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Kinetics and Mechanism of Catalyzed Reactions

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ABSTRACT

A central atom is found in a complex compound. Generally, this central atom is a metal which is surrounded by a group of neutral molecules or anions. These surrounding molecules are co-ordinated to the central atom with the help of pair of electrons residing in the donor atoms. A metal ion is in equilibrium with the surrounding molecules resulting in the formation of metal complex. A stability constant is used so as to measure the extent of interaction between two species in case of equilibrium. The current article highlights the kinetics and mechanism of catalyzed reactions.

1. Introduction

The rate of a reaction depends on the activation energy. It is observed that activation energy and rate of a reaction are indirectly proportional to each other i.e. the rate of a reaction tends to increase on increasing the activation energy and vice-versa. Hence, for a higher rate of a chemical reaction, it is needed that the activation energy should be low.

To minimize the activation energy, some catalysts are used in chemical reaction so that the rate of reactions can be enhanced. Enzymes can be used as biological catalysts.

The surrounding molecules around the central atom are also known as ligands. Suppose, there is a metal 'M' and 'A' is a ligand then the association of metal and ligands results into the formation of complex species ranging from MA_1, MA_2, MA_3……MA_n.

Assume that the complex species formed as a result of this association; have only one nucleus and the obtained product is not soluble in water. In that case, the equilibrium can be written as:

$$M + A \Longleftrightarrow MA \qquad K_1 = [MA]/ [M]\,[A] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$MA + A \Longleftrightarrow MA_2 \qquad K_2 = [MA_2]/ [MA]\,[A] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$MA_{n-1} + A \Longleftrightarrow MA_n \qquad K_n = [MA_n]/ [MA_{n-1}]\,[A] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where,

'n' represents the maximum co-ordination number of the metal ion 'M'.

'Kn' represents the stepwise stability constant.

There is an alternative method to express the stepwise complex formation equilibrium which is mentioned below:

$$M + A \Longleftrightarrow MA \qquad ß_1 = [MA]/ [M]\,[A] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$M + 2A \Longleftrightarrow MA_2 \qquad ß_2 = [MA_2]/ [MA]\,[A]^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

$$M + nA \Longleftrightarrow MA_n \qquad ß_n = [MA_n]/ [MA_{n-1}]\,[A]^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where,

ß represents the stability constant.

The overall stability constant for 'n' number of metal complexes 'M' is expressed as

$$ß_n = K_1\,K_2 \ldots\ldots K_n \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

The value of $ß_n$ and K_n depends on the ionic strength of medium.

2. Discussion

The following reaction can be used for the metal species which show the charges.

$$M + A \Longleftrightarrow MA \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

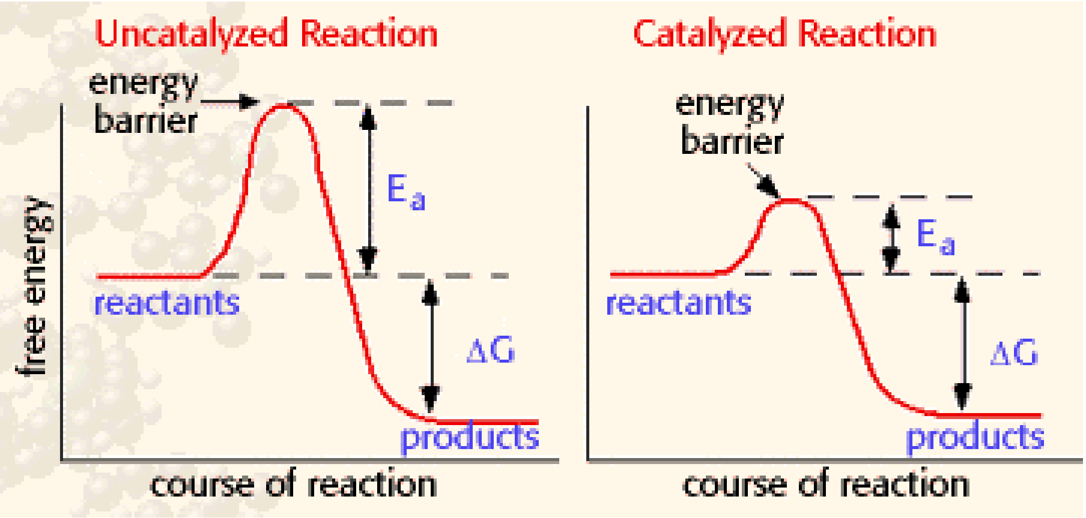
In that case, the thermodynamic stability constant is expressed as:

$$KT = \frac{[MA]}{[M]\,[A]} \times \frac{fMA}{fM \times fA} = K.\ \frac{fMA}{fM \times fA} \quad \ldots\ldots\ldots\ldots (9)$$

where,

'f' represents the activity coefficients

The following figure shows the impact of using catalysts on the activation energy of the reaction.



Here, enzymes can be used as biological catalysts to lower the energy barrier thereby increasing the rate of reaction.

In the last decade, the research activity on the field of biomass conversion to chemicals and fuels has significantly increased as the necessity for the utilization of renewable carbon sources has become more evident. The renewable carbon sources are the carbon dioxide and the biomass, such as triglycerides (fats, vegetable oils), animal byproducts, and organic wastes, predominantly lignocellulosic materials. Triglycerides are transesterified or hydroconverted to get fuel components.

The primary degradative processing of other biomasses involves either gasification, or pyrolysis, hydrolysis, and/or fermentation. The pyro-oils or aqueous solutions obtained in mentioned processes usually give oxygen-rich organic compounds, referred to as platform molecules, which are valuable chemical intermediates. Among them mention must be made about the glycerol and fatty acids obtainable from triglyceride. Abundant platform intermediates are the carboxylic acids having 2 to 6 carbon atoms, including aliphatic mono and dicarboxylic acids, the oxo or hydroxy substituted derivatives thereof, and the furan mono and dicarboxylic acids.

The platform molecules have to be processed to get more valuable chemicals or fuel. In order to get quality fuels the oxygen content of these compounds must be reduced favorably in a catalytic process. Heterogeneous catalysts applying complex bi- or trimetallic catalysts seem to gain more and more significance in the biomass upgrading technologies.

Catalytic hydrodeoxygenation (HDO) is a plausible solution for upgrading oxygen-rich platform materials. The value of the HDO product strongly depends on the catalytic selectivity. For instance, HDO of short chain carboxylic acids can give either gaseous hydrocarbons or liquid phase alcohols, where latter is representing higher value as chemical or fuel component.

3. Analysis

In contrast to Cu-zeolites the Ni-zeolites do not get fully reduced in H2 even above the highest HDO temperature applied in the present study (360 °C). The residual nickel cations stabilize a relatively large fraction of the zeolite in crystalline form. The HDO properties of In-modified Ni-zeolite catalysts (NiIn/Ni,H-zeolite) were not studied yet. The aim of present work was to understand the relationship between the structure and the HDO activity of NiIn/Ni,H-zeolite catalysts using octanoic acid (OA) as model reactant.

Nickel-zeolites (A, X, P) were prepared from NaA (Baylith), NaX (product of the late VEB CKB, Bitterfeld-Wolfen, Germany) and NaP (Crosfield Zeocross) powders, by conventional aqueous ion-exchange using nickel(II)acetate solution. The amount of Ni2+ ions in the applied solution was about equivalent to the ion-exchange capacity of the zeolite. The preparations were designated as 13NiA, 11NiA, 10NiX, and 8NiP where the number gives the Ni content of the sample in weight percent. Bimetallic catalyst precursors were obtained by adding 10 wt.% indium(III)oxide to the Ni-zeolite and grinding the mixture in agate mortar. The catalysts prepared from the precursor by H2-reduction are designated as In13NiA, In11NiA, etc.

The catalytic hydrogenation of OA was carried out in a high-pressure fixed bed flowthrough reactor at 21 bar total pressure in the temperature and space time (or WHSV) ranges of 240-360 °C and 0.3-2 h (or 0.5-3.3 h -1), respectively. Each catalyst precursor was reduced in hydrogen flow in situ in the reactor at 450 °C for 1 h in order to generate active supported metal prior to the catalytic test.

The reactor effluent was cooled to room temperature and the liquid and gas phase products were separated. The liquid was analyzed by a gas chromatograph (GC, Shimadzu 2010) equipped with flame ionization detector and a CPFFAP CB capillary column. The gas was analyzed by an on-line GC (HP 5890) equipped with thermal conductivity detector and Carboxen 1006 PLOT capillary column. The activity and the selectivity of the catalysts were characterized by product distributions represented by stacked area graphs. In this representation, the distance between two neighboring curves gives the yield of the specified product in weight percent.

It is to be mentioned that no bulk indium phase could be detected in any of the above described reduced Ni-zeolite/In_2O_3 composites even below the melting temperature. That can indicate that the melt indium was perfectly dispersed in the pores and on the surface of the support and the nickel metal particles and the high dispersion was retained even at room temperature, where the indium phase must be solid.

4. Conclusions

Indium-modified supported Ni catalysts has been discovered to be highly efficient for reduction of fatty acids by hydrogen. Hydrogen reduction of Ni-zeolites at 450 °C generates nickel particles on the outer surface of the zeolite crystallites. However, the Nizeolites become partially reduced and suffer only partial loss of crystallinity, if any. The indium modification of the Ni particles effectively promotes HDO of carboxylic acids to alcolhols in consecutive steps and hinders mono- or bimolecular alcohol dehydration.

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