Trapping of CH_3O formed from $CO + H_2$

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Methoxy formed on Al_2O_3 from ^{13}CO and H_2 coadsorption on Ni/Al_2O_3 was trapped by C_2H_5OH adsorption and temperature-programmed reaction (TPR). The presence of excess C_2H_5OH significantly increases the rate of $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ formation. The $^{13}CH_3OH$ forms by the reaction of C_2H_5OH with $^{13}CH_3O$ on Al_2O_3. In the absence of C_2H_5OH, TPR following ^{13}CO and H_2 coadsorption did not produce significant amounts of $^{13}CH_3OH$ or $(^{13}CH_3)_2O$.

Keywords: Methoxy; Ni/Al_2O_3; TPR; C_2H_5OH; trapping; ^{13}CO

1. Introduction

Previous temperature-programmed reaction (TPR) studies of the interaction of CO and H_2 on Ni/Al_2O_3 catalysts indicated the presence of two types of reaction sites where CH_4 formed [1,2]. The more active sites were shown to be adsorbed CO on Ni, and the less active sites were concluded to be CH_3O, which formed on the Al_2O_3 support by a spillover process. The presence of CH_3O was conjectured based on the simultaneous formation of CO and H_2 and the H : CO stoichiometry during TPD. Methoxy formation from CO and H_2 has not been detected with IR on Ni/Al_2O_3, but it has been seen with IR on Pt/Al_2O_3 and Pd/Al_2O_3 [3,4]. Moreover, this CH_3O is hydrogenated to CH_4 during TPR on Pt/Al_2O_3 and Pd/Al_2O_3 [3,4]. On Ni/Al_2O_3, the low activity of CH_3O for CH_4 formation indicates CH_3O is not important during steady-state catalytic reaction. In contrast, it may be important on Pt/Al_2O_3 and Pd/Al_2O_3.

The similarity in the behavior of adsorbed CH_3OH and coadsorbed CO and H_2 for both hydrogenation during TPR and decomposition during TPD strongly suggests that CH_3O is present on Ni/Al_2O_3 [5,6]. To directly detect this CH_3O and to study its reaction properties, we trapped CH_3O with C_2H_5OH to form CH_3OH and ethers. Labeled $^{13}CH_3O$ was formed by coadsorbing ^{13}CO and H_2 at elevated temperature. Isotope labeling allows the source of the resulting products during TPR to be readily distinguished. Ethanol was used as a trapping reagent instead of CH_3OH because the resulting ethers were easy to distinguish. Kinnemann et al.

[7,8] reported that C_2H_5OH was an effective trapping reagent for detection of CH_3O on methanol synthesis catalysts. During TPD of C_2H_5OH on our Ni/Al_2O_3 catalyst [6] some carbon-containing products did not completely desorb by 950 K, apparently because surface carbon formed. Because adsorbed species were removed at lower temperatures during TPR and because fewer products formed, TPR was used for these trapping experiments instead of TPD. The TPR spectra for coadsorbed $^{13}CO+H_2$ were compared to TPR spectra of adsorbed C_2H_5OH and of coadsorbed ^{13}CO, H_2 and C_2H_5OH. The detection of $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ in significant quantities when C_2H_5OH was adsorbed with $^{13}CO + H_2$ shows directly that $^{13}CH_3O$ formed from $^{13}CO + H_2$ at 385 K.

2. Experimental

Temperature-programmed reaction (TPR) experiments were carried out on a 5.7% Ni/Al_2O_3 catalyst at ambient pressure in a flow system that has been described previously [1,9,10]. A 100 mg sample of the catalyst (60–80 mesh) was supported on a quartz frit in a 1 cm o.d. quartz reactor, which was placed in an electric furnace. A 0.5 mm o.d. chromel–alumel shielded thermocouple was centered in the catalyst bed and connected to a temperature programmer to control the furnace to provide a constant heating rate of 1 K/s. The carrier gases (He and H_2) at atmospheric pressure flowed over the catalyst at a flowrate of 100 cm^3/min (STP). Immediately downstream, the gas was analyzed with a UTI quadrupole mass spectrometer located in a turbopumped ultrahigh vacuum system.

For TPR experiments, the reduced and passivated catalyst was pretreated for 2 h at 773 K in H_2 flow and then cooled to room temperature. The ^{13}CO was adsorbed for 30 or 60 min (0.05 cm^3 pulses every 30 s) at 385 K in H_2 at 0.8 atm or 2.6 atm. In most experiments, following ^{13}CO adsorption, gaseous C_2H_5OH was adsorbed at 300 K by evaporation of 2 μL from the tip of a liquid syringe. After the catalyst was held for 30 min at 300 K in He flow for equilibration, TPR was carried out by raising the catalyst temperature in H_2 flow at a rate of 1 K/s. In some experiments, following ^{13}CO adsorption, TPR was carried out without C_2H_5OH exposure, and in some experiments C_2H_5OH was adsorbed without ^{13}CO exposure. During TPR, CH_4 ($m/z = 15$), $^{13}CH_4$ (17), H_2O, C_2H_4 (26), CO, ^{13}CO (29), C_2H_6 (30), C_2H_4O (29,43), C_2H_5OH (31,46), $^{13}CH_3OH$ (32,33), CO_2, $^{13}CO_2$ (45), $(^{13}CH_3)_2O$ (47,48), $^{13}CH_3OC_2H_5$ (60,61), and $(C_2H_5)_2O$ (59,74), were detected. Mass 31 was corrected for the cracking fragment from $^{13}CH_3OH$, and the ratio of the remaining mass 31 and mass 46 signals was compared to the C_2H_5OH calibration to determine if $^{12}CH_3OH$ (31) formed. To obtain ^{13}CO spectra, the cracking fractions at mass 29 from $^{13}CO_2$, C_2H_6, $^{13}CH_3OH$, C_2H_4O, C_2H_5OH, and $(^{13}CH_3)_2O$ were subtracted from the mass 29 signals. The signals at mass 17 were corrected for H_2O cracking to obtain $^{13}CH_4$ signals, and the CH_4 signals were obtained by correcting mass 15 for cracking of $^{13}CH_4$, C_2H_6, C_2H_4O, and

C_2H_5OH. Known volumes of pure gases or liquids were injected into the H_2 carrier gas, downstream of the reactor, to calibrate the mass spectrometer. The calibration factor for $(CH_3)_2O$ was used to estimate desorption rates of $(C_2H_5)_2O$, $^{13}CH_3OC_2H_5$, and $(^{13}CH_3)_2O$, and the calibration factor for CO at mass 28 was used to estimate C_2H_4O (mass 29) formation rates.

The 5.5% Ni/Al_2O_3 catalyst was prepared by impregnating Kaiser Al_2O_3 (A-201) to incipient wetness with an aqueous solution of nickel nitrate. After being dried in a vacuum oven for 24 h at 373–383 K, the catalyst was directly reduced in H_2 for 10 h at 773 K, and passivated with 2% O_2 in N_2 at room temperature. Weight loading was measured by inductively coupled plasma. The Ni dispersion of 1.7% was estimated by TPR of CO [6]. Ethanol (USP, 200 proof) was obtained from Midwest Grain Products Co., and the ^{13}CO (99.2% ^{13}C) was supplied by Isotec Inc.

3. Results

3.1. LOW $^{13}CH_3O$ COVERAGE

Temperature-programmed reaction on the 5.7% Ni/Al_2O_3 catalyst is similar to that reported for other Ni/Al_2O_3 catalysts following CO adsorption at 300 K [5,11]. Two distinct CH_4 peaks were observed, due to hydrogenation of CO adsorbed on Ni (peak temperature (T_p) of 445 K) and hydrogenation of CH_3O that formed on the Al_2O_3 by spillover (T_p = 546 K). The amount of $^{13}CH_3O$ was increased by adsorbing ^{13}CO in H_2 flow (ambient pressure) at 385 K for 30 min, and fig. 1 shows the resulting spectra. The two $^{13}CH_4$ peaks were present at 463 and 533 K. Note that most of the ^{13}CO was hydrogenated to $^{13}CH_4$ (110 μmol/g catalyst) and only a small amount of ^{13}CO was seen. Water also formed during TPR and desorbed above 600 K. No significant amounts of $(^{13}CH_3)_2O$ and $^{13}CH_3OH$ were observed. For this low dispersion catalyst the rate of methoxy formation on Al_2O_3 was slow during adsorption at 385 K and the Al_2O_3 surface was not saturated.

Fig. 2 shows the TPR spectra where the same adsorption procedure as for fig. 1 was repeated for ^{13}CO and H_2, and the catalyst was then exposed to 2 μL of C_2H_5OH (350 μmol/g catalyst) in He flow. Note that C_2H_5OH, which adsorbs on Al_2O_3, dramatically changed the ^{13}C product distribution during TPR. Less $^{13}CH_4$ (91 μmol/g catalyst) formed, and instead 10 μmol $^{13}CH_3OH$/g catalyst formed. The $^{13}CH_3OH$ desorbed in a single peak at 525 K in a shape that is almost identical to that for C_2H_5OH desorption. Some ^{13}CO and $^{13}CO_2$ were also observed. In addition, a small amount of $(^{13}CH_3)_2O$ (1.5 μmol/g catalyst) was seen in a single peak at 530 K (fig. 2b). The presence of coadsorbed C_2H_5OH dramatically increased $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ desorption.

The coadsorbed C_2H_5OH was hydrogenated to CH_4 (fig. 2a) in a similar matter to the $^{13}CH_3O$, and this is discussed in detail elsewhere [6]. Some C_2H_6, C_2H_4O,

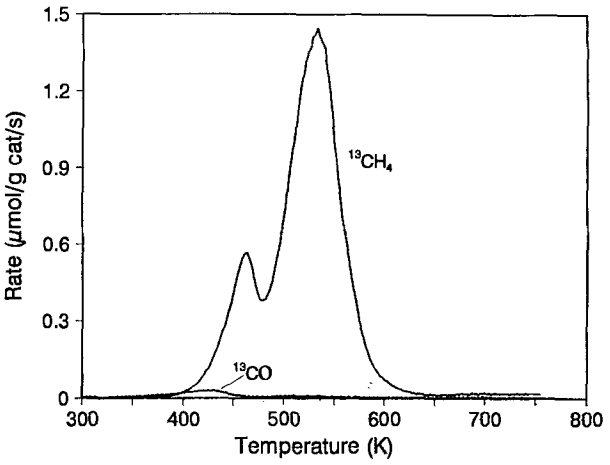


Fig. 1. TPR spectra for ^{13}CO adsorbed in H_2 flow (ambient pressure) for 30 min at 385 K on 5.7% Ni/Al_2O_3.

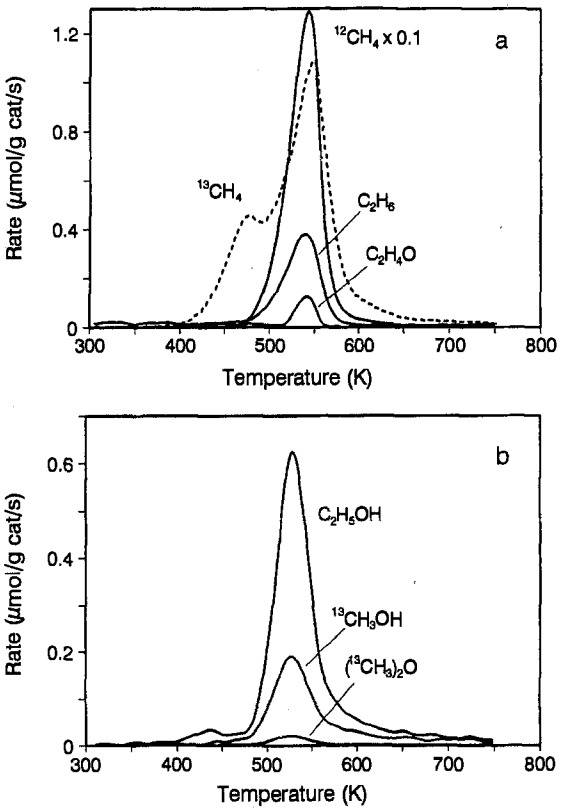


Fig. 2. TPR spectra for ^{13}CO adsorbed in H_2 flow (ambient pressure) for 30 min at 385 K followed by C_2H_5OH adsorption (2 μL) at 300 K on 5.7% Ni/Al_2O_3.

and C_2H_5OH were observed, but 80% of the ^{12}C formed $^{12}CH_4$. No significant amounts of $^{13}CH_3OC_2H_5$ and $(C_2H_5)_2O$ were detected. Water formed during TPR, but is not shown in fig. 2 for clarity. The product amounts are listed in table 1. Within experimental accuracy all the injected C_2H_5OH adsorbed and was detected as products during TPR. Accurate exposure amounts could not be obtained with the liquid syringe.

As expected, when 2 μL of C_2H_5OH was adsorbed alone, neither $^{13}CH_3OH$ nor $(^{13}CH_3)_2O$ were observed during TPR. Ninety-two percent of the total ^{12}C in C_2H_5OH appeared as $^{12}CH_4$ (685 μmol/g catalyst), and the peak shape was the same as the $^{12}CH_4$ peak in fig. 2a. Some C_2H_6 and C_2H_4O were also observed at the same temperature as CH_4, but no significant amount of C_2H_5OH desorbed at this C_2H_5OH coverage in the absence of preadsorbed ^{13}CO and H_2 [6]. At higher C_2H_5OH coverage (4 μL exposure) C_2H_5OH desorbed.

3.2. HIGH $^{13}CH_3O$ COVERAGE

An increase in the $^{13}CH_3O$ coverage, by longer exposure to ^{13}CO and at higher H_2 pressure (2.6 atm), increased the amplitude of the $^{13}CH_4$ signal during TPR. As shown in fig. 3, the high temperature $^{13}CH_4$ peak increased, and 251 μmol $^{13}CH_4$/g catalyst formed. Small amounts of ^{13}CO (9 μmol/g catalyst), $^{13}CO_2$ (0.8 μmol/g catalyst), and $(^{13}CH_3)_2O$ (<0.5 μmol/g catalyst) were detected. No $^{13}CH_3OH$ desorption was observed. When the catalyst was exposed instead to 1 μL of CH_3OH (250 μmol/g catalyst) in He flow at 300 K to obtain a similar coverage of CH_3O on Al_2O_3, the subsequent TPR exhibited the CH_4 (269 μmol/g catalyst) and CO (7 μmol/g catalyst) peaks that were similar to the $^{13}CH_4$ and ^{13}CO peaks in fig. 3.

Table 1
Amounts of products (μmol/g catalyst) formed during TPR on Ni/Al_2O_3

Products	Amounts of products (μmol/g catalyst)			
	low $^{13}CH_3O$ coverage		high $^{13}CH_3O$ coverage	
	no C_2H_5OH	with C_2H_5OH	no C_2H_5OH	with C_2H_5OH
$^{12}CH_4$	<1	587	<2	590
$^{13}CH_4$	110	91	251	161
^{13}CO	3	6	9	7
$^{12}C_2H_6$	–	21	–	21
$^{12}C_2H_4O$	–	8	–	9
$^{13}CH_3OH$	–	10	–	55
$^{12}C_2H_5OH$	–	42	–	55
$^{13}CO_2$	<0.5	2	0.8	3
$(^{13}CH_3)_2O$	–	1.5	<0.5	6
total ^{12}C	<1	729	<2	760
total ^{13}C	113	112	261	238

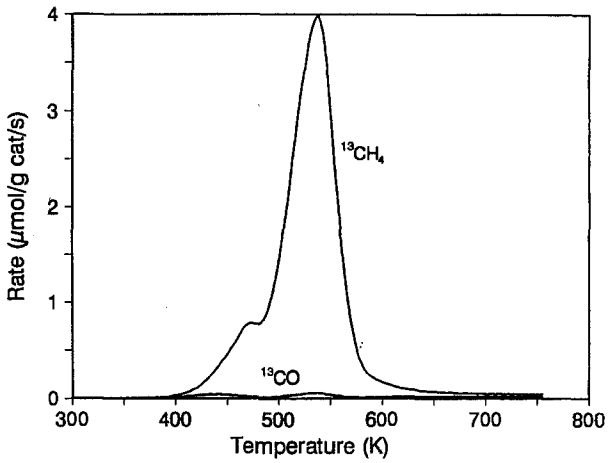


Fig. 3. TPR spectra for ^{13}CO adsorbed in H_2 flow (2.6 atm) for 60 min at 385 K on 5.7% Ni/Al_2O_3.

Less than 1 μmol $(CH_3)_2O$/g catalyst was obtained, and no CH_3OH desorption was detected.

Fig. 4 shows the TPR spectra obtained when the same $^{13}CO + H_2$ adsorption procedure used for fig. 3 was repeated, and the catalyst was then exposed to 2 μL of C_2H_5OH at room temperature. The rates of $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ formation dramatically increased, and 55 μmol $^{13}CH_3OH$ and 6 μmol $(^{13}CH_3)_2O$ per gram catalyst were observed in single peaks at 515 K. The peak temperature and shape of the $^{13}CH_4$ spectrum are similar to those in fig. 3, but the $^{13}CH_4$ amount decreased by 90 μmol/g catalyst to 161 μmol/g catalyst. When ^{13}CO and H_2 coadsorption was followed by 2 μL of CH_3OH exposure, similar results were obtained during the subsequent TPR. Significant amounts of $^{13}CH_3OH$ and ethers ($(^{13}CH_3)_2O$, $^{13}CH_3OCH_3$, and $(CH_3)_2O$) were obtained.

The distribution of ^{12}C-containing products from C_2H_5OH hydrogenation at high $^{13}CH_3O$ coverage is similar to that at low $^{13}CH_3O$ coverage (table 1). Methane was the main product (590 μmol/g catalyst), and similar amounts of C_2H_6 (21 μmol/g catalyst), C_2H_4O (9 μmol/g catalyst), and unreacted C_2H_5OH (55 μmol/g catalyst) were detected. The total number of adsorbed molecules ($^{13}CH_3O$, C_2H_5O, and C_2H_5OH) is estimated to be $1.7 \times 10^{14}/cm^2$ of Al_2O_3. Using C_2H_5OH chemisorption at saturation coverage, Arai et al. [12] determined that the number of adsorption sites on Al_2O_3 was 2.0×10^{14} sites/cm^2.

4. Discussion

Trapping of CH_3O by C_2H_5OH is an effective means to show directly that CH_3O forms from coadsorption of CO and H_2 on Ni/Al_2O_3. The formation of sig-

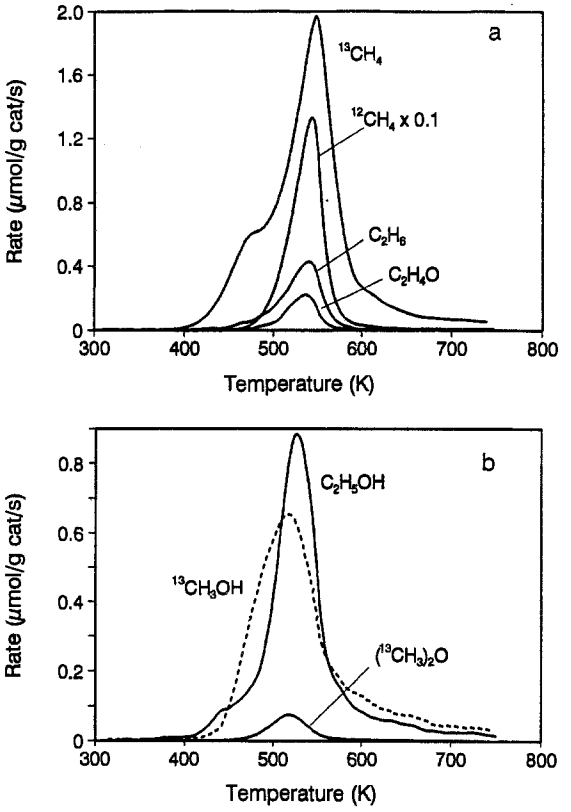


Fig. 4. TPR spectra for ^{13}CO adsorbed in H_2 flow (2.6 atm) for 60 min at 385 K followed by C_2H_5OH adsorption (2 μL) at 300 K on 5.7% Ni/Al_2O_3.

nificant amounts of $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ when C_2H_5OH was adsorbed following ^{13}CO and H_2 coadsorption on Ni/Al_2O_3 indicates that $^{13}CH_3O$ formed on the Al_2O_3 surface from ^{13}CO and H_2. The C_2H_5OH is known to adsorb on the Al_2O_3 surface because essentially the same amount of C_2H_5OH adsorption was observed on Al_2O_3 alone.

During CO and H_2 coadsorption at 385 K, CH_3O forms on Al_2O_3 by spillover, and CO also adsorbs on Ni. During TPR, some CO on Ni hydrogenated to form CH_4 in the lower temperature peak, and the remaining CO forms additional CH_3O on Al_2O_3 by spillover. Then CH_3O on Al_2O_3 is hydrogenated to form CH_4 at higher temperature (fig. 1). More CH_4 formed during TPR in fig. 3 than in fig. 1 because more CH_3O formed on Al_2O_3 because of the longer exposure time and the higher H_2 pressure. Even at the high CH_3O coverage, CH_3OH was not observed during TPR, probably because Ni/Al_2O_3 is not a CH_3OH synthesis catalyst.

On other Ni/Al_2O_3 catalysts and on Pt/Al_2O_3 catalysts, CH_3OH was not observed during TPR following CO and H_2 adsorption to saturation [13,14]. On

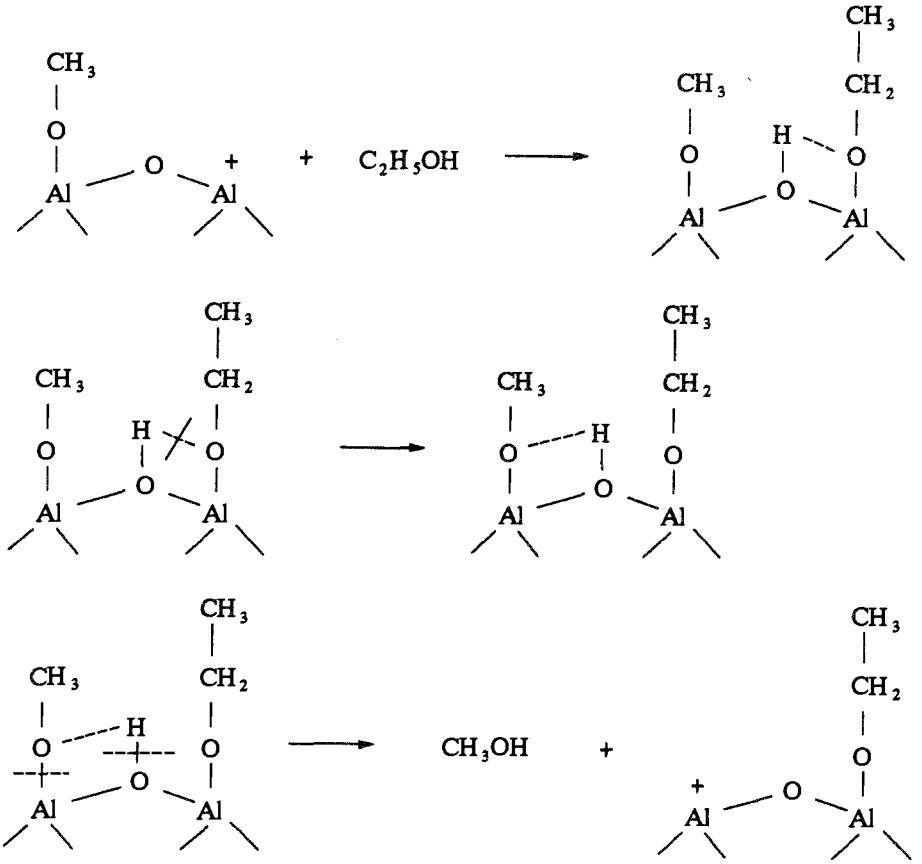
Pd/Al_2O_3, however, a small amount of CH_3OH, 1% of the total adsorbed CO, was detected during TPR at high CH_3O coverage [15]. Palazov et al. [4] observed CH_3O on a Pd/Al_2O_3 catalyst with IR, and proposed that CH_3OH formation was due to hydrogenation of CH_3O on Pd, though they did not detect CH_3O on Pd/SiO_2 under the same conditions. They suggested that CH_4 formed by hydrogenation of CH_xO, which formed on Pd by reaction of adsorbed CO and H or by reverse spillover of CH_3O from Al_2O_3. Methanol formed at high temperature and pressure from CO and H_2 at steady state on supported Pd [16], but at lower pressure and temperature CH_4 was the dominant product [4]. Anderson and Jen [17] analyzed the mobility of CH_3O and H and their reaction to form CH_4 on Al_2O_3 by using atom superposition and electron delocalization molecular orbital theory. They concluded that the reaction of CH_3O and H on Al_2O_3 to form CH_4 was more likely than CH_3OH formation.

4.1. $^{13}CH_3OH$ FORMATION

Following ^{13}CO and H_2 coadsorption, the adsorption of C_2H_5OH significantly increased the amount of $^{13}CH_3OH$ formed during TPR (figs. 2 and 4). 9% of the ^{13}C at low $^{13}CH_3O$ coverage and 24% of the ^{13}C at high $^{13}CH_3O$ coverage was present in $^{13}CH_3OH$ during TPR, and most of the remaining ^{13}C-containing adsorbates were hydrogenated to form $^{13}CH_4$ during TPR. Similar effects were obtained when CH_3OH was coadsorbed instead of C_2H_5OH. Kinnemann et al. [7] and Chauvin et al. [8] used C_2H_5OH to identify a CH_3O intermediate on CH_3OH synthesis catalysts. They injected excess C_2H_5OH liquid (1 mL) into a bulb containing $Cu–ZnAl_2O_4$ or $ZnAl_2O_4$, which had been pretreated with a $CO + H_2$ mixture, and they detected CH_3OH by gas chromatography. They concluded that CH_3OH formed immediately at room temperature due to protonation of the CH_3O groups by C_2H_5OH [8]. Since $^{13}CH_3OH$ desorbed above 400 K in the present study, the same reaction is possible:

$$^{13}CH_3O + C_2H_5OH \rightarrow {}^{13}CH_3OH + C_2H_5O\,.$$

The formation of $^{13}CH_3OH$ may be a multi-step process in which C_2H_5OH first dissociates to form adsorbed H on weak basic sites (Al–O–Al). This H then reacts with adsorbed $^{13}CH_3O$, possibly at elevated temperatures (scheme 1). Previous IR studies [17,12] showed that C_2H_5OH decomposed on Al_2O_3 to form adsorbed C_2H_5O and H. Note that C_2H_5OH desorbs in a sharp peak at 530 K (figs. 2 and 4). Ethanol formation may also be attributed to the reaction of adsorbed C_2H_5O with H on weak basic sites. Spilled-over H, which forms by dissociative adsorption of H_2 on Ni and the spillover onto Al_2O_3, adsorbs on $Al–O^-$ sites (strong basic sites) as OH. This H is unlikely to react with adsorbed $^{13}CH_3O$ to form $^{13}CH_3OH$, since no significant amount of $^{13}CH_3OH$ was observed during TPR following ^{13}CO and H_2 coadsorption at 385 K [13,14].



Scheme 1.

4.2. ETHER FORMATION

The introduction of C_2H_5OH following ^{13}CO and H_2 coadsorption at 385 K also increased the amount of $(^{13}CH_3)_2O$ formed during TPR. Dimethyl ether forms when CH_3OH decomposes on Al_2O_3 and Ni/Al_2O_3 catalysts [6,18–20], and two mechanisms have been proposed for its formation. Jain and Pillai [18] examined dehydration of alcohols over Al_2O_3 at steady state by changing the partial pressure of alcohols. They concluded that $(CH_3)_2O$ formed via a bimolecular reaction between CH_3O on an acidic site and strongly adsorbed CH_3OH on a basic site. Similar models were developed by Padmanabhan et al. [21] and Knözinger et al. [22]. Matsushima and White [19] suggested that ether formed through the interaction of two adsorbed CH_3O. They observed that in the presence of gas-phase CD_3OD, the ether produced during thermal desorption from an Al_2O_3 surface on which CH_3OH had been preadsorbed, was primarily CH_3OCH_3. DeCanio et al. [20] did not observe physisorbed alcohol at the temperature where ether formed,

and they concluded that the reaction was between two alkoxide species and not an alkoxide and a molecularly adsorbed alcohol.

In the present study, $(^{13}CH_3)_2O$ formed during TPR following ^{13}CO adsorption in 2.6 atm H_2 at 385 K, although the amount of $(^{13}CH_3)_2O$ was less than 0.5 μmol/g catalyst (table 1). Since no $^{13}CH_3OH$ was detected, $(^{13}CH_3)_2O$ formation may be due to the reaction between two adjacent $^{13}CH_3O$ species on Al_2O_3, as described by DeCanio et al. [20]. Previous studies on Pd/Al_2O_3 [15] and Pt/Al_2O_3 [14] also detected $(CH_3)_2O$ formation during TPR following CO and H_2 coadsorption at 385 K to high CH_3O coverage.

Note that the amount of $(^{13}CH_3)_2O$ significantly increased when C_2H_5OH was introduced (table 1). The formation of $(^{13}CH_3)_2O$ is unlikely due to a coverage effect, because the total amount of $^{13}CH_3O$ did not change. Instead, $^{13}CH_3OH$, which formed by the reaction between C_2H_5OH and $^{13}CH_3O$, may subsequently react with an adjacent $^{13}CH_3O$ to form $(^{13}CH_3)_2O$. Both reactions for $(CH_3)_2O$ formation, CH_3OH+CH_3O and CH_3O+CH_3O, thus may occur during TPR following CO and H_2 coadsorption and C_2H_5OH adsorption on Ni/Al_2O_3. The reaction between CH_3OH and CH_3O may be faster than the reaction between two CH_3O. TPR of CH_3OH on Ni/Al_2O_3 produced CH_3OH and $(CH_3)_2O$ when excess CH_3OH was adsorbed [6].

4.3. ETHANOL HYDROGENATION

Ethanol directly adsorbs on Al_2O_3 to form adsorbed C_2H_5OH and C_2H_5O species, which have been detected by IR [12,23,24]. The $^{12}CH_4$ peak is the result of C_2H_5O and C_2H_5OH hydrogenation. Ethoxy adsorbed on Al_2O_3 also decomposes to form C_2H_4 and C_2H_4O during TPR, and some C_2H_4 is hydrogenated to form C_2H_6 [25–27]. Kim and Barteau [28] also observed C_2H_4 and C_2H_4O products during TPD of C_2H_5OH on TiO_2. They proposed that C_2H_4O formed by α-H elimination and Al–O bond rupture of a C_2H_5O species. The formation of C_2H_4 was attributed to α-H elimination and C–O bond rupture simultaneously [28].

5. Conclusions

Following ^{13}CO and H_2 coadsorption at 385 K on Ni/Al_2O_3, introduction of C_2H_5OH dramatically increased the rates of $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ formation during TPR. In the absence of coadsorbed C_2H_5OH, no $^{13}CH_3OH$ was detected. The $^{13}CH_3OH$ formed by surface reaction between C_2H_5OH and $^{13}CH_3O$. The formation of $^{13}CH_3OH$ and $(^{13}CH_3)_2O$ directly shows that $^{13}CH_3O$ formed on the Al_2O_3 support following ^{13}CO and H_2 coadsorption. Dimethyl ether formed by reactions both between $^{13}CH_3O$ and $^{13}CH_3OH$ and between two $^{13}CH_3O$ species.

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