Use of TPR / TPO for characterization of supported cobalt catalysts

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The extent of reduction of supported cobalt catalysts is difficult to determine using TPR due to the unknown stoichiometry of reduction and due to the dynamic nature of the measurement. A method is described where, by using a combined TPR/TPO technique, it is possible to determine the extent of cobalt reduction and obtain an estimate of the extent of cobalt–support species formation. The results showed that the extent of metal reduction following hydrogen reduction at 500°C is affected considerably by the type of metal carrier. In particular, the extent of metal reduction decreased with increasing aluminium content of the support material. Decreasing extents of metal reduction could be correlated with an increase in the temperature required for reduction of the nitrate ion during TPR. Increasing the time and temperature of hydrogen reduction results in increased extents of metal reduction.

Keywords: TPR/TPO characterization; cobalt catalysts

1. Introduction

Cobalt catalysts find application in hydrotreating [1] and hydrogenation processes [2] and are promising catalysts for the production of fuels and chemicals via CO hydrogenation [3] and for the synthesis of alkylamines via reductive amination [4]. Bulk metal catalysts pose severe drawbacks in terms of catalytic efficiency and are therefore costly. In order to increase the surface area of the active metallic component (and thus the efficiency), they are frequently supported on high surface area carriers. The support not only aids in the dispersion of the active metallic component, but also increases the thermal stability and therefore the lifetime of the catalyst [5]. Although the support increases metal dispersion, metal losses are sometimes incurred due to the formation of metal–support species. These effects are more pronounced in highly dispersed systems [6].

Supported cobalt catalysts are frequently not reduced completely to the metallic state due to the formation of stable metal–support species [1,7–11]. The extent of cobalt reduction is determined by factors such as the metal loading, the method of catalyst preparation and activation and the type of support used [12]. On Al_2O_3 supported cobalt catalysts, metal reduction is limited due to diffusion of cobalt ions into alumina lattice sites resulting in the formation of cobalt–alumina surface spinels [1,10]. On SiO_2 supported cobalt catalysts, the formation of surface cobalt oxide species [8] and cobalt silicates [11] results in decreased extents of reduction. The formation of these difficult to reduce cobalt–support species represents a loss of the active metallic component and must therefore be minimized.

The extent of reduction of supported cobalt catalysts is difficult to determine by measuring the hydrogen consumption during TPR because of the complicated stoichiometry of the reduction (i.e. besides the reduction of unknown quantities of divalent and trivalent cobalt ions, reduction of the nitrate ion might also occur). In this paper, a method is described which is able to determine the extent of metal reduction and the state of the supported cobalt following reduction using a combined TPR/TPO technique.

2. Experimental

The catalysts were prepared by the incipient wetness impregnation method using an aqueous solution of cobalt nitrate. The concentrations of the impregnating solutions were adjusted to obtain a cobalt loading of 9 wt%. Following impregnation, the catalysts were dried at 100°C for 16 h before storage in a desiccator. The SiO_2 and MgO supports were supplied by Merck and the Al_2O_3 and SiO_2–Al_2O_3 supports were supplied by Kalichemie. The physical characteristics of the supports are listed in table 1. The cobalt nitrate precursor ($Co(NO_3)_2 \cdot 6H_2O$) was supplied by Merck and had a purity greater than 99%.

The reduction behaviours of the catalyst precursors were measured in a temperature programmed reduction (TPR) apparatus. The procedure involved reduction of the catalyst (~0.15 g) in a 60 ml(NTP)/min 5% H_2/N_2 stream as the temperature was raised linearly from 100 to 1000°C at 10°C/min. Hydrogen consumption was measured by a thermal conductivity detector (TCD) using a 60 ml(NTP)/min stream of N_2 as a reference stream. Water formed by metal reduction and precursor decomposition is trapped using 3 Å molecular sieves to avoid interference with the measured signal. The TCD

Table 1
Physical characteristics of carrier materials

Support	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	Al_2O_3 content (wt%)
SiO_2	289	1.16	160	0
γ-Al_2O_3	209	0.45	85	100
MgO	33	0.14	148	0
SiO_2–$1Al_2O_3$	491	1.21	98	1
SiO_2–$4Al_2O_3$	563	0.82	58	4
SiO_2–$9Al_2O_3$	461	0.48	42	9
SiO_2–$13Al_2O_3$	516	0.47	36	13

was calibrated by the temperature programmed reduction of pure metal oxides (CuO, NiO, Co_3O_4 and Fe_2O_3).

Temperature programmed oxidation (TPO) of reduced catalysts was performed in the same apparatus as used for the TPR experiments. The procedure involved initial reduction of the catalyst precursor ($\sim$ 0.50 g) in a 60 ml(NTP)/min 5% H_2/N_2 stream using a temperature programming rate of 10°C/min. The time and temperature of reduction could be adjusted as required. Oxidation of the reduced catalyst was performed in a 60 ml(NTP)/min 2% O_2/He stream as the temperature was raised linearly from 50 to 1000°C at 10°C/min. Oxygen concentrations in the outlet stream were measured by TCD using 60 ml(NTP)/min He as a reference stream. The TCD was calibrated by temperature programmed oxidation of pure metallic Co.

3. Results and discussion

3.1. Temperature programmed reduction

The reduction profiles of the cobalt catalysts supported on various inorganic oxide carriers are shown in figs. 1and 2. The occurrence of multiple reduction peaks indicates the presence of a number of reducible cobalt species present in the catalyst precursor. The most intense peak corresponds to the reductive decomposition of the cobalt nitrate precursor [8,10]. Mass spectroscopic analysis of the effluent gas during this event showed that the decomposition of the cobalt precursor is accompanied by the evolution of the nitrogen oxides NO_2, NO and N_2O. The high thermal conductivity of the dimer N_2O_4, which is not detected using GC-MS, may be responsible for the negative peak sometimes occurring prior to this feature. N_2O_4 can have a higher thermal conductivity than H_2 depending on the temperature in the TCD cell [12]. The hydrogen consumption occurring directly after the peak corresponding to precursor decomposition is assigned to the reduction of CoO formed through cobalt nitrate reduction [8]. This assignment was made on the basis of the two peaks obtained during TPR of unsupported $Co(NO_3)_2$.

Subsequent reduction to metallic cobalt occurs in several steps, the size and location of the peak being dependent on the type of support used. Hydrogen consumption occurring at temperatures greater than 500°C may be assigned to the reduction of cobalt which has some degree of interaction with the support, since bulk cobalt oxide is reduced completely by 500°C [10]. In general, these peaks are due to the reduction of cobalt

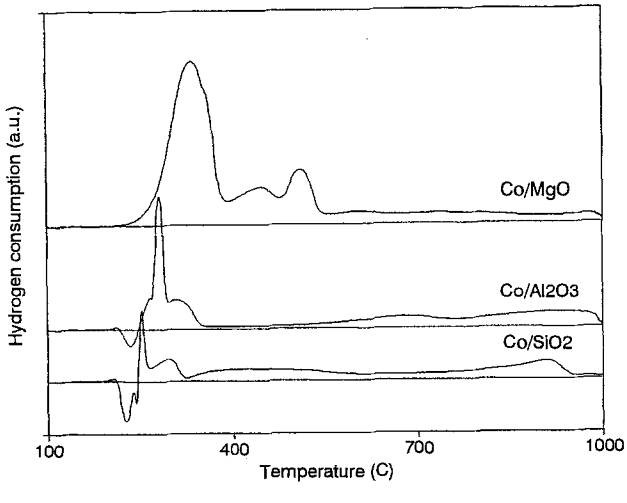

Fig. 1. TPR spectra of SiO_2, Al_2O_3 and MgO supported cobalt catalysts. (100–1000°C at 10°C/min in 60 ml(NTP)/min 5% H_2/N_2.)

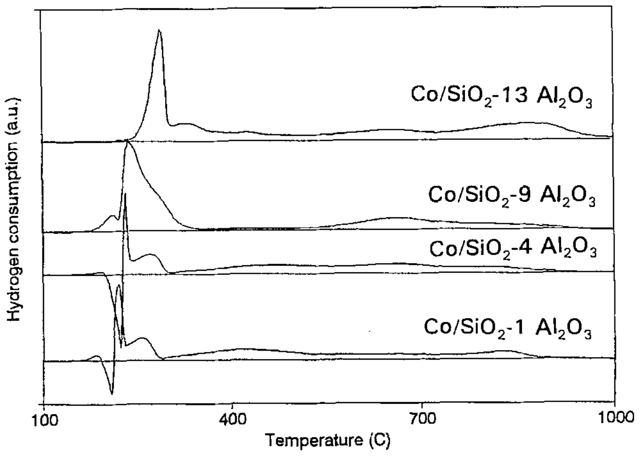

Fig. 2. TPR spectra of SiO_2–Al_2O_3 supported cobalt catalysts with different aluminium contents. (100–1000°C at 10°C/min in 60 ml(NTP)/min 5% H_2/N_2.)

Table 2
Hydrogen to metal ratios and temperature of nitrate reduction during TPR. (100–1000°C at 10°C/min in 60 ml(NTP)/min 5% H_2/N_2)

Catalyst	$(H_2 : Co)_{total}$ (mol : mol)	$(H_2 : Co)_{>500}$ (mol : mol)	$T_{decomposition}$ (°C)
Co/SiO_2	1.33	0.73	239
Co/Al_2O_3	1.64	0.95	282
Co/MgO	3.98	0.87	337
Co/SiO_2-$1Al_2O_3$	1.30	0.57	236
Co/SiO_2-$4Al_2O_3$	1.21	0.70	242
Co/SiO_2-$9Al_2O_3$	1.99	0.78	249
Co/SiO_2-$13Al_2O_3$	2.07	0.95	290

silicates [11], cobalt aluminates [1,10] and surface cobalt oxides [8].

Table 2 lists the hydrogen to cobalt molar ratios (measured by integration of the TCD signal) and the temperature at which reduction of the nitrate ion occurs. Integration of the TCD signal during TPR yields $H_2 : Co$ molar ratios ranging from 1.30 to 3.98. Since reduction of divalent cobalt would yield a $H_2 : Co$ molar ratio of 1 and reduction of cobalt in Co_3O_4 would result in a $H_2 : Co$ molar ratio of 1.33, it is evident that simultaneous reduction of the nitrate ion is also occurring during TPR. Signal integration is further complicated by the release of nitrogen oxides which interfere with the measured thermal conductivity. Integration of the TCD signal, which varies due to hydrogen consumption as well as the release of nitrogen oxides, at temperatures below 500°C therefore does not give an accurate measure of the extent of metal reduction.

Instead, an indirect estimate of the degree of metal reduction can be obtained by measurement of the hydrogen consumption occurring at temperatures greater than 500°C. Above 500°C, reduction of the nitrate ion is complete and all hydrogen consumption can be attributed to reduction of cobalt not reduced below 500°C. Knowledge of the total cobalt content in the catalyst therefore allows the extent of reduction to be calculated assuming that metal reduction is complete by 1000°C and that all cobalt which is reduced above 500°C is divalent. This might not be true for the MgO supported catalyst.

The hydrogen consumption occurring above 500°C increases as the cobalt support is changed from SiO_2 to Al_2O_3 and as the aluminium content in the SiO_2–Al_2O_3 supported catalysts is increased. Increasing the aluminium content of the carrier therefore decreases the reducibility of the cobalt.

The temperature at which the reductive decomposition of the nitrate precursor occurs increases from 239 to 282 to 337°C as the support is changed from SiO_2 to Al_2O_3 to MgO. The increase in the temperature required for precursor decomposition indicates an increase in the degree of precursor–support interaction which would be expected to decrease the reducibility of the supported cobalt. Similarly, the decomposition temperature increases from 236 to 242 to 249 to 290°C as the aluminium content in the SiO_2–Al_2O_3 catalysts is increased from 1 to 4 to 9 to 13 wt%.

Increasing the aluminium content of the carrier material therefore results in an increase in the degree of precursor–support interaction which results in decreased extents of cobalt reduction. The increase in the degree of precursor–support interaction is characterized by an increase in the temperature required for the reductive decomposition of the cobalt nitrate precursor.

3.2. Temperature programmed oxidation

Temperature programmed oxidation (TPO) of unsupported cobalt metal (fig. 3) is characterized by two oxygen consumption maxima at 298 and 583°C, corresponding to the sequential oxidation of metallic cobalt first to CoO and then to Co_3O_4 (reactions (1) and (2)). At a temperature of 872°C, the spinel Co_3O_4 decomposes to form the thermodynamically more stable CoO with a stoichiometric release of oxygen (reaction (3)). The oxygen release during Co_3O_4 decomposition can be correlated to the oxygen uptake during cobalt oxidation in accordance with reaction stoichiometry.

$$Co + \tfrac{1}{2}O_2 \rightarrow CoO \qquad (1)$$

$$3CoO + \tfrac{1}{2}O_2 \rightarrow Co_3O_4 \qquad (2)$$

$$Co_3O_4 \rightarrow 3CoO + \tfrac{1}{2}O_2 \qquad (3)$$

Following reduction of a supported cobalt catalyst, the cobalt is assumed to be present in three forms, viz. as reduced Co metal, as an oxidizable divalent cobalt species and as a non-oxidizable cobalt–support species. All cobalt present on the catalyst surface after hydrogen reduction has been assumed to be either divalent or zero-valent, in accordance with the TPR studies of Arnoldy and Moulijn [10] where it was shown that trivalent cobalt species were reduced completely by 500°C. The amount of non-oxidizable cobalt-support species may be deter-

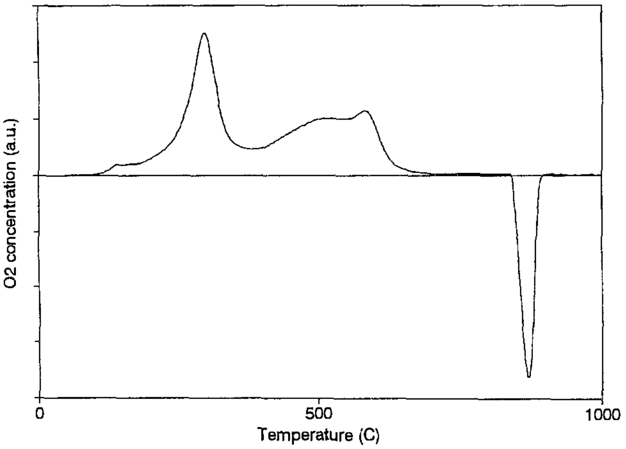

Fig. 3. TPO spectrum of unsupported cobalt metal. (50–1000°C at 10°C/min in 60 ml(NTP)/min 2% O_2/He.)

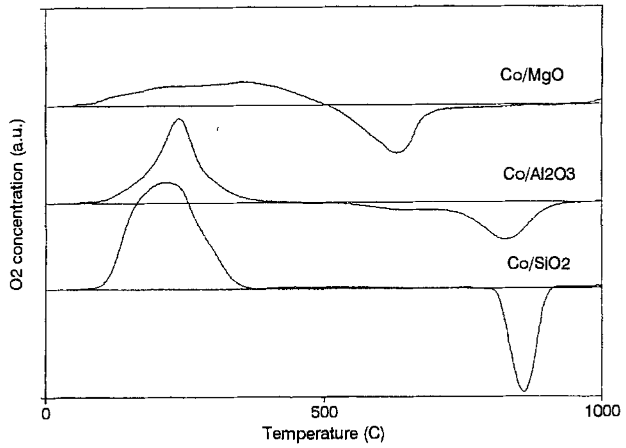

Fig. 4. TPO spectra of SiO_2, Al_2O_3 and MgO supported cobalt catalysts. (50–1000°C at 10°C/min in 60 ml(NTP)/min 2% O_2/He.)

mined directly using TPO by measuring the oxygen release during the high temperature decomposition of Co_3O_4 since this peak represents all cobalt which has been oxidized to trivalent cobalt. Taking into account the stoichiometry of oxidation, the relative peak areas corresponding to oxygen consumption and oxygen release can be used to determine the amount of cobalt metal and the amount of divalent oxidizable cobalt present on the catalyst following reduction. In this manner, the TPO technique can be used to characterize the surface composition of supported cobalt catalysts.

The TPO spectra of the SiO_2, Al_2O_3 and MgO supported catalysts are illustrated in fig. 4. The extent of metal reduction, which has been defined as the amount of metallic cobalt present after reduction relative to the total amount of cobalt in the catalyst, decreases from 42 to 8 to 0% as the support is changed from SiO_2 to Al_2O_3 to MgO (table 3). The results obtained from the TPO measurements of the SiO_2 and Al_2O_3 supported cobalt catalysts showed that the lower extent of reduction in the latter case is due to the presence of residual unreduced divalent cobalt species and not due to increased formation of non-oxidizable cobalt–support species. No reduced metal is observed on the MgO supported catalyst and oxygen consumption corresponds to the oxidation of divalent cobalt to Co_3O_4, i.e. the ratio of oxygen consumption to oxygen release is unity.

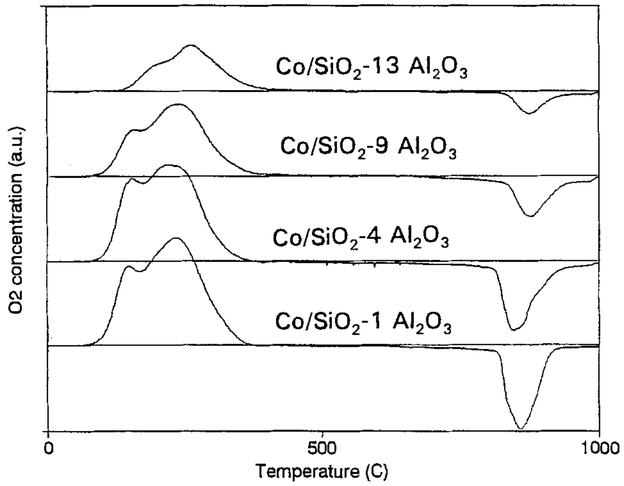

Fig. 5. TPO spectra of SiO_2–Al_2O_3 supported cobalt catalysts with different aluminium contents. (50–1000°C at 10°C/min in 60 ml(NTP)/min 2% O_2/He.)

The TPO spectra of the SiO_2–Al_2O_3 supported cobalt catalysts are illustrated in fig. 5. Increasing the aluminium content in the SiO_2–Al_2O_3 supported catalysts from 1 to 4 to 9 to 13 wt% results in a decrease in the extent of metal reduction from 46 to 40 to 35 to 32%. Increasing the aluminium content thus decreases the extent of metal reduction, in agreement with the measurements obtained during TPR. The decrease in metal reduction with increasing aluminium content is accompanied by a decrease in the levels of unreduced divalent cobalt species and an increase in the levels of non-oxidizable cobalt–support compounds. Aluminium therefore promotes the formation of cobalt–support species which are non-oxidizable up to 1000°C and non-reducible up to temperatures of 500°C.

Increasing the temperature of hydrogen reduction of Al_2O_3 supported cobalt catalysts from 300 to 600°C results in an increase in the extent of metal reduction from 1 to 27% (table 4). The increase in metal reduction is accompanied by a decrease in the level of residual unreduced divalent cobalt species. The concentration of

Table 3

Surface composition and metal oxidation temperatures of supported cobalt catalysts reduced at 500°C for 1 h. (50–1000°C at 10°C/min in 60 ml(NTP)/min 2% O_2/He)

Catalyst	Reduced Co (mol%)	Oxidizable Co (mol%)	Non-oxidizable Co (mol%)	$T_{\text{oxidation}}$ (°C)
Co/SiO_2	42	29	29	215
Co/Al_2O_3	8	65	27	241
Co/MgO	~0	84	16	358
Co/SiO_2–1Al_2O_3	46	44	10	233
Co/SiO_2–4Al_2O_3	40	40	20	213
Co/SiO_2–9Al_2O_3	35	34	31	217
Co/SiO_2–13Al_2O_3	32	24	44	260

Table 4
Surface composition and metal oxidation temperatures of Co/Al_2O_3 catalysts reduced at different temperatures for 1 h. (50–1000°C at 10°C/min in 60 ml(NTP)/min 2% O_2/He)

Reduction temp. (°C)	Reduced Co (mol%)	Oxidizable Co (mol%)	Non-oxidizable Co (mol%)	$T_{\mathrm{oxidation}}$ (°C)
300	1	72	27	195
400	4	70	26	200
450	6	79	15	216
500	8	65	27	241
550	15	53	32	244
600	27	25	48	261

cobalt–support species first decreases and then increases with increasing reduction temperature however. Increasing the reduction temperature thus appears to initiate the reduction of weak cobalt–support species whereas at higher temperatures, there may be increased thermal annealing of residual divalent cobalt with the Al_2O_3 support forming highly stable cobalt–support species such as cobalt–alumina surface spinels [1]. For reduction temperatures lower than 500°C, it is likely that some trivalent cobalt will still be present on the catalyst after activation in hydrogen [10]. This trivalent cobalt will decompose to divalent cobalt at high temperatures with a stoichiometric release of oxygen. This will affect the accuracy of the TPO measurements but will not alter the observed trends.

The temperature at which cobalt oxidation occurs during TPO increases as the reduction temperature is increased. Metal dispersion decreases with increasing temperature of reduction due to sintering and results in larger particles of reduced cobalt metal on the surface of the carrier. Since unsupported cobalt shows a maximum in oxygen consumption at 298°C, it appears that the supported cobalt is becoming more similar in nature to its unsupported counterpart, i.e. the degree of interaction of the reduced metal with the carrier is decreased with increasing reduction temperature.

Increasing the time of Co/Al_2O_3 reduction at 500°C from 1 to 5 to 20 h results in an increase in metal reduction from 8 to 29 to 39% (table 5). This increase in metal reduction is due to the increased reduction of oxidizable divalent cobalt species. The concentration of non-oxidizable cobalt–support species shows no trend with increasing time of hydrogen reduction. The temperature of maximum oxygen uptake decreases with increasing time of reduction at 500°C. There thus appears to be an increased interaction between the reduced metal and the support with increasing time of high temperature reduction since unsupported cobalt metal is characterized by a maximum oxygen uptake at 298°C.

4. Conclusions

The technique of temperature programmed oxidation is valuable for characterizing the surface composition of supported cobalt catalysts. In combination with temperature programmed reduction, TPO can be used to determine optimum activation procedures designed to increase the extent of metal reduction and to minimize the formation of inactive cobalt–support species. The extent of metal–support compound formation is dependent on the type of support used as well as on the time and temperature of catalyst reduction.

The temperature at which the reductive decomposition of the nitrate precursor occurs is linked to the reducibility of the supported cobalt. An increase in the temperature required for reductive decomposition results in a decrease in the extent of metal reduction. The temperature at which oxidation of the supported metal occurs is generally lower than that for unsupported cobalt metal. These differences may be due either to a particle size effect or due to an electronic interaction between the reduced metal and the cobalt support. Since the type of support is known to affect not only particle morphologies but also the adsorption and catalytic properties of supported metal catalysts [13–15], the technique of temperature programmed oxidation may yield

Table 5
Surface composition and metal oxidation temperatures of Co/Al_2O_3 catalysts reduced at 500°C for different times. (50–1000°C at 10°C/min in 60 ml(NTP)/min 2% O_2/He)

Reduction time (h)	Reduced Co (mol%)	Oxidizable Co (mol%)	Non-oxidizable Co (mol%)	$T_{\mathrm{oxidation}}$ (°C)
1	8	65	27	241
5	29	58	13	235
20	40	38	22	211

new insights into observed differences in catalytic performance.

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