Van 't Hoff Institute for Molecular Sciences

HIMS chemists succeed in antagonistic catalysis

Dr. Raveendran Shiju and prof. dr. Gadi Rothenberg, both from the heterogeneous catalysis and sustainable chemistry group at the Van 't Hoff Institute for Molecular Sciences (HIMS) have succeeded in synthesising a robust solid catalyst that combines two antagonistic functions: acid and base.

Using a simple and straightforward synthetic approach, the researchers created a bifunctional surface that combines the advantages of bifunctional enzyme-like catalysis with the ease of separation and robustness of traditional heterogeneous catalysis.

The new family of materials can catalyse one-pot tandem reactions. The bifunctional catalytic activity was demonstrated in tandem deprotection-aldol reactions and deprotection-Henry reactions. The results have been published in the top-tier journal Angewandte Chemie.

Enzyme-like catalysis

Many researchers in heterogeneous catalysis cite enzymes as their model catalysts. Enzymes can efficiently catalyse multistep processes that give various types of biomolecules. Remarkably, many enzymes combine two antagonist catalytic functions, such as an acid and a base.

Examples include the serine proteases that are involved in blood clotting and inflammation in mammals. These enzymes cleave amide bonds. They contain neighboring basic imidazole and acidic carboxylic acid groups. The hydrolysis of phosphate diester linkages in RNA by ribonuclease A (one of the classic model systems of protein science) also involves a concerted interaction of RNA with acidic and basic sites in the enzyme.

But even though the concept looks simple, combining two rival functions in one catalyst, yet keeping them apart so that they do not destroy each other, is no easy task.

Tailoring the acid:base ratio

In collaboration with Dr. Albert Alberts (UvA), Prof. David Brown (Huddersfield, UK) and Dr. Syed Khalid (Brookhaven National Laboratory, USA), Rothenberg and Shiju now managed to create an acid-base bifunctional catalyst that is easy to synthesise as well as easy to separate after reaction.

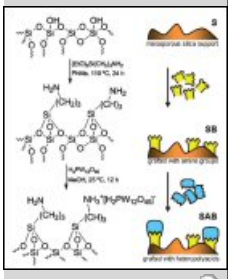
First, they grafted mesoporous silica with aminopropyl groups, making a basic catalyst. Then, they immobilized phosphotungstic acid on some of these groups (see figure). By varying the amount of phosphotungstic acid, the researchers could tailor the acid:base active site ratio.

One-pot tandem conversion

Characterising the materials before and after each step confirmed that the pore structure remained unaltered, keeping the chemically important mesopores that give the catalyst a high active surface area. Furthermore, 31P NMR spectroscopy showed that the Keggin structure of the phosphotungstic acid was maintained after immobilization.

The researchers then applied the catalyst in the one-pot tandem conversion of dimethoxymethylbenzene to trans-1-Nitro-2-phenylethylene. This two-step cascade starts with an acid-catalysed deacetalization, giving benzaldehyde. The benzaldehyde then reacts with nitromethane in a base-catalysed step (a so-called Henry reaction), giving the final nitro product. The results show that both the amino groups and the acid polyanions retain their reactivity. The immobilized polyanions, which are still acidic, catalyze

Rothenberg has a tradition of creating highly colorful illustrations, which often appear on journal covers. Angewandte Chemie selected his latest contribution for its back cover. The active sites on the new catalyst are represented by the iconic Rock 'em Sock 'em Robots. Read more about the illustration at the end of this news item.



Schematic representation of the synthesis of the new catalyst.

the deacetalization, followed by the Henry reaction with nitromethane at the free amino groups.

A key requirement for the tandem deacetalization-nitro-aldol reaction is the ratio between amino groups and polyanions. If all the amino groups are used for polyanion immobilization, the reaction stops at the first step and benzaldehyde is the only product.

The same catalyst also catalyzed another acid-base tandem sequence – deacetalization followed by aldol condensation with malononitrile – showing a wide application scope.

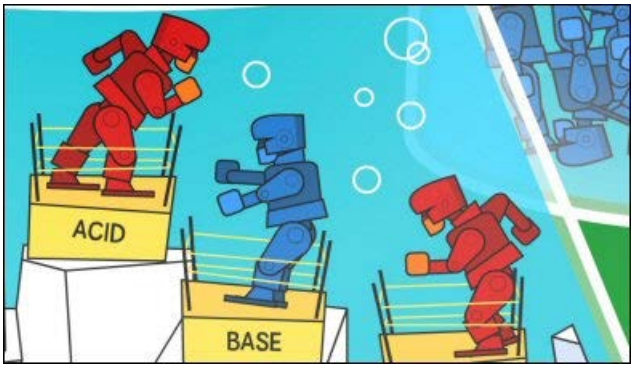
Control reactions in the presence of homogeneous p-toluenesulfonic acid gave no product, due to the neutralization of the catalyst amino groups.

Wide applications

These new catalysts can have wide applications, because they are easy to make and easy to tune. The catalyst can be made predominantly basic, or predominantly acidic, or equally acidic and basic by changing the ratio of polyacid and amine groups. Similar types of catalysts can be synthesized using other heteropolyacids, which further widens the scope of these materials.

Cover illustration

The importance of this new catalyst is reflected by the fact that the results will be featured on the issue cover. Rothenberg has a tradition of highly colorful cartoon cover images, and this is no exception. “When this reaction worked, it immediately clicked in my mind with the image of the red-and-blue Rock 'em Sock 'em Robots toys of my childhood” says Rothenberg; “funnily enough, this was also the first reaction of our illustrator, Itamar Daube, when I sent him the paper and asked him to sketch what he finds from it”. Randy Olson would have approved.



The Rock 'em Sock 'em Robots (or Raving Bonkers, as they were called in the UK) were designed by Marvin Glass and Associates and first manufactured by the Marx toy company in 1964. In the new catalysts, however, the “red” (acid) and “blue” (base) antagonist sites are physically separated in private “boxing rings”. The physical separation on the catalyst surface prevents the acid and base sites from attacking each other, creating a truly bifunctional and tunable acid-base catalyst.

Publication details

Mesoporous Silica with Site-Isolated Amine and Phosphotungstic Acid Groups: A Solid Catalyst with Tunable Antagonistic Functions for One-Pot Tandem Reactions N. Raveendran Shiju, Albert H. Alberts, Syed Khalid, David R. Brown, and Gadi Rothenberg. Angewandte Chemie International Edition 2011. DOI: 10.1002/anie.201101449

Refer to
Complete article
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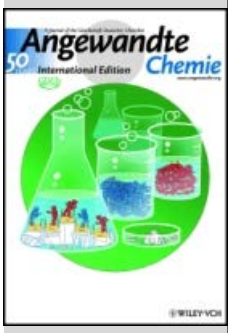

Back cover of the issue of Angewandte Chemie.