Experimental report

17/09/2018

Proposal: **7-05-470**

Council: 10/2016

Title: INS characterization of the carbonylation of methanol using mordenitezeolite

Research area: Chemistry

This proposal is a resubmission of 7-05-463

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Samples: CH3COOCH3
CH3OCH3
Mordenite + CO + CH3OCH3
Mordenite zeolite (Si/Al = 10)
Mordenite + CH3OCH3
Mordenite + CH3COOCH3

Instrument	Requested days	Allocated days	From	To
IN1	5	4	03/04/2018	07/04/2018

Abstract:

Acetic acid is a very important bulk chemical. Currently, the most of acetic acid is produced through the carbonylation of methanol using Iodide promoted Iridium or Rhodium catalysts. As such catalysts are expensive and their large amount is required, their substitution by acid heterogeneous catalysts in the methanol carbonylation, known as Koch process, has been of growing interest in recent years. Among, many solid acid catalysts, zeolites and particularly mordenite (MOR) have shown very high activity, selectivity and stability, being a promising new technology for this particular production.
The carbonylation of methanol and dimethyl ether evolve to the desired acetic acid or ester (acylation process). MOR may be used as a catalyst in this process as it has been shown by previous studies that the rate of methyl acetate synthesis (per total Al content) is the highest on H-MOR (Si/Al=10:1).
The main objective of this project is to study the mechanism of CO + CH3-O-CH3 <=> CH3-COO-CH3 reaction on zeolite mordenite, aiming to detect the possible methoxy adsorbed intermediate. If the methoxy intermediate is not formed, the mechanism must be revised and a new one could be suggested.

The carbonylation process of methanol and dimethyl ether (CH3OCH3, DME) presented in **Figure 1** result in formation of acetic acid or ester, the chemicals which are used in different important industrial synthesis.

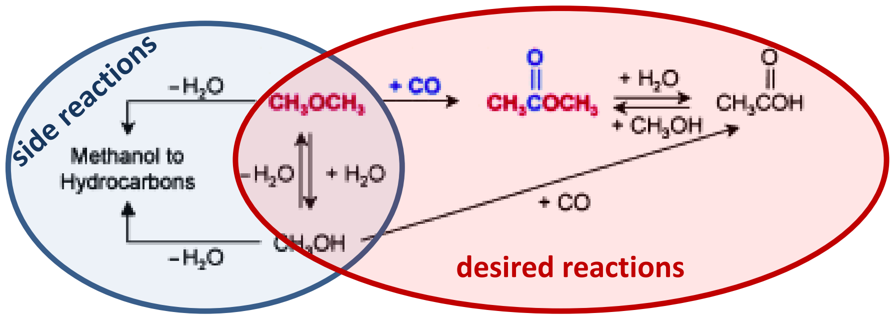


Figure 1. Network of carbonylation, hydration, dehydration, and methanol-to-hydrocarbon chemistries

The carbonylation process should be performed with use of catalysts (such as acidic zeolites) and it occurs concurrently with side reactions [1]. Nowadays, it is a challenge to find acid catalysts that promote carbonylation reaction, while keeping the speed of side reactions as low as possible. In this project, we proposed to study the catalytic activity of mordenite (MOR) zeolite in carbonylation reaction of methanol and dimethyl ether.

It is believed that the carbonylation process presented in **Figure 1** includes two important reactions which lead to the so-called 'methoxy absorbed intermediate':

CH3-O-CH3 + MOR-OH --> **MOR-O-CH3** + CH3-OH (I)

CH3-OH + MOR-OH --> **MOR-O-CH3** + H2O (II)

First, the methoxy adsorbed mordenite is formed as a result of interaction between dimethyl-ether (DME) and pure mordenite (see reaction (I)). Second, Methoxy absorbed intermediate (highlighted in the above mechanism) is produced as a result of the interaction between the acid center of the zeolite and the DME or methanol (see reaction (II)). If the methoxy intermediates are not formed, the mechanism must be revised and a new one could be suggested.

Therefore, the goal of this INS study was to observe the methoxy adsorbed form of mordenite and, hence, confirm the proposed mechanism of the carbonylation reaction.

The experiment consisted in several steps in order to observe the processes described by reactions (I) and (II):

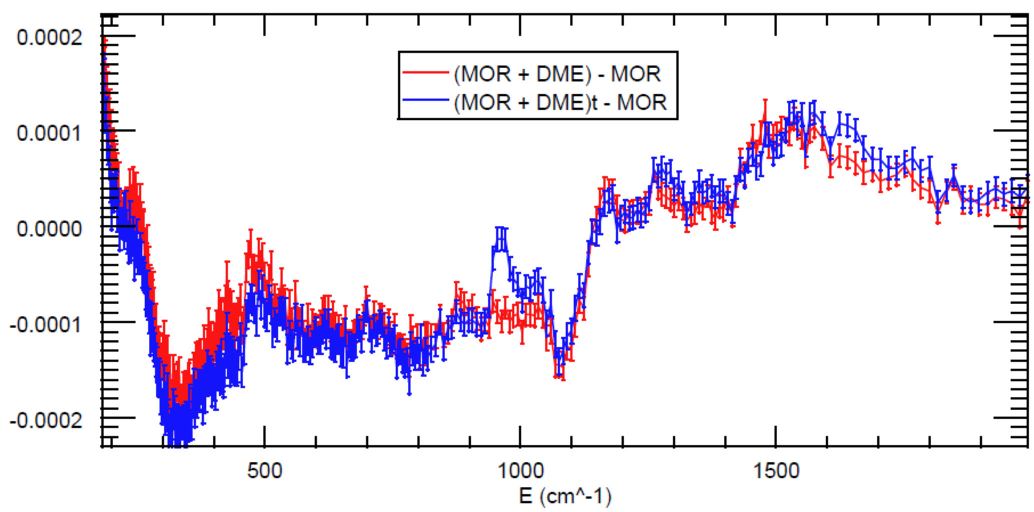
1) It has been measured evacuated MOR sample;

2) Dimethyl-ether (CH3-O-CH3) has been measured as the reference;

3) The sample of DME with MOR have been measured without heating;

4) The sample of DME with MOR have been measured after heating to 400°C.

We supposed that certain amount of heat initiate the reaction between MOR and DME. Thus, in order to observe the possible differences that may occur with (MOR + DME) system after heating we compared 2 spectra (see Figure 2): red spectrum corresponds to the subtraction of the spectrum measured for pure MOR from the spectrum measured for the system (MOR + DME), while blue spectrum corresponds to the subtraction of the spectrum of MOR form the spectrum measured for the system (MOR + DME) after heating. By subtracting the spectrum corresponding to pure MOR we can only observe the changes that happened to DME and, hence its methoxy groups.



It can be seen that a new peak appears at around 980 cm^{-1} after the system (MOR + DME) has been heated. This can be explained by the following: in the initial system DME does not interact with MOR, while after the system is heated the reaction is initiated and the peak found at 980 cm^{-1} might correspond to the newly formed methoxy adsorbed group.

Refernces

[1] P. Cheung et al. , Angew. Chem. Int. Ed. 2006, 45, 1617 –1620.