The Mechanism of the Gas-Phase Esterification of Acetic Acid and Ethanol over MCM-41

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Esterification reactions are conventionally carried out using homogeneous acids, such as sulphuric acid. Especially in view of catalyst separation, the use of heterogeneous catalysts is now heavily pursued. In the current work we have assessed the potential of MCM-41 as a solid esterification catalyst and tested this in esterification of acetic acid and ethanol as a model reaction. Whereas the mechanism for the homogeneously catalysed esterification is long known, this does not hold for the esterification over heterogeneous catalysts. Using transient and steady state experiments, temperature-programmed desorption (TPD), and isotopic labelling experiments, the esterification mechanism over MCM-41 (Si/Al = 16) is studied. Gas-phase esterification of acetic acid with ethanol over MCM-41 (Si/Al = 16) is shown to proceed via a Langmuir–Hinshelwood-type mechanism, involving a protonated acetic acid intermediate. © 2001 Elsevier Science

INTRODUCTION

Esterification reactions are industrially conducted as a homogeneously catalysed batch process. Typical catalysts are (Brønsted acidic) sulphuric acid or (Lewis acidic) Sn–octoate. Brønsted acidic homogeneous catalysts are corrosive and need to be neutralised after reaction (forming salts) and Lewis acidic, metal-containing, catalysts need to be removed carefully after reaction. This can be done for instance by adsorption on bleaching earth, which however leads to the formation of large amounts of waste. The use of heterogeneous catalysts in esterification is preferable since these are easily separated from reactants and products by filtration and allow the use of a continuously operated fixed bed.

Many heterogeneous catalysts have been reported in the literature to be active in esterification; ion exchange resins (1), H–ZSM-5 (2), zeolite Y (3, 4), niobic acid (5), sulphated oxides (6–8), hydrous zirconium oxide (9), and supported heteropolyacids (10). In a concurrently performed study, amorphous catalysts (silica–aluminas), crystalline materials (H–ZSM-5 and H–Beta), and mesoporous hexagonally structured materials (MCM-41) have all been tested on their activity and selectivity in gas-phase esterification. In

this article, the mechanism of the MCM-41-16 catalysed gas-phase esterification of acetic acid and ethanol is the main topic. The structure of MCM-41 catalysts is depicted in Fig. 1.

Although the mechanism of homogeneously catalysed liquid-phase esterification is long known (11), there is still no clarity on the heterogeneously catalysed gas-phase reaction. Chu *et al.* (10) claim that the esterification mechanism of acetic acid with butanol over carbon-supported HPA catalysts proceeds via a protonated alcohol intermediate, but most authors (3, 4, 12) proposed a protonated carboxylic acid as the reaction intermediate. The two possible intermediates, protonated ethanol and protonated acetic acid, are shown in Fig. 2.

Attempts were also made to distinguish between an Eley–Rideal- and a Langmuir–Hinshelwood-type mechanism. Literature data concerning this point are contradictory: several authors (1, 12) claim that the reaction proceeds via a Langmuir–Hinshelwood mechanism, but others propose an Eley–Rideal mechanism (4, 13). Chu *et al.* (10) studied gas-phase esterification of acetic acid with butanol and ethanol over heteropolyacids supported on carbon. They proposed a dual-site Langmuir–Hinshelwood mechanism for the esterification of acetic acid with ethanol, but a single-site Eley–Rideal-type mechanism for esterification of acetic acid with butanol, i.e., butanol adsorbed at the catalyst and acetic acid reacting from the gas-phase. In many cases the discrepancies between proposed mechanisms may be attributed to minor differences in correlation constants when fitting activity data to kinetic equations. In the case of butanol, Chu observed that the activity is found to be proportional to the acetic acid concentration, but in the case of ethanol as the reacting alcohol an optimum in activity is found as a function of the acetic acid concentration. This difference may be explained by the stronger adsorption of butanol as compared to ethanol, and thus both reactions may in fact proceed according to a Langmuir–Hinshelwood mechanism.

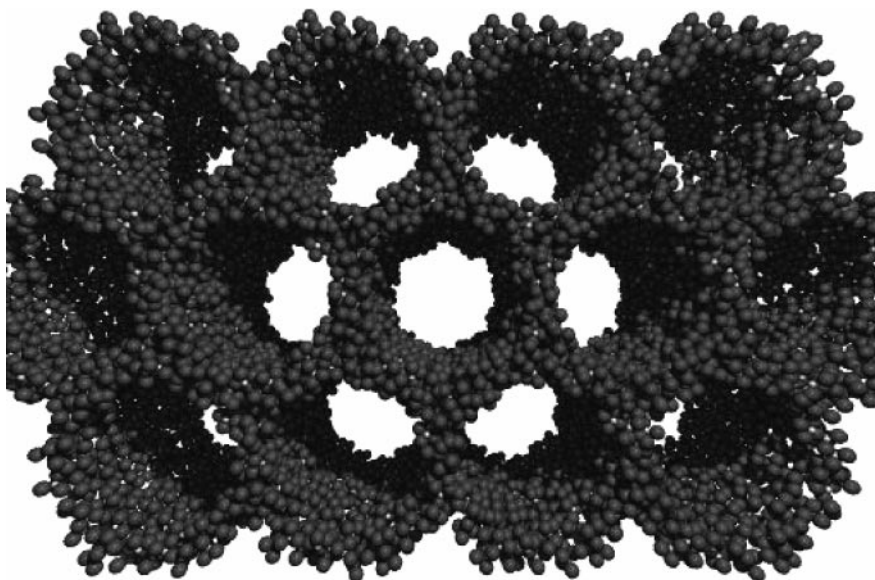Corma *et al.* (3) concluded from a study into the liquid-phase esterification of phenyl acetic acid and

FIG. 1. Impression of the structure of MCM-41. This picture was kindly provided by R. Hanssen, Eindhoven University of Technology.

ethanol/isopropanol over partially exchanged Na–H–Y zeolites that strongly acidic sites form the active sites. From the observation that ethanol dehydration does not correlate to the strength of acidic sites, whereas the esterification reaction does, Corma *et al.* conclude that the reaction proceeds via a protonated carboxylic acid and not via protonated ethanol. Therefore, these reactions apparently do not proceed via the same intermediate.

Santacesaria *et al.* (4) studied the gas-phase esterification of acetic acid and ethanol over HY zeolite. These authors did not find a linear correlation of the activity with the number of acidic sites; therefore, they conclude that two different mechanisms contribute to the activity, only one of them proceeding over the acidic sites.

The aim of this study is to determine unambiguously the mechanism of the gas-phase esterification of ethanol and acetic acid over MCM-41-16. Evidently, there is no agreement in the literature on a generic mechanism of esterification over solid acids. This may mean that the mechanism is different for the various catalysts and substrates or may depend on gas- or liquid-phase operation.

Steady state experiments are performed to determine the order in ethanol and acetic acid. TPD experiments of used catalysts are conducted to measure the surface coverage of both reactants. Both types of experiments should provide indications of the predominant reaction mechanism. The protonated intermediate in the mechanism can unambiguously be determined using step-response transient experiments with isotopically labelled reactants.

EXPERIMENTAL

Step-response transient experiments are performed using a standard flow setup. Acetic acid and ethanol are added in a saturator to an argon flow, which is further on mixed with a helium flow to be able to vary the concentrations and flows independently. Step-response experiments are conducted by switching the feed from an inert flow to a flow with one of the reactants. The second reactant is pre-adsorbed on the catalyst at the reaction temperature, after which the catalyst is flushed with inert for half an hour to ensure the absence of this reactant in the gas-phase. The reaction is monitored by mass spectrometry (MS). Various step-response measurements are conducted in the absence of catalyst to calibrate for the various reactants and products and to ensure a sufficiently fast response time of the analysis equipment.

The temperature range investigated ranges from 398 to 473 K. The reactant concentration is varied from 0.25 to 1.0 vol%, but is typically kept at 0.5 vol%. Temperature-programmed desorption (TPD) experiments are conducted in the same experimental setup, by increasing the temperature from the adsorption or reaction temperature to 723 K at a rate of 10 K/min.

MCM-41 (Si/Al = 16) catalysts were prepared as described by Beck *et al.* (14) and Janicke *et al.* (15). Amberlyst-15
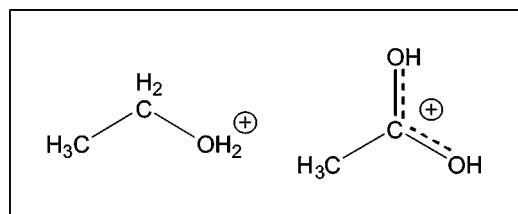

FIG. 2. Possible protonated intermediates in the esterification of ethanol (left) and acetic acid (right).

TABLE 1

Properties of the Catalysts

Catalyst	Code	Producer or literature reference	N_2-BET area (m²/g)	Si/Al ratio
MCM-41-16	MCM-41-16	Refs. (14, 15)	739	16
SiO₂–Al₂O₃–KDC	SA–KDC	Akzo Nobel	322	0.2
SiO₂–Al₂O₃–HA	SA–HA	Akzo Nobel	380	2.6
Amberlyst-15	Amberlyst-15	Aldrich	—	—

(Aldrich) and the silica–aluminas SA–KDC and SA–HA (Akzo Nobel) are used as reference catalysts. The properties of the catalysts can be found in Table 1.

Acetic acid p.a. and ethanol p.a. were obtained from Aldrich. O^{18}–O^{18} acetic acid (95% O^{18}) and O^{18}–ethanol (95% O^{18}) are obtained from Isotec, Inc.

The O^{18}-labelled reactants are injected in the gas stream through a septum and used in adsorption only. Extensive analysis of the fragmentation patterns of ethyl acetate and the O^{18}-labelled reactants was performed to enable the quantitative interpretation of the experiments.

RESULTS AND DISCUSSION

Variation of Reactant Concentration

Four catalysts (SA–HA, SA–KDC, Amberlyst-15, and MCM-41-16) were used in an experiment, consisting of four stages (I–IV) with different reactant concentrations. Either the acetic acid or ethanol concentration was 0.5 vol%, while the concentration of the other reactant was half or double this value. Figure 3 shows that the ester yield over Amberlyst-15 and MCM-41-16 depends on the acetic acid concentration but hardly on the ethanol concentration. In stage III the ethanol concentration is four times higher than
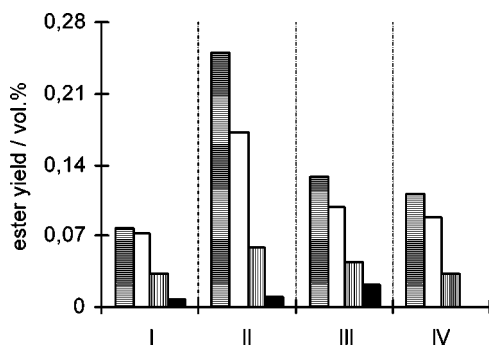

FIG. 3. Concentration dependence of ester yield in gas-phase esterification of acetic acid and ethanol at 448 K over (▤) Amberlyst-15, (▯) MCM-41-16, (▥) SA–HA, and (▮) SA–KDC at 4 concentration sets (vol%): (I) 0.25 acetic acid, 0.5 ethanol; (II) 10 acetic acid, 0.5 ethanol; (III) 0.5 acetic acid, 1.0 ethanol; (IV) 0.5 acetic acid, 0.25 ethanol. Flow is 50 ml/min, 50 mg of catalyst.
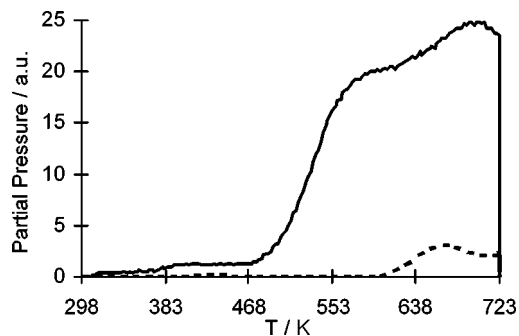

FIG. 4. TPD of MCM-41-16 after reaction of acetic acid with ethanol: black line, ethene (ethanol) partial pressure (a.u.); dashed line, CO_2 (acetic acid) partial pressure (a.u.).

in stage IV, but the ester yield is almost equal in these stages for Amberlyst-15 and MCM-41-16.

SA–KDC, a silica–alumina with a very high Al content, shows the opposite behaviour of MCM-41 and Amberlyst-15; the ester formation is constant, i.e., independent of acetic acid concentration, for the first two stages and increases significantly with higher ethanol concentrations in stages III and IV. SA–HA shows intermediate behaviour; the ester yield over SA–HA depends both on the acetic acid and the ethanol concentration, although more strongly on the acetic acid concentration.

TPD of Used Catalysts

Some of the catalysts are studied after reaction by TPD. To this end, catalysts were selected with varying Al content because the way the conversion depends on the reactant concentrations differs significantly (see Fig. 3). Amberlyst-15 is not incorporated in TPD measurements, as it is not stable at temperatures over 473 K.

For all catalysts similar results were obtained in TPD of pre-adsorbed ethanol and acetic acid. At elevated temperatures ethanol decomposes into ethene and water. Acetic acid also decomposes and forms methane and CO_2. Ethene and CO_2 are therefore monitored to analyse the surface coverage of acetic acid and ethanol during reaction.

MCM-41-16 is more active in esterification than either SA–HA or SA–KDC. MCM-41-16 contains moderately strong acidic sites and its activity in esterification depends on the acetic acid partial pressure (Fig. 3). TPD of a used MCM-41 (Si/Al = 16) catalyst (Fig. 4) yields almost exclusively ethene, indicating high ethanol and low acetic acid coverage on the surface during reaction. This is in good agreement with a reaction order of 0.6 in the acetic acid partial pressure in esterification and the approximately zero order in ethanol, assuming a Langmuir–Hinshelwood-type mechanism. The amount of acetic acid present on SA–HA (24% alumina) during reaction (Fig. 5) is higher than that of MCM-41-16, whereas the silica–alumina KDC (84% alumina) shows the highest acetic acid/ethanol ratio of all
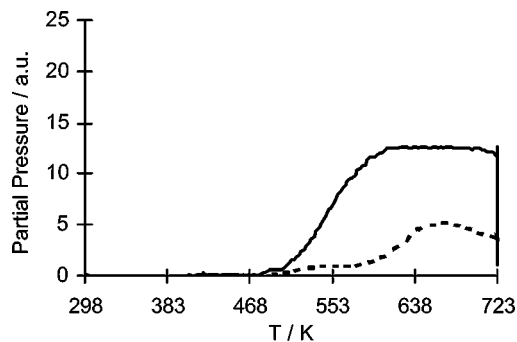
FIG. 5. TPD of SA–HA after reaction of acetic acid with ethanol: black line, ethene (ethanol) partial pressure (a.u.); dashed line, CO_2 (acetic acid) partial pressure (a.u.).

catalysts tested (Fig. 6). The amount of acetic acid present during reaction on the catalytic surface apparently is related to the alumina content. The esterification activity of the catalyst with the highest alumina content and the most acetic acid on the surface during reaction, silica–alumina KDC, is ethanol partial pressure dependent. As mentioned before, the catalyst with high activity in esterification, MCM-41-16, contains mostly ethanol on its surface and the reaction order in acetic acid is high and in ethanol is low.

The steady state esterification of acetic acid with ethanol observed for the various catalysts (Fig. 3), in combination with TPD after reaction (Figs. 4–6), shows that MCM-41-16, the most active catalyst of the three used with TPD, contains mainly ethanol on the surface. The fact that during the esterification reaction alcohol dehydration did not occur, whereas this latter reaction is found to proceed in the presence of ethanol only (as can be seen in Fig. 7), proves that acetic acid is adsorbed on the active sites during esterification. For a higher Al content of the catalyst, the steady state coverage of acetic acid on the catalyst during reaction increases as well. The reaction order in ethanol of the high Al catalysts and the order in acetic acid of the low Al catalysts indicate that both reactants should be adsorbed on the catalyst to react.
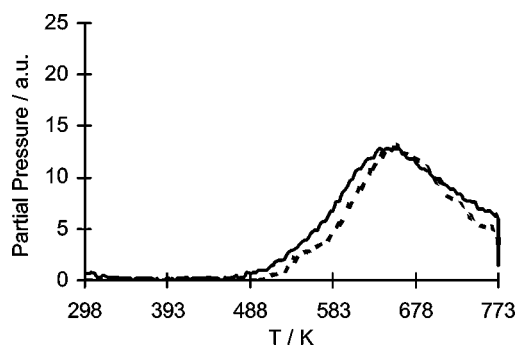

FIG. 6. TPD of SA–KDC after reaction of acetic acid with ethanol: black line, ethene (ethanol) partial pressure (a.u.); dashed line, CO_2 (acetic acid) partial pressure (a.u.).
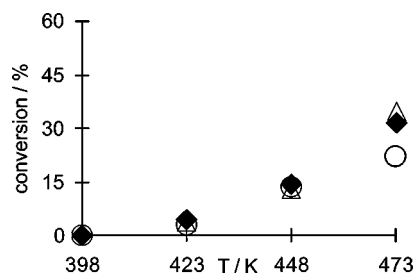

FIG. 7. Conversion of ethanol (0.5 vol% in N_2, flow 50 ml/min) in the ethanol dehydration over 50 mg of catalyst: (○) MCM-41-16; (△) SA–KDC; (◆) SA–HA.

A Langmuir–Hinshelwood mechanism with a protonated acetic acid molecule is thus expected on the basis of these results. This is in agreement with the results of Corma *et al.* (3), who showed that the esterification activity of the tested catalysts depends on the number of strongly acidic sites. This also points at the above-mentioned mechanism since acetic acid is more difficult to protonate than ethanol and thus stronger acidic sites are required.

Transient Experiments

Transient experiments are conducted to verify this mechanism, as these enable the discrimination between an Eley–Rideal and a Langmuir–Hinshelwood mechanism. Using O^{18}–labelled ethanol and acetic acid, one may distinguish between mechanisms involving protonated ethanol and those involving a protonated acetic acid.

MCM-41 (Si/Al = 16) is used as the catalyst in all experiments described in this section. A typical experiment consists of several steps. First, the catalyst is heated in an inert flow at 498 K. Subsequently, either ethanol or acetic acid is pre-adsorbed on the catalyst at the reaction temperature (448 K), with breakthrough being observed by MS. Again, an inert flow is passed over the catalyst for half an hour and subsequently a step change in the concentration of the second reactant is implemented, allowing the reaction to commence. The two experiments are described below.

Reaction of Ethanol with Adsorbed Acetic Acid over MCM-41-16

Acetic acid initially desorbs when ethanol is introduced in the reactor. Subsequently, ethyl acetate formation starts (Fig. 8). Ethyl acetate continues to be formed until all acetic acid is removed from the surface, as is shown by TPD recorded after reaction. The formation of ethyl acetate reaches a maximum soon after introduction of ethanol in the reactor, but ethyl acetate continues to be formed during a considerable time span after this maximum is reached. During the titration of acetic acid by ethanol, the formation of diethyl ether increases, indicating that both reactions proceed over the same active sites.
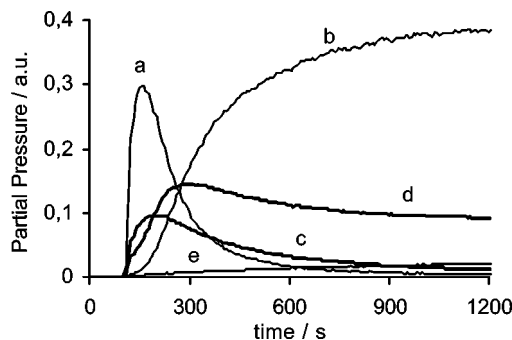
FIG. 8. Product partial pressures following a step change in the ethanol concentration from 0 to 0.5 vol% over MCM-41-16, preadsorbed with acetic acid. $T = 448$ K. (a) acetic acid, (b) ethanol, (c) ethyl acetate, (d) water, and (e) diethyl ether.

FIG. 10. Product partial pressures following a step change in the O^{16}–ethanol concentration from 0 to 0.5 vol% over MCM-41-16, preadsorbed with O^{18}–O^{18}–acetic acid. $T = 448$ K. ($\diamond$) H_2O^{18}, ($\triangle$) O^{18}–O^{16}–ethyl acetate, and ($\square$) O^{18}–O^{18}–ethyl acetate.

Reaction of Acetic Acid with Adsorbed Ethanol over MCM-41-16

During pre-adsorption of ethanol on MCM-41-16, ethanol reacts to diethyl ether and water. At the moment acetic acid is introduced in the reactor, a part of the adsorbed ethanol, water, and diethyl ether is removed from the surface by acetic acid (Fig. 9). Only at this point does the esterification start, suggesting that acetic acid needs to adsorb on the surface to react with ethanol and form ethyl acetate. Again, ethyl acetate continues to be formed for a long period.

Both experiments discussed above indicate that the predominant mechanism is of the Langmuir–Hinshelwood type. In the case of an Eley–Rideal mechanism, an instantaneous maximum would be expected in the ester yield following the introduction of the gas-phase reactant in the reactor. The latter is observed for neither acetic acid nor ethanol as gas-phase reactants. In both cases ethyl acetate is formed during a long period of time after this maximum in ester yield. A maximum in the ester yield is not observed at the moment the pre-adsorbed reactant is desorbed (and therefore in the gas-phase) due to the introduction of the
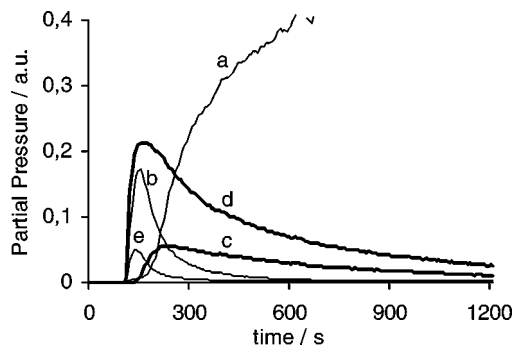
gas-phase reactant. This means that desorption, followed by reaction from the gas-phase (Eley–Rideal), is not a likely explanation for the observation that in both experiments ethyl acetate is formed for a long period of time after the introduction of the gas-phase reactant.

Step-Response Experiments with Adsorbed O^{18}–Labelled Reactants

Results of transient experiments with adsorbed O^{18}-labelled acetic acid and O^{16}–ethanol in the gas-phase are shown in Fig. 10. When the dominant reaction mechanism would proceed via a protonated acetic acid intermediate, any water formed during reaction should contain O^{18} and the ethyl acetate should contain one O^{18} per molecule as well. When, in contrast, the reaction proceeds over a protonated ethanol intermediate, both labeled O-species of acetic acid end up in the ethyl acetate and no H_2O^{18} should be found. From Fig. 11 it is obvious that $O^{16}O^{18}$–ester and H_2O^{18} are formed and no $O^{18}O^{18}$–ethyl acetate is formed.

This experiment unambiguously shows that, for MCM-41-16 catalysts, the esterification proceeds over a

FIG. 9. Product partial pressures following a step change in the acetic acid concentration from 0 to 0.5 vol% over MCM-41-16, preadsorbed with ethanol. $T = 448$ K. (a) acetic acid, (b) ethanol, (c) ethyl acetate, (d) water, and (e) diethyl ether.
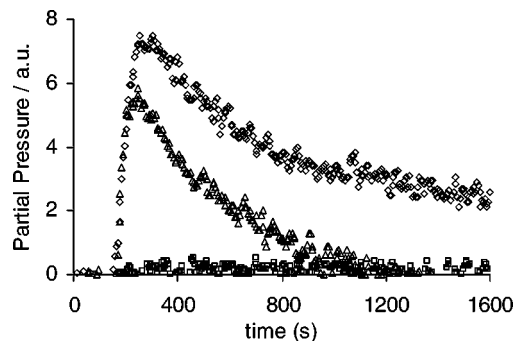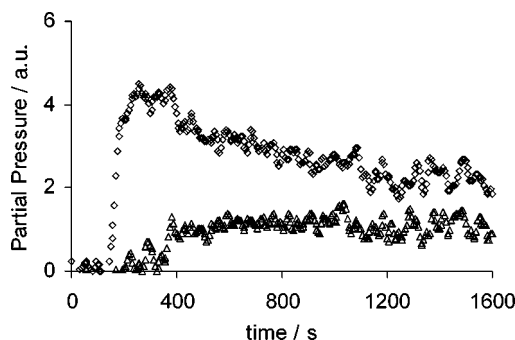

FIG. 11. Product partial pressures following a step change in the O^{16}–O^{16}–acetic acid concentration from 0 to 0.5 vol% over MCM-41-16, preadsorbed with O^{18}–ethanol. $T = 448$ K. ($\diamond$) H_2O^{18} and ($\triangle$) O^{18}–O^{16}–ethyl acetate.

protonated acetic acid intermediate and not over protonated ethanol.

The reverse experiment with adsorbed O^{18}–ethanol and $O^{16}O^{16}$–acetic acid in the gas-phase is shown in Fig. 11. In a reasoning similar to that for the first experiment, O^{18}–water is formed in the case protonated ethanol is the reaction intermediate, whereas $O^{16}O^{18}$–ester is expected in the case of a protonated acetic acid intermediate. Based on the experiment with labelled acetic acid, formation of the O^{18}–ester is expected. However, both O^{18}–ester and O^{18}–water are formed in this experiment. The presence of H_2O^{18} can be understood since H_2O^{18} is formed during diethyl ether formation, accompanying the adsorption of O^{18}–ethanol (see also Fig. 8). Labelled water is partially retained on the surface and desorbs from the surface when acetic acid is introduced, as is seen in Fig. 9. When the esterification proceeds over a protonated ethanol intermediate, the O^{18} of ethanol would end up exclusively in water and no $O^{16}O^{18}$–ethyl acetate would be found. Figure 11 shows that both $O^{16}O^{18}$–ethyl acetate and H_2O^{18} are formed. Therefore, additional evidence is obtained that the reaction mechanism includes protonation of acetic acid.

CONCLUSIONS

The gas-phase esterification of acetic acid and ethanol was investigated over MCM-41 catalysts to elucidate the reaction mechanism. To this end we used step-response experiments, TPD after reaction, steady state kinetic, and isotopic labelling experiments. The experimental results all point to the same conclusion: gas-phase esterification of acetic acid with ethanol over MCM-41-16 proceeds via a protonated acetic acid intermediate and follows a Langmuir–Hinshelwood pathway. The reaction mechanism is therefore similar to that identified for homogeneous

acids: protonation of the adsorbed acetic acid at the acid site followed by a reaction with ethanol.

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