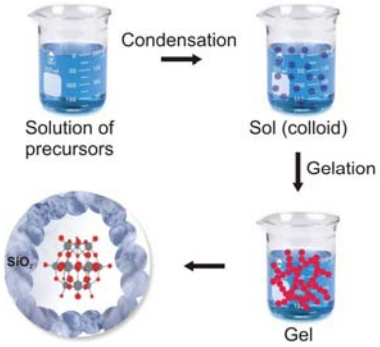
Molybdenum oxide nanoparticles supported on mesoporous silica: A versatile catalyst

National Chemical Laboratory (NCL), Pune has developed an environmentally benign process for the manufacture of nitrobenzene using a solid acid catalyst. This innovation was awarded the silver medal of FICCI-Lokheed Martin Indian Innovation growth program recently. Dr. Mohan K. Dongare and his group at NCL worked on this process that represents a green chemistry approach in which benzene is nitrated using dilute nitric acid over solid acid catalyst in the vapor phase. Nitrobenzene is formed in high yields without use of any sulfuric acid, which is used in the conventional process. Using a solid acid catalyst packed in a tubular reactor, the hazards of handling and storing a large inventory of sulfuric acid is avoided. The capital cost for the plant based on this technology is expected to be lower by 30-40% compared to the conventional processes.

Elaborating further, Dr. Dongare, senior scientist at Catalysis and Inorganic Chemistry Division said, "The development of this novel catalyst originated in 2002 when we were working on another project, namely, the Oxidation of benzene to phenol using nitric acid as an oxidant. NCL team prepared and tried various metal oxide catalysts and found that silica supported molybdenum oxide catalyst was very active. This catalyst gave diversity of products at different temperature using nitric acid as an oxidant. Nitration of toluene was also observed at low temperature with high specificity using this catalyst.



"We further worked on the synthesis of this catalyst using various routes to improve the catalytic activity. Preparation of this catalyst using ethyl silicate-40, a foundry chemical used as binder, as novel silica precursor gave very high surface area (890 m^2/g) and high mesoporosity (80 A^0). The product was stable up to 600 ^0C and did not require any surfactant template. This is probably the first report of a high surface area mesoporous silica produced" informed Dr. Dongare.

Transmission electron microscopy of this catalyst showed molybdenum oxide nanoparticles of 1-2 nm formed on mesoporous silica support.

Besides using for benzene nitration, this catalyst has shown very high activity in many other reactions. One such reaction is transesterification of diethyl oxalate with phenol to form diphenyl oxalate giving 100% selectivity for diphenyl oxalate, which is one of the intermediates for preparation of polycarbonate. NCL scientists have also used this catalyst for the synthesis of tinidazole, an important pharmaceutical compound by condensation/ oxidation reaction without any use of acetic acid, tungstic acid or ammonium molybdate used in the conventional process.

For further reading:

Patents:

- Vapor phase nitration of benzenes over solid catalyst, US Pat 6,791,000 (2004).
- Process for the preparation of 4-nitro-o-xylene, US Pat. 6,825, 388 (2004).
- Process for preparing microporous crystalline titanium silicate, US, Pat. 6,991,678 (2006).

Publications:

- Transesterification of diethyl oxalate with phenol using MoO_3/SiO_2 catalyst, A.V. Biradar, S.B. Umbarkar, M.K. Dongare, Applied Catalysis A: General 285 (2005) 190–195.
- Vapor phase nitration of benzene using mesoporous MoO3/SiO2 solid acid catalyst, S. B. Umbarkar, A. V. Biradar, S. M. Mathew, S. B. Shelke, K. M. Malshe, P. T. Patil, S. P. Dagde, S. P. Niphadkar and M. K. Dongare, Green Chem., 2006, 8, 488–493.
- Synthesis of tinidazole by condensation–oxidation sequence using MoO_3/SiO_2 bifunctional catalyst, J.G. Chandorkar, S.B. Umbarkar, C.V. Rode, V.B. Kotwal, M.K. Dongare, Catalysis Communications 8 (2007) 1550–1555.

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