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Active state of model cobalt foil catalyst studied by SEM, TPR/TPO, XPS and TG

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Abstract

Four states of the cobalt foil catalyst, corresponding to different redox treatment and activity, were defined: oxidised, reduced, active and deactivated. They were investigated by scanning electron microscopy (SEM), temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), X-ray photoelectron spectroscopy (XPS) and thermogravimetric (TG) methods and in the hydrogenation of ethylene used as a test reaction. Particular emphasis was laid on the study of the active state, achieved after the catalyst reduction at moderate temperatures. It was shown that the catalyst preactivated by a series of redox cycles is built of a cobalt oxide layer of a characteristic size and dispersion, which is stuck to the metallic bulk. Reduction at a moderate temperature, prolonged even to several hours, converts only a small fraction of the oxide layer into metallic Co. XPS, TPR and TPO methods distinguished various states of oxygen and cobalt on the surface of the activated or partially activated samples. The results were interpreted in terms of the mechanism of autocatalytic reduction. The deactivation was associated with the structural reconstruction of the surface, taking place either in the reaction mixture during the hydrogenation of ethylene or in hydrogen atmosphere. Formation of the inactive carbon deposit was experimentally excluded.

Keywords: Active state; Model cobalt foil catalyst; SEM

1. Introduction

This work intends to contribute to the studies on catalyst design, being in the main notorious in surface science and catalysis. One possible approach to this problem is to build up a complex model catalyst starting from the characterisation of a one-component material into which new components are gradually added [1]. A few research groups have used such an approach for cobalt foil catalysts of CO and CO_2 hydrogenation [2–7]. In our recent papers [6,7], we have worked out the method of activation of the cobalt polycrystalline foil [5,6] and put forward the models of its activation and deactivation [6,7]. It has been shown that the procedure of activation by a series of subsequent reduction/oxidation cycles at a high temperature leads to a catalyst precursor in an oxidised form which can be then converted into an active catalyst by the reduction at a moderate temperature, the procedure's final and obligatory step. Such a treatment increases the foil activity by 4 orders of magnitude up to a saturation value, characteristic of an active catalyst, and reproducible even after the activity loss in a catalytic reaction. Furthermore, metallic cobalt clusters impinged to the cobalt oxide matrix have been postulated as the active centres for hydrogenation. Their surface concentration, measured by temperature-programmed reduction, has been regarded as the benchmark for the catalyst activity and thus the main parameter of the models of activation and deactivation.

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In this paper, following the threads from these models, we focus on the description of the active surface of the cobalt catalyst obtained from the foil. Since our interest is the catalyst under the closest possible conditions to those of the catalytic process, we engaged the temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO). These were accompanied by the surface methods: scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) and the thermogravimetric method (TG). The catalyst activity was tested in the hydrogenation of ethylene at low temperatures in order to avoid formation of the inactive carbon deposit.

2. Experimental

2.1. Samples

The cobalt foil (Aldrich) of +99.99% purity, 0.1 mm thick, was used as an initial material for the catalyst preparation. Typical samples were rectangle pieces (ca. 6 mm × 5 mm) of a mass between 15 and 17 mg. Their activation procedure consisted of three steps: preactivation, activation proper and regeneration. The preactivation involved about 10 subsequent oxidation and reduction cycles which were carried out under the following conditions: reduction — in 5% (v/v) H_2 in Ar (Linde), at a flow rate of 8.5 cm^3/min for 30 min, at 550°C; oxidation — in 5% (v/v) O_2 in He (Linde), at a flow rate of 8.5 cm^3/min for 30 min at the same temperature. The activation used before each catalytic test involved reducing of a preactivated oxidised sample in pure H_2 usually for 30 min at 250°C. After both the high-temperature reduction and the catalytic test, a catalyst sample was regenerated by oxidation in 5% O_2 at 550°C. The regeneration procedure restored the initial activity of the catalyst. If necessary, reduced samples were passivated before transferring them into a different apparatus. The passivation was carried out in the gas mixture containing 5% O_2 in He, at a flow rate 8.5 cm^3/min for 15 min at 60°C.

2.2. Apparatus

SEM images of the catalyst surface were taken in a scanning electron microscope (Philips XL20). Temperature-programmed experiments were performed in a standard TPR/TPO unit using a thermal conductivity detector (TCD, Valco) which measured an uptake of a reactive gas from the H_2/Ar or O_2/He mixtures. Temperature-programmed reactions were carried out at a heating rate 20°C/min. XPS analyses were carried out in ESCA spectrometer (VSW ESCA100) equipped with a preparative chamber and an HV analytic chamber. Prior to the analyses an oxidised sample was reduced in the preparative chamber which was purged with H_2/Ar 7% (v/v) mixture (Linde) under a flow 10 cm^3/min. The isothermal reduction measurements applied a TG unit (Mettler-Toledo 851e).

2.3. Catalytic tests

The hydrogenation of ethylene was carried out in a microreactor unit operating in a continuous flow of reactants at atmospheric pressure. The products were analysed on a gas chromatograph (Shimadzu 14A with FID detector and packed HayeSep DB column). Quartz reactors (4 mm i.d.) were interchangeable with those used in the TPR/TPO unit. The tests were performed with use of a reaction mixture composed of H_2 and C_2H_4 (6:1), at the temperatures from the range 150 to 300°C. The reaction was initiated by switching on the flow of C_2H_4 to the reactor immediately after the activation of the samples was completed.

3. Results

We define four states of the surface of a preactivated catalyst

- oxidised state: a sample oxidised at 550°C (as during the oxidation in the preactivation step);
- active state: an oxidised sample reduced at 250°C (activation proper);
- deactivated state: an active sample exposed to the reaction mixture for about 2 h at 250°C;
- reduced state: a sample reduced at 550°C (as during the reduction in the preactivation step).

3.1. SEM

The four states of the catalyst surface can be easily distinguished in SEM photographs (Fig. 1). The

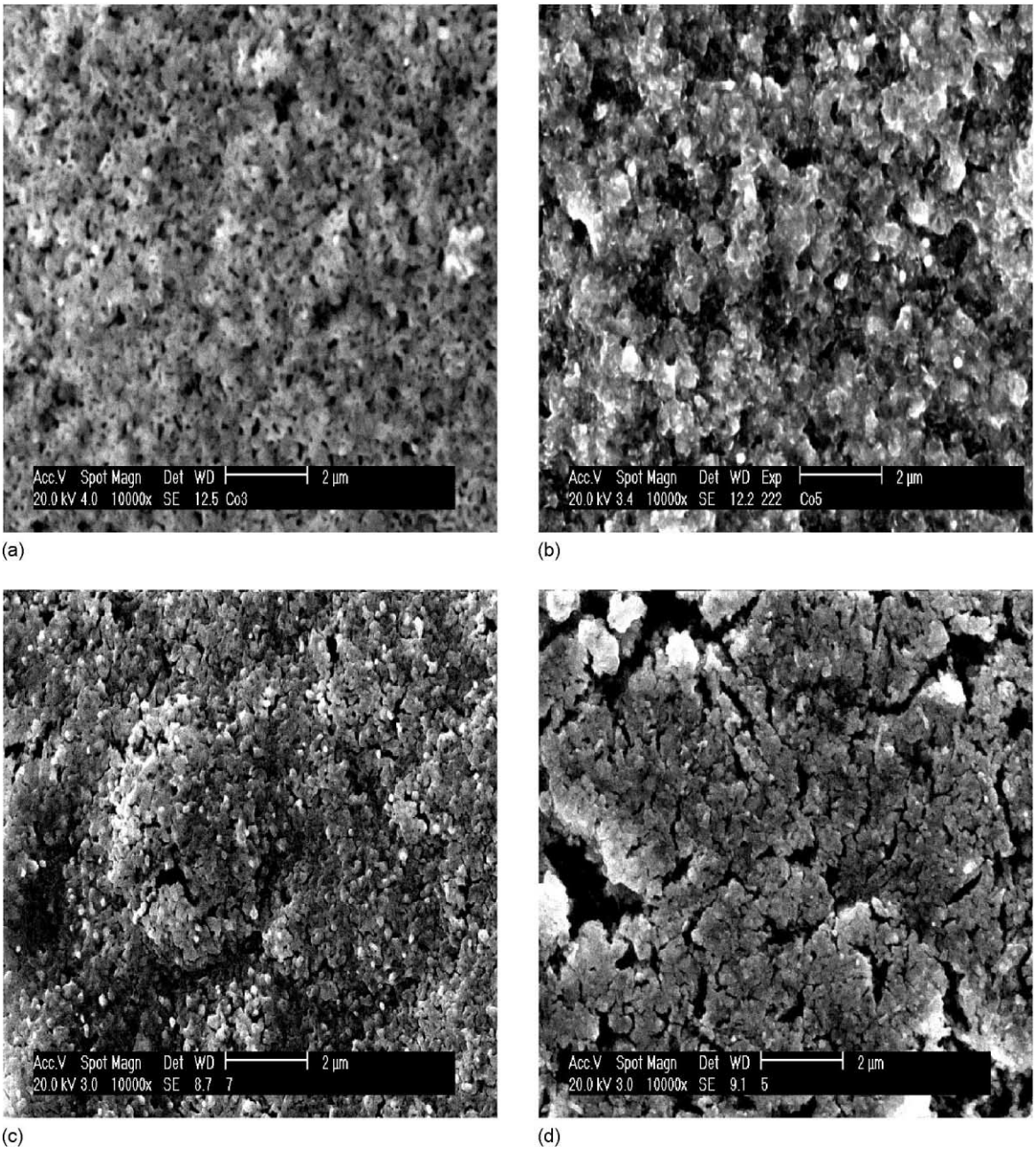
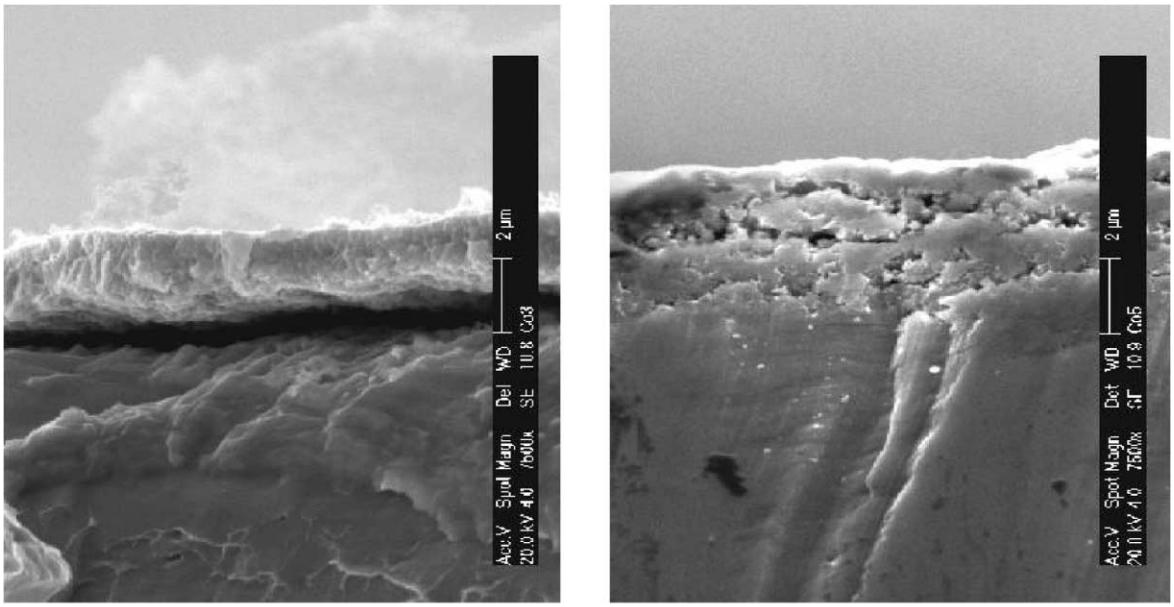


Fig. 1. SEM of the surface of the cobalt catalyst after preactivation (10 000×): (a) oxidised state, (b) reduced state, (c) active state, (d) deactivated state.



(a) (b)

Fig. 2. SEM of the cross-section of the cobalt catalyst after preactivation (7500×): (a) oxidised state, (b) reduced state.

oxidised sample (Fig. 1a) resembles a sponge with many pores, possible routes for gas migration. The reduced sample (Fig. 1b) shows fairly large metallic cobalt grains around 0.6 μm in diameter, distributed evenly on the catalyst surface while the active sample reveals much smaller (0.2 μm) but still well discernible grains. The reaction in hydrogen-rich mixture significantly changes the texture of the surface and the deactivated sample becomes shrunk and rifted (Fig. 1d). A similar effect on the surface is brought about by a 2-h reduction at moderate temperatures.

The extent of oxidation or reduction used in the preactivation procedure can be measured by the thickness of the surface oxide layer that develops on the metallic bulk. Such a layer was observed in SEM of the cross-sections of the oxidised or reduced samples (Fig. 2a and b). From the value of an average thickness of the layer (2 μm), the amount of cobalt atoms in the surface layer was estimated to 4% of the sample total mass. Magnifying the picture 2a, we could notice the boundaries between the cobalt oxide grains of a diameter 0.2 μm. A reduced Co layer whose laminar structure possibly comes from the subsequent reduction and oxidation treatments can be distinguished even after the prolonged reduction at 550°C (Fig. 2b).

3.2. TPR and TPO

The progress of the preactivation was traced down by TPR and TPO experiments. The quantitative results are presented with those of the catalytic tests in Fig. 3. After an initial growth the amount of the reactive cobalt stabilises at 700–800 μmol/(g catalyst) for both TPR and TPO, which corresponds to 4% of the initial sample mass.

In order to get a clearer understanding of the catalyst at the active state, TPR and TPO experiments were performed over a series of the active and partially activated samples (Figs. 4 and 5). The oxidised and reduced samples serve here as standards to which the changes occurring on the catalyst during the mild reduction can be related. The tendency is the longer the activation (mild reduction) time the lower is the temperature of a maximum in a TPR profile. Thus, the oxidised catalyst reveals a narrow maximum at about 430°C (Fig. 4a, curve E), whereas the sample treated with H_2 only for 10 min shows a maximum slightly

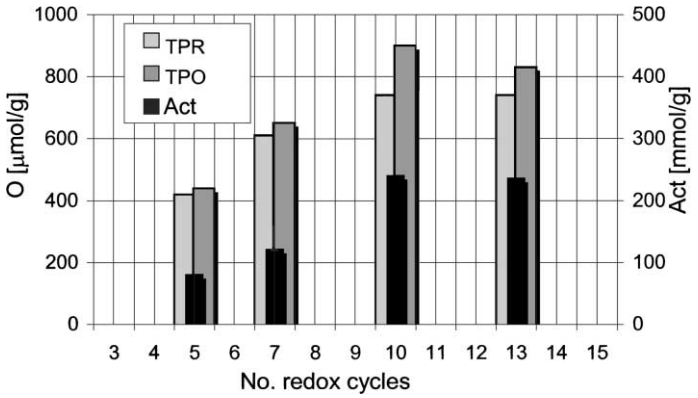


Fig. 3. The dependence of the Co foil activity on the number of redox cycles: TPR — amount of O from CoO converted into H_2O, TPO — amount of O used to form CoO, Act — total amount of ethylene converted during 2 h hydrogenation at 250°C. All values were normalised to the mass of an initial sample.

shifted towards a lower temperature (Fig. 4a, curve A). With the reduction time prolonged to 20 min the TPR profile splits into two small maxima at 210 and 350°C (Fig. 4b, curve B) to finally give, after 30 min, one peak at 240°C and two vanishing ones below 200°C (Fig. 4b, curve C). It is noteworthy that the smallest maximum at 200°C was detected for the deactivated sample (Fig. 4b, curve D). The TPO results show a similar trend with the reduction time (Fig. 5). Two (or three) overlapping peaks with the maxima at 400 and 460°C are detected for the reduced sample (Fig. 5, curve D). A short 10-minute mild reduction gives a very small and broad oxidation peak in the TPO spectra (Fig. 5, curve A), and the reduction prolonged to 30 or 60 min, two more intense oxidation peaks at 310 and 380°C (Fig. 5, curves B and C, respectively). The third small maximum at the lowest temperature (around 200°C) can be distinguished after deconvoluting the B, C and D spectra.

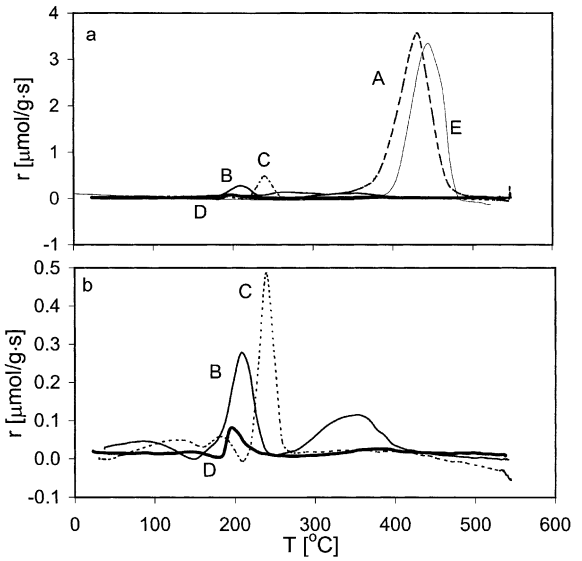


Fig. 4. (a) TPR of the catalyst: (A) oxidised and then reduced at 250°C for 10 min, (B) oxidised and then reduced at 250°C for 20 min, (C) oxidised and then reduced at 250°C for 30 min, (D) deactivated in the flow of H_2:C_2H_4 = 6:1 for 2 h, (E) oxidised at 550°C for 30 min. (b) Curves B–D of (a) scaled up.

3.3. XPS

In an attempt to ascertain the surface composition of the active catalyst XPS analyses were performed on the samples pretreated in situ and ex situ with hydrogen or oxygen, in the similar way as for the TPR and TPO experiments. Since the results of these two series of experiments do not differ between each other only the spectra obtained for the former series are presented in Fig. 6. The binding energies Co 2p 779.95 eV and O 1s 529.9 eV, characteristic of cobalt (+2) oxide, were observed for all studied samples irrespectively of reduction time and temperature. However, due to the broadening of the Co 2p band at around 782 eV small amount of Co^{3+} cannot be excluded. No metallic Co was detected even after the mild reduction prolonged to 60 min (curve C) and the only indication of the progressing reduction was a drop in the

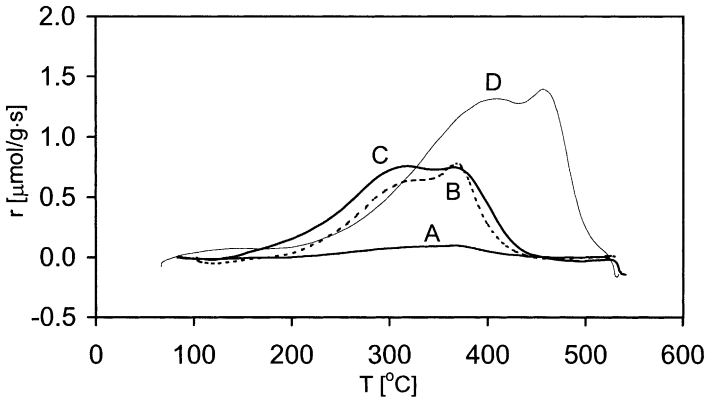


Fig. 5. TPO of the oxidised catalyst: (A) reduced at 250°C for 10 min, (B) reduced at 250°C for 30 min, (C) reduced at 250°C for 60 min, (D) reduced at 550°C for 30 min.

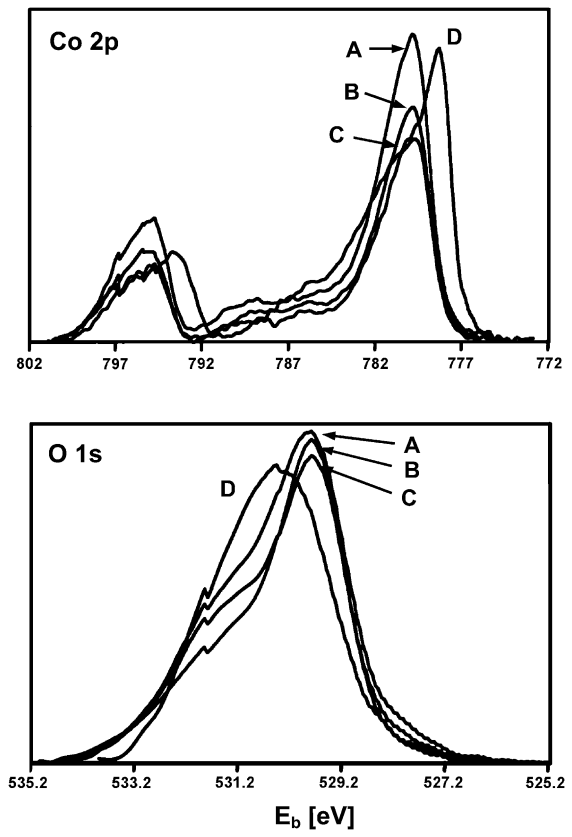


Fig. 6. Co 2p and O 1s lines in XPS of the sample: (A) oxidised at 550°C for 30 min, (B) reduced at 250°C for 30 min, (C) reduced at 250°C for 60 min, (D) reduced at 500°C for 30 min.

intensities of these peaks with the time of hydrogen exposure. The signal of metallic cobalt at 778.2 eV was noted for the samples reduced at 500°C (curve D) and for the deactivated samples. Furthermore, a broad O 1s maxima of the sample reduced for 30 or 60 min at 250°C (curves B and C in a lower picture) may indicate three oxygen states on the surface: O^{2-} in the oxide, and in OH and H_2O molecules.

3.4. TG

The kinetic curve of the mild reduction performed in the flow system at a temperature of 250°C is presented in Fig. 7. An initial apparent increase of the sample mass induced by a gas replacement from Ar to lighter H_2 was subtracted from this curve. After

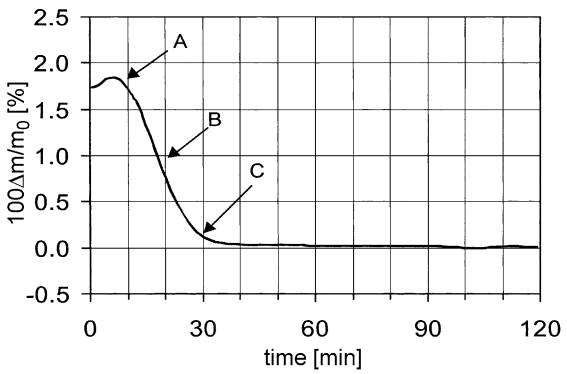


Fig. 7. Reduction of the oxidised catalyst in the flow of H_2 at 250°C in TG: (A) initiation, (B) acceleration, (C) inhibition.

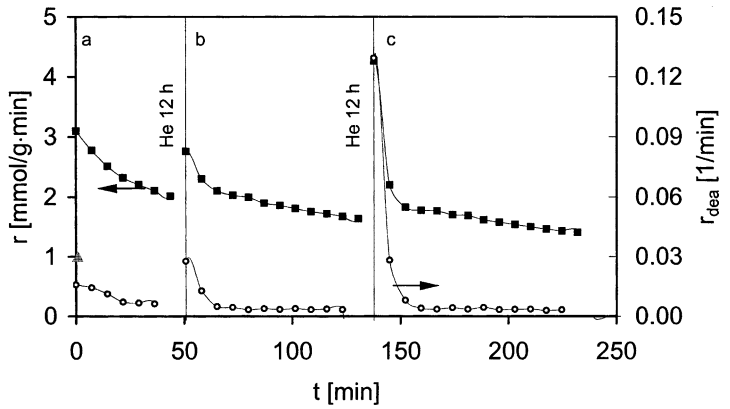


Fig. 8. The hydrogenation of ethylene H_2:$C_2H_4 = 6$:1 at 250°C: (a) on the active catalyst, (b) restarted after 12 h in He at room temperature, (c) as in b; the relative deactivation rate $r_{dea} = -(1/r)(dr/dt)$, where r the reaction rate.

10 min of a slight increase of the sample mass, the reduction begins to accelerate at around 20 min, and practically ends after approximately 35 min. The total reduction degree reaches about 1.7% of the total sample mass, which corresponds to around 50% of the initial oxide layer.

3.5. Catalytic tests

The catalyst was tested in a series of C_2H_4 hydrogenations. Fig. 8a presents a typical time-on-stream profile of the overall reaction rate as well as the relative deactivation rate recorded at 250°C. Under the applied conditions the main product was C_2H_6 (>90%), with small amounts of C_3 hydrocarbons (<5%) and CH_4 (<1%). A high selectivity for C_2H_6 did not change considerably with time. Fig. 8b and c represents the reaction initiated back on the deactivated sample that after the first reaction run was kept under a He flow for 12 h at room temperature. Neither changing the feed composition nor interrupting the reaction by purging the reactor with He had an effect on the relative deactivation rate. However, in the beginning of each reaction run there was a pronounced initial drop in the catalyst activity.

4. Discussion

The preactivation of the cobalt foil catalyst, during which the catalyst gradually develops its surface area, dispersion and activity, results in the formation of a cobalt oxide layer of a characteristic dimension on top of the catalyst metallic bulk. The preactivation procedure applied here, consisting of 10 reduction/oxidation cycles performed at 550°C, produced the 2 μm CoO layer containing about 4% of cobalt from the initial sample, as measured by TPR and TPO (Fig. 3). Had there been Co_3O_4 in the layer, we would have observed oxygen emission during the temperature-programmed experiments carried out in pure He in ascending and descending temperature modes. Although XPS analyses revealed mainly Co^{2+} on the surface of the oxidised catalyst, the traces of Co^{3+} cannot be excluded. Similar findings have already been reported in [8,9], where the phase transition between Co_3O_4 and CoO was observed at 550°C for the bulk oxides and at 350°C for the surface oxides. These observations lead us to postulate that the oxide layer obtained by the preactivation constitutes a kind of a support for metallic active centres being formed during activation of the catalyst by its reduction at moderate temperatures.

Since both the oxidised and the reduced catalysts are inactive in hydrogenation reactions [6], these two states set fairly broad limits within which we can look for an active state of the catalyst operating at lower temperatures. This also implies that the active catalyst must include both cobalt oxide and metallic cobalt. In order to grasp redox properties of the active state, we studied the changes occurring on the catalyst surface at different stages of the mild reduction. The

Table 1
The TPR and TPO results of the oxidised, partially active, active and deactivated samples

Samples	TPR: % CoO remained in the layer	TPO: % CoO remained in the layer	XPS: % surface CoO[a]	TG: % CoO remained in the layer
Oxidised at 550°C for 30 min	100	100	100	100
Reduced at 250°C for 10 min	95	85	95	95
Reduced at 250°C for 20 min	13	–	75	70
Active-reduced at 250°C for 30 min	10	60	70	50
Reduced at 250°C for 60 min	–	50	70	47
Deactivated at 250°C for 2 h	<1	–	63	–
Reduced at 550°C for 30 min	–	0	40[b]	–

[a] Area under the Co 2p peaks related to an oxidised sample assigned as 100%.
[b] Reduced at 500°C in situ.

quantitative results of TPR, TPO, XPS and TG are summarised in Table 1. The TG results give a clear evidence that the mild reduction ends before the whole oxide is used up; under the applied conditions the reduction degree amounts maximum 50% of the oxide layer before exceeding 40 min (Fig. 7). At such a stage of the reduction the catalyst reaches the highest activity in the hydrogenation of ethylene and of CO_2 [6]. The sigmoidal shape of the kinetic reduction curve, observed in Fig. 7, can be interpreted in terms of the autocatalytic mechanism, described in [6], in which initially formed metallic grains become active centres for further hydrogen adsorption. In order to measure the most pronounced effects on the surface, we have performed the other experiments at three characteristic points of this kinetic curve, i.e. after 10, 20 and 30 min, corresponding to the reduction initiation, acceleration and inhibition, respectively. Slow reduction progress in first 10 min, accompanied by a slight increase of the sample mass (corresponding to the adsorption of 0.5 μmol H_2/g catalyst), was also observed by TPR and TPO (Figs. 4 and 5). This may result from a high activation barrier either of hydrogen chemisorption on the oxidised centres or of water desorption. The formation of the second kind of centres, in a reduced form, accelerates the reduction bringing another maximum in the TPR spectra. This low-temperature maximum is characteristic of an activated catalyst (Fig. 4b, curve C). By and large, the mild reduction seems to facilitate both TPR and TPO, forming a dispersed metallic phase seen in Fig. 1d.

Somewhat astonishing, however, is the comparison of the quantitative TPR and XPS results obtained for the activated catalyst. The question arises why on the active samples TG manifested 50% CoO remained in the layer after the mild reduction, TPR only 10% CoO, while XPS exclusively CoO. The XPS results show that reduction proceeds from the bulk of the CoO layer toward the surface and can be accelerated by the temperature rise or by increasing the time of hydrogen exposure (Fig. 6). Schloegl presents analogous XPS results for the activation of iron catalyst for ammonia synthesis [10] indicating that gas–solid interface can only be reduced after reduction of bulk is complete. The driving force for such a segregation of the cobalt metallic phase is surface tension whose value is seven times greater for metallic cobalt than for cobalt oxide [11]. Thus to achieve minimum Gibbs free energy, metallic cobalt tends to contract toward the bulk while cobalt oxide wets cobalt surface. This is facilitated also by a huge difference between diffusion rates of electrons and oxygen anions through the oxide net. On adsorbing on CoO surface, hydrogen reduces surface Co^{2+} to Co but this state is transient and electrons diffuse fast through the "hole" mechanism to the CoO bulk reducing internal Co cations. Simultaneously, large oxygen anions leaving their nodes diffuse slower through the vacancies or grains boundaries to the surface in this way limiting the overall reduction rate. In the light of XPS results oxygen measured by TPR for the deactivated or activated catalyst may originate from the surface region (Fig. 4, curves B–D). The reduction of the sub-oxide layer can be prevented by the sintering of the active metallic layer, what will be discussed later together with deactivation of the catalyst. Summing up, formation of the dispersed metallic cobalt phase is obligatory to achieve active state of the cobalt foil. However, it is not clear what is the role

of CoO present on or near the surface of the active catalyst. The residual CoO may exert a promoting impact on the catalyst activity because the CoO amount decreases with the deactivation progress (Fig. 6). Having investigated a similar system, Jnioui et al. [12] conclude that residual CoO can improve electronic properties of metallic centres.

Studying the reasons for the catalyst activity loss, we have eliminated both the formation of the inactive carbonaceous deposit and the reduction of the cobalt oxide as possible deactivation mechanisms. The latter we have discussed earlier in this paper. The exact information on the conditions under which the carbon deposits occur on the surface of the cobalt foil catalyst during the hydrogenation of ethylene the reader can find in [13], but here we mention only these facts which are necessary to carry on the discussion on deactivation. The results of the temperature-programmed gasification of the deposits proved that the hydrogenation of ethylene did not produce a sufficient amount of the inactive deposit to deactivate the catalyst at temperatures below 300°C. Although ethylene wins the competition with hydrogen for the same active centres even in the excess of hydrogen (2:1) — in this way limiting the reaction rate — the effect is reversible and thus cannot cause deactivation of the catalyst. It is generally accepted that temperatures below 300°C are too low to enhance the condensation of adsorbed forms of ethylene [1,14]. Furthermore it should be pointed out that the deactivation occurs exclusively in an hydrogen atmosphere. No changes in the relative deactivation rate took place after the reaction had been temporarily halted, the reagents cut off and replaced with He for 2 or even 12 h (Fig. 8). Additionally, as observed in SEM, the textures of the catalyst exposed to the reaction mixture or to pure hydrogen at the same temperature are alike. In view of these facts, deactivation of the cobalt foil catalyst at temperatures below 300°C must be a kind of surface reconstruction which occurs in the reducing atmosphere of H_2 and which causes the decrease of the number of active centres for the catalytic reaction. In our previous paper similar findings were interpreted in terms of hydrogen-enhanced sintering [5], but in fact sintering can only be observed at temperatures much higher than those used by us [15], and, what is more, the pictures of the sintered (Fig. 1b) and of the so-called reconstructed surface of the catalyst (Fig. 1d) are substantially different.

The surface reconstruction can help to account for the TPR results which underestimated the amount of CoO in the oxide layer (Fig. 4, curves B–D). The metallic dispersed phase prefabricated in the mild reduction, when exposed to elevated temperatures, may rapidly laminate the cobalt oxide cutting off the routes for the hydrogen diffusion to the oxide remaining in the sublayer. Certainly at lower temperatures, this process is much slower and thus on the catalyst deactivated for 2 h at 250°C the amount of the residual oxygen detected by TPR is lower than on the active one.

5. Conclusions

The knowledge of the structure of one-component catalysts can be instrumental in designing multicomponent catalysts for large-scale industrial applications. This work presents a characterisation of a cobalt foil catalyst to be used for hydrogenation reactions. The surface of the catalyst was modified by reduction/oxidation cycles. The states of the surface produced by these treatments were studied with SEM, TPR, TPO and TG methods, which provided us with complementary information coming from different surface regions of the catalyst. Special attention was paid to the catalyst at the active state. It has been shown that the preactivation procedure by redox cycles develops the CoO layer of a characteristic size and dispersion on the metallic bed of the foil. The layer is a support for the metallic active centres formed during activation by the reduction at moderate temperatures, which has proved to be an autocatalytic process. The extent of this reduction is limited to a surface fraction of the CoO layer. At the active state the catalyst shows the dispersed metallic phase whose surface is enriched with Co^{2+}, O^{2-}, OH and H_2O. This phase, activating as well hydrogenation of ethylene as reduction and oxidation undergoes structural changes in the hydrogen atmosphere lowering its dispersion and activation capacity.

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