TPR and XPS investigations of Co/Al_2O_3 catalysts promoted with Ru, Ir and Pt

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The influence of small amount of noble metals (Ru, Ir and Pt) on the reduction of Co atoms in supported Co catalysts has been investigated by TPR and XPS measurements. The catalysts, containing 8 at% Co and different amounts of promoting metals ($\leqslant 1$ at%) such as Pt, Ir or Ru, were prepared by sequential impregnation. The change in Co reducibility was investigated by XPS to quantify the surface reduction degree of cobalt and by TPR to demonstrate that the presence of the second metal strongly influences the reducibility of the catalysts with TPR shifting to lower temperatures. The efficiency in Co reduction was Ir $>$ Pt $>$ Ru, both at low and high promoter amount, while a complete Co reduction was never found in our operative conditions.

KEY WORDS: cobalt; promotion; characterization; reduction; TPR; XPS

1. Introduction

Cobalt-based catalysts have been widely used for Fischer–Tropsch synthesis (FTS) because of cobalt's intrinsic ability to hydrogenate dissociated carbon species and promote chain growth [1,2]. The properties of Co catalysts for the production of hydrocarbons also depend on the used support material [2–6] and on the nature of Co surface species formed after the catalyst preparation [7,8]. Correlation between Co oxidation state and CO hydrogenation activity was widely reported [7–11] with regards to the difficulty of reducing Co species and the influence of added noble metals (known for having considerable hydrogen dissociation and storage capability) on the reducibility of Co oxides and the resultant ratio of unreduced to metallic Co.

The group VIII noble metals have been suggested to influence catalyst performance in a number of different ways. They may act to promote hydrogen spillover [12], may increase the reducibility of Co [13,14], preserve activity by preventing the buildup of carbonaceous deposits [15], may exhibit cluster and ligand effects [16] and may provide a combination of enhanced Co reducibility and dispersion [17]. It has also been further reported that the addition of a second metal component has no detrimental effect on Co hydrogenation activity [18].

In the present paper, the promotional effects of different amounts of metals (Me) such as Ru, Ir and Pt (0–1 at%) on the reduction of cobalt (8 at% $Co/\gamma\text{-}Al_2O_3$) were investigated.

The higher reducibility of Co/Al_2O_3 due to the presence of Ru atoms was already shown by Goodwin Jr. and coworkers [19,20] who correlated this effect with an increase in CO hydrogenation activity. They concluded that Ru seemed to inhibit the formation of Co species which are hardly reducible or to promote their easy reduction.

Batley *et al.* were the first authors to show the influence of Pt atoms on Co reduction [21]. More recently Holmen and coworkers [22] showed that the presence of Pt atoms has great effects on Co reducibility, and this effect was especially observed on catalysts supported on alumina where the surface cobalt oxides are easily reduced to metallic Co at the usual reduction temperature (350 °C).

Few studies have dealt with Ir promotion, perhaps due to the low activity of this metal for CO hydrogenation [23]. Hanaoka and coworkers [24] suggested a spillover mechanism to explain the higher Co reducibility in cobalt-based catalysts supported on SiO_2 and doped with Ir. In this case, Ir atoms chemisorb hydrogen dissociatively. Thus atomic hydrogen may be thought of migrating over the support and be active in the reduction of cobalt oxides.

In the present paper, all the samples were characterized by XPS (X-ray photoelectron spectroscopy) and TPR (temperature-programmed reduction) to observe and quantify the reducibility of Co oxides in the presence of group VIII metals.

2. Experimental

2.1. Sample preparation

All catalysts used in this study were prepared by incipient wetness impregnation. The γ-alumina, used as support (Engelhard, surface area 110 m^2/g and pore volume 0.54 cm^3/g), was impregnated with an aqueous solution of cobalt nitrate hexahydrate (Fluka) in a single step followed by a reduction in pure hydrogen (99.99% purity grade), at 375 °C for 16 h (flow rate 50 ml_{H_2}/min) to prevent the formation of cobalt aluminates. The reduction schedule included a temperature ramp of 3 °C/min (from room temperature) with 0.5 h holds

Table 1
Results of the XPS analyses performed on the *in situ* reduced samples. (T = 375 °C, t = 16 h, F_{H_2} = 50 ml_{H_2}/min.)

Sample	Co (eV)		Me	Co^0	Me^0
	Co^0	Co^{ox}	(eV)	(%)	(%)
Co8	778.1	780.3	–	26	0
Ru5	–	–	279.8	–	100
Ir5	–	–	60.0	–	100
Pt5	–	–	70.8	–	100
Co8Ru005	778.2	780.4	Nd[a]	31	Nd[a]
Co8Ru01	778.2	780.7	279.6	48	100
Co8Ru05	778.3	780.7	279.7	63	100
Co8Ru1	778.5	780.8	279.5	57	100
Co8Ir005	778.1	780.3	60.3	52	100
Co8Ir01	778.4	780.4	60.2	60	100
Co8Ir05	778.3	780.7	59.9	67	100
Co8Ir1	778.5	780.8	60.0	70	100
Co8Pt005	778.2	780.4	70.8	50	100
Co8Pt01	778.4	780.5	71.2	55	100
Co8Pt05	778.3	780.5	71.1	60	100
Co8Pt1	778.3	780.3	70.9	66	100

[a] Not detectable due to the technique sensitivity limits.

at 100 °C to facilitate water removal and at 200 °C to ensure controlled nitrate decomposition, as described by Bartolomew and Zowtiak [5].

A further impregnation was then carried out on the Co/Al_2O_3 sample with an ethanol solution of $Me(acac)_3$ (Fluka), (Me = Ru, Ir or Pt), followed by drying and calcination at 350 °C for 3 h.

All the prepared catalysts contained 8 at% Co (5 wt%) and Me ranging from 0 to 1 at% (from 0 to 2 wt%) (see table 1) as confirmed by ICP-AES measurements.

Three samples containing Me 5 at% were also prepared with an ethanol solution of $Me(acac)_3$ only, followed by drying and calcination at 350 °C for 3 h, to allow a comparison of the behavior of the monometallic samples with the promoted ones.

Repeated preparation runs yielded samples, both monometallic and promoted ones, with fully comparable features.

2.2. Catalyst characterization

2.2.1. XPS

XPS measurements were performed in an M-Probe Instrument (SSI) equipped with a monochromatic Al Kα source (1486.6 eV) with a spot size of 200 × 750 μm and a pass energy of 25 eV, providing a resolution for 0.74 eV.

With a monochromatic source, an electron flood gun was used to compensate the buildup of positive charge on the insulator samples during the analyses: 7 eV electrons were selected to perform measurements on these catalysts. For all the samples, the Al 2p level was taken as internal reference at 73.6 eV due to a partial overlapping of Ru 3d peaks with C 1s peak (usually used as standard reference).

Co 2p region was fitted assuming a theoretical value of 2 for the ratio Co $2p_{3/2}$ and $2p_{1/2}$ and locking the distance between Co $2p_{3/2}$ and $2p_{1/2}$ at 15.0 eV [29]. The shake-up lines (near the Co $2p_{3/2}$ and near the $2p_{1/2}$ peaks, respectively) were fitted with one peak each.

The accuracy of the reported binding energies (BE) can be estimated to be ±0.2 eV. The quantitative data were also accurately checked and reproduced several times (at least ten times for each sample) and the percentages error is estimated to be ±1% thanks to a severe confidence in spectral decomposition (table 1 data).

All the XPS measurements were performed on the *in situ* reduced samples, treated in flowing H_2 following the same procedure performed after the sample preparation (T = 375 °C, t = 16 h, F_{H_2} = 50 ml_{H_2}/min).

2.2.2. TPR

The experiments were performed using a TPR/O (Thermo Quest Italia). The samples were initially dried under nitrogen at 120 °C for 1 h. After cooling to room temperature, a reducing gas mixture (5 vol% H_2/N_2) was introduced at a flow rate of 30 ml/min. The temperature was increased to 900 °C at a rate of 10 °C/min. The H_2 consumption was detected by a TCD (thermal conductivity detector) and recorded as a function of temperature.

On all the samples. the chemical state of Co before TPR, checked by XPS, was fully oxidized.

3. Results and discussion

Table 1 lists the results obtained by the XPS measurements performed on the *in situ* reduced samples. The composition figures represent atom % (*i.e.*, Cu8Ru1 means Co 8 at% promoted with Ru 1 at%).

A first comparison must be done among the monometallic catalysts: in the same reducing condition it is very easy to reduce all the Me atoms completely (both on Ru, Ir or Pt samples), but it is possible to reduce only 26% of the cobalt atoms present on the surface of the monometallic sample. The different reducibility of Ru and Pt in comparison with Co is a result that was already shown in [26–28].

The introduction of small amounts of a promoter in a Co-based catalyst always maintains a total Me reduction and increases Co reducibility. For both Ir- and Pt-doped catalysts, a constant increase of Co reduction was observed increasing the amount of added promoter with a maximum for the Co8Ir1 sample (70%). In contrast, for Ru-doped catalysts, a maximum is present for Co8Ru05 (this particular trend was always reproduced by XPS on samples prepared by repeated preparation runs, too).

In all the samples, a complete Co reduction was never found.

Only metal or oxides species (mainly Co^{2+}) were found both on based Co catalyst and on promoted ones (see binding energy data (BE, eV) in table 1 [29]). Alloy species were never observed.

Figure 1 shows the results of TPR measurements for the base cobalt catalyst (Co8). In agreement with the data reported in [19,25,26], the cobalt catalyst exhibits two peaks at 180 and 250 °C and a broad reduction feature between

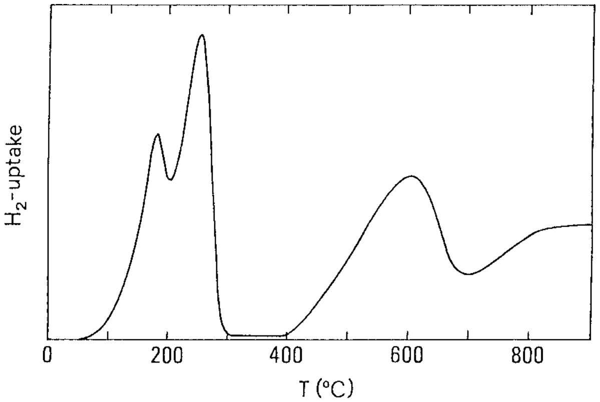

Figure 1. TPR profile for Co8 sample (8 at% Co/Al_2O_3).

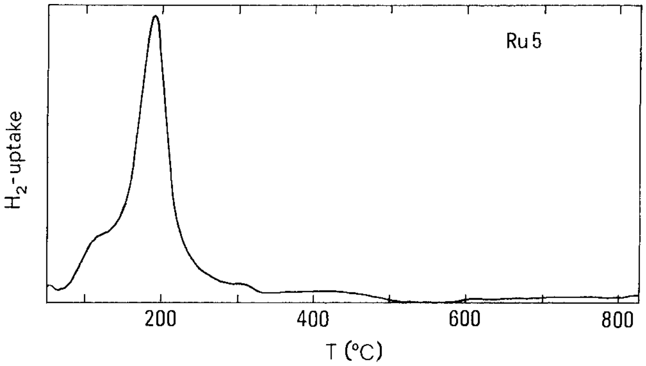

Figure 2. TPR profile for Ru5 sample (5 at% Ru/Al_2O_3).

400 and 800 °C. As shown by Goodwin and coworkers [20], the first peak is due to the complete decomposition of the precursor $Co(NO_3)_2$ and its intensity greatly diminishes by prolonged calcination. The second peak is essentially due to the reduction of Co_3O_4 to Co^{2+}, while the latter broad one is due to the reduction to Co^0 of Co^{2+} atoms, which are interacting with the support (this last peak is not present on unsupported Co_3O_4 [26]).

Even at 900 °C not all the cobalt atoms are completely reduced, as is shown by the increasing TPR profile (figure 1). It is known [26] that hydrogen is still consumed to a great extent between 900 and 1100 °C owing to the complete reduction of the surface $CoAl_2O_4$ spinel.

A completely different behavior of Co/SiO_2 samples is well known as once more reported recently by Kruse and coworkers [30].

Simpler TPR spectra are shown by the other monometallic catalysts. Ru/Al_2O_3 (Ru5) shows two peaks: a small peak at 120 °C and a big peak at 210 °C due to the reduction of RuO_3 to RuO_2 and to RuO_2 to Ru^0, respectively (figure 2). The presence of both the oxides was evident in the unreduced XPS spectra, as already reported in [31].

In contrast, both Pt and Ir monometallic catalysts show one single reduction peak at 280 [32–34] and *ca.* 200 °C [35], respectively (figures not reported for reason of space).

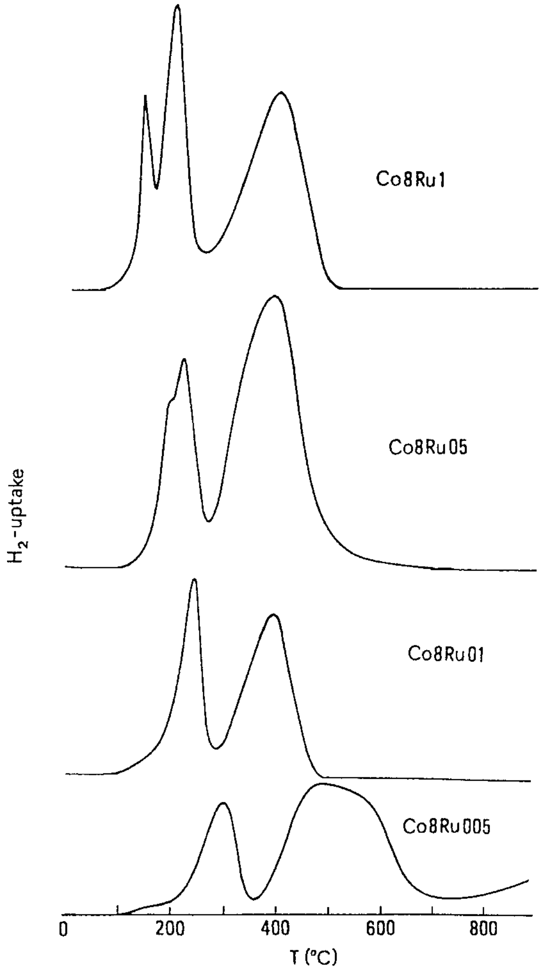

Figure 3. TPR profiles for Co8 samples promoted with different amounts of Ru.

On ruthenium-promoted cobalt catalysts (figure 3), it is possible to observe three main peaks: the first peak is more and more evident and shifts at lower temperature increasing the amount of ruthenium added to the base catalyst. Of course, in this case it is not possible to explain the presence of this peak due to $Co(NO_3)_2$ as the Ru-promoted samples underwent two calcination treatments: a reductive calcination after cobalt impregnation and a second calcination after ruthenium impregnation. Thus it is probable that all $Co(NO_3)_2$ is completely decomposed. Confirmation of this fact is observed on samples Co8Ru01 and Co8Ru005, where this first peak is present only as a small intensity shoulder.

Moreover, this peak is not simply due to Ru reduction because its temperature is too low, compared with Ru/Al_2O_3 (figure 2), its intensity is not proportional to the amount of promoter in the samples and also it shifts to lower temperature increasing the amount of added Ru.

In the light of these considerations, it is possible to assign the first peak (*ca.* 150 °C) to the reduction of a Co species interacting with Ru atoms, the second one to the reduction of both Co_3O_4 to CoO and to RuO_2 to Ru^0. The broad high temperature peak around 600 °C, associated with Co species extremely difficult to be reduced to Co^0, is replaced by a peak at *ca.* 400 °C.

The same behavior was found for Ir- and Pt-promoted catalysts (figures 4 and 5).

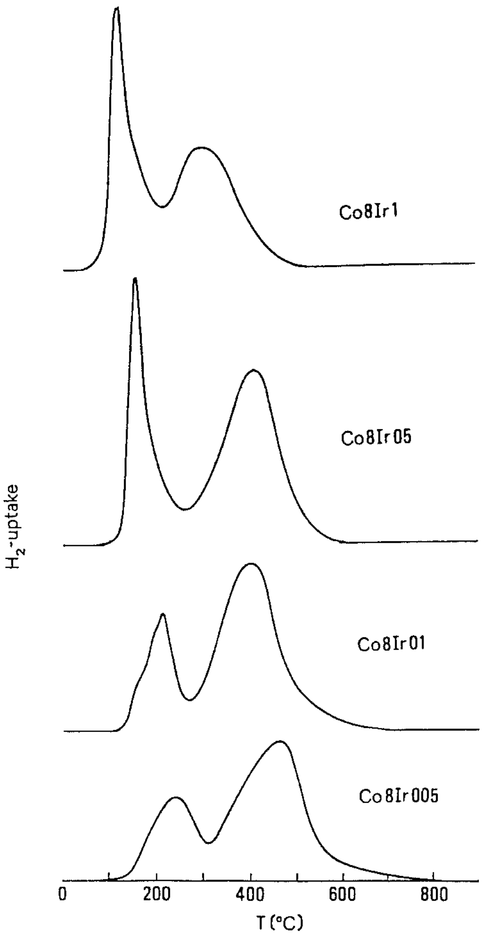

Figure 4. TPR profiles for Co8 samples promoted with different amounts of Ir.

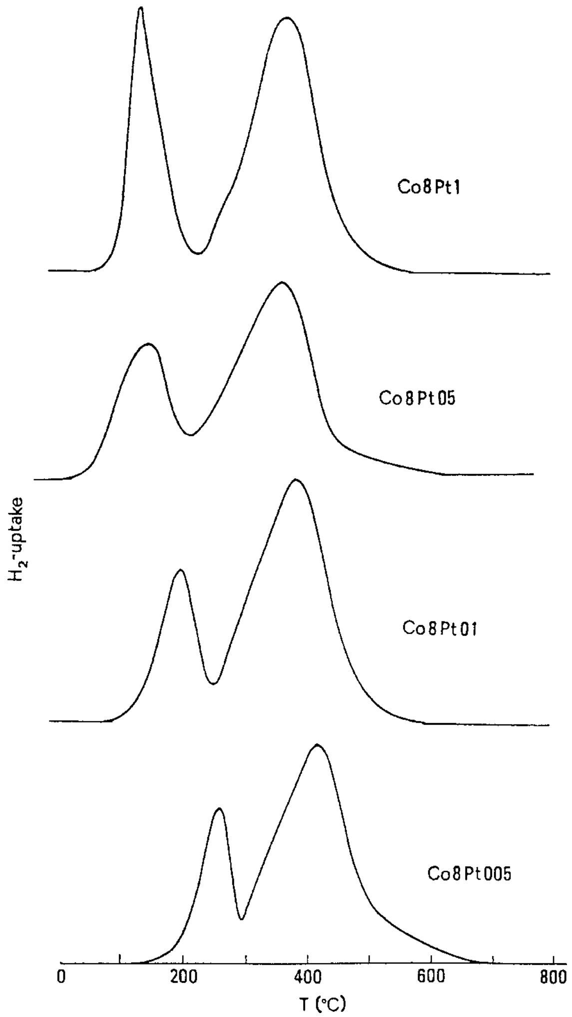

Figure 5. TPR profiles for Co8 samples promoted with different amounts of Pt.

In the former case the situation is similar to Ru promotion: the first peak is present at *ca.* 150 °C, the second at 200 °C and the third one at 400 °C.

In the latter case, the first peak is present at *ca.* 180 °C, the second at *ca.* 280 °C and the third one at 400 °C. In these samples the interacting species between Pt and Co can be observed at a higher temperature (the second peak), as already shown by Holmen and coworkers [22].

In all the studied samples it is interesting to observe the shift of the peaks at lower temperature increasing the amount of promoter in the cobalt-based catalysts (table 2). For example, for Ir-promoted Co catalysts a constant decreasing of the temperature is present both for peak 1 (a difference of 70 °C between the higher and the lower promoter loading) and peak 2 (90 °C) and peak 3 (160 °C). In this latter peak, moreover, the shape of the peak is not as broad as in the Co8 sample.

The difference of temperature of peaks 3 (the peaks at higher temperature) among Co8 and all the promoted catalysts can be correlated with the higher reduction of Co atoms indicated by XPS analyses; that is, it can be assumed as a measure of the easiest reduction of Co oxides interacting with the support. In fact, the larger difference can be observed for Co8Ir1 (315 °C) that also shows the higher Co reduction (70%) among all the tested samples (table 1).

A particular trend is found for the Co8Ru005 sample: it has the lower amount of reduced Co on the surface (as shown by XPS, table 1) and consequently it shows a TPR spectrum (figure 3) with a high temperature and broad peak 3, quite similar to Co8's peak. It seems that at this amount of Ru, the promotion is not so effective.

Table 2 also lists the quantitative data taken from the TPR profiles. These data were obtained determining the amount of hydrogen involved in each peak of TPR experiment and considering completely reduced the promoter metal (as proved by the XPS analyses).

It is interesting to compare these data to those obtained from XPS (see table 1).

The amount of reduced metal is slightly higher when it is measured by TPR than by XPS, except for sample Co8. The TPR experiments were performed reducing the samples till 900 °C, while the XPS measurements were performed at a lower and constant temperature (375 °C); moreover, TPR, is a bulk analysis and thus all the cobalt atoms reached by hydrogen are involved in the measurement.

Table 2
Temperature of TPR peaks.

Sample	$T_{\text{peak 1}}$ (°C)	$T_{\text{peak 2}}$ (°C)	$T_{\text{peak 3}}$ (°C)	$\Delta T_{\text{peaks 3}}$ [a] (°C)	Co^0 (%)	Me^0 (%)
Co8	190	250	615	0	15	–
Ru5	120	210	–	–	–	100
Pt5	280	–	–	–	–	100
Ir5	200	–	–	–	–	100
Co8Ru005	–	300	460–580	35–155	41	100
Co8Ru01	180	240	400	215	54	100
Co8Ru05	180	210	400	215	73	100
Co8Ru1	150	200	400	215	64	100
Co8Ir005	190	240	460	145	72	100
Co8Ir01	170	210	400	215	74	100
Co8Ir05	150	170	400	215	83	100
Co8Ir1	120	150	300	315	88	100
Co8Pt005	270	320	430	195	65	100
Co8Pt01	210	310	410	215	71	100
Co8Pt05	160	280	380	235	76	100
Co8Pt1	140	280	380	235	81	100

[a] Difference between $T_{\text{peak 3}}$ of Co8 and Co8MeX.

Without any dopant promotion (sample Co8), it appears easier to reduce surface cobalt atoms than bulk ones where the cobalt aluminates are largely present.

4. Conclusion

The introduction of even small amounts of a promoter (Ru, Ir or Pt) leads to a high increase of Co reducibility in Co-based catalysts supported on alumina which usually have great problems due to the formation of strong interaction between metal and support. Among the three tested promoters, our results demonstrate that the efficiency in Co reduction is Ir $>$ Pt $>$ Ru, both at lower and higher amounts (in this latter case Ir increases the Co reducibility at the higher extent, 70%) and, furthermore, Ir makes easier the Co reduction decreasing the temperatures for the reduction of the Co oxides present on the catalysts, as demonstrated by TPR measurements.

Finally, it is necessary to remark that all the samples reduced in the operative conditions of this work never show a complete Co reduction to the metal species (checked both by XPS and TPR).

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