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Commentary

C-4 Routes to Methyl Methacrylate: A Sustainable and Environmental Benign Process

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The polymerization process using methyl methacrylate (MMA) has been intensively manufactured owing to poly(methyl methacrylate) (PMMA) is a synthetic thermoplastic with high durability, heat resistance, chemical resistance, light transmission, UV resistant, shattering resistance, optical clarity, high scratch resistance, and so forth. Due to these excellent features, PMMA is patented with trademarks, inclusive of Plexiglas®, Acrylite®, Parapet®, Perspex®, Altuglas®, *etc.* Its incredible role in our daily life is indispensable as we could find PMMA everywhere, such as solar panels, window profiles, lightning, car windows, lights cover, Smartphone screen displays, dental cavity fillings, and so on. Methyl methacrylate (MMA) is the crucial monomer of PMMA, which is also widely used in coatings, paints, adhesives, packaging, sealants, floor polishes, *etc.* [1]. Despite amid the outbreak of coronavirus in 2019, the market demand of MMA is estimated to grow in coming years. The MMA annual growth rate of a market report has forecasted 3.9% CAGR till 2028 [2] while another report has projected a higher growth rate, 4.3% CAGR, in year 2020-2027 [3]. Apparently, MMA is an ignorable material found in our daily routines, especially in automotive, coatings and paintings. Several industrial processes have been engaged to produce a series precursors of MMA, including methacrolein (MAL) and methacrylic acid (MAA) through ACH process, C-2, C-3, and C-4 methods [4,5]. ACH process is economically attractive but it is restraining from the usage of hazardous HCN reactant and co-production of toxic NH_4HSO_4. C-2 process generally presents high selectivity but low one-pass conversion, high preparation costs, and low yield caused by MMA hydrolysis to MAA and methanol; C-3 process suffers from limited starting material (propyne) although it gives high yield of MMA through one-step conversion. The aforementioned literature studies are the pros and cons of ACH, C-2, and C-3 processes in the MAL, MAA or MMA production [5].

On the other hand, C-4 hydrocarbons which comprised of *iso*butane, *iso*butene, *tert*-butyl alcohol, methacrolein (MAL) or 2-methyl-1, 3-propanediol, are the byproducts obtained from petroleum refinery process. Thus, these chemicals are considerably high availability and less hazardous compared to the other methods mentioned. The obtained C-4 materials act as the main feedstocks in chemical industry owing to their intermediates and products have high-commercialised values. This process is also more industrialized practical because the feedstock could produce higher yield of MMA with lower capital costs. By valorizing the byproducts from petroleum to value-added intermediates or products, C-4 process is also in line with Sustainable Global Development, Goal No. 12 Responsible Consumption and Production. To further promote the production of MMA, engineering of appropriate structural catalysts should be studied. There are diverse catalysts used to enhance the conversion, selectivity and yield towards MAL, MAA or/and MMA, such as vanadium pyrophosphate [6], $CsFeCoBiMnMoO_x$ [7], Pd-Pb/γ-Al_2O_3 [8], Bi-doped-styrene-divinyl benzene copolymer (SDB) [9], Cu- and Fe-doped $CsH_3PMo_{11}VO_{40}$ [10], NiAu single atom alloys and so forth [11]. Heteropolyacid is revealed as one of the efficient mixed metal oxides in the oxidation of light alkanes due to its dual functionality, *i.e.* acidity and oxidative properties. The advanced materials, such as layered double hydroxide (LDH), metal-organic framework (MOF), and *etc*, are potential to be functionalized with metal oxide-based materials to give synergistic effects.

Additionally, a cascade pathway from C-4 to MMA should be advocated too. Since both MAL and MAA are the intermediates to produce the desired MMA, therefore *iso*butane or *iso*butene conversion to MAL and MAA are vastly reported. Undeniably, efforts extensively focus on discontinuous processes to MAL or MAA: the oxidative dehydrogenation of *iso*butane or/and *iso*butene to MAL [12-15], oxidative dehydrogenation of *iso*butane to MAA [16,17], and MAL oxidation to MAA [18-23]. In recent years, it is worth noting that the cascade oxidative esterification of MAL to MMA has been investigated [9,11,24,25], nonetheless, on-going studies are still necessary. Directing the discontinuous process to cascade one-step synthetic route is an urge due to the process simplicity and reduced byproducts. This will be prompting energy- and cost-saving with the aim to create a sustainable, eco-friendly environment and economically viable communities.

In short, this research has grown rapidly with possessing great potential in the field of industrial catalysis, which great strides in synthetic transformation process and catalysts engineering. This is making towards environmental cleanliness and sustainable process.

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