

The sixth Green and Sustainable Chemistry Award
Awarded by the Minister of Economics, Trade and Industry

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Development of Green Chemical Processes Catalyzed by Solid Heteropolyacids

With close collaboration between industry and academia, the study of this group on solid heteropolyacid catalysts has successfully led to the establishment of very competitive green-chemical processes of ethylacetate and acetic acid productions. Here, both basic and applied researches of supported and unsupported heteropolyacid catalysts contributed very much to the development of these green chemical processes. Heteropolyacids are the catalyst materials which have intensively been studied in Japan and several large-scale industrial processes were industrialized also in Japan. Hence, heteropolyacid catalysts may be called Japanese original catalysts, or industrial catalysts made in Japan. It is to be remarked that the achievement is the first example of the industrial chemical processes using heteropolyacids as solid acid catalysts, although there had been several industrial processes, in which heteropolyacids are utilized for liquid-phase reactions as acid or oxidation catalysts and for a gas-phase reaction as an oxidation catalyst.

The process of ethylacetate production was developed by Showa Denko K.K. and started into operation in 1999. However, it still had the problem of serious catalyst deactivation (SiO₂-supported heteropolyacids) at the time. This group carried out a collaborative work to figure out the cause of the catalyst deactivation and finally ascertained that the catalyst deactivation was mainly caused by the oligomerized ethylene formed during the reaction. The oligomerization and deactivation was significantly suppressed by thorough reduction of impurities of SiO₂ support and optimization of the layer-structure of heteropolyacid on the surface of SiO₂, which can be controlled by the support modification and catalyst preparation. In addition to the improvement of catalyst, the operation conditions including reaction temperature and water vapor pressure were carefully optimized. This led to tremendous increase in the catalyst life (>> 2 years) under the highly-loaded conditions. It was further confirmed that, instead of ethylene alone, a mixture of ethylene and ethanol derived from a biomass can be used as a feedstock in this process. This has an advantage to deal with a price volatility of ethylene. The improved process has reduced the emission to almost zero and the energy consumption by 40% in comparison to the conventional H₂SO₄ process.

The technology of controlling the layer-structure of heteropolyacid on SiO₂ as described above was applied to SiO₂-supported Pd-heteropolyacid catalyst that was used for the synthesis of acetic acid directly from ethylene (developed and operated by Showa Denko K.K.) and remarkable improvement was successfully achieved. The basic research of this group revealed that ethylene is oxidized through a Wacker-type oxidation and this knowledge helped very much to optimize the layer-structure of heteropolyacid on SiO₂. This process is suited for small to medium size plants distributed geographically.

In addition to the development of above two industrially successful green-chemical processes, the group developed several other supported heteropolyacid catalysts that showed very high activity and selectivity for the alkylation and acylation reactions and also for reactions in water as a water-tolerant solid acid. So, these catalysts have a great potential to replace aluminum chloride and sulfuric acid that are conventionally used for acid-catalyzed chemical processes. It may be stated, therefore, that this research and development is a good example of green and sustainable chemistry achieved by close industry-academia collaboration.