Study on the mechanism of ethanol synthesis from syngas by in-situ chemical trapping and isotopic exchange reactions [1]

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The mechanism of ethanol synthesis from syngas over promoted rhodium catalysts has been studied by chemical trapping and isotopic exchange experiments. Mono-deuterated acetaldehyde (CH_3CDO) was formed in chemical trapping reaction with $CO + D_2$ as the syngas source and CH_3I as the trapping agent, indicating that formyl adspecies was a C_1-intermediate in the ethanol synthesis. In the experiment of in-situ chemical trapping and isotopic exchange reactions with $D_2^{18}O$ followed by purging with methanol in N_2 stream, $CH_2DC^{18(16)}OOCH_3$, $CH_3C^{18(16)}OOCH_3$ and $CH_3CH_2^{18}OH$, $CH_3CH^{18}O$ were formed, showing the existence of ketene and acetyl intermediate adspecies and the occurrence of oxygen-isotope exchange between these intermediates and $D_2^{18}O$, respectively. Based on the mode of oxygen-isotope exchange between ketene (as well as acetyl) intermediate adspecies and the water formed in reaction, the isotopic repartitioning previously observed by Takeuchi and Katzer [1] can be explained without recourse to the hypothesis of the existence of highly strained oxirene intermediate. These results give further support to the ethanol-formation mechanism proposed by us [2]. Besides these, with substitution of D_2 for H_2 in the syngas conversion reaction, noticeable deuterium inverse isotope effects both on methanol and on ethanol formation were observed.

Keywords: Mechanism of ethanol synthesis; rhodium-based catalysts; chemical trapping reaction; isotopic exchange reaction

1. Introduction

Much attention has been paid to the mechanism of ethanol synthesis from syngas since the discovery that rhodium-based catalysts promoted by certain reducible metal-oxides, such as Fe_2O_3, MnO or TiO_2 can catalyze the conversion of syngas to ethanol with fairly high activity and selectivity [3,4]. Many reaction mechanisms have been proposed, but a unified view has not been

reached so far. It is generally accepted that $\underline{C}H_x$ ($x = 2$ or 3; an underlined chemical symbol signifies an adspecies) is among the C_1-intermediates in the formation of both hydrocarbons and oxygenates in the syngas-conversion reactions, but there are divergent views on the mechanism of $\underline{C}H_x$ formation from syngas; some investigators [4] propose that the $\underline{C}H_x$ species is derived via a dissociative mechanism from partial hydrogenation of the surface "active" carbon derived from CO dissociation over Rh metal; while some others [5] suggest that it is formed via an associative mechanism from a formyl intermediate, $H\underline{C}O$, by hydrogenolysis. Thus it is desirable to confirm the presence of the formyl intermediate in order to further strengthen the argument for the proposed associative mechanism [2] of $\underline{C}H_x$ formation from syngas over the promoted rhodium catalysts.

Regarding the pathway for the conversion of ketene intermediate [1,6] into ethanol over rhodium-based catalysts, Takeuchi and Katzer [1] have performed an interesting experiment with $^{12}C^{18}O / ^{13}C^{16}O$ mixtures as the CO source in the syngas for the ethanol synthesis reaction and discovered that the isotopic repartitioning of ^{13}C and ^{18}O in the product ethanol is compatible neither with the hydrocondensation mechanism nor with the mechanism in which CO is inserted into a metal-methyl bond followed by direct hydrogenation to form acetaldehyde and ethanol. This led them to propose a mechanism where ketene and oxirene adspecies were supposed to be two key intermediates. These authors' explanation for the observed isotopic composition of ethanol was based on a reversible interconversion between ketene and oxirene and the exchange reaction of oxirene. As oxirene is a highly strained species, ketene conversion to oxirene would be energetically unfavorable. Moreover, oxirene and ethyleneoxide species have not been detected experimentally in syngas-conversion to ethanol over rhodium catalysts. So it is also desirable to establish a basis for a more plausible explanation for Takeuchi and Katzer's isotopic-scrambling experimental results.

As we used $CO + D_2$ to carry out the syngas conversion reactions in the formyl trapping experiment, we also investigated the effects of deuterium isotope on both the rate of ethanol formation and that of methanol formation.

2. Experimental

CATALYST PREPARATION

Promoted rhodium catalysts were prepared by isovolumetric impregnation techniques. Silica gel beads (Qingdou Marine-Chemical Factory product, 30–40 meshes, 300 m^2/g, 0.9 ml/g pore volume) were impregnated with the mixed methanol solution of metal nitrates or chlorides of rhodium and promoter cations such as Mn^{2+}, Fe^{3+}, Li^+, Ti^{4+}, followed by pumping away the solvent

methanol at room temperature and then drying and heating in air at 573 K for one hour. The sample thus obtained was transferred into a fixed-bed micro-reactor and reduced with hydrogen (or CO so as to obtain a hydrogen-free sample for one special experiment of chemical trapping with CH_3I) at 673 K for two to eight hours. The rhodium loading in the catalyst was 2% by weight in each case.

SYNGAS CONVERSION REACTION

Syngas conversion reaction was carried out in a micro-reactor at 493 K, atmospheric pressure, 1000 h^{-1} space velocity. Reaction products were analyzed by an on-line FID-GC with a GDX-103 column (2 m, 353 K).

FORMYL TRAPPING WITH CH_3I

After running the $CO + D_2$ reaction for enough length of time (two hours), formyl intermediate was identified by chemical trapping reaction with CH_3I as trapping agent, according to the following equation: $H\underline{C}O + \underline{C}H_3 = CH_3CHO$. As acetaldehyde is one of the reaction products, the use of $CO/2D_2$ instead of $CO/2H_2$ was to avoid ambiguity when CH_3I was used as the trapping reagent. The experiment was carried out as follows: after reduction of catalyst at 673 K for two hours with D_2, the $CO/2D_2$ reaction was conducted at 493 K, atmospheric pressure and the products were also analyzed by an on-line FID-GC. Two hours later, the trapping reaction was performed with an excess of CH_3I (0.5 ml) injected onto the catalyst surface which was at the reaction temperature and the trapping-reaction products were collected in an ice-salt cold trap. Samples collected were analyzed by means of GC-MS, with the use of a Finnigan MAT4510 GC-MS spectrometer for data recording and the accompanying microprocessor for the deduction of the G.C background.

IN-SITU CHEMICAL TRAPPING AND OXYGEN-ISOTOPE EXCHANGE REACTIONS WITH $D_2{}^{18}O$

After the steady state of syngas conversion reaction was reached, a definite proportion of $D_2{}^{18}O$ vapor was introduced with the syngas into the catalyst bed by allowing the syngas to bubble through liquid $D_2{}^{18}O$ (the abundance of ^{18}O is 90%) maintained at definite temperature to carry out the in-situ chemical trapping and isotopic exchange reactions. Reaction products were collected in a liquid-nitrogen cold trap for four hours. In view of the strong adsorption of acetic acid, methanol in N_2 stream was introduced into the catalyst bed to convert acetic acid adspecies into methyl acetate until no more methyl acetate was detected in the gaseous effluent. The thawed condensates were analyzed by GC-MS to give the isotopic repartition of ^{18}O in acetaldehyde, ethanol, and methyl acetate.

3. Results and discussion

FORMYL TRAPPING

Adding an alkylation reagent to convert formyl species present on the catalyst surface into the corresponding aldehyde is a common method for formyl trapping [7] and methyl iodide is a highly effective methylation reagent widely used as formyl trapping agent. The MS patterns of acetaldehyde formed in the $CO + 2D_2$ reaction and formed in the trapping reaction with CH_3I are shown in fig. 1. By comparison of (b) with (a), it was obvious that there are two species of acetaldehyde formed in the trapping reaction, one is unlabelled, i.e., CH_3CHO ($m/e = 44$); the other is mono-deuterated, i.e., CH_3CDO ($m/e = 45$). The CH_3CDO was the expected product from the D$\underline{CO}$ trapping reaction, but it was unexpected that CH_3CHO was also found in an amount comparable with CH_3CDO. Since D_2 instead of H_2 was used with CO to conduct the ethanol synthesis reaction, the formation of CH_3CHO seemed to be puzzling. After the possibility of contamination from any impurities in D_2 and CH_3I and from the residual hydrogen on the SiO_2 used as catalyst carrier was excluded, it became obvious that the formation of CH_3CHO must be related to the methyl group in CH_3I. When the "blank" trapping reaction with CH_3I was carried out only in the presence of CO over the Rh-Mn(1:1)/SiO_2 catalyst prereduced at 523 K in flowing CO, CH_3CHO was still found, indicating that cis-insertion of CO into the $\underline{C}H_3$ from the CH_3I to form $CH_3\underline{C}O$, must have taken place, as well as dehydrogenation of some of the $\underline{C}H_3$ to give $\underline{H}$, which then reacted with the $CH_3\underline{C}O$ to give CH_3CHO. Thus this clearly indicates that, in the formyl trapping reaction following $CO + 2D_2$ reaction, there are two possible pathways for the formation of CH_3CDO. One is trapping of D$\underline{C}O$ by methylation, the
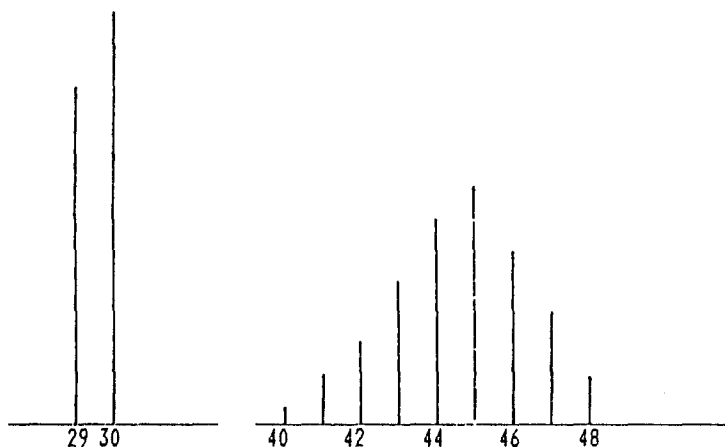

Fig. 1. MS pattern of acetaldehyde formed by trapping reaction with CH_3I after the $CO + D_2$ reaction over a Rh-Mn/SiO_2 catalyst.

Table 1
Effects of purging time of Ar on the amount of CH_3CDO trapped and the relative $\underline{D}$ surface concentration *

Purging time (min)	Amount of CH_3CDO trapped (mmol/mlcat $\times 10^4$)	Relative $\underline{D}$ surf. conc.
0	7.4	100.0
1	4.8	30.5
3	3.7	4.3
5	3.2	2.0
13	0.3	1.3

* The catalyst used was $Rh-Mn/SiO_2$. 1:1.

other is trapping of $\underline{CO}$ plus $\underline{D}$ by deuteration of CH_3CO formed by CO insertion into $\underline{CH_3}$ derived from CH_3I. In other words, CH_3I can trap $\underline{CO} + \underline{D}$ probably almost as easily as it can trap the $D\underline{CO}$ species. In order to make sure that some of CH_3CDO is actually derived from $D\underline{CO}$, the catalyst surface was purged with Ar before the trapping reaction was conducted. The effects of purging time on the percentage of CH_3CDO in total acetaldehyde formed and on the corresponding surface concentration of $\underline{D}$ were investigated and the results shown in table 1. The $CH_3CDO\%$ was found to decrease much less slowly with purging time during the initial five minutes, in comparison with the corresponding decrease in $\underline{D}$ concentration. On the other hand, the $\underline{D}$ concentration was found to change only slightly with purging time from five to thirteen minutes, while the $CH_3CDO\%$ fell much more rapidly. These results indicate that a considerable proportion of the CH_3CDO formed in the formyl trapping reaction was actually derived from methylation of $D\underline{CO}$ and that dissociation of the $D\underline{CO}$ into $\underline{D} + \underline{CO}$ might have taken place to some extent, especially when the surface concentration of $\underline{D}$ had dropped to a low level during the purging. Note that many systematic formyl-trapping experiments with CH_3I and with $(CH_3)_2SO_4$ over a series of catalysts active for alcohol formation have been reported in the literature [8,9]; but it has not been mentioned that dehydrogenation of some of the methyl group from trapping agent might occur, and that cis-insertion of CO into $\underline{CH_3}$ followed by hydrogenation of the resulting acetyl adspecies to give acetaldehyde might also take place in the trapping experiments, in the presence of $\underline{CO}$ and $\underline{H}$. Kuznetzov et al. [5] have observed formyl species during the initial syngas conversion reaction over Rh/La_2O_3 catalyst with ^{13}C NMR. This result and the result of the present paper give further support that formyl adspecies is really a C_1-intermediate in ethanol synthesis reaction.

IN-SITU CHEMICAL TRAPPING REACTION AND OXYGEN-ISOTOPE EXCHANGE RE-
ACTION

As $D_2{}^{18}O$ is a kind of water doubly labelled by D and ^{18}O, it can be used both
as trapping agent for ketene and acetyl intermediates and as the source of ^{18}O
for oxygen-isotope exchange of those species containing carbonyl [10]. With this
as trapping agent, $CH_2DC^{18(16)}OOCH_3$ and $CH_3C^{18(16)}OOCH_3$ are formed in
the in-situ chemical trapping reaction followed by purging the catalyst with
methanol-containing N_2 stream, and the relative proportions of the mon-
odeuterated and the undeuterated esters vary with the relative proportions of
the in-situ trapping agent and D_2 (table 2), as in the case of in-situ chemical
trapping with CH_3OD previously reported by us [6], indicating once again that
the in-situ chemical trapping is in competition with further hydrogenation of
ketene and acetyl, and that ketene and acetyl adspecies are two C_2-inter-
mediates in the ethanol synthesis reaction. With $D_2{}^{18}O$ as the source of ^{18}O in
the in-situ oxygen-isotope exchange reaction, ethanol as the main C_2-oxygenate
formed contains more than 40% of ^{18}O-ethanol ($CH_3CH_2{}^{18}OH$), as shown in
table 3. Since a blank test shows that the percentage of ^{18}O exchange between
ethanol and $D_2{}^{18}O$ over $Rh\text{-}TiO_2/SiO_2$ catalyst is only 2.8% under the same
conditions but in the absence of syngas, it can be concluded that the ^{18}O-ethanol
formed in the in-situ oxygen-isotope exchange reaction is derived predominantly

Table 2
Isotopic composition of methyl acetate produced by in-situ chemical trapping reaction with $D_2{}^{18}O$
followed by purging with methanol in N_2 stream over $Rh\text{-}TiO_2/SiO_2$ (493 K, 1 atm, 1000 h^{-1})

Feed comp.	percentage in total AcOMe *	
$D_2{}^{18}O/H_2/CO$ (mol. ratio)	$CH_3C^{18}OOCH_{3+}$ $CH_2DC^{18}OOCH_3$	$CH_2DC^{18}OOCH_{3+}$ $CH_2DC^{16}OOCH_3$
0.14/2/1	14.9	6.9
0.30/3/1	35.8	12.3
0.22/2/1	36.4	13.2
0.15/1/1	52.2	25.2

* Includes CH_3COOCH_3, $CH_3C^{18}OOCH_3$, $CH_2DCOOCH_3$, $CH_2DC^{18}OOCH_3$.

Table 3
Isotopic composition of C_2-oxygenates produced by in-situ isotopic exchange exchange reaction of
oxygen over $Rh\text{-}TiO_2/SiO_2$ (493 K, 1 atm, 1000 h^{-1})

Feed comp. $D_2{}^{18}O/H_2/CO$	$CH_3CH_2{}^{18}O\%$ in acetaldehyde	$CH_3CH_2{}^{18}OH\%$ in ethanol
0.14/2/1	13.5	43.1
0.30/3/1	26.7	43.2
0.22/2/1	28.8	46.2
0.15/1/1	51.6	43.9

Table 4

In-situ chemical trapping reaction and isotopic exchange reaction of oxygen with $D_2{}^{18}O$ followed by purging with methanol in N_2 stream over Rh-TiO$_2$/SiO$_2$ (493 K, 1 atm, 1000 h^{-1})

Feed comp.	percentage in C_2^+-O * (mol%)		
$D_2{}^{18}O/H_2/CO$ (mol. ratio)	$CH_3CH_2{}^{18}O$	$CH_3CH_2{}^{18}OH$	total AcOMe
0.14/2/1	0.8	39.6	2.0
0.30/3/1	1.8	38.9	3.1
0.22/2/1	1.5	42.2	3.4
0.15/1/1	7.6	32.3	11.8

* Includes acetaldehyde, ethanol, methyl acetate.

from hydrogenation of its ^{18}O-containing precursors, such as adspecies of ^{18}O-ketene, ^{18}O-acetyl, and ^{18}O-acetaldehyde, formed by isotopic exchange reactions of the corresponding ^{16}O organic adspecies with $D_2{}^{18}O$, most probably through reversible hydration and dehydration of the carbonyl functional groups. As acetaldehyde adspecies can not be converted into methyl acetate by a hydration reaction, the formation of four species of methyl acetate having different isotopic compositions and ^{18}O-ethanol as well as ^{18}O-acetaldehyde in the in-situ chemical trapping reaction and the oxygen-isotope exchange reaction with $D_2{}^{18}O$ reveals that ketene and acetyl intermediates can take part in two types of hydration reactions. One is irreversible, i.e., the trapping reaction, leading to the formation of acetic acid; the other is reversible hydration and dehydration, leading to isotopic exchange and the formation of ^{18}O-ethanol and ^{18}O-acetaldehyde. The experimental results (table 4) show that the sum of the ^{18}O-ethanol% and ^{18}O-acetaldehyde% in the total C_{2+}-O is much larger than the total AcOMe%, implying that the reversible hydration and dehydration reactions can actually take place faster than the trapping reaction. Based upon these experimental results, the mechanisms for the in-situ chemical trapping reaction and oxygen-isotope exchange reaction are shown in fig. 2.

As mentioned in the introduction, Takeuchi and Katzer [1] explained the observed isotopic composition of ethanol based on the existence of the highly
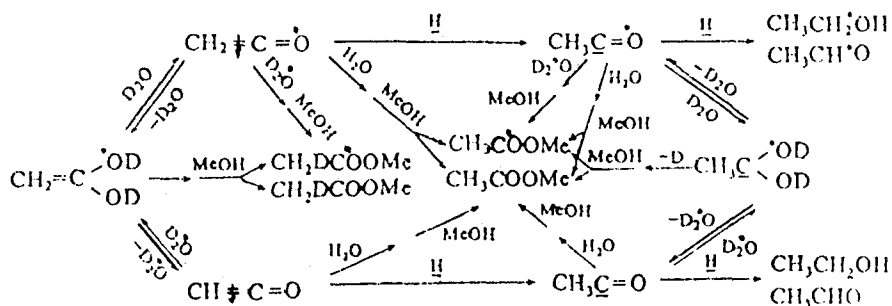

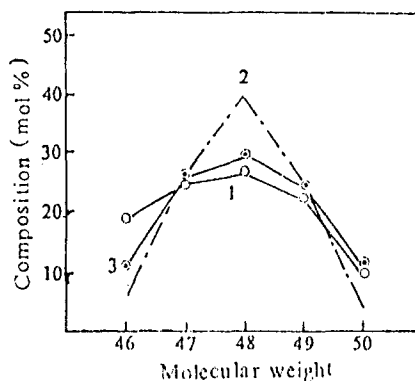Fig. 2. Scheme for the mechanism of in-situ trapping reaction and isotopic exchange reaction of oxygen.

Fig. 3. Isotopic composition of ethanol; 1. experimental results, 2. calculated according to partially dissociative model, 3. calculated with two times of isotopic exchange of oxygen between ketene and water formed in reaction.

strained oxirene adspecies as a ketene isomer. Several authors [11,12] have raised doubts about this explanation. Deluzarche et al. [12] proposed an alternative explanation for Takeuchi and Katzer's results based on the probable reactions of reversible and repeatable oxygen-isotopes exchange between water and adsorbed formaldehyde or acetaldehyde, but they did not produce any experimental evidence. Furthermore, if all the ethanol were derived from hydrogenation of the adsorbed ^{18}O-acetaldehyde, then the ^{18}O-ethanol% in the ethanol would be the same as the ^{18}O-acetaldehyde% in the acetaldehyde; but this is not the case, as shown in table 3. Accordingly, we suggest that the oxygen-isotope exchange reaction between ketene (as well as acetyl) intermediate and water should be considered. Based on the mode of oxygen-isotope exchange of ketene (as well as acetyl) with water formed in the ethanol-synthesis reaction and the isotopic composition of CO in Takeuchi and Katzer's experiment, the isotopic composition of ethanol can also be obtained by statistical calculation, as shown in fig. 3. The experimentally determined isotopic composition is completely different from that calculated by Takeuchi and Katzer based on a half-dissociation model (e.g. CO insertion into M-CH3 bond). But with the assumption that oxygen-isotope exchange can take place twice between ketene (as well as acetyl) and water formed in the reaction, the isotopic composition calculated by us lies very closely to the experimental data. Thus Takeuchi and Katzer's experimental results can be explained without resort to the hypothesis of the existence of highly strained oxirene intermediate. This further supports the ethanol-formation mechanism proposed by us [2].

DEUTERIUM INVERSE ISOTOPE EFFECTS IN METHANOL AND ETHANOL FORMATION

The effect of deuterium isotope on the rate of a hydrogenation reaction is often used to investigate whether hydrogen is involved in the rate-determining

Table 5
H_2/D_2 isotope effect in syngas conversion reaction (493 K, 1 atm 1000 h^{-1}, $CO/H_2(D_2) = 1/2$)

Catalyst	C^D/C^H	Y^D_{MeOH}/Y^H_{MeOH}	Y^D_{EtOH}/Y^H_{EtOH}
Rh/SiO$_2$	1.2	–	2.1
Rh-Mn/SiO$_2$ 1:1	1.3	1.9	1.5
Rh-Mn/SiO$_2$ 1:2	1.3	2.0	1.8
Rh-Fe/SiO$_2$ 1:0.3	1.2	–	1.4
Rh-Li/SiO$_2$ 1:0.3	1.3	–	1.8

C denotes the percentage of CO conversion, and Y the yield of product per hour.

step or not. So far, no work concerning the effects of deuterium isotope in the syngas on the rates of ethanol synthesis and methanol synthesis over rhodium catalysts has been reported in the literature. In the present work, we carried out a series of ethanol-synthesis reactions with $CO/2D_2$ and with $CO/2H_2$ as the syngas in order to study deuterium isotope effect, and the results are summarized in table 5. Over all the catalysts, the rate of ethanol formation in $CO + 2D_2$ reaction is 1.4–2.1 times that in $CO + 2H_2$ reaction. Over the Rh-Mn/SiO$_2$ (molar ratio of Rh/Mn = 1:1 or 1:2) catalyst, on which methanol is also formed, the rate of methanol formation in $CO + 2D_2$ reaction is faster by about a factor of two than that of methanol formation in $CO + 2H_2$ reaction. These results indicate that both methanol formation and ethanol formation show noticeable deuterium inverse isotope-effects in syngas conversion over rhodium-based catalysts. From this result it may be inferred that the rate-determining steps involved in both methanol formation and ethanol formation are, very probably, in each case a step of hydrogenation (or deuteration), though the two steps are apparently not the same, for according to Ichikawa [13], the activation energies for these two reactions are different.

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