Selective Oxidation and Oxidative Dehydrogenation of Ethane and Propane

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Abstract: Recent growth in shale gas production in the US has contributed to reduction in natural gas price and has made plenty of ethane and propane available at low cost for use as a chemical feedstock. This has led to the construction of several new crackers and propane dehydrogenation (PDH) units. However, selective oxidation can provide an alternative route to directly convert the alkane to value added products such as propane to acrylic acid, propane ammoxidation to acrylonitrile, and ethane to acetic acid. The progress made in selective oxidation and the attractive economics of selective oxidation routes will be discussed.
Keywords: Selective Oxidation, Oxidative Dehydrogenation, Alkane feedstock.

1. Introduction

The shale gas revolution in the United States has made petrochemical raw materials such as ethane, propane and butane available in plenty at sharply lower costs. The availability of this feedstock provides opportunities for utilizing newer routes to produce valuable chemicals. The selective oxidation of lower alkanes provides a direct route to produce chemicals such as acetic acid, acrylic acid and acrylonitrile. The one-step oxidation routes can provide a process with lower capital and operating costs as well as lower environmental impact. Achieving a selectivity and productivity that is commercially attractive is one of the main challenges of selective oxidation processes.

The results reported in recent years for selective oxidation of lower alkanes to carboxylic acids as well as oxidative dehydrogenation to olefins indicate that substantial progress has been made in improving the catalyst selectivity. The progress reported in the patent and journal literature as well as some of our assessments in this area will be discussed. The current dominant routes for production of the above chemicals will be compared with the one-step selective oxidation routes. The economic and environmental benefits that selective oxidation routes could potentially provide will be illustrated.

2. Research Methods

Comprehensive searches of patents as well as journal articles were carried out on routes for selective oxidation and oxidative dehydrogenation of lower alkanes. The experimental results reported were analyzed to identify the best results achieved over the years for each process. A more detailed study of the patents was also performed to determine the most promising catalysts and the methods that have been employed to improve the catalyst performance. From this assessment, the most suitable catalyst compositions for each process and the current status of the technology can be inferred.

The raw material cost savings is one of the major benefit provided by the selective oxidation process. Based on the best results reported in the literature, and the latest feedstock prices, raw material costs for the selective oxidation route has been calculated and compared with the raw material cost for the current dominant route.

3. Results and discussion

The most successful catalysts for selective oxidation/ammoxidation and oxidative dehydrogenation of ethane and propane have been complex multimetallic oxides containing several metals, especially the ones containing Mo, V, Nb and Te. Further catalyst performance improvements have been achieved by addition of promoters to the catalyst composition as indicated in Table 1 below, and also through improvements to the catalyst preparation method. The advances made in catalysts for each of the processes will be discussed.

Table 1. Catalyst compositions showing one of the best results reported in literature for selective (amm)oxidation and oxidative dehydrogenation processes.

Process	Catalyst Composition	Selectivity to Target product	References
Ethane to Acetic acid	MoVNbSbCaPd	91	1, 2
Propane to Acrylic acid	MoVTeNbSm	98	3
Propane ammoxidation to Acrylonitrile	MoVSbNbTiLu	69	4
Ethane ODH to ethylene	MoVNbTe	98	5
Propane ODH to propylene	V/CeO2	97	6

The economics of the above processes have been analyzed by estimating the raw material cost per ton of product, considering a range of selectivities and raw material prices. An illustration is shown below for the ethane to acetic acid process in Figure 1. Using the best results reported in the literature, the new processes can be compared with the current dominant industrial process in terms of the raw material costs.

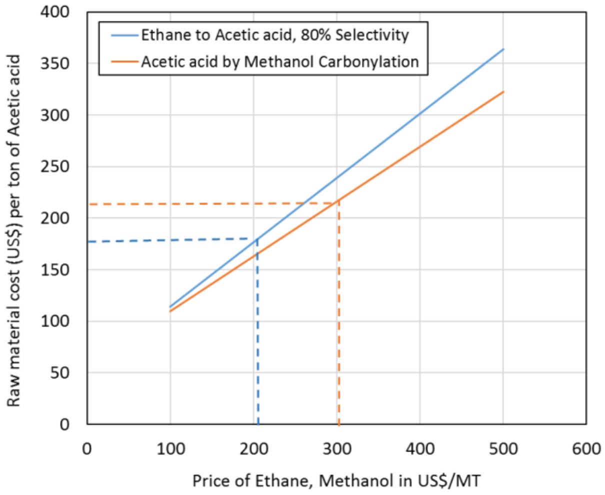

Figure 1. Raw material cost estimate for acetic acid production by ethane oxidation compared to methanol carbonylation. Dotted lines show the raw material cost at current US Gulf coast prices.

The illustration in Figure 1 shows that at current ethane and methanol prices, and 80% selectivity, the SABIC ethane to acetic acid technology can be economically attractive, compared to the methanol carbonylation process. A similar assessment would be presented for the other selective oxidation routes as well. In addition, the other practical challenges that must be overcome for widespread commercial adoption of the selective oxidation and ODH routes will be discussed in the talk.

4. Conclusions

Selective oxidation of lower alkanes is becoming more attractive for commercial application. Further improvement in performance and addressing the practical issues related to catalyst scale up and long-term catalyst stability would help in making these routes a reality.

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