Trapping of CH$_3$O formed from CO + H$_2$

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Methoxy formed on Al$_2$O$_3$ from $^{13}$CO and H$_2$ coadsorption on Ni/Al$_2$O$_3$ was trapped by C$_2$H$_5$OH adsorption and temperature-programmed reaction (TPR). The presence of excess C$_2$H$_5$OH significantly increases the rate of $^{13}$CH$_3$OH and ($^{13}$CH$_3$)$_2$O formation. The $^{13}$CH$_3$OH forms by the reaction of C$_2$H$_5$OH with $^{13}$CH$_3$O on Al$_2$O$_3$. In the absence of C$_2$H$_5$OH, TPR following $^{13}$CO and H$_2$ coadsorption did not produce significant amounts of $^{13}$CH$_3$OH or ($^{13}$CH$_3$)$_2$O.

Keywords: Methoxy; Ni/Al$_2$O$_3$; TPR; C$_2$H$_5$OH; trapping; $^{13}$CO

1. Introduction

Previous temperature-programmed reaction (TPR) studies of the interaction of CO and H$_2$ on Ni/Al$_2$O$_3$ 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$_3$O, which formed on the Al$_2$O$_3$ support by a spillover process. The presence of CH$_3$O 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$_2$O$_3$, but it has been seen with IR on Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ [3,4]. Moreover, this CH$_3$O is hydrogenated to CH$_4$ during TPR on Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ [3,4]. On Ni/Al$_2$O$_3$, the low activity of CH$_3$O for CH$_4$ formation indicates CH$_3$O is not important during steady-state catalytic reaction. In contrast, it may be important on Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$.

The similarity in the behavior of adsorbed CH$_3$OH and coadsorbed CO and H$_2$ for both hydrogenation during TPR and decomposition during TPD strongly suggests that CH$_3$O is present on Ni/Al$_2$O$_3$ [5,6]. To directly detect this CH$_3$O and to study its reaction properties, we trapped CH$_3$O with C$_2$H$_5$OH to form CH$_3$OH and ethers. Labeled $^{13}$CH$_3$O 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$_3$OH because the resulting ethers were easy to distinguish. Kinnemann et al.
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[7,8] reported that C₂H₅OH was an effective trapping reagent for detection of CH₃O on methanol synthesis catalysts. During TPD of C₂H₅OH on our Ni/Al₂O₃ 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 ¹³CO+H₂ were compared to TPR spectra of adsorbed C₂H₅OH and of coadsorbed ¹³CO, H₂ and C₂H₅OH. The detection of ¹³CH₃OH and (¹³CH₃)₂O in significant quantities when C₂H₅OH was adsorbed with ¹³CO + H₂ shows directly that ¹³CH₃O formed from ¹³CO + H₂ at 385 K.

2. Experimental

Temperature-programmed reaction (TPR) experiments were carried out on a 5.7% Ni/Al₂O₃ 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 H₂) at atmospheric pressure flowed over the catalyst at a flowrate of 100 cm³/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 H₂ flow and then cooled to room temperature. The ¹³CO was adsorbed for 30 or 60 min (0.05 cm³ pulses every 30 s) at 385 K in H₂ at 0.8 atm or 2.6 atm. In most experiments, following ¹³CO adsorption, gaseous C₂H₅OH 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 H₂ flow at a rate of 1 K/s. In some experiments, following ¹³CO adsorption, TPR was carried out without C₂H₅OH exposure, and in some experiments C₂H₅OH was adsorbed without ¹³CO exposure. During TPR, CH₄ (m/z = 15), ¹³CH₄ (17), H₂O, C₂H₄ (26), CO, ¹³CO (29), C₂H₆ (30), C₂H₄O (29,43), C₂H₅OH (31,46), ¹³CH₂OH (32,33), CO₂, ¹³CO₂ (45), (¹³CH₃)₂O (47,48), ¹³CH₃OC₂H₅ (60,61), and (C₂H₅)₂O (59,74), were detected. Mass 31 was corrected for the cracking fragment from ¹³CH₃OH, and the ratio of the remaining mass 31 and mass 46 signals was compared to the C₂H₅OH calibration to determine if ¹²CH₃OH (31) formed. To obtain ¹³CO spectra, the cracking fractions at mass 29 from ¹³CO₂, C₂H₆, ¹³CH₃OH, C₂H₄O, C₂H₅OH, and (¹³CH₃)₂O were subtracted from the mass 29 signals. The signals at mass 17 were corrected for H₂O cracking to obtain ¹³CH₄ signals, and the CH₄ signals were obtained by correcting mass 15 for cracking of ¹³CH₄, C₂H₆, C₂H₄O, and