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DEVELOPMENT OF NEW TECHNOLOGY FOR OBTAINING DI-ISOPRPYL ETHER FROM ISO-PROPYL ALCOHOL USING TECHNOLOGY OF AEROSOL NANOCATALYSIS

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ИЗУЧЕНИЕ НОВОЙ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ДИИЗОПРОПИЛОВОГО ЭФИРА ИЗ ИЗОПРОПАНОЛА В УСЛОВИЯХ ТЕХНОЛОГИИ АЭРОЗОЛЬНОГО НАНОКАТАЛИЗА

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An improved production of Di-isopropyl ether based on technology of aerosol nanocatalysis, through the dehydration of isopropanol using a vibrating fluidized bed reactor on a Na-X zeolite catalyst. The overall process involves a single stage synthesis of DIPE, by contacting the isopropanol feed on a zeolite catalyst using aerosol nanocatalysis technology, while controlling parameters of vibration (Gigahertz) and temperature (Celsius). DIPE product is recovered using fractional distillation, by separating the liquid product using a fractional distillation column, in order to produce DIPE free from water.
Key words: *aerosol nanocatalysis, DIPE, isopropanol, NaX zeolite*

1. Introduction

The need to eliminate lead-based octane enhancers in gasoline has provided an incentive for the development of processes to produce high octane gasoline blended with lower aliphatic alkyl ethers as octane boosters. Oxygenates such as lower molecular weight alcohols and ethers, particularly isopropanol (IPA) and di-isopropyl ether (DIPE) are in the gasoline boiling range and are known to have high blending octane numbers [1].

Di-isopropyl Ether (DIPE), although not currently produced at an industrial level, represents an important option as an oxygenate due to its anti-knocking properties and low volatility among other features. Although it presents a disadvantage of auto-oxidation with the subsequent production of low solubility and explosive peroxides. To neutralize this effect, the addition of anti-oxidants which does not allow the production of more peroxides than the ones formed during MTBE synthesis [2].

The need to find or develop DIPE as an alternative oxygenate, was as a result of the environmental issue like water poisoning that Tert-Methyl Butyl Ether (MTBE) causes, and it being resistant to degradation by chemical and biological means. While in comparison with Tert-Ethyl Butyl Ether (ETBE), the high cost of ethanol which is used as a reactant in synthesizing ETBE, has brought about doubts about it being an economically viable option.

DIPE has shown to be very promising, because it has a high octane number of 105,and has shown an optimal value of vapor pressure, when compared to that of MTBE, it's not yet shown to be toxic to the environment, and no research so far has been done on it causing adverse systemic effects or tissue toxicity, it's also been said it reduces NO_x emissions , in comparison with MTBE [1]. DIPE can also be applied to gasoline the same way MTBE and ETBE are currently being applied as shown in (table 1).

Table 1

Comparison of the basic properties of ethers used as additives to increase the octane number of gasoline

Indicators	MTBE	ETBE	DIPE
Density at 20°C kg/m^3	746	746	750
Blending Octane (R+M)/2	110	112	105
Water Solubility	4.3	1.2	2.0
Reid Vapor Pressure (RVP)	8.0	4.0	5.0
Boiling Point, °C	55	73	69
Oxygen Content	18.2	15.7	15.7

Currently in the industry DIPE is produced as a byproduct in the production of isopropanol by the reaction of isopropylene and water. However, there are various suggestions for obtaining DIPE from propylene and water in a single stage and a two-stage process of isopropyl alcohol and also from acetone [3], unlike other ethers DIPE utilizes propylene from the refinery and does not depend on an outside supply of alcohol. Mobil Research and Development Corporation has developed a new process that converts propylene and water to DIPE [3].

$$2C_3H_6 + H_2O \leftrightarrow C_3H_7OC_3H_7 \quad (1)$$

Preparation of DIPE involves a combination of reactions in contact with a particular catalyst which catalyze the formation of DIPE simultaneously over different routes.

DIPE is usually produced by dehydration of isopropanol (IPA), isopropanol is produced by the hydration of propylene

$$C_3H_6 + H_2O \leftrightarrow C_3H_7OH \quad (2)$$

There is also formed some by products DIPE, by a series of equilibrium reactions, whose some total maybe expressed by

$$2C_3H_6 + H_2O \leftrightarrow C_3H_7OC_3H_7 \quad (3)$$

Isopropanol can also be partially dehydrated to DIPE, in accordance with the

$$2C_3H_7OH \leftrightarrow C_3H_7OC_3H_7 + H_2O \quad (4)$$

This reaction is acid catalyzed, and also reversible.

DIPE can also be prepared by reacting propylene with propanol, this can be expressed by

$$C_3H_6 + C_3H_7OH \leftrightarrow C_3H_7OC_3H_7 \quad (5)$$

It is very possible, that partial dehydration of isopropanol to DIPE can be achieved using a particular type of catalyst for such reactions and under appropriate conditions, there can also be achieved simultaneously with the dehydration, some alcoholysis of propylene (its addition is optional) to form additional DIPE.

Currently, the reactors mostly used in the industries for the synthesis of DIPE are fixed bed type reactors, which involve high temperature, high pressure, and acidic catalysts. These catalytic systems usually encounter challenges that involve:

- The need for constant regeneration of catalyst.
- The use of high concentration of catalyst (about 700kg/m^3 of reactor).
- Necessity of permanent supply of a catalyst since after 1-2 seconds of work, additional losses of the catalyst due to abrasion takes place.

A successful synthesis of DIPE depends on a lot of factors which are:

- Temperature
- Pressure
- Ratio of catalyst and type of catalyst in the reactor
- The feed , i.e. proportion of free propylene (if applied) to IPA in the feed
- Catalyst contact time (which is inversely proportional to LHSV)
- Activity of the catalyst

It is difficult to interrelate the various parameters that have been disclosed, this is where the purpose of my research comes in, which involves the synthesis of ethers: DIPE, using the technology of Aerosol Nano catalysis (AnC) on a Vibrating Fluidized Bed (AnCVFB). This technology was developed by Professor M.A Glikin in Severodonestk, Ukraine [4].

This AnC technology is based on the mechanochemical effect arising under constant mechanical action of the catalytically active material. The catalyst system of AnC technology involves a dispersing material.

During the continuous motion of the dispersing material, in a vibrating bed, the vibrations ensure that there is always constant friction and grinding of the catalytically active material, which induces the mechanochemical activation (MCA) of the catalyst, which leads to a change in the thermodynamic potentials of the activated catalytically active material by giving it induced surface defects grinding to nano sized state.

2. Analysis of the current level of research in the field of AnC.

Implementation of catalytic processes under AnC technology (without support) reduces the amount of catalytically active substance (up to 10^6 fold) and removes restrictions (mechanical and thermal) associated with the use of a supported catalyst [4]. Thus it is possible to reduce the flow temperature, in which by doing so, removes the possibility of producing unwanted reactions and increases feed conversion.

Initially aerosol nanocatalysis technology has been implemented in a catalytic system with the catalyst system operating like that of the fluidized bed.

This process is called aerosol nanocatalysis fluidized bed (AnCFB - Aerosol nanoCatalysis with Fluidized Bed). In this process, the mechanochemical activation of the catalyst was carried out by dispersing the fluidized material. In this embodiment, the technology required significant costs of reagents and compliance with tight gas dynamic modes.

The next step was the development of another technology of AnC installation which was Aerosol nanocatalysis technology using vibrating bed layer. Where mechanochemical activation of the catalyst is carried out by vertical reciprocating movements of laboratory reactor and a catalyst system located inside it [5].

The process was named aerosol nanocatalysis in vibrating bed layer (AnCVB - Aerosol nanoCatalysis with Vibrating Bed).The efficiency of reactor with a capacity of vibro-impact layer was higher than the reactor with the fluidized bed, in addition, there were new possibilities for controlling the kinetics of the process [6]. The vibration enables the ideal mixing of reactants on the catalytic surface, resulting in high catalytic activity, as reactants will have equal and easy access to the catalyst surface.

CONCLUSIONS

- Implementing the basic principles of AnC technology in a vibrating fluidized bed in the synthesis of DIPE using isopropyl alcohol (IPA) as the feed.
- Understanding the influence of catalyst activity to the selectivity of DIPE as a product using AnC technology using various catalysts.
- Understanding the correlation of different temperature, pressure ranges in the dehydration of isopropanol (IPA) to DIPE.
- Evaluating the rate of production of DIPE calculated in gm-mols/hr/gm of catalyst (active ingredients only) in the reactor (gm/hr/gCat).
- Determine the best conditions for DIPE synthesis using AnC technology.
- Qualitative mathematical processing and analysis of experimental data with a well-defined optimal regime of the synthesis project.

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Филиппс Тобенна Чимдиади, Кудрявцев С.А., Гликина И.М. Изучение новой технологии получения диизопропилового эфира из изопропанола в условиях технологии аэрозольного нанокатализа

Изучены свойства эфиров, в том числе диизопропилового эфира. Проанализированы методы их получения и механизм протекания реакции. Рассмотрены преимущества и недостатки этих методов. Предложена новая технология получения ди-изопропилового эфира из изопропанола в условиях аэрозольного нанокатализа в реакторе с виброожиженным слоем катализатора (цеолитм NaX). Проанализированы условия возможного протечения процесса. Определена методика определения эфиров методом фракционной перегонки смеси.

Ключевые слова: *аэрозольный нанокатализ, диизопропиловый эфир, изопропанол, цеолит NaX*

Філіппс Тобенна Чімдіаді, Кудрявцев С.О., Глікіна І.М. Вивчення нової технології отримання діізопропілового ефіру з ізопропанолу в умовах технології аерозольного нанокаталізу

В статті наведені дослідження властивостей етерів на прикладі діізопропілового етеру. Проаналізовані методи їх отримання та механізм перебігу реакції. Розглянуті переваги та недоліки промислових методів отримання етерів. Запропоновано нову технологію для отримання діізопропілового етеру з ізопропанолу в умовах аерозольного нанокаталізу в реакторі із віброзрідженим шаром каталітичної системи NaX. Проведено аналіз можливих технологічних параметрів перебігу нового процесу. Визначено методику аналізу продуктів реакції шляхом фракційної перегонки суміші.

Ключові слова: *аерозольний нанокаталіз, діізопропіловий етерр, ізопропанол, цеоліт NaX*

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