



Extended activity of zeolite catalysts with CO₂ as reaction medium

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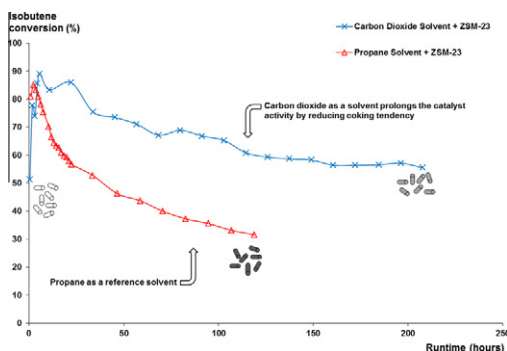
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HIGHLIGHTS

- ▶ CO₂ is a potential solvent option for industrial applications.
- ▶ The catalyst activity maintained on a higher level with CO₂ solvent.
- ▶ Lower carbon dioxide emissions are expected due to the steadier catalyst activity.
- ▶ CO₂ results differ in selectivity compared to propane solvent.
- ▶ Standard engineering simulation tools give valuable information of phases.

GRAPHICAL ABSTRACT



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ABSTRACT

Isooctane is a typically used vehicle fuel component. However, the synthesis of isooctane is limited due to the coking phenomenon when using zeolite catalysts. In this paper the suitability of CO₂ as a solvent for zeolite based acid catalytic reactions was studied in general and isobutene dimerization in particular. The special focus of this study was to clarify whether using CO₂ as a solvent reduces coking compared to propane, which was used as a reference solvent in this case. The reaction was carried out in a 50 cm³ continuous stirred tank reactor with two solid acid catalysts, ZSM-5 and ZSM-23 zeolites. Besides the desired dimerization reaction, the oligomerization reaction was also considered. The study also includes determination and discussion on phase conditions. Calculations based on thermodynamic methods show that the reaction phase may change during the experiment from a single phase (liquid, gas or supercritical) to a two phase domain (coexistence of vapor and liquid). Experiments with the ZSM-23 catalyst gave initial isobutene conversion of above 80%. The conversion with CO₂ was approx. 56% after ~200 h whereas with propane it was approx. 32% after about 120 h. These results were similar also over the ZSM-5 catalyst. The reduced coking tendency results in lower carbon dioxide emissions as the need for burning off the coke in catalyst regeneration is decreased. The results show that carbon dioxide is a potential solvent for industrial purposes as it prolongs the catalyst activity due to a reduced coking tendency.

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1. Introduction

Isooctane (2,4,4-trimethylpentane) can be used as a gasoline component because it provides the necessary high octane number boost for gasoline to avoid coking phenomena inside an internal combustion engine. Isooctane has also low vapor pressure, but

does not contain aromatic compounds or sulfur. Gasoline is a mixture of hydrocarbons, including 2-methoxy-2-methylpropane (MTBE). However, MTBE causes environmental and health concerns and the legislation in a few countries has limited its use. MTBE can be substituted with isooctane [1–9]. A common way to synthesize isooctane is through the dimerization of isobutene (2-methyl-2-propene) to form isooctene (2,4,4-trimethylpentene) followed by hydrogenation. The other method to produce high quality gasoline components is alkylation of isobutane with *n*-butene [2,10,11].

In heterogeneous solid acid catalytic reactions and also for silica alumina based acid catalysts, the coking phenomenon is a typical problem [3–5,12–16]. Coking decreases the operation period of a catalyst and decreases process efficiency. During isooctene synthesis, coking occurs as the reaction proceeds through oligomerization. The undesired heavier molecules are formed which cannot be removed from the catalyst surface and pores by the reaction solvent [3–5,9,12,14,15,17,18]. New promising and highly selective catalysts are presented as optional alternatives to substitute mineral acids in olefin oligomerization. Zeolites still remain attractive catalysts commercially since oligomerization requires a regenerable and stable catalyst with effective acidic properties for synthesis [19,20]. However, it is difficult to maintain high catalyst activity for prolonged periods [12,14]. Traditionally catalyst activity has been restored through a heating process operation [10,21]. This operation has disadvantages, however, such as catalyst degradation when frequently carried out, and generating carbon dioxide attributing to global warming. Therefore, it is both environmentally and economically preferable to develop new processing alternatives.

Supercritical carbon dioxide (scCO₂) solvent can potentially decelerate the coking phenomenon and maintain high catalyst activity. Supercritical carbon dioxide also dilutes and transports undesired heavier molecules off the catalyst surface [3–5,9,12,14,16,17,22]. Carbon dioxide emissions are reduced as the longer operation period allows a less frequent need for coke burning and provides an alternative use for CO₂. This means indirect decrease in CO₂ emissions. Alkylation is among the most widely studied reactions on solid acid catalysts with scCO₂ [11]. However, the use of supercritical CO₂ solvent has not been studied in the dimerization of isobutene. Advances of scCO₂ to the reactants is discussed widely in the literature [23]. However, less research interest has been put on proper fluid phase determination of reaction mixtures. In this study applied thermodynamic tools have been used in the phase determinations of reaction mixtures.

The aim of this research was to study the impact of the solvent on the catalyst behavior in the dimerization reaction of isobutene wherein CO₂ and propane are comparatively used as a reaction medium, propane being used as a reference solvent. Another aim was to apply thermodynamic tools to the phase determinations.

2. Materials and methods

2.1. Materials

Commercial isobutene delivered by AGA Oy was used as a reagent in the studied dimerization reaction. Two commercially available catalysts delivered by Zeolyst International were used, namely zeolite ZSM-23 (structure type MTT) and zeolite ZSM-5 (structure type MFI) [24]. Coke formation dependence on the catalyst structure was studied with two 10-member ring zeolites where ZSM-5 has a three dimensional and ZSM-23 has a one dimensional structure. The catalysts were prepared to have similar aluminum contents.

BET specific surface areas were 370 m²/g for the ZSM-5 catalyst and 110 m²/g for the ZSM-23 catalyst. BET measurements were

done with a sorptomatic 1900 automatic physisorption–chemisorption apparatus (Carlo Erba instruments). Data were evaluated with Data master version 2 software. The surface area was calculated with the BET equation (Brunauer–Emmett–Teller). Silicon and aluminum contents were determined with Buker S4 X-ray fluorescence (XRF) spectrometry equipped with a Rh end-window X-ray tube. According to the XRF analysis the aluminum content and the Si/Al ratio for ZSM-5 were 1.8 wt.% and 23.8 mol/mol, respectively. The values for ZSM-23 were 2.1 wt.% and 19.7 mol/mol. For analysis, a 0.5 g sample was mixed with lithium tetraborate, melted at 1623 K (1350 °C) and poured into a mold. The resulting glass bead was a homogeneous solid solution, which allows accurate determination of aluminum and silica. This method is superior to wet methods, which suffer from limited solubility of zeolites in acids. The total acidity of the catalysts was measured with temperature-programmed desorption of ammonia (NH₃-TPD) using an Altamira AMI-100 instrument. The total acidity of ZSM-5 was 380 μmol/g and that of ZSM-23 was 690 μmol/g. The sample size was 40 mg. The total acidity was measured by desorption of NH₃ as a function of temperature. The acidity of the zeolites was calculated from the amount of NH₃ adsorbed at 473 K (200 °C) and desorbed between 373 K (100 °C) and 773 K (500 °C). The NH₃-TPD instrument was equipped with a thermal conductivity detector (TCD) manufactured by Gow Mac. A ramp rate of 20 °C/min was applied and the temperature was linearly raised to 773 K where it was held for 30 min. The quantification was made using pulses of known volume of 10% of NH₃ in He.

Two different reagent–solvent mixtures were used as reaction feeds: the first was the focus of the study and the second a reference. The first mixture was commercially prepared (±2%), and its composition was 75 wt.% carbon dioxide, 24 wt.% isobutene and 1 wt.% hexane. Hexane was added to be used as an internal standard. The second mixture was prepared from commercial gases. It consisted of 75 wt.% of propane, 24 wt.% of isobutene and 1 wt.% of hexane. In order to feed the second mixture, nitrogen was added to increase the total pressure.

All feed compositions were confirmed by gas chromatography (GC) using a flame ionization detector (GC-FID), except CO₂ and nitrogen that are not detectable with an FID. A negligible amount of nitrogen dissolves into propane and remains in the feed flow, and this nitrogen is accounted for in the reaction phase determination part in Sections 3.1 and 3.2. However, it was assumed that the role of a small amount of inert N₂ was negligible in terms of the study target and was therefore not analyzed. Commercial nitrogen gas was also used to purge the apparatus and to perform pressure-checks.

2.2. Experimental apparatus

The experimental system is schematically shown in Fig. 1. The safe operating limits of the apparatus were 10 MPa and 573 K. Number 1 in the figure refers to the feed vessel for the reagents. The vessel was weighed and the results were recorded in real time. The feed from the vessel was directed to a membrane pump (Lewa FC1W) equipped with a 2 μm filter (2). The head of the pump was cooled (Lauda RM6) with glycol to avoid cavitations. The target temperature was set to 263 K.

The pressure reactor (Parr-reactor) was made of stainless steel and its type was a continuous stirred tank reactor (CSTR) with an internal volume of 50 cm³. The stirring (350 rpm) was realized by a cubic shaped metal gauze basket operated by an electric motor. There were four agitating blades attached to the basket to enhance stirring. A catalyst bed was placed inside the basket. A thermocouple was placed inside the reactor to monitor internal reactor temperature, rather than the temperature at the reactor wall. An external electrical jacket was used to heat the reactor.

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