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Journal of Catalysis 236 (2005) 21–33

JOURNAL OF CATALYSIS

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The detailed kinetics and mechanism of ethyl ethanoate synthesis over a Cu/Cr_2O_3 catalyst

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Received 1 July 2005; revised 30 August 2005; accepted 1 September 2005

Abstract

Ethyl ethanoate is produced industrially in a process that came on-stream in March 2003 using liquid ethanol as the feed. The catalyst was Cu/Cr_2O_3, and the reactor temperature was 473 K. The selectivity to ethyl ethanoate was 95%. Detailed kinetic and mechanistic studies of this process were conducted in a multipurpose microreactor system, using an on-line mass spectrometer controlled and interrogated by computer. Isothermal frontal gas adsorption chromatography experiments using ethanol as the adsorbate in the temperature range 300–473 K found that a H_2 pulse was detected immediately after the ethanol contacts the catalyst. The fact that H_2 evolved from the Cu/Cr_2O_3 catalyst at 300 K indicates that the dehydrogenative adsorption of ethanol to form an adsorbed ethoxy species $[(CH_3CH_2O)_{(a)}]$ occurred on the Cu component of the catalyst. A plot of the logarithm of the amount of H_2 evolved on adsorption against the reciprocal of the adsorption temperature gives an activation energy to adsorption of 31 $kJ\,mol^{-1}$. Temperature-programmed studies on the adsorbed ethoxy species showed that some of these ethoxy species dehydrogenated at 425 K with a surface activation energy of 94 $kJ\,mol^{-1}$ to form the adsorbed acetyl species $(CH_3CO)_{(a)}$. The adsorbed ethoxy and acetyl species combined on the surface to form adsorbed ethyl ethanoate. The ethyl ethanoate desorbed at a peak maximum temperature of 680 K. Ammonia temperature-programmed desorption experiments produced a desorption peak for NH_3 at 680 K, revealing the existence of a strong Brönsted acid site on the surface of the Cr_2O_3. Thus the ethyl ethanoate desorbing at 680 K was bonded to the Cu/Cr_2O_3. Temperature-programmed reaction (TPR) studies, in which ethanol was passed continuously over the Cu/Cr_2O_3 catalyst while raising the temperature linearly with time and monitoring the products of reaction continuously on the mass spectrometer, gave an overall activation energy of 92 $kJ\,mol^{-1}$ for ethyl ethanoate formation, the same as that for the dehydrogenation of the adsorbed ethoxy species to form an adsorbed acetyl, suggesting that this might be the rate-determining step for the reaction. TPR studies of ethanol over unsupported polycrystalline Cu gave identical results to those of the Cu/Cr_2O_3 catalyst, confirming that Cu is the active component of the catalyst.

Keywords: Ethyl ethanoate; Copper/chromia catalyst; Kinetics and mechanism; Temperature programmed desorption/reaction

1. Introduction

Ethyl ethanoate is an industrially important bulk chemical used primarily as a solvent in the paints, coatings, and inks industries. It is produced commercially by one of three processes: (i) esterification of ethanol by acetic acid, (ii) addition of ethene to acetic acid, or (iii) the dimerisation of ethanol over CaO (the Tischenko reaction). Recently, a new process has been commercialised in which ethyl ethanoate can be synthesised without the need of acetic acid or ethanal [1,2]. In this process ethyl ethanoate is synthesised from a liquid ethanol feed at liquid hourly space velocities between 0.5 and 2 h^{-1} over a Cu/Cr_2O_3 catalyst at 493 K and 15 atmospheres. The selectivity to the product ethyl ethanoate is $>95\%$.

Unlike the esterification of ethanol by acetic acid or the addition of ethene to acetic acid, both of which require the backup of large petrochemical installations comprising hydrocarbon crackers, steam reformers, methanol synthesis, and acetic acid plants, the new process is stand-alone and can use ethanol produced by fermentation from renewable feedstocks, such as

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doi:10.1016/j.jcat.2005.09.012

sugar cane or corn. The process is highly tolerant of a wide range of impurities in the feed and thus can use inexpensive grades of ethanol. Its only byproduct is H_2, which, if the plant is sited near industry, can be exported.

This paper reports a detailed investigation of the kinetics of adsorption, desorption, and surface reaction of ethanol on a well-characterised Cu/Cr_2O_3 catalyst. These studies provide a detailed mechanism of the reaction.

2. Experimental

All of the experiments were conducted in the in situ multipurpose reactor described previously [3–5]. This is a single stainless steel tube reactor (20 cm long, 0.4 cm) connected via a heated capillary to an on-line mass spectrometer (Hiden Analytical, Warrington, UK). The mass spectrometer is capable of following 16 masses continuously with temperature/time. The reactor is housed in a stainless steel block that can be cooled to 77 K (for total area measurements) by pumping liquid N_2 through it. The metal block can be heated to 1100 K in a controlled manner using a Newtronics controller to control the cartridge heaters housed in the block. The thermocouple used to provide the catalyst temperature to the Newtronics controller is housed in the catalyst bed.

The catalyst was characterised by (i) temperature-programmed reduction (TPR) [3], (ii) by N_2 adsorption at 77 K using gas adsorption chromatography for measurement of the total area and (iii) by N_2O reactive frontal chromatography for measurement of the Cu metal area [4]. The adsorptive capacity of the catalyst was determined by isothermal frontal gas adsorption chromatography and by temperature-programmed desorption (TPD) [3]. The kinetics of the reaction were determined by TPR and isothermal rate measurements. The mechanism of the reaction was elucidated by temperature-programmed reaction spectroscopy (TPRS) [3].

2.1. Catalyst

The experiments were carried out on a commercial Cu/Cr_2O_3 catalyst with a Cu:Cr ratio of 1:1, reduced in H_2/He as described below. It had a total surface area of 13.8 $m^2\ g^{-1}$ and a copper metal area of 7.6 $m^2\ g^{-1}$ measured in situ by N_2O reactive frontal chromatography [4]. The catalyst was supplied by Süd-Chemie.

The role of the Cu component of the catalyst was determined by conducting TPR studies of ethanol on unsupported polycrystalline Cu. The unsupported polycrystalline Cu was prepared in situ by temperature-programmed reduction of CuO (BDH) in a fashion identical to that used for the Cu/Cr_2O_3 catalyst. The polycrystalline Cu had a surface area of 2.2 $m^2\ g^{-1}$.

2.2. Reaction mixture

A 12% C_2H_5OH/He stream was prepared by bubbling He though C_2H_5OH held in a saturator at 303 K. The cracking patterns of the reactant ethanol (C_2H_5OH) and product ethyl ethanoate ($CH_3CO_2C_2H_5$) together with those of possible intermediates [e.g., ethanal (CH_3CHO)] and of side products [e.g., methylethyl ketone ($CH_3COC_2H_5$) and crotonaldehyde] were all determined on the mass spectrometer. A mass/charge ratio (m/z) of 31 (the CH_2OH fragment) was taken as characteristic of ethanol; an m/z ratio of 69 was taken as characteristic of ethyl ethanoate. Other m/z ratios included 43 for ethanal, 71 for butanol, 18 for water, and 2 for dihydrogen.

3. Results and discussion

3.1. Characterisation of the bonding of the H_2 to the Cu and Cr_2O_3 components of the Cu/Cr_2O_3 catalyst

Fig. 1 is the TPR profile obtained by heating the Cu/Cr_2O_3 catalyst in H_2/He (5% H_2, 101 kPa, 25 $cm^3\ min^{-1}$) from ambi-

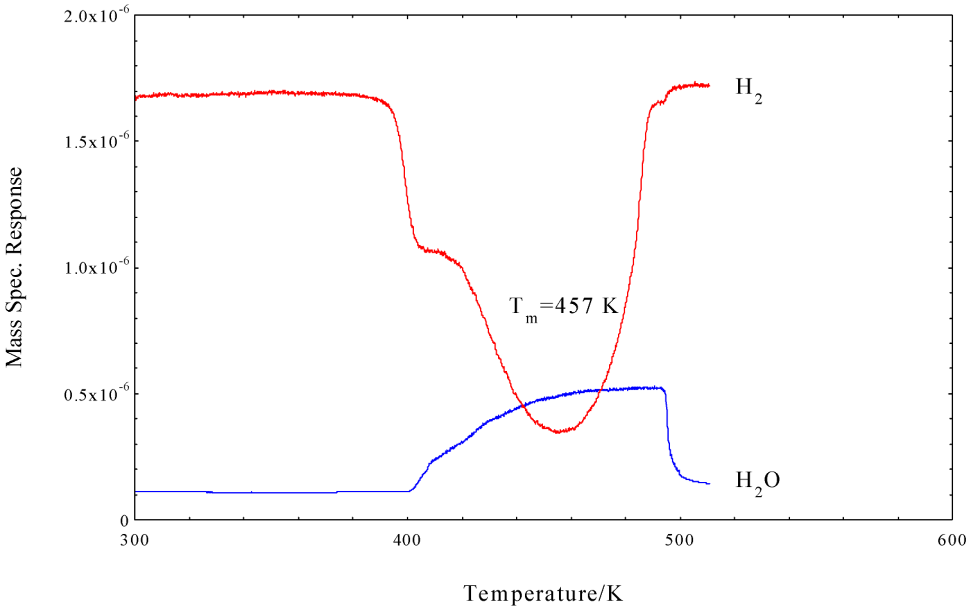

Fig. 1. TPR profile obtained by heating the Cu/Cr_2O_3 catalyst in H_2/He (5%/H_2, 101 kPa, 25 $cm^3\ min^{-1}$) from ambient to 600 K at 0.5 K min^{-1}.

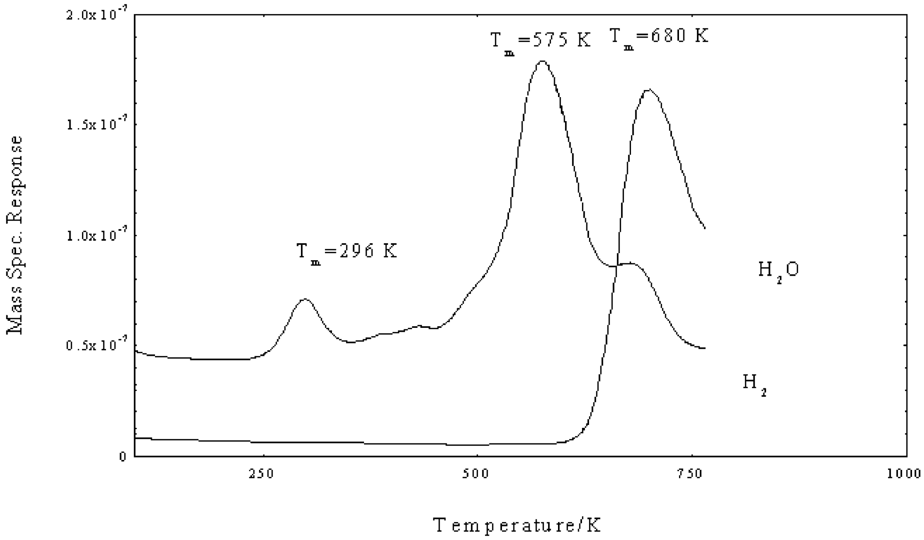

Fig. 2. TPD spectrum of H_2 and H_2O from a Cu/Cr_2O_3 catalyst which had been reduced in H_2 as described in Fig. 1. The reduced catalyst was cooled to 200 K in the H_2/He before being heated at 5 K min^{-1} from 200 to 1000 K.

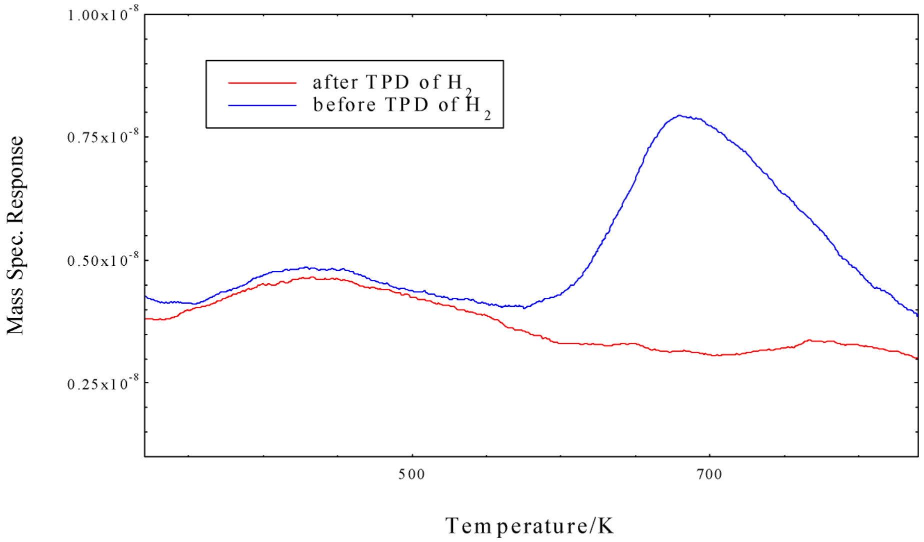

Fig. 3. TPD spectrum of NH_3 from Cu/Cr_2O_3 catalyst on which all the H_2 desorption states at 296, 375, 430, 575 and 680 K exist (black curve). The grey curve is the NH_3 desorption spectrum from the Cu/Cr_2O_3 catalyst which had all of the H_2 desorption states removed by temperature programming.

ent temperature to 600 K at a rate of 0.5 K min^{-1}. The shoulder in the reduction profile at 410 K probably originated from the reduction of the surface oxygens atom. Indeed, on that basis, using a crude deconvolution of the peaks by dropping a vertical at 415 K predicts a Cu dispersion of 17%. The Cu dispersion calculated from the Cu area measuring 7.8 $m^2\ g_{cat}^{-1}$ or 15.6 $m^2\ g_{Cu}^{-1}$ was 16%, giving reasonable support for the proposition. The H_2 and H_2O signals returned to baseline at temperatures $>$500 K, indicating complete reduction of the copper oxide component of the catalyst. However, to ensure complete reduction, the catalyst was held at 500 K under the H_2/He stream for a further 16 h.

Fig. 2 shows the TPD spectrum of H_2 and H_2O from the Cu/Cr_2O_3 catalyst. Thus was obtained by first reducing the catalyst in H_2/He as described above, then lowering the temperature to 200 K in the H_2/He (5% H_2) stream. The flow was then switched to He and the temperature raised from 200 to 1000 K at a rate of 5 K min^{-1}, following $m/z = 2$ (H_2) and $m/z = 18$ (H_2O).

The peak at 296 K represents the recombinative desorption of H atoms on the surface of the Cu [5]. The small peaks at 375 and 430 K probably originated from H atoms located beneath the surface of the Cu [5]. Therefore, the H_2 desorption peaks at 575 and 680 K derived from the Cr_2O_3 component of the Cu/Cr_2O_3 catalyst.

The H_2 peak desorbing at 680 K derived from a strong Brönsted acid site on the surface of the Cr_2O_3. This can be demonstrated by the NH_3 desorption spectra shown in Fig. 3. The NH_3 was dosed on to the reduced Cu/Cr_2O_3 catalyst from a NH_3/He (5% NH_3, 101 kPa, 25 $cm^3\ min^{-1}$) stream at 300 K. The blue line represents the NH_3 desorption spectrum from a catalyst containing all of the H desorption states shown in Fig. 2. The

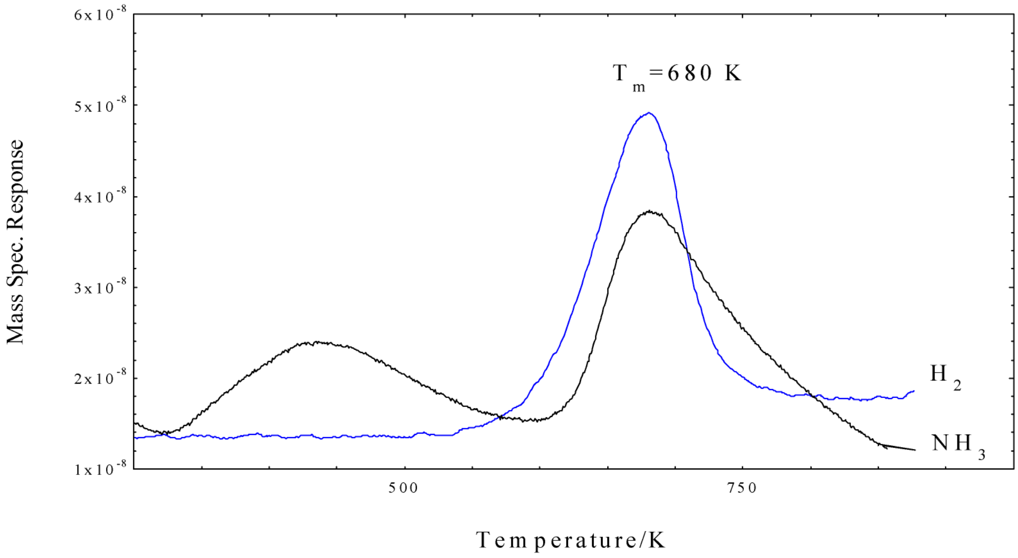

Fig. 4. NH_3 TPD spectrum from the Cu/Cr_2O_3 catalyst from which the H_2 desorption states at 296, 375, 430 and 575 K had been desorbed. The coincident desorption of NH_3 and H_2 is from NH_3 being adsorbed as NH_4^+ on the Brönsted acid site.

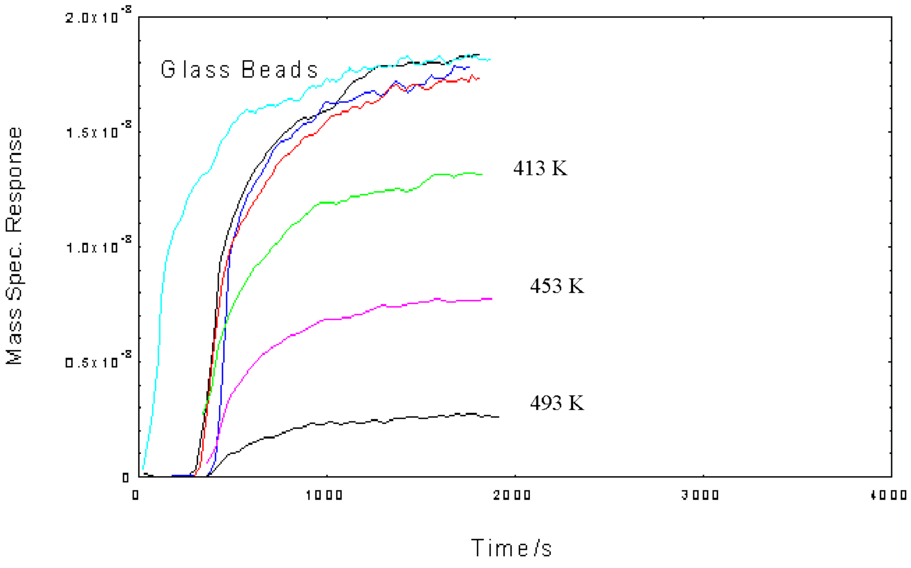

Fig. 5. The time dependence of the ethanol signal obtained by dosing C_2H_5OH/He (12%) on to the reduced and H desorbed Cu/Cr_2O_3 catalyst at 303, 343, 373, 413, 453 and 473 K.

red line in Fig. 3 represents the NH_3 desorption spectrum from which all of the adsorbed H atoms had been desorbed. The NH_3 peak at 680 K was lost. The NH_3 peak at 453 K was unchanged and was probably due to a Lewis acid site on the Cr_2O_3.

Additional evidence for the 680 K H_2 desorption peak being a Brönsted acid is provided in Fig. 4, which shows the NH_3 desorption spectrum from the Cu/Cr_2O_3 catalyst from which the H_2 desorption states at 296, 375, 430, and 575 K had been desorbed by raising the temperature to 600 K in He and cooling to 300 K before adsorbing the NH_3. The figure shows only one H_2 desorption peak at 680 K. The NH_3 peak at 680 K is coincident with that of the H_2, indicating that they derived from a common species—probably the NH_4^+ species. The NH_3 desorbing at 453 K was unaffected by the desorption of H_2 in this temperature range, so its bonding to the Cr_2O_3 was not through a H atom. As stated above, the bonding of the NH_3 in this state to the Cr_2O_3 was probably to a Lewis acid site on the Cr_2O_3.

3.2. Isothermal ethanol adsorption on the Cu/Cr_2O_3 catalyst

Fig. 5 shows the time dependence of the development of the ethanol peak ($m/z = 31$) when the C_2H_5OH/He (12%) ethanol mixture was diverted over the reduced and H desorbed Cu/Cr_2O_3 catalyst, held at 303, 343, 373, 413, 453, and 473 K. The figure also shows the time dependence of the development of $m/z = 31$ peak when the ethanol/He mixture was diverted over glass beads held at 303 K.

Little reaction appeared to occur on the catalyst at 303, 343, or 373 K, because the $m/z = 31$ signal from the catalyst held at these temperatures for >1400 s was roughly the same as that

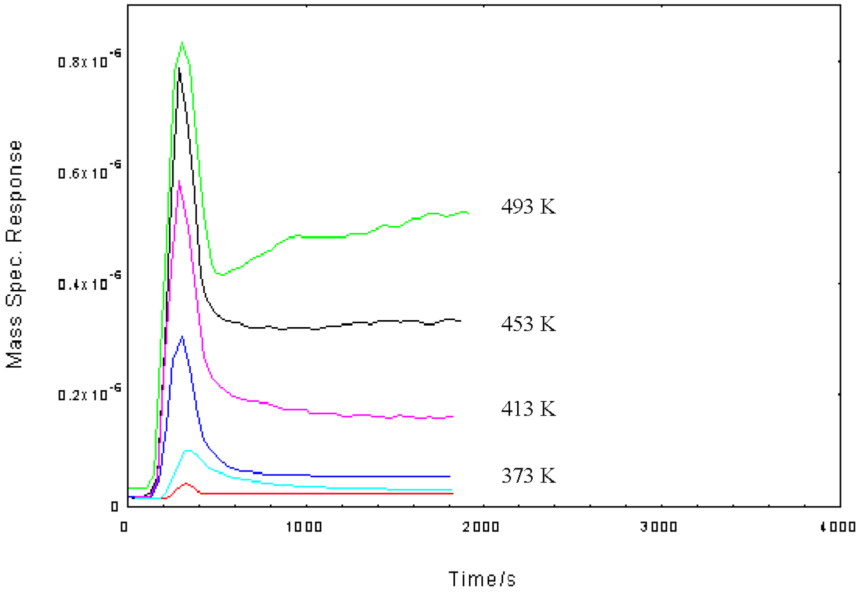

Fig. 6. The H_2 pulse obtained by dosing C_2H_5OH/He (12%) on to the reduced and He desorbed Cu/Cr_2O_3 catalyst at 303, 343, 373, 413, 453 and 493 K.

obtained from glass beads. Clearly, however, significant steady-state conversion of the ethanol occurred over the catalyst above 373 K, as evidenced by the fact that the long-term steady-state value of $m/z = 31$ signal dropped from 1.8×10^{-8} mbar at 303 K to 1.3×10^{-8} mbar at 413 K, 0.8×10^{-8} mbar at 453 K, and 0.3×10^{-8} mbar at 493 K.

Surprisingly, however, when the dihydrogen signal was monitored during the dosing of the ethanol on to the catalyst, the H_2 peak produced clearly indicates that ethanol was chemisorbed on the catalyst at 303 K and above (Fig. 6). A distinct dihydrogen peak was obtained in the temperature range 303–373 K, with the $m/z = 2$ signal returning roughly to its baseline value on completion of the dihydrogen pulse. This process likely occurred on the Cu component of the catalyst, because associative desorption of atomic hydrogen adsorbed on Cu occurs at 303 K [2] and at 575 and 680 K on the Cr_2O_3 (see above). Little or no reaction of the chemisorbed ethoxy species occurs below 373 K, because the long-term $m/z = 2$ signal is barely above baseline in this temperature regime. The peak in the H_2 signal results from the initial interaction of the ethanol with the clean Cu surface. The adsorption of the ethoxy species resulting from the interaction effectively poison the surface to further reaction to an extent determined by the temperature. Thus the chemisorption process is

$$CH_3CH_2OH(g) + 2Cu \rightarrow CH_3CH_2CO(a) + H(a), \qquad (1)$$

$$H(a) + H(a) \rightarrow H_2(g), \qquad (2)$$

where the subscripts “a” and “g” refer to adsorbed and gas phase species, respectively. The steady-state evolution of H_2 at 413 K and above results from the dehydrogenation of the adsorbed ethoxy species.

Two important quantities can be calculated from the dihydrogen peaks shown in Fig. 6: (i) the activation energy for the adsorption of ethanol to form the adsorbed ethoxy species [reaction (1)] and (ii) the surface coverage of the ethoxy species on the Cu, because every H_2 molecule formed corresponds to two adsorbed ethoxy species.

Fig. 7 is an Arrhenius plot of the natural logarithm of the amount of H_2 produced in the pulse versus $1/T$ in the temperature range 303–413 K. The H_2 pulse at 413 K was integrated even though the H_2 signal did not return to its baseline value by extending the descending part of the peak to the baseline. The activation energy for the adsorption of ethanol as ethoxy obtained from this plot was 31 $kJ\,mol^{-1}$.

Table 1 lists the amounts of H_2 evolved in the temperature range 303–493 K (0.5 g catalyst) and the derived ethoxy coverage of the Cu component of the catalyst. It can be seen from the table that the ethoxy coverage of the Cu is submonolayer at temperatures <373 K. The average Cu atom site density on the three low-index Cu crystal faces [Cu(111), Cu(110), and Cu (100)] was 1.4×10^{15} sites cm^{-2} [4]. The value of 0.58×10^{15} ethoxyl species per cm^2 of Cu at 373 K (approximately half monolayer) is probably saturation coverage of the Cu by the ethoxy species due to the difficulty of packing such a large species on the surface.

It is clear from the table that the ethoxy coverages of the Cu at temperatures above 453 K calculated from the amount of H_2 evolved are greater than monolayer. Multilayer coverage of the catalyst by an ethoxy species is impossible, and so both adsorption and reaction are occurring in the pulse. Because the only product observed in the pulse is H_2 (the $m/z = 43$ signal shows no pulse), the form of this reaction appears to be dehydrogenation of the adsorbed ethoxy species

$$CH_3CH_2O(a) + Cu \Longleftrightarrow CH_3CHO(a) + H(a) \qquad (3)$$

and

$$CH_3CHO(a) + Cu \Longleftrightarrow CH_3CO(a) + H(a), \qquad (4)$$

followed by associative desorption of the adsorbed H(a) [reaction (2)].

Corroborative evidence that reaction occurs above 373 K can be found in the increasing loss of gas phase ethanol ($m/z = 31$)

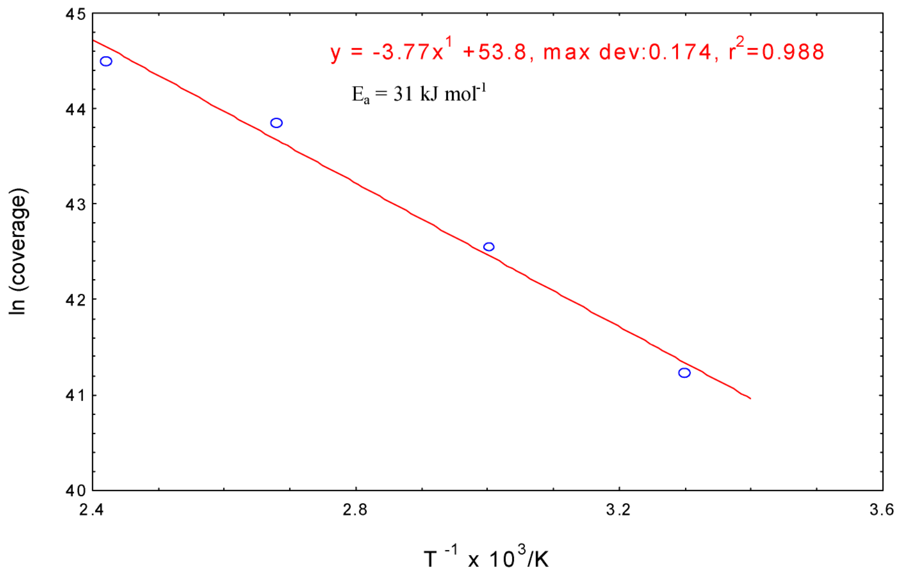

Fig. 7. Arrhenius plot of ln[H_2] versus I/T from H_2 pulses observed after dosing C_2H_5OH/He (12%) on to the reduced and H desorbed Cu/Cr_2O_3 catalyst at 303, 343, 373 and 413 K.

Table 1
Ethoxy coverage of the Cu as a function of the adsorption temperature

Dosing temperature (K)	Evolved H_2 (molecules, $\times 10^{19}$)	C_2H_5(a) species ($\times 10^{19}$)	C_2H_5O(a) coverage of Cu (cm^{-2}, $\times 10^{15}$)
303	0.08	0.16	0.04
333	0.3	0.6	0.18
373	1.1	2.2	0.58
413	2.1	4.2	1.1
453	2.7	5.4	1.4
493	3.5	6.4	1.7

at 413 K and above (Fig. 5) together with the increase in the steady-state values of both the $m/z = 2$ (H_2) (Fig. 6) and $m/z = 43$ (Fig. 8) signals. The $m/z = 43$ signal is a minor cracking fraction of ethanol and ethyl ethanoate but a major one of ethanal.

3.3. TPR of ethanol over the Cu/Cr_2O_3 (1:1) catalyst

Fig. 9 shows the TPR profile obtained by passing the C_2H_5OH/He stream (12% C_2H_5OH) continuously over the Cu/Cr_2O_3 (1:1) catalyst while raising the temperature from ambient to 523 K at 5 K min^{-1}. The m/z ratios 31 (C_2H_5OH), 2 (H_2), 18 (H_2O), 61 ($CH_3CO_2C_2H_5$), 56 ($CH_2OHCH_2CH_2CH_3$), and 43 (C_2H_5OH, $CH_3CO_2C_2H_5$ and CH_3CHO) were followed continuously on the mass spectrometer as the temperature was raised. The figure indicates that whereas the H_2 signal rose continuously from room temperature, the significant increase in this signal occurred only above 400 K. This, then, was the temperature of the onset of reaction. A small water peak can also be seen at the onset temperature of 400 K, so that the evolving H_2 reduced not fully reduced Cu by the initial reduction in H_2He.

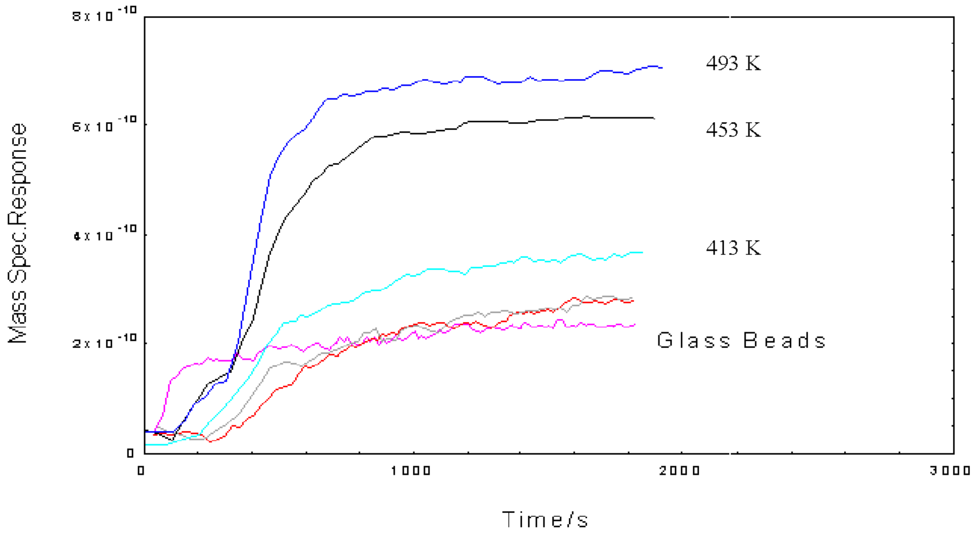

Fig. 8. The time dependence of the $m/z = 43$ signal (possibly ethanol) obtained by dosing C_2H_5OH/He (12%) on to the reduced and H desorbed Cu/Cr_2O_3 catalyst at 303, 343, 373, 413, 453 and 493 K.

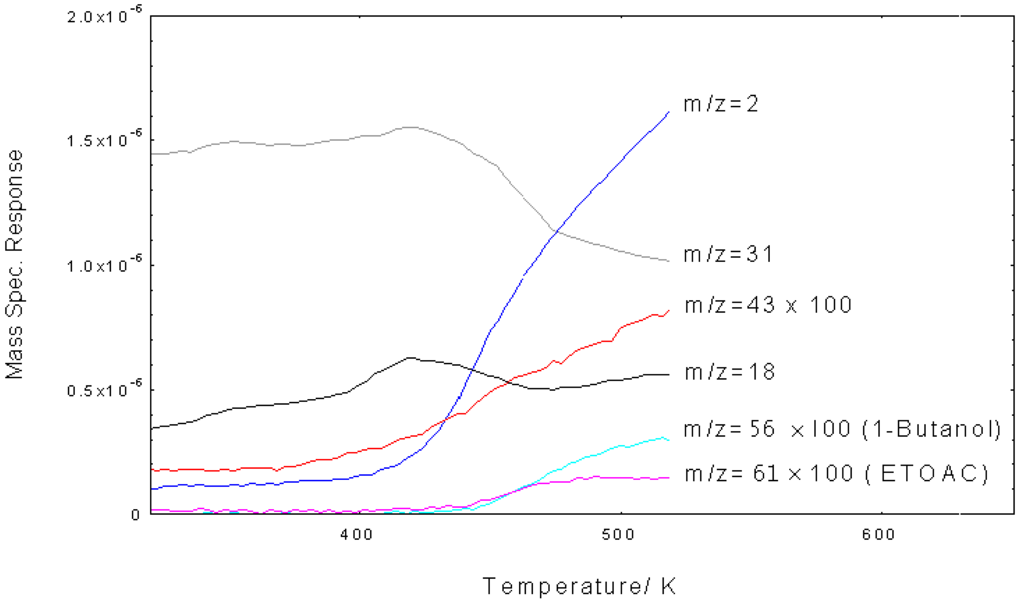

Fig. 9. TPR profile obtained by flowing C_2H_5OH/He (12%) continuously over the reduced and H desorbed Cu/Cr_2O_3 catalyst while raising the temperature from ambient to 523 K at 5 K min^{-1}.

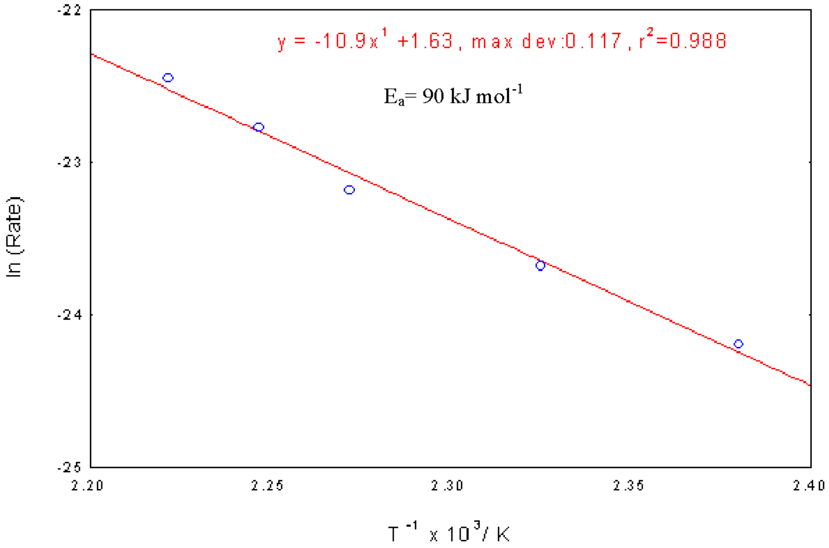

Fig. 10. Arrhenius plot of the logarithm of the ethyl ethanoate signal ($\ln m/z = 61$) versus I/T observed by temperature programmed reaction shown in Fig. 9.

It is possible to obtain the activation energy for the formation of ethyl ethanoate from Fig. 9. A plot of the natural logarithm of the rate of production of ethyl ethanoate (the $m/z = 69$ signal) versus $1/T$ (K) at the initial stages of reaction when there is negligible reverse reaction gives the activation energy for the reaction. This plot in the temperature range 420–431 K is shown in Fig. 10; the activation energy obtained from it was 91 kJ mol^{-1}. Note that from Fig. 9, above 473 K, the ethyl ethanoate signal ($m/z = 61$) became invariant with temperature, even though the $m/z = 31$ signal (ethanol) continued to fall, albeit at a slower rate above 473 K than in the temperature range 433–473 K. Therefore, the ethyl ethanoate reaction reached equilibrium at 473 K. Above 473 K, the ethanol continued to react, forming byproducts, as evidenced by the continued increase in the $m/z = 71$ signal (butanol) and in the $m/z = 43$ signal (possibly ethanal) above 473 K. This suggests that byproduct formation is a high-temperature phenomenon.

Because the formation of ethyl ethanoate from ethanol is essentially the dimerisation of ethanol,

$$2CH_3CH_2OH \Longleftrightarrow CH_3CO_2C_2H_5 + 2H_2, \tag{5}$$

then

$$\frac{d[H_2]}{dt} = \frac{2d[CH_3CO_2C_2H_5]}{dt} = A_e^{-E/RT} P_{C_2H_5OH} \tag{6}$$

or

$$\ln\frac{d[H_2]}{dt} = \ln 2 + \ln\frac{d[CH_3CO_2C_2H_5]}{dt}$$
$$= \ln A - E/RT + \ln P_{C_2H_5OH}. \tag{7}$$

A plot of the natural logarithm of the rate of production of dihydrogen $\ln(d[H_2]/dt)$ versus $1/T$ in the initial stages of reaction

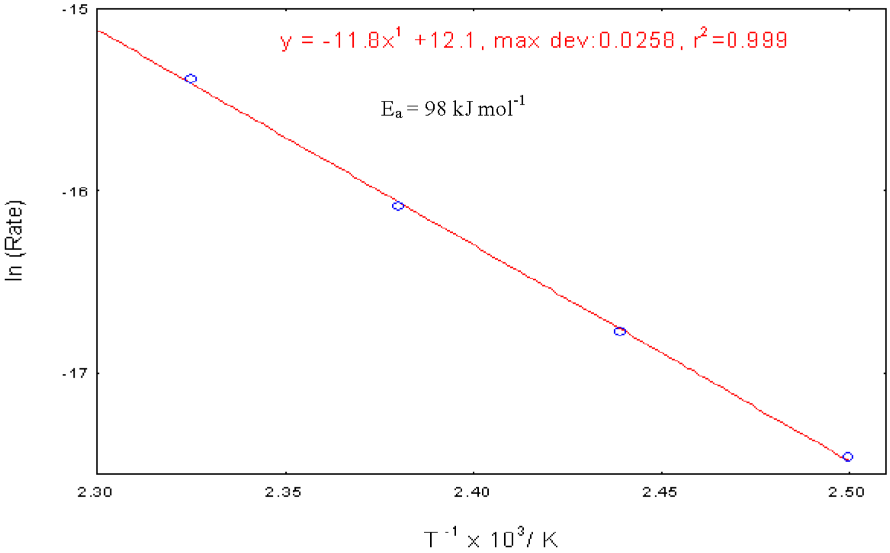

Fig. 11. Arrhenius plot of the logarithm of the H_2 signal versus I/T obtained by temperature programmed reaction shown in Fig. 9.

should give the activation energy for the production of ethyl ethanoate. Such a plot in the temperature range 420–431 K is shown in Fig. 11, from which an overall activation energy for ethyl ethanoate formation of 98 $\mathrm{kJ\,mol^{-1}}$ is obtained. Because we have greater sensitivity for the $m/z = 2$ (H_2) signal in the mass spectrometer relative to the $m/z = 61$ signal, the value of 98 $\mathrm{kJ\,mol^{-1}}$ for the activation energy for ethyl ethanoate formation obtained from the temperature dependence of the H_2 signal is probably more accurate than the value 90 $\mathrm{kJ\,mol^{-1}}$ obtained from the $m/z = 61$ signal.

The activation energy for ethyl ethanoate formation might be obtained from the increase in the steady-state value of the H_2 signal with increasing temperature (Fig. 6) or from the decrease in the steady-state value of the C_2H_5OH signal with increasing temperature (Fig. 5). Values of 30 $\mathrm{kJ\,mol^{-1}}$ are obtained from both in the temperature range 453–493 K. These values are considerably lower than the value of 98 $\mathrm{kJ\,mol^{-1}}$ obtained from the activation energy for the ethyl ethanoate formation from the initial rate of H_2 production. These lower values are a result of significant back-reaction at 453 and 493 K: that is, the reaction is near equilibrium at these temperatures.

3.4. *Reaction mechanism resulting from TDSS ethanol dosing experiments and TPR studies*

The temperature-dependent $C_2H_5OH(g)$ adsorption studies showed that the C_2H_5OH adsorbed as ethoxy and that the adsorbed ethoxy species was easily dehydrogenated to form an acetyl species [Figs. 5 and 6; reactions (1), (3), and (4)],

$$CH_3CH_2OH + 2Cu \Longleftrightarrow CH_3CH_2O(a) + H(a), \tag{1}$$

$$CH_3CH_2O(a) + Cu \Longleftrightarrow CH_3CHO(a) + H(a), \tag{3}$$

$$CH_3CHO(a) + Cu \Longleftrightarrow CH_3CO(a) + H(a). \tag{4}$$

Reaction of the adsorbed ethoxy species with the adsorbed acetyl species produced adsorbed ethyl ethanoate,

$$CH_3CH_2O(a) + CH_3CO(a) \Longleftrightarrow CH_3CH_2OOCCH_3(a), \tag{8}$$

which then desorbs,

$$CH_3CH_2OOCCH_3(a) \Longleftrightarrow CH_3CH_2OOCCH_3(g). \tag{9}$$

It is impossible to conclude from the data obtained thus far whether the rate-determining step in the reaction is the surface reaction of adsorbed ethoxy species with adsorbed acetyl species [reaction (8)], desorption of the ethyl ethanoate [reaction (9)], or a combination of the two. However, as we show later, desorption of ethyl ethanoate is rate-determining.

The generic form of the overall rate expression for the rate of production of ethyl ethanoate resulting from reactions (1)–(9) would be

$$\frac{dP_{CH_3CH_2OOCCH_3}}{dt} = \frac{K_1k_3k_4k_8k_9P_{CH_3CH_2OH}}{1 + K_9P_{CH_3CH_2OOCCH_3} + K_2P_{H_2}} \tag{10}$$

from which it can be seen that the overall activation energy of 98 $\mathrm{kJ\,mol^{-1}}$ for the production of ethyl ethanoate is a complex function of the sum of the activation energies for the adsorptive dehydrogenation of ethanol and of the dehydrogenation of the adsorbed ethoxy and ethanal (E_1, E_3, and E_4) plus the energy barriers for the surface reaction (E_8) and for the desorption of ethyl ethanoate (E_9) divided by the ethyl ethanoate and hydrogen equilibrium heats of adsorption (ΔH_9 and ΔH_2). A consequence of deconvoluting the overall reaction into its component elementary reactions is that it explicitly shows that the first dehydrogenation of an adsorbed ethoxy species produces an adsorbed ethanal species [reaction (3)] that could desorb as ethanal,

$$CH_3CHO(a) \Longleftrightarrow CH_3CHO(g) + Cu. \tag{11}$$

That the reaction is >95% selective to ethyl ethanoate and that negligible amounts of ethanal are detected in the gas phase (note that the $m/z = 43$ signal in Fig. 9 is multiplied by 100) implies that the activation energy for dehydrogenation of the adsorbed ethoxy species E_4 is much smaller than the desorption activation energy of adsorbed ethanal E_{11}.

White and colleagues found that selectivity in ethanol dehydrogenation depends critically on the dispersion of the Cu [6,7].

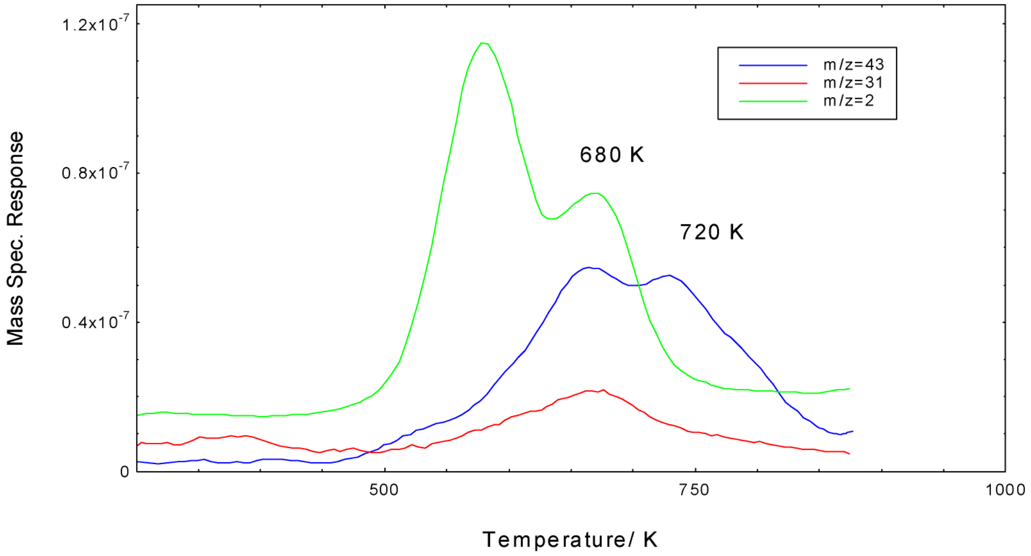

Fig. 12. TPD spectrum obtained by dosing ethyl ethanoate in He (17%) at 493 K on to a reduced Cu/Cr_2O_3 catalyst at 493 K on which the 680 K desorbing H state only existed.

They found that isolated Cu atoms catalysed the dehydrogenation of ethanol to acetal only, whereas multiple Cu ensembles produced ethyl ethanoate (73%) in addition to acetal (27%). Assuming spherical Cu particles, the average diameter of the Cu in the Cu/Cr_2O_3 catalyst is ∼400 Å, whereas that in the polycrystalline Cu is ∼3000 Å. If high selectivity in ethanol dehydrogenation to ethyl ethanoate requires large Cu particles, then it is not surprising that the materials used here produce ethyl ethanoate almost exclusively.

3.4.1. *TPD and TPR spectroscopy studies of C_2H_5OH and $CH_3CO_2C_2H_5$ on the Cu/Cr_2O_3 catalyst*

The combined techniques of TPD and TPR spectroscopy (TPRS) provide added detail to the elementary reaction model described by reactions (1)–(4), (8), and (9) in terms of specific desorption activation energies using TPD and surface reaction mechanisms using TPRS.

3.4.2. *Ethyl ethanoate adsorption on Cu:Cr (1:1) studied by TPD and TPRS*

The catalyst was reduced in an identical manner to that described to produce Fig. 1. However, after 16 h reduction in H_2/He (5%) at 508 K, the temperature was lowered to 473 K, at which point the flow was switched to He (101 kPa, 25 min^{-1}) for 30 min to remove the H adsorbed on Cu while leaving the H adsorbed on the Cr_2O_3. The ethyl ethanoate was then dosed on by passing He (101 kPa 25 $cm^3\,min^{-1}$) through ethyl ethanoate maintained at 300 K in a saturator, producing a 17% mixture of ethyl ethanoate in He. The ethyl ethanoate/He mixture was passed over the reduced catalyst held at 493 K for 30 min. The temperature was lowered to ambient under the ethyl ethanoate/He stream. The flow was then switched to He (101 kPa, 25 $cm^3\,min^{-1}$) for 30 min, and the temperature was raised from ambient to 900 K under the He stream. The TPD/TPRS spectrum so produced is shown in Fig. 12.

The H_2 desorption spectrum shows the characteristic peaks at 580 and 680 K. Nothing desorbs coincident with the H_2 peak at 580 K; however, both $m/z = 43$ and $m/z = 31$ fragments desorb coincident with the 680 K H_2 peak. These derive from the desorption of ethyl ethanoate bound to the surface of the Cr_2O_3 through the strong Brönsted acid site described earlier. The $(m/z = 31)$:$(m/z = 43)$ ratio is not that of the cracking pattern of ethyl ethanoate, and so the adsorbed ethyl ethanoate must undergo some degree of hydrogenolysis by the Brönsted acid hydrogen as it desorbs,

$$CH_3CH_2OOCCH_3(a) + 2H(a) \Longleftrightarrow CH_3CH_2OH(g) + CH_3CHO(g). \tag{12}$$

This reaction is not complete; a fragment appears to be left on the surface that desorbs at 720 K as a $m/z = 43$ peak. This fragment could be an acetyl species that is hydrogenated to ethanal,

$$CH_3CO(a) + H(a) \Longleftrightarrow CH_3CHO(g) + 2Cu. \tag{13}$$

If the desorption of ethyl ethanoate from the Brönsted acid site is assumed to be of first order, then the desorption activation energy from that site calculated from the value of the peak maximum temperature (680 K) for a desorption pre-exponential term of 10^{13} s^{-1} is 180 $kJ\,mol^{-1}$ [8]. This is greater that the overall value of 98 $kJ\,mol^{-1}$ obtained from TPR experiments; the difference derives from the complex function of the sum the activation energies for adsorption, surface reaction, and desorption found in Eq. (10), which produce an overall activation energy of 98 $kJ\,mol^{-1}$ while still containing in that rate expression a value of 180 $kJ\,mol^{-1}$.

It should also be noted that a small $m/z = 31$ (ethanol) peak is observed at 300 K. This probably results from the hydrogenation of an ethoxy species adsorbed on Cu,

$$CH_3CH_2OH(g) + 2Cu \Longleftrightarrow CH_3CH_2O(a) + H(a). \tag{1}$$

3.4.3. *TPD/TPRS of ethanol from Cu:Cr (1:1)*

3.4.3.1. Adsorption temperature 493 K Fig. 13 is the spectrum obtained on temperature programming after dosing

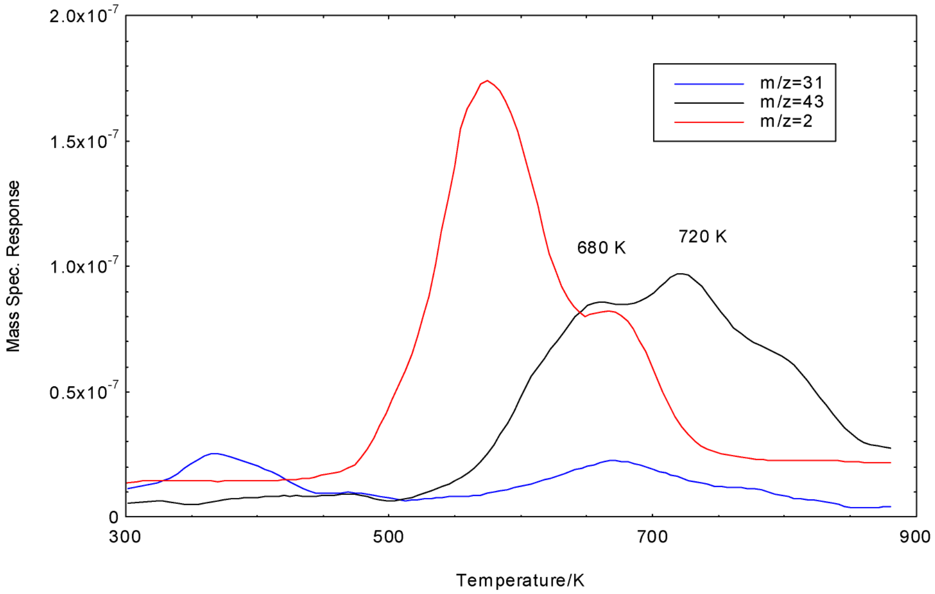

Fig. 13. TPD spectrum obtained by dosing C_2H_5OH/He (12%) on to a reduced Cu/Cr_2O_3 catalyst at 493 K on which the 680 K desorbing H state only existed.

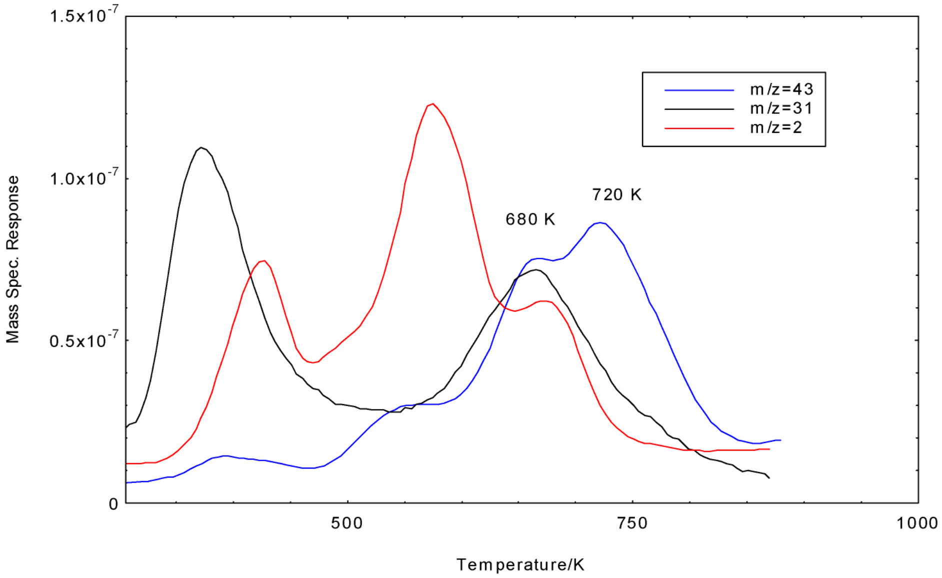

Fig. 14. TPD spectrum obtained by dosing C_2H_5OH/He (12%) on to a reduced Cu/Cr_2O_3 catalyst at 303 K on which the 680 K desorbing H state only existed.

CH_3CH_2OH (12% in He, 101 kPa, 25 $cm^3\,min^{-1}$) onto the Cu:Cr (1:1) catalyst held at 493 K for 30 min. After the ethanol was dosed at 493 K, the temperature was lowered to ambient in the ethanol stream. The flow was then switched to He for 30 min, after which the temperature was raised at a rate of 5 $K\,min^{-1}$. The spectrum produced is virtually identical to that obtained after ethyl ethanoate was dosed on to the catalyst at 493 K. Therefore, the ethanol adsorbs and reacts on the surface at 493 K, forming ethyl ethanoate. This ethyl ethanoate is bound to the catalyst through the strong Brönsted acid site, desorbing on hydrogenation at 680 K in coincident H_2, CH_3CH_2OH, and CH_3CHO peaks.

There are two major differences in the spectra obtained after ethanol dosing and after ethyl ethanoate adsorption. The first of these is a larger high-temperature fragment remaining on the Cr_2O_3 desorbing as $m/z = 43$ (possibly CH_3CHO) in two peaks at 720 K and 840 K. The second is the larger ethoxy species existing on the surface of the Cu, desorbing as CH_3CH_2OH at 360 K.

3.4.3.2. Adsorption temperature 303 K Fig. 14 is the spectrum obtained after dosing CH_3CH_2OH/He (12% CH_3CH_2OH, 101 kPa, 25 $cm^3\,min^{-1}$) onto the Cu:Cr (1:1) catalyst for 30 min at 303 K. After the CH_3CH_2OH/He was dosed, the flow was then switched to He for 30 min, after which the temperature was raised at a rate of 5 K min. Keep in mind that catalyst pretreatment involved reduction at 503 K for 16 h in H_2/He (5% H_2, 101 kPa, 25 $cm^3\,min^{-1}$), followed by desorption of the hydrogen adsorbed on the Cu in a He flow (101 kPa, 25 $cm^3\,min^{-1}$) at 503 K for 30 min.

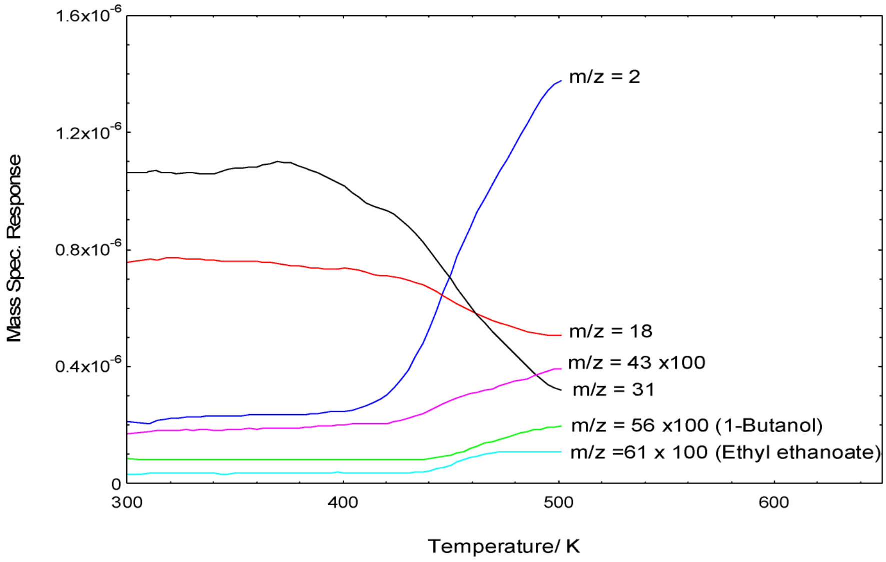

Fig. 15. TPR profile obtained by flowing C_2H_5OH/He (12%) continuously over the reduced and H desorbed unsupported polycrystalline Cu catalyst while raising the temperature from ambient to 523 K at 5 K min^{-1}.

It is possible to measure the coverage of the Cu/Cr_2O_3 catalyst by ethanol at 303 K from the frontal uptake shown in Fig. 5. Integration of ethanol uptake at 303 K on the Cu/Cr_2O_3 in Fig. 5 can be obtained from the time difference to ethanol breakthrough on the catalyst minus the time difference on glass beads; this value is 400 s. The total number of molecules adsorbed is therefore

$$\text{Molecules adsorbed} = \frac{NPVt}{RT}, \qquad (13)$$

where N is Avogadro's number (6.023×10^{23}), P (atm) is the partial pressure of ethanol (0.12), V ($cm^3\,s^{-1}$) is the flow rate (25/60), t (s) is the time to breakthrough (400), R ($cm^3\,atm\,K^{-1}\,mol^{-1}$) is the gas constant (82.058), and T (K) is the adsorption temperature (303).

Substituting these values into Eq. (13) gives a value of 4.9×10^{20} molecules adsorbed. The weight of catalyst used was 0.5 g, and its total surface area was 13.8 $m^2\,g^{-1}$, so that the coverage of the catalyst by ethanol at 300 K in equilibrium with gas phase ethanol (0.12 atm) is approximately 5 monolayers. Only a small fraction of that (4% ML) is adsorbed as the ethoxy species (Table 1). Some of this physically adsorbed ethanol will desorb during the 30 min of He flow before temperature programming. That some remains is evidenced by the ethanol desorption peak at 370 K in Fig. 14, which constitutes 70% of the initially adsorbed ethanol.

However, some of the adsorbed ethanol is dehydrogenated during temperature programming. This is shown by the H_2 peak beginning ~20 K after the onset of ethanol desorption and maximising at 425 K. The total amount of the H_2 is 3.8×10^{14} atom cm_{Cu}^{-2}, 27% of a monolayer of the Cu (Fig. 14).

In the lower temperature regime (300–373 K), we know that the H_2 evolution derives from the dehydrogenation of ethanol to form an adsorbed ethoxy species (see the discussion of Fig. 6). Above 373 K, H_2 evolution occurs by the dehydrogenation of the adsorbed ethoxy species to form adsorbed acetyl species. The amount of H formed up to 373 K is 5.5×10^{13} atom cm_{Cu}^{-2} corresponding to a coverage of ethoxy species of 5.5×10^{13} species cm_{Cu}^{-2}. The amount of H formed by the dehydrogenation of ethoxy species to form the acetyl species is 3.2×10^{14} atom cm_{Cu}^{-2}. Because the dehydrogenation of the ethoxy species to form the acetyl species involves the loss of two H atoms [reactions (3) and (4)], the coverage of the adsorbed acetyl species is 1.6×10^{14} acetyl species cm_{Cu}^{-2}.

It is evident from Fig. 14 that the ethoxy and acetyl species combine to form ethyl ethanoate. This appears to migrate from the Cu to the Brönsted acid site, where it desorbs at 680 K. The remaining acetyl species [$\sim 1 \times 10^{14}$ acetyl species cm_{Cu}^{-2}] are hydrogenated and desorb as ethanal at 720 K.

It is possible to obtain an estimate of the activation energy for the dehydrogenation of the adsorbed ethoxy species by analysing the temperature dependence of the line shape of the H_2 desorption peak. The fact that the peak is symmetric about the peak maximum indicates that this desorption is associative and so, not surprisingly, is a second-order process. We can use the result that line shape analysis of the second-order H_2 desorption peak from Cu, whose peak maximum temperature is 300 K, produces a desorption activation energy of 67 kJ mol^{-1} to construct a graph of desorption activation energy against peak maximum temperature. Using this graph, the peak maximum temperature of 425 K for the dehydrogenation of adsorbed ethoxy species corresponds to an activation energy of 94 kJ mol^{-1} for this process—a value similar to that for the overall production of ethyl ethanoate.

3.4.4. *TPR of ethanol with polycrystalline copper*

That copper is the primary active component of the catalyst can be seen on the TPR profile obtained by passing ethanol (12% in He, 101 kPa, 25 $cm^3\,min^{-1}$) over polycrystalline Cu while raising the temperature at a rate of 5 K min^{-1} (Fig. 15). The polycrystalline Cu was produced by reducing CuO (BDH)

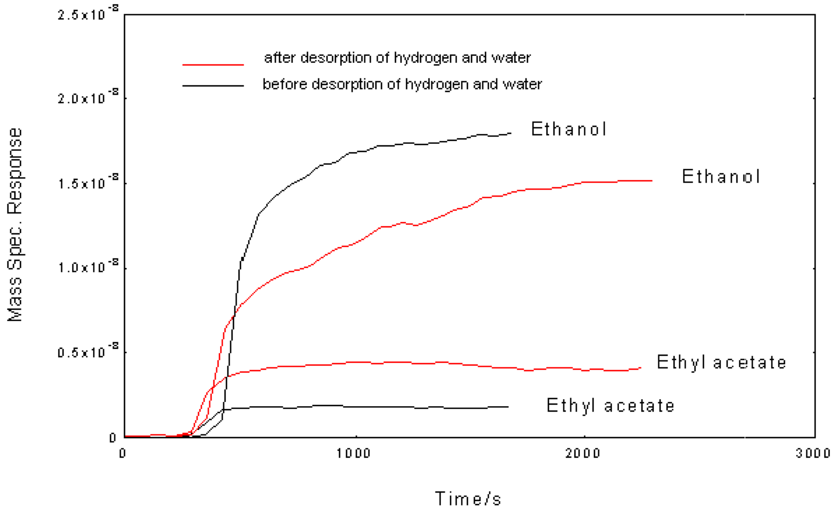

Fig. 16. The effect of removing the 680 K H desorbing Brönsted acid site from the reduced Cu/Cr_2O_3 catalyst on the ethanol conversion and ethyl ethanoate production at 493 K.

in H_2/He (5% H_2) in a fashion identical to that for the Cu/Cr_2O_3 (1:1) catalyst.

The TPR profile of CH_3CH_2OH with Cu (Fig. 15) is virtually identical to that obtained with the Cu/Cr_2O_3 catalyst (Fig. 9). The onset of H_2 production occurs at about 400 K, and ethyl ethanoate formation occurs at 440 K. The slight difference between Cu and Cu/Cr_2O_3 is that the Cu has a slightly stronger temperature dependence than the Cu/Cr_2O_3. Thus the activation energy for ethyl ethanoate formation on Cu derived from Fig. 15 is 120 $kJ\,mol^{-1}$, compared with 98 $kJ\,mol^{-1}$ from Cu/Cr_2O_3.

The fact that in TPR studies, unsupported Cu and the Cu/Cr_2O_3 catalyst exhibit both the same product spectrum and nearly the same temperature dependence of that product spectrum confirms that the Cu component of the catalyst is the source of its activity. Next, we demonstrate that the Brönsted acid site not only is unnecessary for the activity of the Cu/Cr_2O_3 catalyst, but also is positively associated with the activity of the catalyst.

3.4.5. Effect on activity of the removal of Brönsted acid site species from Cr_2O_3

Although it is clear that the adsorption of ethanol and the surface reaction of the adsorbed ethoxy and acetyl species to form ethyl ethanoate takes place on the Cu component of the Cu/Cr_2O_3 catalyst, we have suggested that the activity of the Cu/Cr_2O_3 catalyst could be inhibited by difficulty in desorbing the ethyl ethanoate product, which is strongly held on the Brönsted acid site of Cr_2O_3. Having reduced the catalyst in the normal way, the Brönsted acid site and the OHs on the Cr_2O_3 were removed by ramping the temperature from 503 to 903 K in He. The temperature was then lowered to 493 K under the He and the flow switched from He to CH_3CH_2OH/He (12% CH_3CH_2OH, 101 kPa, 25 $cm^3\,min^{-1}$).

The resulting effect on ethanol conversion and on ethyl ethanoate formation is shown in Fig. 16. The steady-state rate of ethyl ethanoate formation increased by a factor of 2.5. This increased rate of formation of ethyl ethanoate did not diminish with time, remaining constant for ∼1 h. Thus the H_2 produced by the reaction of ethanol to form ethyl ethanoate did not reestablish the Brönsted acid site or the OHs on the Cr_2O_3.

The steady-state rate of ethyl ethanoate formation in the presence of the Brönsted acid site is a pseudoequilibrium value, because the standing surface concentration of ethyl ethanoate on this site was higher than would be achieved in its absence. The reverse reaction on the surface was increased by this higher standing concentration of adsorbed ethyl ethanoate on the Brönsted acid site.

4. Conclusions

1. Ethanol adsorbs on to the Cu component of Cu/Cr_2O_3 catalysts as an ethoxy species with an activation energy of 31 $kJ\,mol^{-1}$.
2. The ethoxy species adsorbed on the Cu component of the Cu/Cr_2O_3 catalyst is dehydrogenated to an acetyl species with an activation energy of 94 $kJ\,mol^{-1}$.
3. The ethoxy and acetal species adsorbed on the Cu react to form adsorbed ethyl ethanoate molecule that migrates over the Cu to a Brönsted acid site on the Cr_2O_3, where it is strongly adsorbed. Assuming first-order desorption, this has an desorption activation energy of 180 $kJ\,mol^{-1}$.
4. The rate-determining step in the reaction is the desorption of the product ethyl ethanoate molecule from this Brönsted acid site, which, assuming first-order desorption, has a desorption activation energy of 180 $kJ\,mol^{-1}$.
5. The overall activation energy for the production of ethyl ethanoate over the Cu/Cr_2O_3 (1:1) catalyst obtained by line shape analysis of the initial rates of ethyl ethanoate formation in TPR experiments is 98 $kJ\,mol^{-1}$, which is the same as that for the dehydrogenation of the adsorbed ethoxy species to form an adsorbed acetyl species. That the two values are identical is a coincidence deriving from the complex function of the activation energies in the overall rate expression for ethyl ethanoate formation. It does not

indicate that the dehydrogenation of the adsorbed ethoxy species is rate-determining.

6. The steady-state rate of ethyl ethanoate production obtained over the Cu/Cr_2O_3 (1:1) catalyst is a pseudoequilibrium, because removing the Brönsted acid site and of the OHs adsorbed on the Cr_2O_3 increases the steady-state rate at 493 K by a factor of 2.5.
7. The H_2 produced by the production of ethyl ethanoate from ethanol does not reestablish the Brönsted acid site on the Cr_2O_3.
8. In a TPR experiment with ethanol over polycrystalline Cu, the temperature of the onset of ethyl ethanoate production and the temperature dependence of the byproducts formed are the same as those on the Cu/Cr_2O_3 (1:1) catalyst. Thus copper is the active component of the catalyst.

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