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Role of catalysis in sustainable chemistry

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Abstract

Background: Sustainable Chemistry aims at the design of products which minimize the use and generation of harmful substances which have an adverse effect on the environment. Sustainable Chemistry is based on the 12 Principles of Green Chemistry enunciated by Paul Anastas and John Werner in the 90's, which provide a blueprint for sustainable development. Among these, the use of catalysts to improve atom economy and yield of reactions is most important. Catalysts are the pillars of Green Chemistry and worldwide, there is a constant search for novel catalysts.

Atom economy of a chemical reaction is a theoretical measure of the amount of starting material which has got converted into the desired useful product and is a reliable metrics of the greenness of a reaction.

%Atom economy =[mass of desired product]/[total mass of all products]100

Thus, 100% atom economy means 0% waste.

Green catalysts are preferred because of their distinct advantages:

1) better atom economy,
2) minimum waste production,
3) ecofriendly products and emissions,
4) reusability

Methods: Illustration1: The atom economy of the extraction of iron from its ore using carbon can be calculated as follows:

$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$

Mass of reactants=2[2x55.84 + 3x16] + 2[12] = 355.36 amu

Mass of products =4[55.84] + 3[44] =355.36 amu

The desired product is Fe

% Atom economy= [mass of desired product/total mass of all products] X 100

= [4(55.84)/355.36] x 100 = 62.85%

Illustration 2: Aniline can be prepared by old and new methods

The old method used FeCl3.HCl as the catalyst

$4C_6H_5NO_2 + Fe + 4H_2O \rightarrow 4C_6H_5NH_2 + 4Fe_2O_3$

Nitrobenzene Aniline

% Atom economy=35%

The new method uses Nickel catalyst at 3000C and 5 psi pressure.

$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

% Atom economy=72%

Illustration 3: Adipic acid is a very important starting material for the manufacture of Nylon 6.

Adipic acid

The conventional method uses carcinogenic benzene as the starting material, Ni/Al_2O_3 as the catalyst and nitric acid as the oxidizing agent. Nitric acid produces nitrous oxide N_2O which contributes to the greenhouse effect and destruction of ozone in the stratosphere.

The reaction takes place in 3 steps and has atom economy 55.7%

In the new method (greener method), the starting material is Cyclohexene, Na_2WO_4 is the catalyst and 30 % H_2O_2 is the oxidizing agent. This one step synthesis proceeds in aqueous medium at a lower temperature and has atom economy 67%.Both the reactant and product are environmentally benign.

2) Optimization of reaction yield

A catalyst should improve the yield of a reaction.

Illustration 4: Ibuprofen is an analgesic drug just like Aspirin (Acetyl Salicyclic acid)

Ibuprofen

2-Methylpropyl benzene is the starting material for both the conventional and new methods of synthesis.

2-Methylpropylbenzene

The original synthesis required 6 steps and resulted in the production of secondary by products which were a waste.The catalyst anhydrous $AlCl_3$ was not efficient as it got hydrated and was rendered ineffective.The yield was 40%

The new method uses Raney nickel as catalyst which can be recycled and reused. The yield is 77%

Illustration 5 : Nickel catalyst increases the yield of hydrogenation of propene to almost 100%

$CH_3CH=CH_2 + H_2 \rightarrow CH_3CH_2CH_3$

Propane

RESULTS

Consumption indicators in Ukraine decreased from 11.5358 DID in 2013 to 10.0884DID in 2015 and increased from 11.0792 DID in 2016 to 12.4731 DID in 2018.

The consumption in the United Kingdom has decreased from 18.2765 DID in 2013 to 16.2636 DID in 2018, despite a slight increase in 2014 (18.5068 DID).

Throughout the study period, antibiotics were consumed more in the United Kingdom than in Ukraine. The largest difference in antibacterial for systemic use consumption between the two countries was recorded in 2015 (1.8 times).

Conclusion

Sustainable Chemistry focuses on the design of products that minimizes the use and generation of hazardous starting materials. The use of green catalysts improves atom economy and efficiency of reactions.

Sustainable Chemistry should be incorporated in a big way in the curriculum to understand the principles of Green Chemistry based on the 3R's –Reduce, Reuse and Recycle and to learn to modify the existing processes to make them environmentally friendly.

Keywords: Sustainable Chemistry, Green catalysts, atom economy, reaction yield, biocatalysts, enzymes, nanocatalysts, phase transfer catalysts.

Introduction

In the last few decades, there has been a constant and vigorous debate between Development and Conservation of the environment. Man has been consuming natural resources at an alarming rate leaving behind toxic byproducts which are hazardous to the environment. Today, there is a general acceptance that there should be a balance between development and conservation.

Overview of Principles of Green Chemistry

The 12 Principles of Green Chemistry [1-3] provide a blueprint for sustainable development.

1) The generation of waste products should be minimized. It is better to prevent the formation of waste rather than clean it up after its generation.

2) Atom economy of a process should be so designed that maximum amount of reacting material is converted into the desired product.

3) The use and generation of toxic materials should be avoided.

4) Non toxic chemical substances should be used as starting materials in reactions.

5) The use of auxiliary substances like solvents and separating agents should be minimized .Green solvents like water should be used in preference to halogenated organic solvents. Green Chemistry aims at solvent free reactions.

6) Energy consumption in reaction should be minimized and ideally reactions should be carried out at ambient temperature.

7) Renewable feedstock like biomass should be used as starting materials instead of non renewable feedstock like crude oil.

8) Reactions should be carried out with minimum number of steps. Steps like derivatization, protection and de-protection of functional groups in molecules should be avoided as far as possible.

9) Catalysts should be used to increase reaction rates as they are superior to stoichiometric reagents. Catalysts increase the atom economy and yield of reactions

10)The products of a reaction should degrade easily to harmless substances and should not pose a threat to the environment.

11) The generation of hazardous substances should be monitored by sensitive analytical methods.

12) Chemically safer substances with minimum potential of accidents should be used. Solids and non volatile liquids have less risk of accidents compared to gases and volatile liquids.

Methods

1)Improvement in Atom Economy

A catalyst should improve the atom economy of a reaction

Atom economy of a reaction is a theoretical measure of the amount of starting material that ends up as the desired final product.Atom economy is the most widely used metrics to measure the greenness of a reaction.

% Atom Economy = [Mass of desired product/Total mass of all products] X 100

Thus greater the % atom economy ,more green (efficient) is the reaction.ie 100% atom economy means 0% waste.

Atom economy can be maximized by designing the synthesis so that the final desired product contains the maximum proportion of the starting material and few or no atoms are wasted.This can be achieved by use of a suitable catalyst.

2) Optimization of reaction yield

A catalyst should improve the yield of a reaction.

Discussion

A catalyst is a substance which accelerates the rate of a reaction but remains chemically unchanged at the end of the reaction ie. its chemical composition and amount remains unchanged. A catalyst takes an active part in the reaction but does not appear in the end product of the reaction.

A catalyst lowers the minimum energy required for the reaction to take place and hence increases the rate of reaction. This energy threshold called Energy of Activation (E) is related to the absolute temperature T by the Arrhenius equation, k=A e-E/RT where k is rate constant, R is the gas constant and A is a constant. Temperature has the most profound effect on rate of reaction.

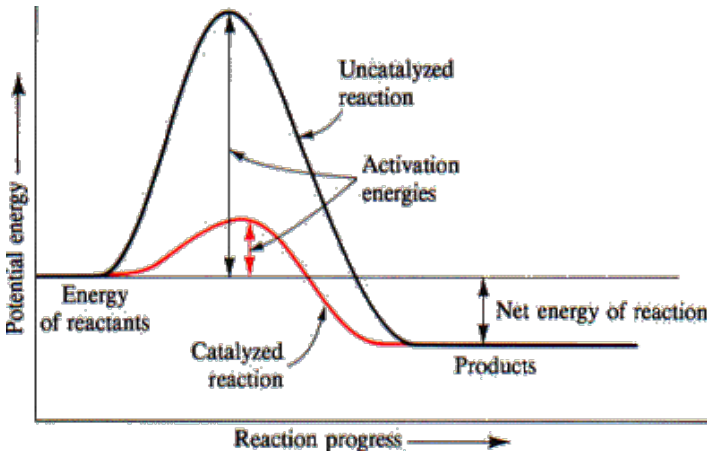

Fig.1:Effect of catalyst on rate of reaction

E and E' are the energies of activation of the uncatalyzed and catalyzed reactions respectively .

Since E' < E, the rate of the catalyzed reaction k' > rate of uncatalyzed

reaction k.

Mechanism of catalysis

The catalyst forms an unstable short lived intermediate with the reactant.The intermediate then decomposes to give the product and the catalyst comes out unchanged.

Reactant + Catalyst ---------→ Intermediate

Intermediate ----------→Product + Catalyst

Example : Friedel Craft's reaction using anhydrous AlCl3 as catalyst

$CH_3COCl + an.AlCl_3 \longrightarrow CH_3COCl.AlCl_3$

Acetyl chloride Intermediate

$CH_3COCl.AlCl_3 + C_6H_6 \longrightarrow CH_3COC_6H_5 + HCl + AlCl_3$

Acetophenone

$CH_3COCl + C_6H_6 \longrightarrow CH_3COC_6H_5 + HCl$

Some industrial catalysts used on a large scale are :

1) Aluminosilicates ($Al_2O_3 + SiO_2$) in cracking of petroleum to give smaller fractions,
2) Fe along with Mo as promoter in the manufacture of ammonia by Haber's process,
3) V_2O_5 in the manufacture of sulphuric acid by Contact Process
4) Raney nickel in hydrogenation of ethylene to ethane and propene to propane.

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