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Sulfur-Resistant Platinum Hydrogenation Catalysts

There is increasing awareness of the damaging effects on human health caused by the pollution from diesel fuelled vehicles, especially the harm due to the presence of particulate matter of 10 μm or less. The aromatic particulates content of diesel fuel is known to be a primary source of pollution, and legislation and research have been directed towards reducing the levels in diesel fuels (1).

In order to comply with new specifications, petroleum refiners may use an additional hydrotreating procedure, usually with a relatively inactive metal sulfide catalyst, which requires severe operating conditions. Alternatively a two-stage process can be used, the second-stage being hydrogenated by very active noble metals. However, catalyst poisoning by the sulfur compounds in the petroleum feedstock is a problem, and a first stage hydrotreatment is needed to reduce the sulphur to below 10 ppm.

Researchers from CANMET in Canada have now studied two molecular sieve catalysts, impregnated with platinum, for their resistance to sulfur poisoning during hydrogenation of the aromatics of synthetic crude distillates (2). The molecular sieves they examined were a sodium montmorillonite, made into a pillared inter-layered clay (PILC), and Y-zeolite. The feedstocks used were middle distillate fractions from a synthetic crude oil, from Canadian oil sands, which have significantly different properties to conventional fuels.

The Y-zeolite had a much higher microporosity than the PILC, while the parallel-plate formations in the PILC create a unique structure with interior galleries having well-dispersed ion-exchange sites.

They found an acceptable hydrogenation activity for platinum clusters supported in Y-zeolite, when a distillate feedstock, containing 140 ppm sulphur and 50 ppm nitrogen, was upgraded. There was also an improved poison resistance to the feedstock, which contains sulfur levels at least an order of magnitude higher than required for conventional catalysts. The platinum/Y-zeolite catalyst functioned at temperatures signifi-

cantly lower than those for conventional hydrotreating catalysts with superior activity for the hydrogenation of middle distillate aromatics. This is attributed to the structure of the Y-zeolite supercage, producing well-dispersed electron-deficient platinum metal clusters. Although the platinum/PILC catalyst had no enhanced resistance to sulfur poisoning, its unique structure may be useful in ring opening reactions for naphthene in middle distillate feedstocks.

References

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Sulfur Removal by Platinum

Petroleum and natural gas contain sulfur, and its removal by hydrodesulfurisation produces hydrocarbons and hydrogen sulphide, which may be removed via the Claus process. In the Claus process, sulfur is recovered from hydrogen sulfide in a two-stage process in which hydrogen sulfide is mixed with oxygen to yield water and sulfur dioxide, the latter then reacts with more hydrogen sulfide to produce sulfur and water.

Researchers from McGill University, Canada, have now produced a homogeneous platinum catalyst which mimics the Claus process (A. Shaver, M. El-khateeb and A.-M. Lebuis, *Angew. Chem., Int. Ed. Engl.*, 1996, 35, (20), 2362-2363). They report on the reaction of *cis*-[(PPh₃)₂Pt(SH)₂] (*cis*-2) with sulfur dioxide, to produce [(PPh₃)₂PtS₂O] (1). Both complexes catalyse the Claus reaction.

The catalytic cycle proposed for this reaction involves adduct formation between *cis*-2 and sulfur dioxide, followed by sulfur dioxide insertion into the sulfur-hydrogen bond. Elimination of water produces (1), which reacts with hydrogen sulfide to cleave the platinum-sulphur bonds and regenerate *cis*-2. The other cleavage product was not detected, and may be a key intermediate in the process.