Institution: University of Liverpool

Unit of Assessment: 8 - Chemistry

Title of case study: Economical and beneficial environmental impact on industrial production of ethyl acetate

1. Summary of the impact

Studies into the deactivation and regeneration of heteropoly acid catalysts, which took place in the group of Professor Ivan Kozhevnikov at Liverpool University since 1996, resulted in the large-scale industrial application of these catalysts in BP's process for the synthesis of the widely used solvent ethyl acetate, thus making significant economic and environmental impact. This process, trademarked AVADA (for **A**d**V**anced **A**cetates by **D**irect **A**ddition of acetic acid to ethylene), was launched in 2001 at Hull, UK, on a scale of 220,000 tonnes p.a., then the world's largest ethyl acetate production plant. The impact continued through the REF period from 2008 to 2013. In October 2011, the AVADA process produced 56% of the ethyl acetate in Europe (245,000 tonnes p.a. production capacity and $340m p.a. factory gate value), being the second largest in the world after the Zhenjiang 270,000 tonnes p.a. ethyl acetate plant in China. Over the REF period, the AVADA process produced 1.2 million tonnes of ethyl acetate worth $1.7 billion. The AVADA process makes ethyl acetate with 100% atom efficiency, avoiding the use of ethanol as an intermediate. It beats conventional processes in environmental friendliness by reducing energy consumption by 20% and feedstock losses by 35%, thus removing more than 100,000 tonnes p.a. of wastewater stream. At the heart of the AVADA process is a highly efficient heteropoly acid catalyst that is responsible for its superior performance. Implementation of measures improving catalyst stability and resistance to coking, which originated from collaboration between the Kozhevnikov group and BP Chemicals, prevented otherwise fast catalyst deactivation to create an economically viable process.

2. Underpinning research

Catalysis by heteropoly acids (HPAs), also known as polyoxometalates, has attracted much interest both in fundamental and applied research because of its potential to generate significant economic and environmental benefits (Kozhevnikov, I.V., *Catalysis by Polyoxometalates*, Wiley, Chichester, 2002). Systematic studies of HPA catalysts at the molecular level have led to a series of large-scale industrial applications, such as the hydration of olefins and the oxidation of methacrolein to methacrylic acid. Prof. Kozhevnikov is a world-leading expert in catalysis by HPAs; he became involved with HPA catalysis early on, since the mid-1970s, and published over 150 widely recognized research outputs in this field, including the pioneering work on acid catalysis by HPAs (Kozhevnikov, I.V., *Chemical Reviews*, **98**, 171-198 (1998); *J. Mol. Catal. A* **262**, 86-92 (2007); *J. Mol. Catal. A* **305**, 104-111 (2009), total citation score 1436). The majority of HPA catalytic applications use the most stable and easy available Keggin HPAs comprising heteropolyanions of the formula $[XM_{12}O_{40}]^{n-}$, where X is the heteroatom (e.g. P^{5+}, Si^{4+}) and M is the addendum atom (e.g. Mo^{6+}, W^{6+}). HPAs are non-volatile compounds possessing very strong Brønsted acidity which is superior to that of mineral acids and conventional solid acid catalysts. This makes them promising solid acid catalysts for various reactions both in gas and liquid phases. However, the relatively low thermal stability of HPAs and difficulty of catalyst regeneration had always been obstacles to their commercialisation, rendering their use in heterogeneous acid catalysis rather limited. The key problem was catalyst lifetime, since the heteropoly acids usually suffered rapid deactivation and loss of activity.

In the 1990s, BP Chemicals were facing the challenge of relocating ethyl acetate manufacturing capacity around Europe to a more efficient site, by implementing a significantly improved production process. Ethyl acetate is manufactured on a large scale and is used in surface coatings, inks, and pharmaceuticals. The state-of-the-art BP site at Hull was chosen as the new location for the commercial plant.

BP Chemicals came up with a new solution for ethyl acetate production, trademarked AVADA. The new technology converts ethylene and acetic acid in the gas phase with 100% atom efficiency directly into ethyl acetate using a highly active HPA catalyst, without the usual intermediate stage of esterification which would have required another feedstock chemical, ethanol. By avoiding ethanol the new technology represents a significant advance – a true step change. Exploratory work on the AVADA process was carried out at BP Sunbury-on-Thames Research Centre by the team led by Dr Martin Atkins and at BP Research and Technology Centre at Hull by the technology team led by Dr Mark Howard. Their progress was hampered by the short catalyst lifetime due to fast deactivation of the HPA catalyst caused by its coking and poisoning.

In 1996, Kozhevnikov, then Senior Research Fellow in the Leverhulme Centre for Innovative Catalysis (LCIC), Department of Chemistry, University of Liverpool, was invited by BP Chemicals, an Industrial Affiliate with the LCIC at that time, to collaborate with their team at Sunbury on the development of the HPA catalyst for the AVADA process. Kozhevnikov set up a research group in Liverpool, which included two PDRA's, Dr S. Holmes and Dr M. R. H. Siddiqui, funded by BP Chemicals. The aim of their research was to gain an insight into the nature of the coke formed on the surface of supported HPA catalysts and the effect of the coke on the HPA. This was investigated using ^{13}C and ^{31}P solid state NMR, XPS and TPO/TGA in combination with fixed-bed reactor studies of aerobic coke gasification. It was found that catalyst modification with platinum group metals, such as palladium, significantly reduced the temperature of coke removal to allow for catalyst regeneration without HPA degradation (*Catal. Lett.* **66**, 53-57 (2000)). Particularly important was the finding that addition of polar molecules (n-donors) such as water, methanol etc. to the feed could greatly reduce coking of HPA catalysts thus improving catalyst life without the need for frequent catalyst regeneration (*Appl. Catal. A* **214**, 47-58 (2001)).

The result of this collaborative research was the development of effective methods to improve the stability and lifetime of the HPA catalysts. These processes include both prevention of catalyst coking as well as regeneration of HPA catalysts. The main results of these studies have been published in the papers listed below.

3. References to the research (indicative maximum of six references)

* Three references to indicate the quality of the research.

1. *Siddiqui, M.R.H., Holmes, S., He, H., Smith, W., Coker, E.N., Atkins, M.P., Kozhevnikov, I.V. Coking and regeneration of palladium-doped $H_3PW_{12}O_{40}/SiO_2$ catalysts. *Catal. Lett.* **66**, 53-57 (2000). DOI: 10.1023/A:1019083103395 (citation score 24).
2. *Kozhevnikov, I.V., Holmes, S., Siddiqui, M.R.H. Coking and regeneration of $H_3PW_{12}O_{40}/SiO_2$ catalysts. *Appl. Catal. A* **214**, 47-58 (2001). DOI: 10.1016/S0926-860X(01)00469-0 (citation score 48).
3. *Kozhevnikov, I.V. Sustainable heterogeneous acid catalysis by heteropoly acids. *J. Mol. Catal. A* **262**, 86-92 (2007). DOI: 10.1016/j.molcata.2006.08.075 (citation score 87).
4. Alsalme, A.M., Wiper, P.V., Khimyak, Y.Z., Kozhevnikova, E.F., Kozhevnikov, I.V. Solid acid catalysts based on $H_3PW_{12}O_{40}$ heteropoly acid: Acid and catalytic properties at a gas-solid interface. *J. Catal.* **276**, 181-189 (2010). DOI: 10.1016/j.jcat2010.09.014 (citation score 18).

5. BP Chemicals as the Industrial Affiliate with the Leverhulme Centre for Innovative Catalysis at Liverpool University (1987 to 1998) supported this project through their membership fee (£25,000 p.a.). In addition, they also supported two post-docs and provided support in kind including access to facilities and staff time. Support from EPSRC: Novel solid acid materials based on polyoxometalates, grant EP/F014686/1, 2007-2010 (£99,174).
6. Web references can alternatively be found at: **http://tinyurl.com/livchemref**

4. Details of the impact

The new AVADA catalyst developed by BP (EP0757027, 1997) consists of a bed of silica beads impregnated with silicotungstic HPA. The catalyst showed excellent initial activity in the synthesis of ethyl acetate, but unfortunately deactivated very quickly and with irreversible loss of activity. The main cause of deactivation was extensive catalyst coking which blocked catalyst acid sites leading to the loss of acidity. As a result, the catalyst life was too short to be economically viable, which put the AVADA project at risk of closure.

Kozhevnikov made the crucial suggestion of an alternative approach to the problem of catalyst deactivation, viz prevention of catalyst coking and poisoning by adding n-donors to the reaction feed, rather than attempting a ‘cure’ (regeneration). Kozhevnikov demonstrated that addition of water to the olefin feedstock was an extremely effective coke inhibitor over HPA catalysts (*Appl. Catal. A* **214**, 47-58 (2001)).

Based on these results, the first advance implemented was co-feeding 3–8% of water (steam) together with ethylene and acetic acid to the catalytic reactor. This reduced dramatically the amount of coke deposited on the catalyst surface. It also improved the stability of the heteropoly acid on the silica surface. The second measure developed was the installation of a silico-alumina guard bed to protect the HPA catalyst from poisoning by basic impurities in the feed and corrosion metal ions. Altogether these measures, originating from collaborative research between Kozhevnikov’s group and BP Chemicals, allowed significant prolongation of catalyst life to about one year and were crucial to the commercial success of the AVADA process.

The ethyl acetate plant at Hull achieved continuous sustained operation during its first year in commercial production. The purity of the product was excellent – 99.98%, the best ever. The low volatility of the HPA helped the catalyst to survive the reactor’s extremes of heat and pressure, thus allowing long periods of uninterrupted operation for the plant. Interestingly, the HPA catalyst, which is now produced by Johnson Matthey, is practically unchanged from the one used in the initial stage of process development. It is the implementation of the right process conditions, based on fundamental research, that has made the great improvement to the process efficiency.

Regarding its environmental friendliness, the AVADA process is by far ahead of conventional ethyl acetate syntheses (*Green Chemistry*, 2003, **5**, G78-C81; DOI: 10.1039/b304290c). Traditional ethanol esterification units produce as much water as they do ethyl acetate and therefore require treatment and disposal of this waste stream. In the AVADA process, elimination of ethanol as intermediate eliminated the transport of some 60,000 tonnes of ethanol by road and removed more than 100,000 tonnes p.a. of wastewater stream. The other main technology in the market, Tischenko condensation, uses an acetaldehyde feedstock. This is less efficient than producing ethyl acetate directly from a modern ethylene cracker and also produces waste streams from the aluminium salts used as catalyst. Compared to conventional processes, AVADA's energy consumption is about 20% lower and feedstock losses are some 35% less than in conventional esterification with benefits to CO_2 emissions (*Green Chemistry*, 2003, **5**, G78-C81).

The AVADA technology is potentially interesting for other acid-catalysed processes such as the manufacturing of fuels, detergents and lubricants using heterogeneous acid catalysis. The AVADA process won the AstraZeneca Award in Green Chemistry and Engineering in 2002 (*Green Chemistry*, **5**, G78-C81 (2003)).

In 2008, BP sold the ethyl acetate and related vinyl acetate monomer businesses to INEOS Enterprise, a Swiss headquartered petrochemical group, for an undisclosed amount. At that time each facility had 250,000 tonnes p.a. capacity and together employed around 40 people (www.knak.jp/big/ineos.htm).
According to the recent ICIS Chemical Business report (October 2011), the INEOS (former BP) plant at Hull (245,000 tonnes p.a. production capacity, $340m p.a. factory gate value) by far dominates ethyl acetate production in Europe (56% of the total 440,000 tonnes p.a.), being the second largest in the world after the Zhenjiang 270,000 tonnes p.a. capacity ethyl acetate plant in China (http://www.icis.com/Articles/2011/10/24/9501870/european+chemical+profile+ethyl+acetate.html).

Over the REF period from 2008 to 2013, the AVADA process produced 1.2 million tonnes of ethyl acetate of the total value of $1.7 billion and reduced the wastewater stream by 0.5 million tonnes compared to the conventional ethanol esterification process.

In his letter of corroboration, Dr Mark Howard, Technology Vice President, Conversion Technology Centre, BP International Ltd., Saltend, Hull, states *"Kozhevnikov's group, in close cooperation with BP's team at Sunbury, set out to investigate coking and regeneration of HPA catalysts. This contributed to the development of effective strategies for maintaining the stability of the HPA catalyst which were implemented to achieve economically viable catalyst lifetime. Recently sold to INEOS as part of BP's rationalisation of its portfolio, the AVADA plant is still in operation."*

5. Sources to corroborate the impact (indicative maximum of 10 references)

The contribution of the Leverhulme Centre for Innovative Catalysis at the Department of Chemistry, University of Liverpool, to the success of AVADA process is acknowledged in a special publication by the General Technology Manager, BP Chemicals (Dobson, I.D., "Leaps of innovation", *Green Chemistry*, **5**, G78-C81 (2003) (DOI: 10.1039/b304290c)). Similar publication appeared earlier in the BP journal *Frontiers*, August 2002, p. 12-14. Both state "the ethyl acetate development work was ... widely collaborative ..., calling on the cooperation of chemists, chemical engineers process developers, catalyst manufacturers and research departments in several universities, *particularly the Leverhulme Centre of Liverpool University in the UK* and Waterloo University in Canada."

The letter of corroboration is provided by the Technology Vice President, Conversion Technology Centre, BP International Ltd., Saltend, Hull.