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REACTIONS OF COBALT FORMATE ON SUPPORTS

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ABSTRACT

The thermal decomposition of support cobalt formate has been studied by GC and XPS. In accordance with the peak temperatures and the composition of the gas products in helium, the peaks may be divided into four groups indicated by α, β, γ and ϵ. Weak interaction between $Co(HCOO)_2$ and the support gave peak α. For $Co(HCOO)_2/MgO$, the reaction of surface Mg^{2+} with $HCOO^-$ dissociated from Co^{2+} led to the decomposition being analogous to that of formic acid on MgO, yielding peak β. In the case of $Co(HCOO)_2/HY$, the zeolite behaved as a dehydration catalyst to give peak γ at lower temperatures. Peak ϵ resulted from the desorption of CO_2 on La_2O_3. When thermal decomposition was carried out in hydrogen, the CH_4 yield depended on the nature of the support. Among the supports studied, $La_2O_3-Al_2O_3$ is the most efficient for methanation and the support plays a role not only in dispersing the metal, but also in adsorbing and transferring CO_2.

INTRODUCTION

The possibility of preparing small metal particles on various supports obtained by decomposition of supported complexes has received a great deal of attention [1,2]. The energy problem has initiated great interest in the study of the hydrogenation of carbon oxides catalysed by highly dispersed systems. This synthesis is particularly important for producing a clean energy fuel from abundant coal resources instead of using more limited petroleum naphtha supplies.

Chemists who strive for a better understanding of the fundamentals of catalysis favour the study of simple reactions. Formic acid can decompose in three directions and the analytical determination of the reaction products is easily performed. Thus the decomposition of formic acid has frequently been used to determine the factors which can affect the catalytic selectivity of metal and metal oxides [3–5].

Our recent work in the decomposition of supported complexes has been reported [6,7], and the various stages in the decomposition of the complexes

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and the interaction with the supports, as well as the methanation reaction, have been monitored by various techniques [6]. The present paper reports on the thermal decomposition of cobalt formate supported on silica, magnesia, HY-zeolite, γ-alumina and lanthana–alumina. As will be shown, the different natures of the supports lead to quite different decomposition reactions. The primary concern of this work is to evaluate the effect of the supports. Attention is also paid to the methanation of carbon oxides during the thermal decomposition in hydrogen.

EXPERIMENTAL

Materials

The $Co(HCOO)_2 \cdot 2H_2O$ used was of analytical grade; silica, γ-alumina, magnesia and HY-zeolite were used as described elsewhere [7,8]. Lanthana–alumina was prepared by heating $La(NO_3)_3/Al_2O_3$ obtained by impregnation of γ-Al_2O_3 with an aqueous solution of $La(NO_3)_3$ with an La_2O_3 content of around 4.0 wt.%. Samples of supported $Co(HCOO)_2$ were prepared by impregnation of supports with an aqueous solution of $Co(HCOO)_2$ and then dried in vacuo at 60 ° C. The samples were analysed for cobalt by atomic absorption spectrophotometry following heating in air at 450 ° C. The cobalt content was around 2.5 wt.%.

Instrumentation

The gas chromatographic measurements were made as described elsewhere [9]. The X-ray photoelectron spectra were obtained using a Perkin–Elmer PH5300 photoelectron spectrometer. Mg $K\alpha$ X-radiation (1253.6 eV) was used. Three measurements were made for each sample. In each case the carbon 1s line was recorded and all the spectra were referenced to this line (285.0 eV). With this method, it is possible to locate the photoelectron peaks reproducibly to within 0.2 eV.

RESULTS

As may be clearly seen from Fig. 1, when unsupported $Co(HCOO)_2$ decomposed in He, CO_2, H_2 and CH_4 were expelled in the range 220–310 ° C. For $Co(HCOO)_2/MgO$, thermal decomposition gave peaks α and β; the former was similar to that of the unsupported material, while the major products of the latter were CO_2 and H_2. The initial decomposition of $Co(HCOO)_2/HY$ was at about 200 ° C, and CO was first released (peak γ), followed by peak α. Figure 2 shows that only peak α was found in He for

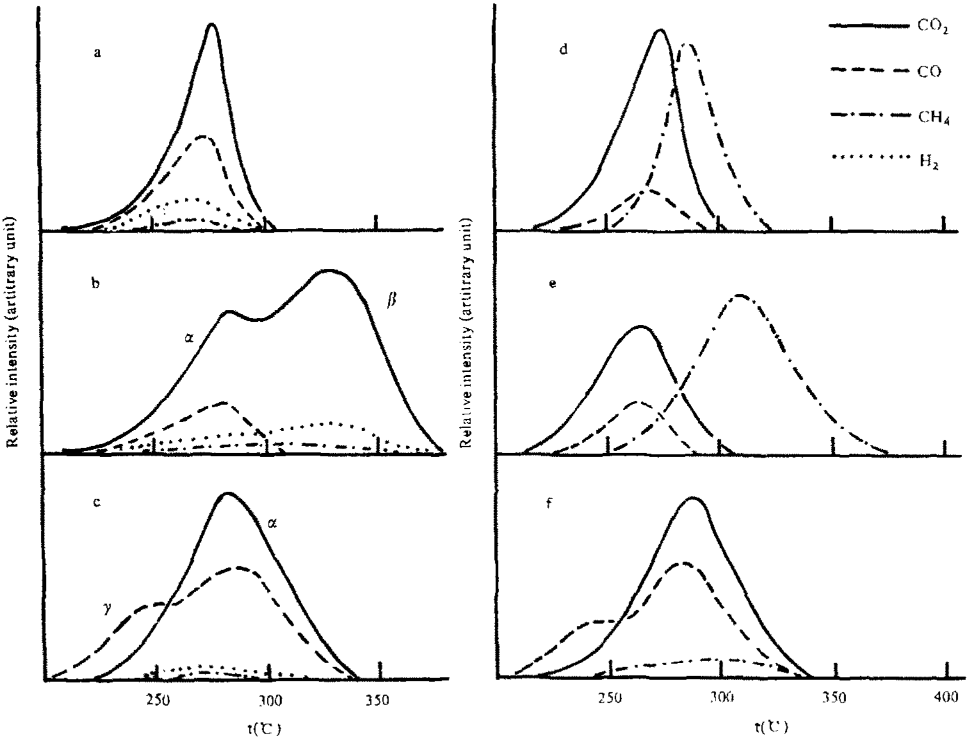


Fig. 1 Thermal decomposition in He: a, $Co(HCOO)_2$; b, $Co(HCOO)_2/MgO$; c, $Co(HCOO)_2/HY$; and in H_2: d, $Co(HCOO)_2$; e, $Co(HCOO)_2/MgO$; f, $Co(HCOO)_2/HY$. (H_2O is omitted.)

$Co(HCOO)_2/SiO_2$ or $Co(HCOO)_2/Al_2O_3$, while thermal decomposition of $Co(HCOO)_2/La_2O_3$–Al_2O_3 gave additional CO_2 at higher temperatures (peak ϵ). When thermal decomposition was carried out in hydrogen, a considerable amount of CH_4 was formed because of the methanation of CO_2 and CO. The CH_4 yield depends on the nature of the support and among the supports studied, La_2O_3–Al_2O_3 is the most efficient.

As shown in Fig. 3, for $Co(HCOO)_2$ and $Co(HCOO)_2/Al_2O_3$ the binding energy of $Co(2p_{3/2})$ of the product in He was 777.8 eV, indicating that Co metal was formed. On the basic support, MgO, the XPS peak split into two parts, the shoulder (777.9 eV) is close to that of Co metal, while the bigger peak has a binding energy of 779.8 eV which may be assigned to CoO. This suggests that CoO was the major solid product on MgO.

DISCUSSION

The thermal decomposition reactions of unsupported $Co(HCOO)_2$ in He may be divided into two types [10]:

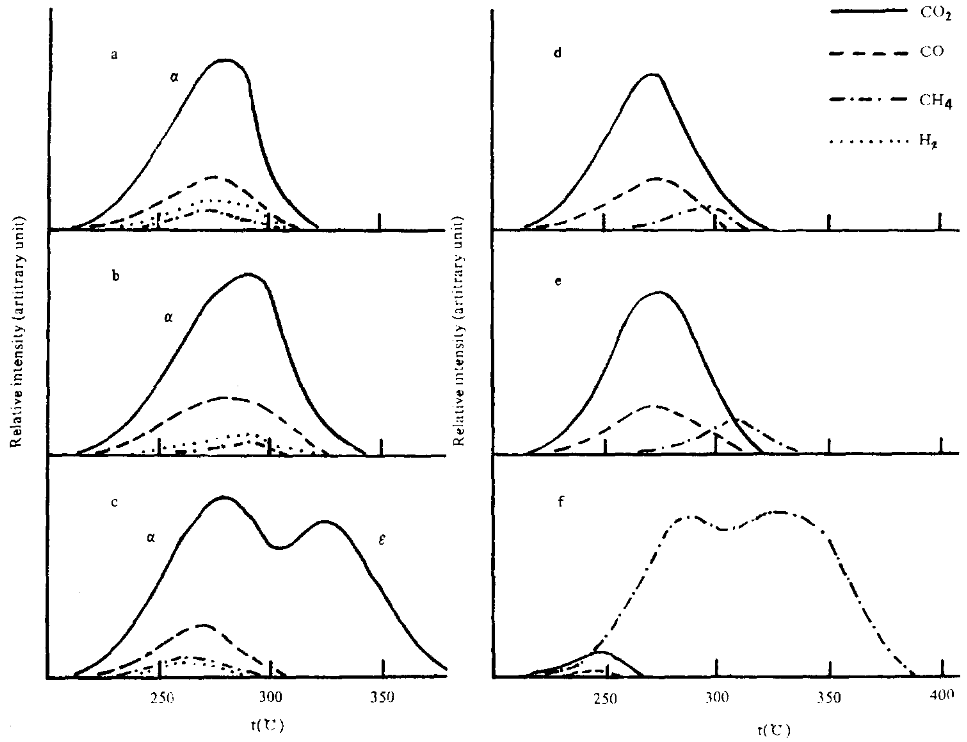


Fig. 2. Thermal decomposition in He: a, $Co(HCOO)_2/SiO_2$; b, $Co(HCOO)_2/Al_2O_3$; c, $Co(HCOO)_2/La_2O_3-Al_2O_3$; and in H_2: d, $Co(HCOO)_2/SiO_2$; e, $Co(HCOO)_2/Al_2O_3$; f, $Co(HCOO)_2/La_2O_3-Al_2O_3$. ($H_2O$ is omitted.)

$$Co(HCOO)_2 \longrightarrow Co + H_2 + 2CO_2 \qquad (1)$$

$$Co(HCOO)_2 \longrightarrow Co + CO + CO_2 + H_2O \qquad (2)$$

with reaction (1) predominant. Peak α of the supported material might correspond to these reactions, implying that there was no obvious chemical interaction between $Co(HCOO)_2$ and the supports, and in this case the effect of the supports was to disperse $Co(HCOO)_2$ on the surface. For the $Co(HCOO)_2/MgO$ system, hydrolysis of some of the Co^{2+} ions might take place so that $Co(OH)_2$ was formed on the surface during impregnation, due to the basicity of MgO. As a result, on MgO $Co(OH)_2$ decomposed to yield CoO:

$$Co(OH)_2 \longrightarrow CoO + H_2O \qquad (3)$$

The formation of CoO was confirmed by the XPS study. On the other hand, the reaction of Mg^{2+} on MgO with $HCOO^-$ dissociated from Co^{2+} led to the formation of a surface compound, whose thermal decomposition was analogous to that of formic acid on MgO [5], and therefore the dehydro-

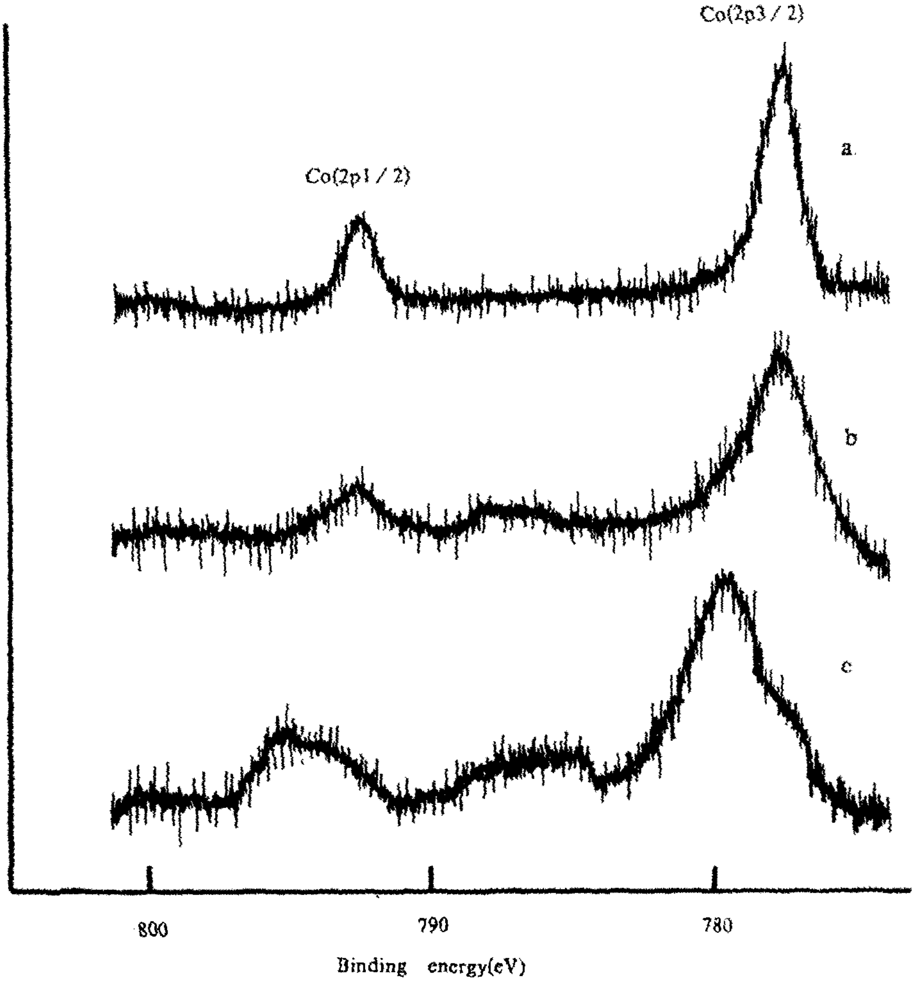
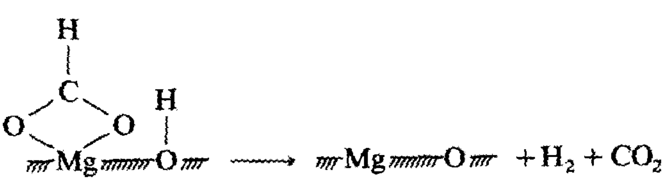


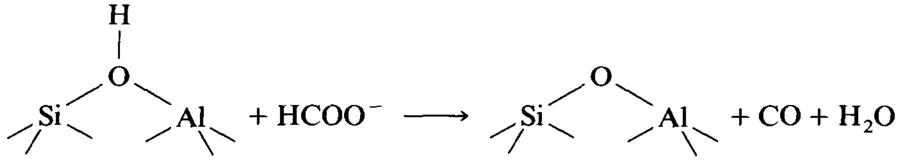
Fig. 3. X-ray photoelectron spectra of decomposition products in He at 400 °C: a, $Co(HCOO)_2$; b, $Co(HCOO)_2/Al_2O_3$; c, $Co(HCOO)_2/MgO$.

genation reaction took place, giving peak β:

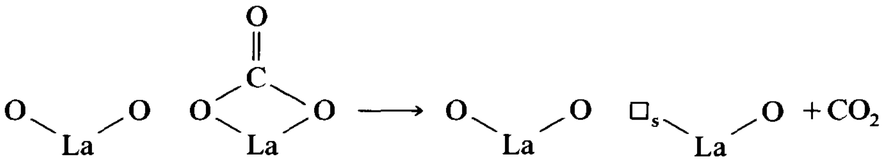


$$\text{HC(O)(O)Mg–O(H)} \longrightarrow \text{Mg–O} + H_2 + CO_2 \qquad (4)$$

Molecular orbital calculations showed that a proton linked to an oxygen interconnecting SiO_4 and AlO_4 tetrahedra in silica–alumina is very strongly acidic, while a proton of silica or alumina is weakly acidic [11,12]. In the case of $Co(HCOO)_2/HY$, the zeolite behaved as a dehydration catalyst to give peak γ at lower temperatures; the proton played an important role:


(5)

For the lanthana–alumina support, the Al_2O_3 surface was covered with La_2O_3. Based on IR spectroscopy, the adsorption of CO_2 on La_2O_3 was illustrated by the results of Rosynek and Magnuson [13] who proposed the formation of two surface carbonate species on La_2O_3 at different temperatures. Spectral evidence for unidentate carbonate species disappeared at 300 ° C, and was followed by complete removal of the bidentate structures at > 350 ° C [13]. During the decomposition of $Co(HCOO)_2/La_2O_3$–Al_2O_3, some of the CO_2 released from $Co(HCOO)_2$ adsorbed on the La_2O_3 surface of lanthana–alumina and peak ϵ resulted from the desorption of CO_2 at higher temperatures


(6)

where $\square_s$ denotes the surface vacancy.

It is interesting that the high CH_4 yield was obtained from the decomposition of $Co(HOO)_2/La_2O_3$–Al_2O_3 in hydrogen. Most probably,the support not only disperses the metal, but also adsorbs and transfers CO_2.

In conclusion, the present method not only offers an easy approach to the understanding of the decomposition processes of supported complexes, but also suggests a novel approach to the search for new efficient catalysts.

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