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The mechanisms of ethene and propene formation from methanol over high silica H-ZSM-5 and H-beta

Morten Bjørgen [a,*], Finn Joensen [b], Karl-Petter Lillerud [c], Unni Olsbye [c], Stian Svelle [c]

[a] *Norwegian University of Science and Technology, Department of Chemistry, N-7491 Trondheim, Norway*
[b] *Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark*
[c] *University of Oslo, Department of Chemistry, N-0315 Oslo, Norway*

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ABSTRACT

Selectivity control is a key issue in the zeolite facilitated conversion of methanol to hydrocarbons. This work addresses: (a) How the zeolite topology (MFI versus BEA) determines the type of intermediate participating in the catalytic cycle thereby controlling the ethene/propene product selectivity in the methanol to alkenes reaction, and (b) to what extent light alkene formation occurs via aromatic and alkene reaction intermediates for H-ZSM-5. Three catalyst samples have been studied in experiments relying on isotopic labeling. For H-beta, penta- and hexamethylbenzene are involved in an aromatics based hydrocarbon pool type mechanism leading predominantly to propene and the higher alkenes (a very low yield of ethene is observed), whereas for H-ZSM-5, the lower methylbenzenes are the aromatic intermediates and represent the major route for ethene formation. For H-ZSM-5, an alkene based and an aromatics based catalytic cycle for product formation are distinguishable. By conducting co-reaction experiments (MeOH + propene or MeOH + *p*-xylene) over H-ZSM-5 we were able to evaluate the relative rates of ethene and propene formation from both the alkene and the aromatics based catalytic cycles.

1. Introduction

The current high and stable oil prices have sparked interest, both commercially and scientifically, in the development of technologies and processes that may utilize natural gas or coal (or even biomass) rather than liquid petroleum as the source of transportation fuels and raw materials for the petrochemical industry. This situation is manifested by the interest in Fischer–Tropsch based technologies for diesel production from natural gas or coal via synthesis gas (H_2 + CO). However, high octane gasoline and light alkenes for polymerization are not the primary products from a conventional Fischer–Tropsch reactor, and other options must be pursued in order to meet increasing demands of these products. Methanol, which may also be manufactured from synthesis gas, constitutes a convenient chemical intermediate in this respect, because when reacted over solid, acidic zeolite catalysts, methanol may be transformed into gasoline (MTG—methanol to gasoline) and/or alkenes (MTO/MTP—methanol to olefins/propene), depending on catalyst choice and process conditions.

The MTG reaction was discovered and later commercialized by Mobil Oil in 1986, when a plant dimensioned for an annual gasoline production of 600 000 tons over a MFI zeolite catalyst came on stream in New Zealand [1]. However, the gasoline part of the MTG plant was later shut down due to decreasing crude oil prices and only the methanol synthesis step remained in operation [1]. Haldor Topsøe A/S later developed the Topsøe integrated gasoline synthesis (TIGAS) process, in which the methanol synthesis and the gasoline synthesis are integrated in one loop [2]. Two alternatives currently exist for light alkenes production from methanol. The Norsk Hydro/UOP MTO process, which is based on the SAPO-34 catalyst, yields a flexible mixture of ethene and propene [3], whereas Lurgi's MFI based MTP alternative predominantly produces propene with some gasoline as by-product [4]. Lurgi recently announced the successful commercialization of the MTP process with a plant expected to come on stream in 2008 [4].

The understanding of the reaction mechanism of the conversion of methanol to hydrocarbons (MTH) has been greatly advanced over the past years [1,5–7]. Current consensus now favors an *indirect* reaction cycle [8–10] known as the hydrocarbon pool mechanism. Rather than being based on coupling of C_1 entities from methanol or dimethylether, this mechanism involves a series of steps where methanol is added to the hydrocarbon pool, resulting in C–C bond formation and subsequent alkene production. Several studies have shown that methylbenzenes may

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[*] Corresponding author. Tel.: +47 73 59 48 46; fax: +47 73 55 08 77.
E-mail address: morten.bjorgen@chem.ntnu.no (M. Bjørgen).

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constitute the hydrocarbon pool. For example, in H-SAPO-34, propene may be lost from hexamethylbenzene via a series of rearrangements and the resulting trimethylbenzene molecule is then methylated three times by methanol in order to close the catalytic cycle [11]. In the H-beta zeolite, hexamethylbenzene also displays a high reactivity, but the heptamethylbenzenium cation appears to be even more relevant for propene and butene formation [12,13]. Recent research has shown that there are major mechanistic differences from one catalyst topology to another [7]. For H-ZSM-5, we have shown that, *e.g.* hexamethylbenzene is an insignificant reaction intermediate compared to the lower aromatic homologues [7]. Moreover, an additional catalytic cycle, based on repeated alkene methylation and cracking reactions is to some extent in operation over H-ZSM-5. For example, a propene molecule may be sequentially methylated by methanol to give a hexene molecule. Subsequent cracking of this hexene molecule into two propene molecules will result in the net formation of a propene molecule from three methanol molecules.

In this contribution, we compare the mechanisms for conversion of methanol to hydrocarbons over H-ZSM-5 (medium channel dimensions) and H-beta (large channel dimensions) and link the ethene yield to the nature of the active, aromatic reaction intermediates. Further, so far no attempts have been made to address the relative importance of alkenes and aromatics as intermediates within the frame of this recently introduced dual cycle concept [7]. This is addressed by co-reacting ^{13}C MeOH and ^{12}C propene or ^{12}C *p*-xylene over H-ZSM-5, in an attempt to study the reactions of methanol with typical intermediates from each catalytic cycle.

2. Experimental

2.1. Catalysts

Two H-ZSM-5 samples with Si/Al = 50 (ZeoChem AG) and 140 (Zeolyst International) and a dealuminated zeolite H-beta (Si/Al = 120, PQ Zeolites) have been used. H-ZSM-5 (Si/Al = 50) consists of particles of average size ~1 μm, whereas H-ZSM-5 (Si/Al = 140) consists of somewhat larger particles of average size ~3 μm. The H-beta sample consists of particles of average size around 0.2 μm. The H-ZSM-5 (Si/Al = 140) and H-beta samples have been characterized extensively previously [7,14,15].

2.2. Reaction studies

All reactions were carried out at 350 °C in a fixed bed reactor using 60 mg catalyst. The catalyst powder was compressed to wafers that were crushed and sieved to obtain particles in the size range 0.25–0.42 mm. Methanol, either ^{13}C enriched (Cambridge Isotope Laboratories, 99% ^{13}C purity) or ordinary ^{12}C methanol (BDH Laboratory Supplies, >99.8% chemical purity) was fed by passing a controlled He carrier gas stream through a saturation evaporator. Three types of experiments, all involving methanol feed, were performed in order to obtain mechanistic information:

(1) By using two separate and identical feed lines, it was possible to switch from ^{12}C to ^{13}C methanol without otherwise disrupting the experimental conditions. Ordinary ^{12}C methanol (130 hPa, $\text{WHSV}_{\text{MeOH}} = 7\ \text{g}\ \text{g}^{-1}\ \text{h}^{-1}$) was reacted for 18 min at 350 °C. After switching to ^{13}C methanol feed, the isotopic compositions of effluent compounds were determined at increasing ^{13}C methanol reaction times (0.5, 1, and 2 min). Immediately after the final effluent analysis (*i.e.* after ~ 2 min of ^{13}C methanol reaction), the reaction was quenched and the material retained inside the zeolite channels was analyzed (see below).

(2) ^{13}C-methanol (130 hPa, $\text{WHSV}_{\text{MeOH}} = 7\ \text{g}\ \text{g}^{-1}\ \text{h}^{-1}$) was reacted alone for 18 min at 350 °C. Then, a minor flow of pure ^{12}C-propene (0.17 N mL/min) was added as a co-reactant to the He/methanol stream, resulting in a propene partial pressure of 4.3 hPa and a ^{13}C:^{12}C carbon ratio of 10. The propene flow was kept small in order keep the system as equal to the pure methanol system as possible. After a total of 20 min on stream (2 min of co-reaction) effluent analyses were carried out and immediately after, the reaction was quenched and the organic material retained in the zeolite was analyzed (see below).

(3) Finally, co-reaction experiments with ^{13}C methanol and ^{12}C *p*-xylene were performed, also at 350 °C. In this case, both reactants were fed from the beginning of the experiment and the methanol feed rate ($\text{WHSV}_{\text{MeOH}}$) was increased to $25\ \text{g}\ \text{g}^{-1}\ \text{h}^{-1}$. *p*-Xylene was fed ($\text{WHSV}_{\text{xylene}} = 2.5\ \text{g}\ \text{g}^{-1}\ \text{h}^{-1}$) by saturating part of the He stream. The obtained partial pressures of methanol and xylene were 90 and 2.7 hPa, respectively, giving a ^{13}C:^{12}C carbon ratio of 4. Effluent analysis was carried out after 20 min of reaction.

2.3. Analysis of organic material retained in the zeolite

After being removed from the reactor and rapidly cooled to room temperature, a part of the catalyst mass (40 mg) was transferred to a screw-cap Teflon vial and dissolved in 1.0 mL 15% HF. Thereafter, 1.0 mL CH_2Cl_2 (Fluka puriss) was added to the thus obtained solution to extract the liberated organic molecules from the aqueous phase. After phase separation, the CH_2Cl_2 extract was analyzed using GC–MS. The technique of dissolving the zeolite crystals in HF to recover confined constituents by extraction has been used earlier in related studies [7,16] and was introduced by Guisnet and co-workers [17].

2.4. Chromatography

The reactor effluent was analyzed by an on-line GC–FID. The isotopic compositions of the retained compounds (extracted from the HF aqueous phase) and effluent were analyzed on two GC–MS set-ups in order to obtain adequate separation of all compounds, from C_2 to C_{12}. A thorough description of the chromatographic set-up has been given previously [7].

3. Results and discussion

As pointed out in Section 1, previous research has indicated fundamental differences between ethene and propene in the MTH reaction, both with respect to formation and further reaction [7]. In the present study, we have conducted several experiments to obtain a more complete description of the formation mechanisms and roles as intermediates played by the light alkenes and the methylbenzenes. First, we study the incorporation of methanol into both the gas phase products and the reaction intermediates trapped within the zeolite voids by switching from ^{12}C to ^{13}C methanol for both H-ZSM-5 and H-beta. Based on the findings thus obtained, co-reaction of ^{13}C methanol and ^{12}C propene or ^{12}C *p*-xylene was carried out over H-ZSM-5, in order to study the reactions of methanol species selected to be representative for two groups of reaction intermediates within the dual cycle concept [7].

3.1. Composition of retained hydrocarbons and gas phase products for H-ZSM-5 and H-beta

Table 1 lists conversion and selectivity data (carbon based) for the two H-ZSM-5 samples and the H-beta sample after 15 min on stream of methanol conversion ($\text{WHSV} = 7\ \text{g}\ \text{g}^{-1}\ \text{h}^{-1}$) at 350 °C. The two H-ZSM-5 samples give fairly similar results, except that