Nitration of Toluene and Nitrotoluene with Solid Acids

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Nitrotoluenes (NT) and dinitrotoluenes (DNT) are important intermediate products in the chemical industry. They find use in the production of polyurethanes, pharmaceutical compounds, dyes, perfumes, explosives, pesticides and fertilisers. The main drawback of the present industrial mixed-acid process is the production of huge amounts of spent acid. An alternative solution is strongly desired because the reconcentration and the regeneration of spent acid is very energy intensive.

In this work the suitability of solid acids for the nitration of toluene to both mono- and dinitrated products was studied. The advantages would be the easy regeneration of solid acids through a thermal treatment and a facilitated separation of the catalyst from the products. Moreover, in the case of zeolites it would be possible to introduce shape-selectivity and to shift the product composition in favour of the more required 4-nitrotoluene (4-NT) and eventually 2,4-dinitrotoluene (2,4-DNT). One of the key issues in the successful application of solid acids in the nitration of toluene and NT to DNT is the handling of the water in the reaction mixture.

For a liquid-phase batch reaction at ambient or slightly higher temperature a solid acid with a high concentration of acid sites is required. Zeolites were inactive under those conditions because of their low concentration of acid sites and the resulting strong mediating effect of water on acidity. Only supported sulphuric acid on silica was capable of providing the required high density of acid sites, although amounts of sulphuric acid greater than stoichiometric were required to bind the water present in the reaction mixture.

The water formed during the reaction and also present in the 65 wt% nitric acid used as nitrating agent is the crucial variable governing the activity of a solid acid. An efficient
removal of the water during a nitration reaction is possible with two different methods: a continuous flow vapour-phase reaction and a liquid-phase reaction with simultaneous distillation.

In the vapour phase nitration of toluene, NT was observed as a reaction product, whereas the formation of DNT was negligible with all solid acids tested. Preshaped silica impregnated with sulphuric acid was the most active catalyst but a continuous loss of sulphuric acid with time-on-stream occurred. Deloxan, showing relatively good activity and stability, was more promising although the loss of nitric acid through disproportionation to NO₂ was substantial. H-beta was stable in the highly acidic reaction medium used and provided a higher para-to-ortho ratio than other zeolites such as ZSM-5, ZSM-12 and mordenite, but deactivated after 5-10 hours on-stream. The decrease in activity and para-selectivity with time-on-stream was reversible and was linked to the formation of strongly bound (by)products blocking the micropore system. The para-selectivity of mordenite could be improved by the creation of a mesoporous system. The vapour phase nitration may become interesting for the production of NT if the high para-selectivity of H-beta is desired and if the deactivation of the catalysts can be better controlled.

The reaction with simultaneous distillation was the only case where true catalytic formation of DNT using classical natural solid acids and 65 wt% nitric acid as only reactant was observed. Zeolite beta was less active than supported liquid acids but gave an exceptionally high 2,4-DNT selectivity (up to 94%), compared to 74-79% obtained with all other solid acids. Supported liquid acids were not stable under those reaction conditions because a loss of the impregnated acid occurred.

The nitration of toluene and 2-NT with a variety of zeolites and solid acids using acetyl nitrate as nitrating agent was investigated with the aim to elucidate the reasons for the exceptionally high selectivity observed with beta zeolites. Beta zeolites with the smallest crystallite size were the most selective catalysts, whereas macromolecular zeolite H-beta and dealuminated mordenite did not show enhanced para-selectivity. Depending on the batches of beta used, a 4-NT selectivity of up to 73% was obtained using an equimolar amount of nitrating agent. Using 2-NT as reactant, an unexpectedly high selectivity towards 2,4-DNT of up to 94% could be reached.