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Determination of formate decomposition rates and relation to product formation during CO hydrogenation over supported cobalt

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ABSTRACT

The concentration and reactivity of the formate species present at the surface of a supported cobalt catalyst were investigated by *in situ* diffuse reflectance FT-IR spectroscopy (DRIFTS). The specific concentration of formates under a CO/H_2 feed was determined through calibration curves determined from reference samples prepared by impregnation with sodium formate. Two types of formates reactivity were observed upon removal of CO from the feed. The decaying period of the fastest decomposing species ("fast formats") was identical to that of the carbonyl adsorbed on the metallic cobalt phase, suggesting that the fast formates were produced by spill-over of CO adsorbed on the metal onto the support. The slowest decomposing formates were at least one order of magnitude less reactive than the fast formates. The comparison of the rate of formation of methanol measured under steady-state reaction to that of decomposition of formates indicated that only the fast formates could potentially be an intermediate in the formation of methanol. The rate of formation of methane and propene, the main products observed under our reaction conditions, were yet markedly higher than that of fast formate decomposition. Therefore, the formation of hydrocarbons involved surface intermediates other than the formates observable by DRIFTS.

1. Introduction

Synthetic fuels and base chemicals can be produced through the conversion of synthesis gas ("syngas", a mixture of carbon oxides and dihydrogen) [1]. The nature of the reaction mechanism of the Fischer–Tropsch synthesis over cobalt-based catalysts is still a matter of debate [2,3]. Whether chain growth occurs via hydrocarbon fragments or involves partially oxygenated intermediates has raised particular attention.

Several studies have reported *in situ* FT-IR data with a view at understanding the nature of surface species formed under reaction conditions. Various types of CO(ads) are reported, the exact nature of the adsorption sites of which are quite complex to unravel [4,5]. Smith et al. proposed that chain growth leading to ethanol involved two different cobalt sites in CuCo-based samples, on one of which CO was not dissociating [6]. Kollár et al. reported that several oxygenated compounds were formed at the surface of 15% Co + 0.5% Pt supported on oxides [7]. In the case of a Co-Mg-O sample, Schweicher et al. showed that the surface formates observed by DRIFTS were irrelevant for the formation of ethane [8].

Formates have been proposed as reaction intermediates in the synthesis of methanol over copper-based catalysts [9–11]. Different formate species were reported over Cu/$ZnAl_2O_4$ and those were proposed to exhibit different reactivity for the formation of methanol or the reverse water-gas shift reaction [12].

We recently reported a two-fold reactivity of the formates present at the surface of Siralox®-supported cobalt used for CO hydrogenation [13]. The objective of the present study was to determine whether or not these formates could be considered as reaction intermediates in the formation of some of the products observed. Therefore, the rate of decomposition of formates was compared to that of the main reaction products monitored, i.e. methane, propene and methanol. The rate comparison was carried at three different temperatures around 220 °C, which is typically used for Fischer–Tropsch synthesis over cobalt-based catalysts.

2. Experimental

The 14 wt.% Co/Siralox® (5% silica–95% alumina) catalyst was supplied by IFPEN. The surface area of the sample was 129 m^2/g. The average particle size of the calcined sample was 12 nm, estimated

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from the line broadening of the Co_3O_4 diffraction peaks corresponding to index plans 422 ($2\theta = 55.9°$) and 511 ($2\theta = 59.4°$) using Scherrer's equation [14,15]. The XRD patterns (not shown) were recorded on a Bruker D5005 diffractometer using the radiation Cu(Kα). High purity Ar, CO and H_2 were purchased from l'Air Liquide. The gases were used without further purification.

DRIFTS experiments were performed at ambient pressure with a high temperature DRIFT cell (from Spectra-Tech®) fitted with KBr windows, using a collector assembly. A description and properties of the cell can be found elsewhere [16]. The spectrophotometer used was a Nicolet 6700 (ThermoFischer Scientific) fitted with a liquid-N_2 cooled MCT detector. The DRIFT spectra were recorded at a resolution of 4 cm^{-1} and 8 or 32 scans accumulation depending on the -resolution desired. The DRIFTS spectra are reported as log ($1/R$), where R is the sample reflectance. This pseudo-absorbance gives a better linear representation of the band intensity against surface coverage than that given by the Kubelka–Munk function for strongly absorbing media such as those based on metals supported on oxides [17]. The contribution of gas-phase CO was subtracted using a CO(g) spectrum collected at the reaction temperature over SiC, which enabled a perfect correction [18].

The catalysts were pre-reduced at 450 °C for 1 h in a flow of 55 STPmL min^{-1} of 60% H_2 in Ar. The samples were then cooled to the reaction temperature. The feed composition was: 30% CO + 60% H_2 in Ar, unless otherwise stated. The total flow rate was 30 ml min^{-1}, unless otherwise stated. The gas hourly space velocity (GHSV) was about 18,000 h^{-1}. The CO conversion was always lower than 5% at all temperatures and therefore the DRIFTS cell could be considered as a differential reactor. Note that the maximum concentration of methanol measured at the cell exit was ca. 50 ppm, while the thermodynamic equilibrium concentration corresponding to our feed at 220 °C and 1 bar is ca. 1000 ppm.

The reactor effluent was analyzed both using an Inficon quadrupolar mass spectrometer and a FT-IR gas-cell fitted in a Nicolet spectrometer. The IR gas-cell exhibited a 2 m-long pathlength and enabled measuring concentration of reaction products in the tens of ppm. Several m/z fragments were recorded over the mass spectrometer over the 2–80 m/z range.

3. Results and discussion

The 14% Co/Siralox was pre-treated under H_2 at 450 °C for 60 min to reduce part of the cobalt oxide into a metallic state. The extent of cobalt reduction was not assessed *in situ*, but alumina-supported cobalt samples (non-promoted by a noble metal) reduced under similar conditions would typically display a level of reduction comprised between 60 and 80% [19–22]. The DRIFTS spectra (Fig. 1) obtained at steady-state (ca. 22 h of time on stream) at 210 and 230 °C were essentially identical in nature to that collected at 220 °C, which was already discussed elsewhere [13].

In short, the bands at 2927 and 2856 cm^{-1} were mostly due to stretching vibrations of methylene ($-CH_2-$) groups, typical of long carbon chain alkanes which may accumulate in the catalyst pores as waxes. The band at 2032 cm^{-1} is typical of CO linearly adsorbed on a metallic surface of cobalt [1,23,24]. The bands at 1592 cm^{-1} (asymmetric OCO stretching), 1392 cm^{-1} (C–H bending) and 1378 cm^{-1} (symmetric OCO stretching) can be assigned to formate species on the alumina surface [25,26]. The C–H stretching modes and other combination bands usually located in the region 2700–3000 cm^{-1} were not resolved because of the overlap of the C–H stretching bands of hydrocarbons. The band at 1462 cm^{-1} (associated with a band at ca. 1590 cm^{-1} that was masked by that of the formates) was related to carboxylate species.

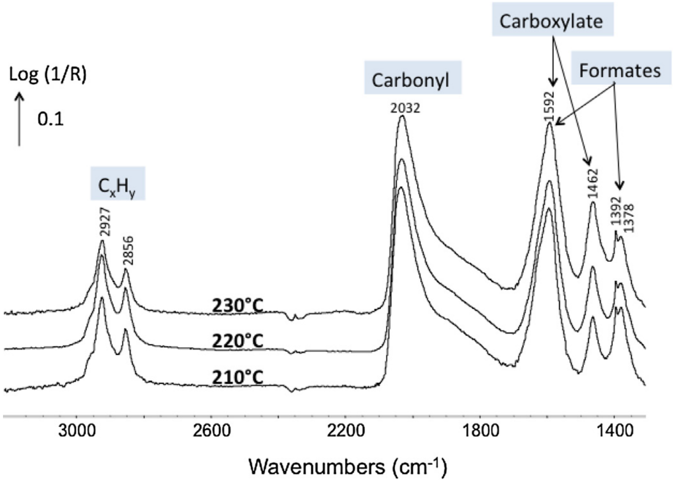

Fig. 1. *Operando* DRIFTS spectra collected at 210, 220 and 230 °C after 22 h on stream. Feed: 30% CO + 60% H_2 in Ar. The signal of the sample at the corresponding temperature under H_2 following reduction at 450 °C was used as background. The spectrum of CO(g) was subtracted.

The concentration of formates on the 14% Co/Siralox was estimated using reference samples of known concentrations of sodium formates deposited on a plain alumina (67 $m^2\,g^{-1}$), which typically leads to formate coordinated two-fold to the alumina surface at low loadings. The use of this calibration technique was already demonstrated on other supports for the same purpose [27,28]. The formate DRIFTS signal was integrated over the range 1411–1307 cm^{-1} (Fig. 2A). Other bands of formates could not be used because of the overlapping with the signals of C–H stretching of hydrocarbons (around 3000 cm^{-1}) and carboxylate species (around 1600 cm^{-1}). The calibration curve obtained by using the three standards resulted in a linear relation between formate concentration and DRIFTS band intensity (Fig. 2B). Note that the use of higher loadings of sodium formate led to the presence of new bands that we assigned to plain ionic sodium formate crystals (not shown).

More work would yet be needed to ascertain the bonding mode of formates during impregnation of the alumina with sodium formates, e.g. whether a species doubly coordinated to the alumina surface is formed or if the formate species is still bound to the sodium cation. These species could possibly exhibit different molar extinction coefficient. In any case, the similarity between the band positions of the standard samples and that obtained on the operando spectra suggests that those were similar in structure.

The variation of the carbonyl and formate DRIFTS signals following the removal of CO from the feed was monitored at 210, 220 and 230 °C. Each of these signals decayed and the logarithm of the signals normalized to those taken at steady-state are given in Fig. 3. The decay of the logarithm of the relative formate band area was not uniform and could be approximately decomposed into two linear sections, as already reported earlier for the data at 220 °C [13]. A fast decay associated with so-called "fast" formates was initially observed (red line in Fig. 3), which was followed by a markedly slower decay, associated with so-called "slow" formates.

The slopes of the line fitting the fast formate and slow formate section were the apparent rate constants of decomposition k_{FF} and k_{SF}, respectively, expressed in Hz in Table 1. The k_{FF} and k_{SF} values were essentially turn-over frequencies (TOF) of formate decomposition. The apparent rate constant of decomposition of the fast formates k_{FF} was more than an order of magnitude higher than that of the slow formates k_{SF} (Table 1), indicating that the former species was much more reactive than the latter. The apparent rate constant of decomposition of slow formates was essentially constant at the three temperatures considered, suggesting that slow