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Short Commentary

The Synthesis of Medical Intermediate Adamantane

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Adamantane is a highly symmetrical clathrate hydrocarbon with a ring-tetrahedral structure. It is a camphor-smelling colorless crystalline solid with a density of 1.07 kg/L at room temperature. As the structure is highly symmetrical and compact, and the hydrogen atoms are easily replaced by other groups, it has a wide range of applications in these fields: medical intermediate, high-density fuel, lubricant, new photoelectric material et al. Therein, for the medical intermediate field, adamantane can be used to synthesize amantadine, rimantadine, amantanium bromide, memantine et al., which shows the talents to treat diseases effectively such as influenza virus, parkinson's syndrome, chronic hepatitis C and more. At present, the method to synthesize adamantine is to use dicyclopentadiene produced in refinery as the raw material, which would experience the hydrogenation to tetrahydrodicyclopentadiene firstly and further isomerization to adamantine. For the hydrogenation process, the typical hydrogenation catalysts like Raney Ni, Pd/Al_2O_3 can be qualified for completing the reaction. While for the isomerization process, it possesses more technical problems and attracts more research attention correspondingly. There are four main isomerization methods based on four different types of catalyst: (1) $AlCl_3$; (2) super acid; (3) ionic liquid; (4) zeolite.

$AlCl_3$ method is the current industrial production method of adamantine with autoclave as the reactor. It has the positive characteristics of easy operation, high catalytic activity and high yield of adamantane, but this method would produce a large amount of black tar. Further, $AlCl_3$ is highly toxic and acidic, easily causing body damage to the operators, and the post-reaction treatment is so complicated that more processes and cost are required. Therefore, from the perspective of the green and sustainable development trend, this method will be phased out in the future. Super acid method uses super acid as catalyst for example CH_3SO_3H-SbF_5 to synthesize adamantane. Super acid is more acidic than 100% sulfuric acid, so it shows high catalytic activity and high adamantane yield. However, the super acid owns these disadvantages: high synthesis cost, strict requirements for the equipment, the poor stability, causing a large distance to the practical application as a result. Ionic liquid method uses ionic liquid as catalyst to synthesize adamantane. Ionic liquid is a kind of liquid salt composing of anions and cations at room temperature. Due to its almost no vapor pressure, good solubility, good conductivity and stable properties, it has been widely studied in many fields. For the synthesis of adamantane, the most outstanding characteristics of ionic liquid method are mild reaction conditions, good selectivity of adamantane, and solvent free. But the synthesis of ionic liquid itself is difficult and high-cost, as well as the weak tolerance to impurities, which limits its further industrial large-scale application.

Zeolite method makes use of zeolite to synthesize adamantine. Zeolite is a kind of synthetic or natural crystalline silicate or silicaluminate. It has achieved great successful applications in the field of purification, oil refining, separation etc. Due to the characteristics of mature synthesis technology, low cost, easy regeneration, easy separation and low pollution, it has been widely investigated in many relevant researches, and been considered to replace the existing intermittent method and realize continuous synthesis into adamantane. However, zeolites have to face the problems of low catalyst activity, poor product yield, and easy coking. Once these issues are solved, this method would have more widely practical applications.

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