Evidence for support effects in metal oxide supported cobalt catalysts

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ABSTRACT
Cobalt supported on a number of different metal oxides are often used in the Fischer–Tropsch (FT) reaction. No obvious rationale for the composition of the metal oxide used exists. In this paper we examine the possibility that some form of interaction between the metal and the metal oxide support exists which enhances the activity of the Co metal. To this effect, we have supported Co metal on a series of metal oxides of different degrees of reducibility: (i) Al₂O₃ which is unreducible under FT conditions, (ii) ZrO₂ which can be reduced to a small extent under FT conditions, and (iii) ZnO which can be reduced to a measurable degree under FT conditions. The postulate was that the more reducible support will have the greater number of trapped electrons at anion vacancies, and so will have the greater possibility of transferring these electrons from the support to the metal, giving rise to a sequentially greater metal/metal oxide interaction. We have previously shown that temperature programmed desorption/decomposition of formate species adsorbed on Cu/ZnO/Al₂O₃ (methanol synthesis catalysts) has been able to identify adsorption sites on: (i) the Cu metal, (ii) the ZnO, (iii) Al₂O₃ and (iv) at the Cu/ZnO interface. Here we have used the same probe reaction, namely the adsorption and temperature programmed desorption/decomposition of a formate species, to identify and predict the extent of metal/metal oxide interaction. The whole system, the kinetics of the decomposition of the formate used, and the different forms of metal oxide support used constituted a predictive possibility of what would constitute an active metal oxide supported Co catalyst on (i) Co supported on Al₂O₃, on (ii) Co supported on ZrO₂ and (iii) on Co supported on ZnO. The ZnO support is shown to provide the greatest extent of charge transfer from the support to the Co, evidenced by the lowest temperature for desorption/decomposition of the formate of all the supports used, and the largest amount of CO in the product spectrum. The in situ N₂O reactive frontal chromatography measurement of the Co metal area showed the formate species to be closely packed on the Co.

1. Introduction
Chemical reactions which are catalysed by metals are usually accomplished under the aegis of oxide supports. While the major effect of the oxide support is to stabilize a high dispersion of the metal other, potentially important, effects have been attributed to these oxide supports. These include:

(a) Metal support interaction, sometimes referred to as strong metal support interaction (SMSI) by aficionados [1],

Schematic diagram of closely packed formate species on Co, showing the overlap of the electron charge clouds, demonstrating the possibility of reaction between neighbouring formate strands (red balls: O atoms, grey balls: C atoms, white balls: H atoms and blue balls: Co atoms)
after high temperature reduction in H2 was erroneous, non-reducible supports include Al2O3, and SiO2 which temperatures up to, or even greater than 400 °C. These the conductivity increased by a factor of 16 [6].

d) Spill-over of H atoms from the metal to the oxide support leading to the phenomenon termed “synergy at a distance” [4]. The phenomenon known as “strong metal support interaction” was first reported by Tauster, Fung and Garten [1] following their observation that the Pt component of a Pt/TiO2 catalyst was unable to adsorb hydrogen or CO after high temperature (>700 K) reduction in H2. Their explanation of the phenomenon was that the high temperature H2 reduction removed anions from the support and that the Pt atoms bonded more strongly on the Ti3+ ions at the vacancy than to other Pt atoms. On the basis of this model it was predicted that the reactivity of the Pt metal would change because of the changed electronic structure of the metal resulting from the new bonding.

This was the accepted explanation of the phenomenon from 1978 to 1983. In 1983, however, Cairns and co-workers [4], using Rutherford back scattering, showed that the elimination of the adsorptive capacity of the Pt was brought about by the migration of a sub-oxide of the TiO2 support over the surface of the Pt metal, encapsulating it.

While the explanation of the origin of the reduction in the adsorptive capacity of the Pt on Pt/TiO2 catalysts after high temperature reduction in H2, was erroneous, the importance of the reducibility of the support and of anion vacancies at the support-metal interface remains.

In a series of papers, Vannice demonstrated that a “new site at the metal-support interface consisting of an O vacancy or a Ti5+ cation adjacent to at least one clean Pt atom” was the site which was responsible for the selective hydrogenation of carbonyl groups in olefins or other unsaturated carbonyl compounds [5].

Another form of metal support interaction is that the electronic properties of the support play an important role in the reactivity of the metal nanoclusters. This was clearly demonstrated in the oxidation of CO on Pt supported on TiO2 [6,7]. The electron transport properties of the TiO2 were modified by changing the annealing temperatures of the TiO2 which had been deposited on SiO2 (1 0 0) wafers between 623 and 773 K. This produced three stoichiometric types of TiOx:(i) TiO2, (ii) TiO1.7, and (iii) TiO1.9. The turnover frequency for CO2 production per surface Pt atom increased by a factor of 20% for Pt (TiO1.7) relative to Pt (TiO2) while the conductivity increased by a factor of 16 [6].

Most supports, however, cannot be reduced at temperatures up to, or even greater than 400 °C. These non-reducible supports include Al2O3, and SiO2 which are among those most commonly used in catalysis. The role of these supports, then, appears to be simply to provide and stabilize as high a dispersion of the metal as possible. The morphology of the metal on these supports would be determined by the particle size of the support, with no electronic perturbation of the metal accruing from the support.

Zinc oxide is another commonly used support. It can be reduced, however. It is reduced to a limited extent by H2 at temperatures ≥330 °C and to a greater extent by CO in the same temperature regime [8,9]. Metals supported on ZnO therefore have the possibility of being electronically perturbed by transfer of electrons from anion vacancies at or near the metal/ZnO interface. These vacancy sites are more likely to occur at the metal/ ZnO interface since the sticking probability of hydrogen on ZnO is usually lower than that on the metal and so the ZnO is reduced at the interface by spill-over of H atoms from the metal to the ZnO [2].

Zinc oxide has been an important and integral component of the industrial methanol synthesis catalyst since having been patented in 1966 [10]. The catalyst is Cu/ZnO/Al2O3 (60/30/10). There have been many theories about the role of the ZnO in this catalyst. Most of these derive from the fact that ZnO was the original catalyst, discovered by Mittasch in 1923, for the synthesis of CH3OH from CO/H2 mixtures [9]. These theories include: (i) synergy between Cu and ZnO deriving from a Cu+ ion being proposed to be substituted for a Zn2+ ion in the ZnO lattice, this Cu+ ion was suggested to be the active centre in the reaction, (ii) spill-over of H atoms from the Cu to the ZnO to promote reaction on the ZnO [12] or (iii) reaction at the anion defects at the Cu/ZnO interface [3]. None of these, however, has been shown to apply [13].

What has been demonstrated, however, is that pre-treatment of the catalyst in H2 in the manner used normally for reducing the CuO to Cu metal (reduction in H2/He(5% H2, 1 bar, 25 cm3 min−1) raising the temperature from ambient to 240 °C at 5 C min−1) raising the temperature from ambient to 240 °C at 5 C min−1 and holding the temperature at 240 °C for 16 h under the H2(He flow) produces anion defects in the ZnO surface at a level (approximately 80% of a monolayer) not seen by reduction of pristine ZnO under the same conditions [14]. These defects were only detected by dosing formic acid on the surface when they were observed by the coincident desorption of CO, CO2 and H2 at 217 °C. This was interpreted as being due to a formate species being adsorbed on the defects in the ZnO, which were located in the vicinity of the Cu/ZnO interface. They were not detected by CO2/H2 co-dosing which produced monobidentate formate species on the Cu only; the CO2 in the CO2/H2 feed healed the defects in the ZnO [14].

Formic acid therefore is a particularly useful probe molecule for the detection of anion defects on the ZnO component of ZnO supported metal catalysts.
Given the potential importance of the non-stoichiometry of the support surrounding electron donation from the oxide support, we decided to embark on a systematic study of the phenomenon. The metal studied was Co since the work would act as background information for the Fischer–Tropsch reaction. The Co was supported on Al₂O₃, ZrO₂ and ZnO. These supports were of different reducibility with Al₂O₃ being the least reducible, ZrO₂ intermediate and ZnO being the most reducible of the three. The number of anion defects, containing trapped electrons, produced by reduction would increase along the series and so the oxide electron donation effect would be expected to be greatest for ZnO and least for Al₂O₃.

Since we have previously shown that the temperature programmed desorption/decomposition spectrum of the adsorbed formate species produced by dosing formic acid on to Cu/ZnO, Cu/Al₂O₃ and Cu/ZnO/Al₂O₃ surfaces provides a fingerprint of the adsorption and reaction sites on the individual components of these catalysts, here we use the same reaction to determine the nature of the adsorption and reaction sites on: (i) Co/Al₂O₃, (ii) Co/ZrO₂ and (iii) Co/ZnO catalysts to determine if the differently reducible supports produce different degrees of electron donation from the oxide support to the Co metal. As a basis for comparison it also reports on the characterisation of unsupported Co metal.

This paper therefore reports on the use of the adsorption of formic acid as the probe molecule in the characterisation of unsupported Co metal and of the Co surfaces produced by Al₂O₃, ZrO₂ and ZnO supports.

2. Experimental

2.1. Pre-treatment of the adsorbents

Prior to dosing the HCO₂H, the Co/Al₂O₃, Co/ZrO₂ and Co/ZnO catalysts were reduced in a H₂/He stream (5% H₂, 101 kPa, 25 cm³ min⁻¹) raising the temperature from ambient to 530 °C at 3 °C min⁻¹ and holding the temperature at 530 °C for 30 min under the H₂/He stream to ensure complete reduction. The flow was then switched from H₂/He to He and held at 530 °C for 20 min under the He flow to desorb all the hydrogen before cooling to 30 °C.

The pre-treatment accorded the pristine ZnO prior to dosing the HCO₂H it was simply to raise the temperature from ambient to 530 °C at 5 °C min⁻¹ under a He flow (101 kPa, 25 cm³ min⁻¹) and hold it at 530 °C for 20 min under the He flow before lowering the temperature to 30 °C under the He flow. This was done to desorb any adventitiously adsorbed CO₂ or H₂O (i.e. OH) species which would have complicated the interpretation of the HCO₂H desorption spectrum from the ZnO.

2.2. Dosing formic acid on to the adsorbents

The formic acid was dosed on the Co/Al₂O₃, Co/ZrO₂, Co/ZnO catalysts and on to ZnO alone from a He/HCO₂H stream (3.38% HCO₂H, 101 kPa, 25 cm³ min⁻¹). The He/HCO₂H feed was produced by bubbling the He through the HCO₂H contained in the saturator held at 20 °C by means of an oil bath in order to maintain a constant temperature during dosing. The HCO₂H was dosed on to the catalysts for 20 min at 90 °C, after which the temperature was lowered to 30 °C under the He/HCO₂H stream. The flow was then switched to He (101 kPa, 25 cm³ min⁻¹) for approximately 20 min until no HCO₂H was seen on the mass spectrometer. Temperature programming was then begun at 5 °C min⁻¹ from 30 to 530 °C following H₂, H₂O, CO, CO₂, HCO₂H and m/z = 29, 31, 32 continuously on the mass spectrometer. Where there is coincident desorption of two or more species, by the tenets of temperature programmed reaction spectroscopy, these derive from the desorption/decomposition of a common intermediate or, as has been recently suggested, by the interaction of vicinal adsorbates [15]. (For full detail of experimental techniques refer to Ref. [15].)

The dosage of HCO₂H corresponding to a partial pressure of 3.38% for 20 min is 3.1 × 10^⁻¹⁰ L. The partial pressure of 3.8% atmospheres is insufficient to produce multilayer adsorption but the high dosage will ensure saturation coverage of the adsorbent with the HCO₂H at the adsorption temperature of 90 °C.

2.3. The adsorbents

The Co/ZnO and Zr adsorbents were commercial catalysts supplied by BP.

The Co/Al₂O₃ and Co/ZrO₂ adsorbents were prepared by impregnation of cobalt ammine carbonate solutions onto the respective supports. The cobalt loadings achieved were as follows, Co/Al₂O₃ 17.4 wt-%, Co/ZrO₂ 5.2 wt-% on a reduced catalyst basis.

The catalysts were crushed before use, retaining the 200–300 μ fraction.

3. Results and discussion

3.1. Formate decomposition/desorption from unsupported polycrystalline Co metal

Figure 1 is the temperature programme desorption spectrum obtained after having dosed HCO₂H on to unsupported Co metal at 90 °C. It shows two peaks. The first is at 227 °C and comprises CO, H₂ and CO₂ in the ratio 1:1:1. The second is at 240 °C and comprises CO₂ and H₂ only. The amounts (molecule/g catalyst) of the components of each of the peaks of all of the catalysts studied are listed in Table 1a. Also listed in Table 1a are the peak maximum temperatures of all of the components of each of the peaks of all of the catalysts and their position activation energies, obtained using the Redhead equation [16].

The second peak at 240 °C of CO₂, H₂ (2:1) has the stoichiometry at HCO₂H. That it desorbs at CO₂ and H₂ and not as CO₂ and H₂ only and not as CO, H₂, CO₂ suggests that it derives from a bidentate formate.
This interpretation of the data conforms with our previous observation of mono- and bi-dentate formate species on Cu in which the bidentate species desorbs at 155 °C and the mono-dentate species desorbs at 130 °C [17]. The higher peak maximum temperatures for the desorption of formate species from Co, relative to Cu, are consistent with the higher Co–O bond strength [18] while the difference in peak maximum temperatures for mono- and bi-dentate formate species on Co (240 °C bi, 227 °C mono-) compared with Cu (155 °C(bi), 130 °C (mono-)) is roughly the same. On polycrystalline Cu both the monodentate and bidentate formates decompose/desorb as CO₂/H₂. Bowker and co-workers suggest that this is triggered by the formate bending through 90° until the H of the formate interacts with the surface Cu atom where it is abstracted [19]. This is considered to be the rate determining step for the HCO₂ Cu system. Here, however, since we have dosed formic acid on to saturation coverage, it is possible that the decomposition mechanism is the interaction between vicinal adsorbed formate species as we have described previously [15]. The selectivity to CO₂(SCO), i.e. the % of the total CO + CO₂ desorbed in the desorption/decomposition of the 227 °C peak, is 43%.

This is the baseline experiment for the interaction of HCO₂H with Co which is used to determine the effect of the support on the Co.
3.2. Formate decomposition/desorption from Al₂O₃ supported Co

Figure 2 is the temperature programmed desorption spectrum of HCO₂H dosed on to the Co/Al₂O₃ which had been reduced in the method described in the experimental section. It should also be pointed out that temperature programming was begun only after all the gas-phase and physisorbed HCO₂H was removed from the system in a He stream. A small H₂ peak and a larger H₂O peak were observed during the dosing of the HCO₂H on to the reduced Co/Al₂O₃ catalyst. The evolution of H₂ probably results from the formation of the formate on the Co metal while the H₂O peak probably results from dehydration of the formic acid on the Al₂O₃.

Two distinct peaks are observed. The first is at 220 °C, comprising CO, H₂ and CO₂. The second is at 290 °C and comprises CO with shoulders of H₂ and CO₂. The amounts of the compounds desorbing (molecule/(g catalyst)) are listed in Table 1a. Previous studies on Al₂O₃ have shown that the coincident desorption of CO (principally) H₂ and CO₂ at 290 °C following the adsorption of HCO₂H is due to decomposition of a formate species adsorbed on the Al₂O₃ [12]. Therefore, the CO, H₂, CO₂ (1:0.3:0.3) peak seen here at 290 °C derives from the decomposition/desorption of a formate species adsorbed on the Al₂O₃ component of the Co/Al₂O₃ catalyst. Therefore, the coincident desorption of CO, H₂ and CO₂ at 220 °C in a ratio of 1:1:1 following HCO₂H adsorption on an Al₂O₃ supported reduced Co catalyst is characteristic of a formate species which is adsorbed on polycrystalline Co. The selectivity to CO(SCO) in the desorption/decomposition of the formate species adsorbed on Co supported on Al₂O₃ is 50%. (The amounts of the individual compounds listed in Table 1a were obtained by manual deconvolution of the peaks at 220 and 290 °C shown in Figure 2 and applying the pre-determined calibration constant.)

A better understanding of the adsorption process and of the mechanism of the desorption is to be found by calculating the coverage of the Co by the formate adsorbate. For this, it is necessary to have a determination of the Co metal area of the Al₂O₃ supported Co. The measurement of the Co metal area is obtained by the technique of N₂O reactive frontal chromatography (N₂O RFC), a technique which has been patented for all the elements of first row of the transition series [20]. The N₂O reactive frontal chromatogram carried out at 60 °C for Co supported Al₂O₃ is shown in Figure 3. Integration of the N₂ produced between 6 and 10 min gives a measure of the O atom coverage of the Co. (The m/z 28 signal observed at times > 10 min is a cracking fraction of the m/z = 44 signal).

### Table 1b. Peak maximum temperatures/°C, desorption/decomposition activation energies/kJmol⁻¹, molecular composition of peak/molecule (g catalyst)⁻¹, coverage of Co by (CO + CO₂)/molecule/cm⁻²Co.

| Catalyst | Tₘ/ °C | E_d/ kJ mol⁻¹ | Peak composition / molecules/g catalyst | Coverage of Co by (CO + CO₂)/molecule / cm² Co |
|----------|--------|---------------|---------------------------------------|---------------------------------------------|
| Co / Al₂O₃ | 220 | 136 | CO / 1.1 x 10¹⁰ CO₂ / 1.1 x 10¹⁰ H₂ / 3.5 x 10²² | 4.2 x 10¹⁵ |
| Co / ZnO | 192 | 128 | CO / 2.4 x 10¹⁵ CO₂ / 7.7 x 10¹⁵ H₂ / 2.1 x 10¹⁹ | 2.4 x 10¹⁴ |
| Co / ZnO | 162 | 120 | CO / zero CO₂ / 2.3 x 10¹⁰ | 2.4 x 10¹⁵ |

Figure 2. Temperature programmed desorption/decomposition of formate adsorbed on Al₂O₃ supported polycrystalline Co.
The CO, CO\textsubscript{2} H\textsubscript{2} peak at 173 °C has a selectivity to CO (S\textsubscript{CO}) of 64%. The selectivity to CO (S\textsubscript{CO}) of the higher temperature peak (the 200 °C peak) is lower at 58%. Therefore, the selectivity to CO (S\textsubscript{CO}) of the desorption/decomposition of formate adsorbed on Co supported on ZrO\textsubscript{2} is higher for the lower peak maximum temperature for the decomposition.

This is clear evidence for the ZrO\textsubscript{2} support providing strong metal support interaction by transferring electrons from defect sites on the ZrO\textsubscript{2} to the Co metal, the pre-reduction process used here having been shown to be capable of producing anion vacancies on the ZrO\textsubscript{2} [22]. This electron transfer from the ZrO\textsubscript{2} support to the Co metal, which it supports, increases the electron density in the Co metal. This increased electron density in the Co provides a source of electrons to the antibonding orbitals of the adsorbed formate, so lowering the peak maximum temperature for the decomposition of the adsorbed formate and increasing the selectivity to CO (S\textsubscript{CO}) of that peak [23].

Since the O:Co ratio is 1:1 [21], and since the average low index Co surface atom density is 1.6 × 10\textsuperscript{15} atom cm\textsuperscript{-2}, then each Co surface atom (corresponding to each gas phase N\textsubscript{2} molecule) corresponds to an area per Co atom of 6.25 × 10\textsuperscript{-16} cm\textsuperscript{2}.

Using this value, from the amounts of (CO + CO\textsubscript{2})/g catalyst, the coverage of the Co by formate species is >2 ML. For this to occur, the formate species must be closely packed on the Co in a form not dissimilar to that shown in Figures 4 and 5. Decomposition of this overlayer must occur by the interaction of vicinal formate species and not as a result of bending through 90° so that they interact with free Co atoms. (A listing of the coverage of the Co on the 220 °C peak (molecules/cm\textsuperscript{2} Co) by CO + CO\textsubscript{2} of the Al\textsubscript{2}O\textsubscript{3} and on the 162 °C peak by CO\textsubscript{2} and the 192 °C peak (molecules/cm\textsuperscript{2} Co) on the ZnO supported Co is given in Table 1b.

### 3.3. Formate decomposition/desorption from ZrO\textsubscript{2} supported polycrystalline Co metal

Figure 6 is the temperature programmed desorption spectrum obtained after having dosed HCO\textsubscript{2}H on to ZrO\textsubscript{2} supported polycrystalline Co metal. It shows a peak of CO, CO\textsubscript{2} and H\textsubscript{2} at 200 °C with a peak of CO\textsubscript{2} and shoulders on the CO and H\textsubscript{2} signal at 173 °C and a peak of CO and H\textsubscript{2} at 330 °C.

The H\textsubscript{2}, CO peak observed at 330 °C is ascribed to a formate adsorbed on the ZrO\textsubscript{2} support. It is clear from this that formate adsorbed on ZrO\textsubscript{2} is more strongly held than that on Al\textsubscript{2}O\textsubscript{3} where the CO/H\textsubscript{2} peak is observed at 290 °C from HCO\textsubscript{2}H adsorbed on Co/Al\textsubscript{2}O\textsubscript{3} (Figure 1) and at 267 °C for HCO\textsubscript{2}H adsorbed on Cu/Al\textsubscript{2}O\textsubscript{3} [14].

The CO, CO\textsubscript{2} H\textsubscript{2} peak at 173 °C has a selectivity to CO (S\textsubscript{CO}) of 64%. The selectivity to CO (S\textsubscript{CO}) of the higher temperature peak (the 200 °C peak) is lower at 58%. Therefore, the selectivity to CO (S\textsubscript{CO}) of the desorption/decomposition of formate adsorbed on Co supported on ZrO\textsubscript{2} is higher for the lower peak maximum temperature for the decomposition.

This is clear evidence for the ZrO\textsubscript{2} support providing strong metal support interaction by transferring electrons from defect sites on the ZrO\textsubscript{2} support to the Co metal, the pre-reduction process used here having been shown to be capable of producing anion vacancies on the ZrO\textsubscript{2} [22]. This electron transfer from the ZrO\textsubscript{2} support to the Co metal, which it supports, increases the electron density in the Co metal. This increased electron density in the Co provides a source of electrons to the antibonding orbitals of the adsorbed formate, so lowering the peak maximum temperature for the decomposition of the adsorbed formate and increasing the selectivity to CO (S\textsubscript{CO}) of that peak [23].
Interestingly, the coincident evolution of \( m/z \) fragments 29, 31 and 32 are characteristic of methanol. Therefore, when the two formate species decompose, some of the hydrogen released in this reaction, hydrogenates the remaining adsorbed formate species to methanol. The peak at 247 °C has a selectivity to methanol of 15%, while peak at 260 °C has a selectivity to methanol of 5%.

### 3.5. Formate decomposition/desorption from polycrystalline Co supported on ZnO

Figure 8 is the temperature programmed desorption spectrum obtained after having dosed HCO\(_2\)H on to ZnO supported polycrystalline Co metal. It shows a peak of CO, CO\(_2\) and H\(_2\) at 192 °C with a shoulder of CO, CO\(_2\).
This evidence suggests that the ZnO support donates more electrons to the Co than any other support. The increased electron density on the Co weakens the CO bond strength of the adsorbed formate by donation of these electrons to the antibonding orbitals of the formate adsorbed on the electron modified Co [23]. The ZnO support therefore affects the morphology of the surface of the Co and also the electron configuration of the Co.

It is clear that the ZnO support has a profound effect on the activity of the Co metal it supports, predisposing it to lower the activation energy for the breaking of a C-O bond of an adsorbed formate species which we

and H$_2$ at 162 °C (Table 1a lists the partial pressures of each of the peaks).

The selectivity to CO, $S_{(CO)}$ of the 162 °C shoulder is zero because the CO and H$_2$ peaks coincide so the adsorbate is a bidentate formate. The important conclusion that derives from this should be pointed out here, namely that the ZnO support affects not only the electron charge density on the Co metal through what has been termed on occasion the SMSI effect, but it also affects the morphology of the Co metal it supports.

The CO peak at 192 °C is the lowest temperature CO peak observed. It has a selectivity to CO ($S_{(CO)}$) of 67%.

This evidence suggests that the ZnO support donates more electrons to the Co than any other support. The increased electron density on the Co weakens the CO bond strength of the adsorbed formate by donation of these electrons to the antibonding orbitals of the formate adsorbed on the electron modified Co [23]. The ZnO support therefore affects the morphology of the surface of the Co and also the electron configuration of the Co.

It is clear that the ZnO support has a profound effect on the activity of the Co metal it supports, predisposing it to lower the activation energy for the breaking of a C-O bond of an adsorbed formate species which we

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**Figure 7.** Temperature programmed desorption/decomposition spectrum of formate adsorbed on polycrystalline ZnO.

**Figure 8.** Temperature programmed desorption/decomposition spectrum of formate adsorbed on polycrystalline Co supported on ZnO.
regard as a salient indicator of its lowering the activation energy for the Fischer–Tropsch reaction since the breaking of the C–O bond of an adsorbed intermediate is one of the key elementary steps in Fischer–Tropsch synthesis.

4. Conclusions

(i) The activation energy for the decomposition of a formate species adsorbed on metal oxide supported Co is determined by the nature of the metal oxide support.

(ii) In a series of different oxide supports which included Al₂O₃, ZrO₂ and ZnO, the lowest value of the peak maximum temperature for the decomposition of formate adsorbed on Co (435 °C, \( E_d = 107 \) kJ mol\(^{-1} \)) is for ZnO supported Co.

(iii) Decomposition of the adsorbed formate on ZnO supported Co results in the coincident evolution of CO, CO₂ and H₂ at 435 °C (\( E_d = 107 \) kJ mol\(^{-1} \)) with a selectivity to CO (\( S_{CO} \)) of 67%. This combination of the lowest activation energy for the decomposition of the adsorbed formate (107 kJ mol\(^{-1} \)) and the highest selectivity to CO (67%) is caused by the ZnO providing the highest level of electron transfer from the support to the Co metal – the highest degree of metal support interaction of all the supports used.

(iv) Since C–O bond scission is an essential elementary reaction on the Fischer–Tropsch reaction co-ordinate, a ZnO supported Co catalyst would be expected to have the lowest activation for the Fischer–Tropsch reaction and therefore to provide the most active F–T catalyst of the group, Co/Al₂O₃, Co/ZrO₂, and CoZnO.

Highlights

- The activity of Co is shown to be dependent on the chemical composition of the metal oxide on which it is supported. This is evidence for electron donation from the oxide support to the metal.
- The activation energy for the desorption/decomposition of a formate species adsorbed on Co is a useful indicator of electron donation from the oxide support to the metal.
- In a series of different metal oxide supports, including Al₂O₃, ZrO₂ and ZnO, the lowest value of the activation energy for the desorption/decomposition of the formate species adsorbed on Co is provided by the ZnO support.
- The formate species adsorbed on Co desorbs/decomposes into CO, CO₂ and H₂ at the same peak maximum temperature. The selectivity to CO (\( S_{CO} \)) is highest for the ZnO support, while the peak maximum temperature is lowest for this support. This is a clear indication of the largest extent of electron transfer from this support to the metal compared with the other supports.

Disclosure statement

No potential conflict of interest was reported by the authors.

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