \tag{3}$$

$$\mathrm{ROOH} + \mathrm{Me^{II}} \longrightarrow \mathrm{RO^{\bullet}} + \mathrm{Me^{III}OH} \tag{4}$$

$$\mathrm{ROOH} + \mathrm{Me^{III}OH} \longrightarrow \mathrm{ROO^{\bullet}} + \mathrm{Me^{II}} + \mathrm{H_2O} \tag{5}$$

$$\mathrm{RO^{\bullet}} + \mathrm{RH} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{ROH} \tag{6}$$

The initiation reaction [Eq. (1)] is typically very slow; once formed, the radicals quickly react with dissolved oxygen to form peroxy radicals ($ROO^{\bullet}$) [Eq. (2)]. Such peroxy radicals are stabilized in different ways, for example, by formation of a hydroperoxide [Eq. (3)]. The main role of the metal ions is to catalyze the homolytic decomposition of the intermediate hydroperoxide (ROOH) according to Equations (4) and (5). As a result of this decomposition, metal ions generate chain-initiating radicals, which form alcohols as oxidation products according to Equation (6). Only those metals that exist in two oxidation states with comparable stability are active catalysts for the hydroperoxide decomposition. Besides Cu^+/Cu^{2+} and Fe^{2+}/Fe^{3+}, Co^{2+}/Co^{3+} and Mn^{2+}/Mn^{3+} are suitable. Until now,

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0570-0833/00/3905-0888 $ 17.50+.50/0

reactions of the type described (namely, the metal ion catalyzed decomposition of hydroperoxides) have been predominantly catalyzed by dissolved metal salts. Handling and reprocessing large amounts of metal-containing solutions, however, causes the well-known environmental problems. Furthermore, free-radical chain reactions do not yield terminal oxyfunctionalized alkanes preferentially because of the decreasing relative stability of tertiary to secondary to primary carbon atoms. Therefore, a major goal in research on catalytic oxidations in the liquid phase is the discovery of catalysts that suppress the autoxidation by free radicals and catalyze the oxidation by mechanism 2 (see above). Catalytic oxidations via oxometal intermediates are the main reaction path for the oxidation of hydrocarbons in the gas phase. This mechanism is called the Mars van Krevelen mechanism.[5]

In this context, the above mentioned publications from the group of J. M. Thomas are worth mentioning.[1] These authors report the oxidation of linear alkanes (namely, *n*-pentane, *n*-hexane, *n*-octane) with molecular oxygen under mild reaction conditions (373–403 K; 1.5 MPa). They employed cobalt- and manganese-containing aluminophosphate catalysts of structural type 18 (AEI; structure code of the International Zeolite Association (IZA)) and 36 (ATS) with respective pore diameters of 0.38 nm and 0.65 × 0.75 nm (Figure 1). The structure of $AlPO_4$-18 consists of perpendicularly arranged 8-ring channels, while $AlPO_4$-36 possesses a one-dimensional channel system with 12-ring channels. The addition of cobalt and manganese salts to the synthesis gel and an appropriate choice of synthesis parameters results in the formation of molecular sieves, in which cobalt and manganese ions (≈4 atom % of the Al^{III} ions)[1] are isomorphously substituted in tetrahedral positions. The regioselectivity observed for the oxidation of *n*-hexane on CoAPO-18 and MnAPO-18 is remarkable: after a reaction time of 24 h 60 % of the oxidation products are oxyfunctionalized at the terminal carbon atom and an additional 36 % are oxidized in the 2-position (hexan-2-ol, hexan-2-one). Interestingly, the corresponding acid (1-hexanoic) is formed with a high selectivity of 54 %. Analogous results have been obtained for the oxidation of *n*-octane, while the oxidation of *n*-pentane predominantly results in the formation of pentan-2-one and pentan-3-one. In contrast to the autoxidation in a homogeneous (liquid) phase, a dramatic enhancement in the regioselectivity of the reaction is observed for *n*-alkanes with sufficiently long alkyl chains to give products oxyfunctionalized in the 1-position. Thomas et al. demonstrated that these exceptionally high selectivities for the oxidation of terminal carbon atoms are only achieved with cobalt- or manganese-containing aluminophosphates of AEI structure. Similar regioselectivities are not observed over molecular sieves with larger pore diameters, for example, with $AlPO_4$-5 or $AlPO_4$-36 structures. These experimental findings are rationalized by Thomas et al.[1, 2] as being a consequence of the narrow pore openings of molecular sieves with the $AlPO_4$-18 (AEI) structure, which allow access of only slender hydroperoxide intermediates to the pore interior, where they can interact with the active metal site in an "end-on" configuration. The molecular sieve acts in a selective way, analogous to the protein mantle of an enzyme or the bulky ligand of a metal complex.[6, 7] The mode of operation of these novel oxidation catalysts requires, however, that the cobalt and manganese ions remain incorporated in the zeolite framework and do not leach into the reaction mixture, where they work in the dissolved form (homogeneous catalysis). Experimental evidence that no leaching occurs is often difficult to produce, because metal ions in solutions may already possess sufficient catalytic activity at ppm concentrations.[5, 8] To test for leaching, the catalyst is filtered from the hot reaction mixture and if the catalyzed reaction stops as a consequence of the catalyst removal, then it can be considered as a first hint of true heterogeneous catalysis. (In this context, it is important to point out that termination of the reaction after filtration of the cold reaction solution is not unambiguous evidence for the presence of a heterogeneously catalyzed reaction. Cooling down the reaction mixture may result in the heterogenization of the (previously dissolved) metal ions as a result of adsorption on the solid, that is, the molecular sieve.) On the basis of the results (termination of the reaction after filtration of the hot reaction mixture) reported by Thomas et al., one can conclude that the transition metal cations remained in the aluminophosphate framework. Nevertheless, the authors explicitly point out elsewhere that the conversion has to be kept low (< 10 %) to minimize the danger of leaching by polar reaction products (particularly carboxylic acids), which are formed in large amounts.

With respect to the reaction mechanism, Thomas et al. provide experimental data[1] that suggest the participation of

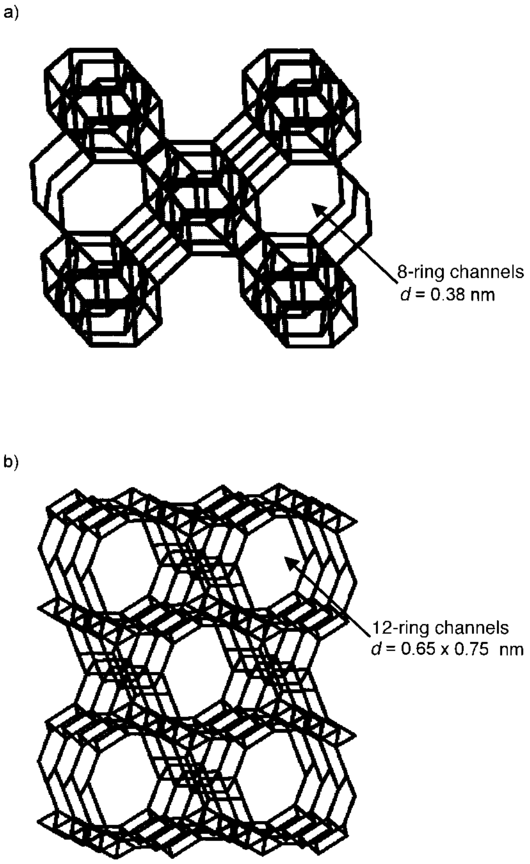

Figure 1. Structure of the aluminophosphates $AlPO_4$-18 (a) and $AlPO_4$-36 (b).

free radicals in the reaction: Addition of a free-radical initiator (*tert*-butylhydroperoxide) largely reduces the otherwise observed induction period; addition of a free-radical scavenger (hydroquinone) largely reduces the reaction rate.

Only limited propositions can be made concerning the long-term stability of these catalysts. From the published conversion/reaction time curve, it follows that the reaction stops at a 6 to 10% conversion of the *n*-alkanes. A possible explanation for the observed catalyst deactivation, besides leaching of the metal into the solution, is the blocking of the catalytically active sites by polar reaction products. The experimental finding that a regeneration of the catalyst by washing with methanol and subsequent calcination at 550 °C is possible, supports the assumption of a blocking of the active centers or pores rather than a loss of active sites by leaching.

The catalytic materials based on crystalline, microporous cobalt- and manganese-containing aluminophosphates proposed by Thomas et al. represent a promising approach to the development of novel catalysts for the selective oxyfunctionalization of linear alkanes with molecular oxygen in the liquid phase. Meanwhile, it has been shown that such catalysts are also suitable for the epoxidation of alkenes with air[9] and the Baeyer–Villiger oxidation of ketones to lactones.[10] Although many questions (leaching, long-term stability, structure of the active site,[11] uniformity of the active sites towards activity, and selectivity, etc.) require further investigations, the recently presented results of Thomas et al. open new horizons for the selective oxidation of hydrocarbons with O_2 in the liquid phase.

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