Chapter 2
Advances in Catalytic Technologies for Selective Oxidation of Lower Alkanes

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ABSTRACT

The main challenge for selective oxidation catalysis has always been achieving an economically viable selectivity. In this chapter, the advances made around the last decade in catalyst development for the selective oxidation of C2-C4 alkanes to carboxylic acids and olefins are discussed. To assess the progress made and to study the trends, particular attention has been given to the results reported in patents. A review of the developments reported in the research literature and new knowledge about the catalysts and their functioning have also been summarized. A comparison with existing processes is provided to obtain an idea of which selective oxidation routes are approaching closer to commercial implementation. Finally, some of the challenges that the selective oxidation routes must overcome for widespread commercial adoption are discussed and suggestions for future research are provided.

INTRODUCTION

This chapter discusses the recent advancements made in heterogeneous catalysts for the selective oxidation of light alkanes to obtain oxygenated products such as carboxylic acids. Since oxidative dehydrogenation carried out a low temperatures, is closely related, the production of olefins using this route is also discussed. In the review of the literature, particular attention has been given to the patent literature, especially patents published since 2000. Based on the assessment of the published literature, the current status, opportunities for further advancement of the technologies and their commercial implementation are discussed.

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The continued sustainability of the chemical industry is dependent on moving to lower cost feedstocks and obtaining products with fewer processing steps. In this context, the selective oxidation of alkanes offers an attractive route to directly convert the alkanes into value added oxygenated products. Selective oxidation of alkanes offers the possibility of a lower cost as well as a lower environmental impact process.

Activation of lower alkanes such as ethane, propane and butanes through an oxidative dehydrogenation process offers advantages such as no equilibrium limitations, operation at a lower temperature, no coke formation on catalyst and control on downstream product impurity or selectivity (Karim, Al-Hazmi, & Al-Andis, 1999). Controlling selectivity to the desired product and developing catalyst with the required activity remains the key challenge in selective oxidations.

The replacement of existing routes by selective alkane oxidation can bring about huge environmental and economic benefits. As an example, the commercial process for methacrylic acid production is based on the acetone-cyanohydrin route involving three process steps, use of hydrogen cyanide as a raw material and production of ammonium bisulfate as a co-product (Jing, Katryniok, Dumeignil, Bordes-Richard, & Paul, 2014). Development of a selective isobutane oxidation process would provide a one-step route to methacrylic acid, using a lower cost raw material and with lower negative impact on the environment (Jing, Katryniok, Dumeignil, Bordes-Richard, & Paul, 2014). This illustrates the need for the chemical industry to pursue research towards the development of selective oxidation catalysts that would make these routes competitive with the existing technology.

Although offering several advantages, partial oxidation of alkanes does have its own set of limitations. The oxygen concentration fed to the reactor has to be limited to be outside the explosive limit, which puts limitations on the amount of hydrocarbon converted per pass. Loss of selectivity due to further oxidation of the desired products, removal of reaction heat, possibility of runaway (Grabowski, 2006) and avoidance of hotspots in the reactor are other potential issues in selective oxidation processes.

Oxidation catalysis has the greatest potential for improvement in the chemical industry, and substantial progress has been made. However, selective oxidation routes need to offer a substantial benefit over the existing routes to be successful. The yield and selectivity targets needed to make many of the processes economically viable have not yet been achieved (Cavani F., 2010). The best results reported in the literature indicate that some of the processes such as ethane oxidative dehydrogenation to ethylene and propane to acrylic acid are quite promising. Further activity and selectivity improvement and process intensification approaches such as combining separation and reaction steps could make these processes attractive for commercialization.

In this chapter, the goal has been to review the literature on selected routes, focusing especially on advances made over the last decade. The trends in the patent as well as research literature have been assessed and any new understanding obtained has been summarized. Another objective was to identify what research approaches have been successful to make advances in catalyst performance. The key challenges faced in each of the new routes are discussed and suggestions are provided on what is needed to make the new process technology based on selective oxidation replace an existing process.

The scope of this chapter has been limited to selective oxidation and oxidative dehydrogenation carried out at low temperatures, using molecular oxygen as the oxidant. Therefore, the ammoxidation of propane to acrylonitrile, although closely related to propane oxidation, is not discussed. The use of other oxidants such as N_2O and CO_2 and oxidative dehydrogenation carried out at high temperatures are not covered in this chapter. Oxidation of *n*-butane maleic anhydride is a well-established commercial process, and is excluded from the discussion in this chapter to focus more on the emerging technologies.