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CO hydrogenation on cobalt-based catalysts: tin poisoning unravels hollow-CO as a main surface intermediate.

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Abstract: Site poisoning is a powerful method to unravel the nature of active sites or reaction intermediates. The nature of the intermediates involved in the hydrogenation of CO was unraveled by poisoning alumina-supported cobalt catalysts with various concentrations of tin. The rate of formation of the main reaction products (i.e. methane and propylene) was found to be proportional to the concentration of multi-bonded CO, likely located in hollow sites. The specific rate of decomposition of these species was sufficient to account for the formation of the main products. These hollow-CO are proposed to be main reaction intermediates in the hydrogenation of CO under the reaction conditions used here, while linear CO are mostly spectators.

Synthetic fuels and base chemicals can be obtained from both fossil and renewable sources through the catalytic conversion of synthesis gas ("syngas", a mixture of carbon oxides and dihydrogen) [1,2,3,4]. Cobalt-based catalysts are the most important formulations regarding the conversion of syngas to synthetic fuels via Fischer-Tropsch synthesis [3]. The nature of the reaction mechanism of the Fischer-Tropsch synthesis is still a matter of debate, as well as the nature of the active sites [5,6,7,8].

Infrared spectroscopy is a powerful technique for investigating the surface sites and the nature of the reaction intermediates, especially because CO is both a reactant and a molecular probe that can be used to characterize metal surfaces under reaction conditions. IR studies were previously used to investigate the role of formates, which had been proposed as a precursor of methane or methanol [9]. Our recent quantitative IR studies have shown that formates located near to the alumina-cobalt interface could potentially be the sole precursors of methanol, while not those of methane and propene, which were the main reaction products [10]. The present contribution will now quantitatively investigate the role of adsorbed CO present over alumina-supported cobalt catalysts.

We recently reported that the most active cobalt sites were possibly those associated with the formation of bridged/multi-

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bonded CO, which are thought to be located at the particle edges or steps. This conclusion was reached by noting that the poisoning of cobalt by chloride affected more the IR band intensity associated with this bridge/multi-bonded CO than that of linear (i.e., on-top) CO [11].

In 1980, Fujimoto and his group suggested for the first time that bridged carbonyls could be active intermediate during CO hydrogenation over Ru and Rh catalysts [12]. On both catalysts, bridged CO were hydrogenated (mainly to methane) at a lower temperature than that needed to hydrogenate linear CO. Several other groups proposed that bridged CO formed over cobalt-based catalysts could be involved in the catalytic activity [13,14,15,16,17,18,19,20,21,22], yet no quantitative structure-activity relationship has yet been reported to the best of our knowledge.

We report herein a quantitative *operando* diffuse reflectance FT-IR spectroscopy (DRIFTS) study in which the hydrogenation of CO is monitored on Sn-modified Co/Al₂O₃ catalysts under differential reaction conditions. DRIFTS enables monitoring the state of the cobalt surface, in particular the various adsorbed CO species formed under reaction conditions [23,24,25]. Sn was used as a modifier because it is expected to remain strongly adsorbed on the cobalt active phase, unlike chlorine used in our previous study, and does not adsorb CO under our conditions [26,27], thereby facilitating DRIFTS spectra interpretation.

The description of the experimental setup and the preparation of the catalyst samples (Table 1) are detailed in the experimental section (See Supporting Information).

Table 1. Specific surface area, metal loading and cobalt dispersion of the asprepared catalysts.

Sn/Co	BET surface	Co	Sn	Metal disper-	Adsorbed CO ^b	Adsorbed H ₂ ^c
ratio	Area (m²/g)	wt.%	wt.%	sion ^a %	µmol/g	µmol/g
Co	113	15.3	0	7.0	143 ± 10	73
1/120	107	14.3	0.24	9.8	160 ± 10	50
1/60	102	14.4	0.52	9.2	156 ± 10	33
1/30	119	14.3	1.1	7.0	103 ± 6	2

a: from TEM analyses

b: from SSITKA experiments, see Fig. S5

c: from chemisorption experiments, see Fig. S6

Typical TEM micrographs show that the cobalt particle size distribution is narrow and centered for all samples around 9-12 nm (Fig. S1.A to D). Metal (essentially cobalt) dispersions based on the TEM-derived size distributions are reported in Table 1.

The combined catalytic and DRIFTS experiments were carried as follows. About 25 mg of sample were placed in the

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DRIFTS cell and reduced *in situ* at 450°C for 1h. The temperature was then set at 220°C and the feed (30%CO+ 60% H₂/He) was introduced. The reactions were carried out at atmospheric pressure.

Typical operando DRIFTS spectra recorded over a period of 18 h are shown in Fig. S2 for the Sn-free catalyst and are similar to those described in details elsewhere [11,23]. In brief, the bands at ca. 3000-2800 and below 1650 cm⁻¹ are essentially related to hydrocarbon waxes and formates/CO₂ adsorbed on the support, respectively. The bands of main interest to this study are adsorbed on metallic cobalt: on-top (linearly) at 2031 cm⁻¹ and bridged/multi-bonded species below 2000 cm⁻¹. The intensity of these bands was essentially constant after 3 h, except for those associated with waxes that continued growing with time.

The rates of formation of the main products measured at the outlet of the DRIFTS cell are shown in Fig. S3. The selectivity to methane and propene of the samples could not be determined with any satisfactory precision because of the low level of CO conversion (well below 5%, inducing a large relative error on selectivities). Shi *et al.* [28], who developed the synthesis method used here to prepare the Sn-free sample, reported at 1.0 MPa selectivities to methane and propene of 40% and 2%, respectively. The selectivity to methane obtained here at atmopheric pressure should be larger and methane be by far the main reaction product. The data reported here were focused on rates of product formation, which could be determined directly without using CO conversion by neglecting the change of moles of gases due to the reaction at these low levels of conversion.

An induction period of about 3 h was observed during which the rates of formation decreased rapidly before becoming steadier (Fig. S3). The Sn-free sample (red symbols) was the most active catalyst, as the activity markedly decreased with increasing content of tin. The DRIFTS and activity data are consistent with an initial surface reconstruction taking place over ca. 3 h, as suggested earlier [23], while the slower long term deactivation may be partly related to wax deposition.

The contribution of gas-phase CO on the DRIFTS spectra could be precisely subtracted according to the method reported elsewhere [29], to facilitate the analysis of adsorbed CO bands. The signal obtained at pseudo-steady-state (i.e. > 20 h on stream) of the Sn-modified samples was compared to that of the Co/alumina (Fig. 1). Band intensities were normalized with respect to the signal maximum in this region, which turned out to be located at 2031 cm⁻¹ in all spectra. This position corresponds to linearly bound CO on metallic cobalt.

Interestingly, the intensity of the bridged/multi-bonded CO located in the region below 2000 cm⁻¹ decreased gradually with increasing Sn content. A decomposition of the DRIFTS bands was carried out to determine the contribution of bridged species (Fig. S4). A single band located at ca. 1860 cm⁻¹ was sufficient to satisfactory represent the DRIFTS signal in this region. According to Weststrate *et al.* [30], this band can be assigned to CO adsorbed on hollow sites (thereafter noted "hollow-CO"). The molar fractions of linear and hollow-CO could be determined from the proportion of hollow-CO DRIFTS bands (Fig. S4), taking into account that the molar absorption coefficient of linear CO is twice as high as that of hollow-CO [30].



Figure 1. Operando DRIFTS spectra collected after 23h at 220°C under 30%CO+ 60% H₂/He over (Red) Co/alumina and the Sn-modified samples (Black) Sn/Co = 1/120, (Blue) Sn/Co = 1/60 and (green) Sn/Co = 1/30. Total flow was 30 ml min⁻¹. The signal of gaseous CO was subtracted. The spectra were normalized with respect to the 2031 cm⁻¹ band.

The specific concentrations of reversibly adsorbed CO over each of the samples were determined through isotopic exchange under reaction conditions at 220°C. Typical normalized exchange plots obtained during the exchange ¹²CO-¹³CO are shown in Fig. S5 and the results are gathered in Table 1. The number of CO reversibly adsorbed was essentially unchanged (ca. 150 µmol/g) for the two samples least loaded with Sn as compared to the case of the Sn-free sample (Table 1). A significant lower CO adsorption capacity (ca. 103 µmol/g) was only noted for the most Sn-loaded material.

The effect of Sn on the adsorption of H_2 was also investigated (Fig. S6) and is discussed in details in the SI (section Discussion D1).

The plots of the rates of formation of methane and propene as a function of the concentration of hollow-CO (assumed to be equal to the product of the concentration of reversibly adsorbed CO and the molar fraction of hollow-CO) are given in Fig. 2.A. Linear relationships were obtained, highlighting a direct correlation between the concentration of hollow-CO and the rate of formation of the two major reaction products.

The minor offset of the data points at the highest concentration (Fig. 2.A, red symbols) is likely due to an underestimation of the true concentration of adsorbed CO from the SSITKA experiments (Table 1). In fact, the rate plots as a function the IR band fraction, which is not affected by the lower precision of the SSITKA data, exhibit much clearer linear relationships (Fig. 2.B.). The data used to draw Fig. 2.B were collected from *operando* experiments carried out entirely on the DRIFTS cell, while those in Fig. 2.A also relied on supplementary data obtained from the plug-flow SSITKA reactor, hence leading to lower precision. Overall the data clearly indicate that hollow-CO was, at least, a marker of the catalytic activity, if not a main reaction intermediate.

A large number of other samples were tested, which differed in the nature of the pre-treatment (Table S1). Essentially linear relationships were obtained when the product rate vs. hollow-CO fraction of all these samples was plotted (Figure S7), stressing

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the universal nature of the relationship between hollow-CO and catalytic activity over this type of Co-Sn formulations.



Figure 2. Methane (circles) and propene (triangles) production as a function of the concentration of hollow-CO expressed (A) in μ mol/g and (B) as a molar fraction of adsorbed CO determined by DRIFTS measured over the alumina-supported cobalt (red symbols) and the three Sn-modified samples: Sn/Co = 1/120 (Black), Sn/Co = 1/60 (Blue) and Sn/Co = 1/30 (green). Total flow was 30 ml min⁻¹.

Additional experiments were carried out to estimate the initial decomposition rate of adsorbed CO by removing CO(g) from the feed. The decomposition rate of adsorbed CO over the Sn-free sample was ca. 5-fold faster under H₂ than under He (Fig. 3). This indicates that adsorbed CO was mainly decomposed through hydrogenation to hydrocarbons rather than desorption to CO(g) over the most active sample.

In contrast, essentially identical decomposition rates under H_2 and He were obtained for the sample most poisoned with tin, Co/Sn = 30:1 (Fig. 3). This indicates that adsorbed CO mostly desorbed as unreacted CO(g) over the least active sample, which exhibited the largest proportion of linear CO (Fig. 1). These observations underline that linear CO were unreactive spectators.

Interestingly, the initial rate of CO decomposition was almost identical over the Sn-free sample under He and the most poisoned sample (whether under He or H_2) (Fig. 3). It is likely that at 220°C surface diffusion allowed rapid transfer of adsorbed CO between hollow-CO and linear CO sites. Thus,

hollow-CO, which are expected to be more strongly bonded than linear CO, were probably removed in the absence of H_2 through transfer onto sites forming linear species before desorbing as CO(g).

The decay of the DRIFTS signal of adsorbed CO under H_2 followed first order kinetics for all samples (Fig. S8), suggesting uniform decomposition in all cases, even when both hollow and linear CO were present in similar proportions. Such behaviour is again consistent with a rapid exchange of adsorbed CO between hollow and top sites at 220°C, decomposition occurring then through the fastest pathway available: hydrogenation if hollow sites were available, otherwise through desorption as CO(g) on top sites. The rate constant of decomposition under H_2 was determined from the slope of best fit lines (Fig. S8).



Figure 3. Logarithm of the DRIFTS band area of CO(ads) present over (red symbols) Sn-free Co/alumina and (green symbols) Co/Sn = 30:1 sample at 220°C under a stream of 20 mL min⁻¹ of (circle) pure H₂ and (triangle) pure He as a function of time following the removal of CO(g). The feed was composed of 30% CO + 60% H₂/He prior to CO removal. The rate constants of CO(ads) decomposition were equal to the absolute value of the slope of the corresponding lines.

The specific rate of decomposition of hollow-CO could thus be calculated (i.e. rate = rate constant x hollow-CO concentration) and compared to the specific rates of methane and propene formation (Fig. 4). The decomposition rate of hollow-CO was similar or higher than the sum of methane and propene formation. These observations would be fully consistent with hollow-CO being a main surface intermediate in the formation of these hydrocarbons under the present conditions. The difference between the two rates could be associated mostly with the formation of higher hydrocarbons, which were not measured here, and some desorption as CO(g). The rate difference of ca. 50% is actually consistent with a selectivity to methane of ca. 50% expected at atmospheric pressure.

In conclusion, the present quantitative operando study of syngas reaction over cobalt-based catalysts demonstrates quantitative relationships between hollow-CO species (i.e. IR mol fraction and decomposition rates) and the rate of formation of the main reaction products methane and propene. More work COMMUNICATION

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is needed to determine the exact nature of these crucial reaction sites and confirm their relevance at higher operating pressures.



Figure 4. Rates of formation of methane and propene, and rate of decomposition of hollow-CO after 22h at 220°C over Al_2O_3 -supported cobalt and three Sn-modified samples. Feed: 30% CO + 60 % H_2 in He, P = 1 atm.

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Keywords: Fischer-Tropsch reaction• Bimetallics • Heterogeneous catalysis • Kinetics • Reactive intermediates

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