



ELSEVIER

Journal of Molecular Catalysis A: Chemical 111 (1996) 113–122

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

# Genesis of cobalt oxide-induced surface structure in $\text{PtCo}_x/\text{Al}_2\text{O}_3$ catalysts

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Received 26 October 1995; accepted 20 April 1996

## Abstract

Molecular approach to surface structure of the  $\text{PtCo}_x/\text{Al}_2\text{O}_3$  ( $x = 0\text{--}0.67$ ) samples prepared by co-impregnation with aqueous solution of  $\text{H}_2[\text{PtCl}_6]$  and  $\text{Co}(\text{NO}_3)_2$  as precursors, has been investigated by means of X-ray photoelectron spectroscopy during the drying–calcination–reduction sequence of preparation. Ion exchange between the chloride ligands and oxygen ions during calcination in oxygen of the samples containing constant loading of Pt and increasing amount of Co, was induced by cobalt oxide at high cobalt content. Simultaneously, CoO was anchored to alumina surface, whereby, after subsequent reduction, a novel CoO-modified-support interface was developed and metallic platinum and intermetallic Pt–Co species were formed. As a result, the estimated dispersion of Pt,  $D_{\text{Pt}}$  passed through a shallow minimum over the various composition. Similar trend was observed for the reaction rate in the CO hydrogenation suggesting that the catalytic activity of the  $\text{PtCo}_x/\text{Al}_2\text{O}_3$  samples is related to platinum, while product selectivity is primarily controlled in a complex manner by the platinum particles on the CoO-modified support. The present work represented how molecular approach in the genesis of a bimetallic catalyst helps in understanding the mechanism of the catalytic reaction.

**Keywords:** Pt; Co; XPS; Surface structure; Co effect; Bimetallic catalysts; CO + H<sub>2</sub> reaction

## 1. Introduction

Platinum is a widely applied precious metal in catalysis and is a component of many bimetallic catalysts [1–3]. Catalytic performance of the alumina supported cobalt could significantly be improved in the presence of platinum [4,5] which is likely attributed not only to enhanced reduction of the Co ions facilitated by platinum, but to the Pt-modified surface

structure, as well. Vice versa, similar effects can also be anticipated on the addition of cobalt to platinum catalyst.

In an earlier work [4], a series of Pt–Co samples was studied in which the total metal content was kept constant, but the Pt/Co ratio changed from sample to sample. Although from these measurements conclusions about the formation of cobalt surface phase (CSP) and its effect on the platinum/alumina interface (e.g. platinum dispersion) could be drawn, but the effects could not be quantified.

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The ultimate goal of the present paper is to receive quantitative information about the changes in the surface structure of the alumina supported Pt in the presence of increasing amount of Co, while keeping the platinum content constant. To follow the development of the surface structure, X-ray photoelectron spectroscopy is applied after each step of sample preparation (drying, calcination and reduction). The CO hydrogenation as test reaction is also used to correlate the catalytic performance with the surface structure.

## 2. Experimental

### 2.1. Sample preparation

The samples were prepared by co-impregnation of  $\gamma$ -alumina (Woelm, BET surface area is  $160 \text{ m}^2/\text{g}$ ) with aqueous solution of  $\text{H}_2[\text{PtCl}_6]$  (and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (Ipatieff method). The platinum content of the samples was  $412 \mu\text{mol g}_{\text{cat}}^{-1}$  in all cases. Simultaneously, four bimetallic ( $\text{PtCo}_x/\text{Al}_2\text{O}_3$ ) samples were prepared in which the Pt content was constant ( $412 \mu\text{mol g}_{\text{cat}}^{-1}$ ) and the molar fraction of cobalt ( $x$ ) referred to platinum varied in the range of 0.1 (1/9), 0.25 (1/4), 0.43 (3/7) and 0.67 (2/3).

After wetting alumina with the solution containing the precursors, time was allowed for complete leaching of the liquid phase and the samples were dried in a water bath in air at about 330 K for 8 h. The samples after impregnation (from now on as prepared state) were then calcined in a stream of oxygen at 573 K for 1 h and were subsequently reduced in a stream of hydrogen at 573 K for 1 h. The reduction steps were carried out in situ either in a small reactor chamber attached to the ESCA machine or in the catalytic reactor.

### 2.2. XPS measurements

XPS measurements were carried out using a KRATOS ES-300 type ESCA machine. After

calcination the catalyst powder was pressed ( $4 \text{ kN cm}^{-2}$ ) into a copper grid in which it was measured by XPS. Then, the samples were reduced in a small chamber directly attached to the UHV chamber. The conditions of the reduction were identical to that were described above. In this procedure the sample was transferable to the analysis position without exposing it to air. After reduction the XPS spectra were again recorded.

During spectra recording the hemispherical analyzer worked in fixed retarding ratio (FRR) mode. The slits were set to fully opened position in order to be able measure the sample with maximum sensitivity. For excitation Al  $K\alpha$  X-ray line was used (150 W). In the experiments the pressure in the UHV chamber did not exceed  $10^{-6} \text{ Pa}$ .

The Al 2s line of 119.30 eV binding energy (BE) was used as an internal BE reference. The Co 2p XPS regions were evaluated with a one-parameter peak-synthesis method [4]. In the XPS measurements, Pt 4d, Co 2p, Al 2s, C 1s, O 1s and Cl 2p transitions were recorded in all cases. The BE positions of the C 1s and the O 1s peaks were 284.8 eV (dried and calcined samples only) and 531.3 eV, respectively. The estimated limits of error of the peak positions are  $\pm 0.2 \text{ eV}$ .

Changes (but not the absolute value) in the Pt dispersion ( $D_{\text{Pt}}$ ) and cobalt dispersion ( $D_{\text{Co}}$ ) were estimated by the area ratios of the Pt 4d/Al 2s and Co 2p/Al 2s peaks, respectively, while the latter was referred to the bulk molar ratio of cobalt to aluminium ( $D_{\text{Co tot}}$  is calculated by  $\{\text{Co } 2p_{\text{tot}} / \text{Al } 2s\} / \{n_{\text{Co}} / n_{\text{Al}}\}_{\text{bulk}}$  where  $\text{Co } 2p_{\text{tot}}$  is the total Co 2p area). Based upon the limitation in the XPS data, the error in the dispersion measurement was  $\pm 0.07$ .

### 2.3. Catalytic measurements

0.5 g sample of the calcined powder catalyst was placed into a quartz reactor tube of about 1 cm inner diameter, ID. After in situ reduction the sample was cooled down to the reaction

temperature (523 K) in  $H_2$ , then the gas flow was switched for reactant mixture of  $H_2/CO$  (2:1) at 1 bar with a flow rate of  $30 \text{ cm}^3 \text{ min}^{-1}$ . After a given time elapsed, the effluent gas mixture was fed into a Girdel 300 gas chromatograph for analysis. The products were separated in a Hayesep R (2 m, 1/8" ID) column and analyzed by flame ionization detector, FID. In order to maintain the differential conditions the conversion was kept below 10%. The catalytic activity data were calculated on the basis of the CO converted into products. The selectivity of a given product displays its molar percentage in the product mixture. The olefin selectivity ( $S_{C=}$ ) data represent the molar percentage of unsaturated hydrocarbons in the  $C_2$ – $C_4$  products. The  $C_{2+}$  selectivity ( $S_{C_{2+}}$ ) expresses the molar percentage of  $C_2$ – $C_4$  hydrocarbons among all products.

### 3. Results and discussion

Changes in the chlorine content of the samples during preparation was also followed by XPS. The binding energy (BE) of the Cl  $2p_{3/2}$  transition was found to be at  $198.8 \pm 0.2 \text{ eV}$  in each case. This value is close to that obtained for chlorinated alumina surfaces [6]. After calcination the surface chlorine content remained practically unchanged, while after reduction it dropped to about one fourth of its initial value. The result proves that during impregnation the alumina surface is chlorinated. The surface chlorine content is significantly decreased by reduction, but some chlorine is still retained by the surface.

In the as prepared samples, the BE of the Pt  $4d_{5/2}$  transition was around 316.5 eV as shown in Fig. 1a. The value is well below that expected for the  $[\text{Pt(IV)Cl}_6]^{2-}$  complex, but practically the same as measured for  $[\text{Pt(II)Cl}_4]^{2-}$  [4]. On the other hand, under the same condition EXAFS, UV–VIS spectroscopy measurements indicated the presence of Pt(IV) chloro-complex on the surface [7]. The disagreement between

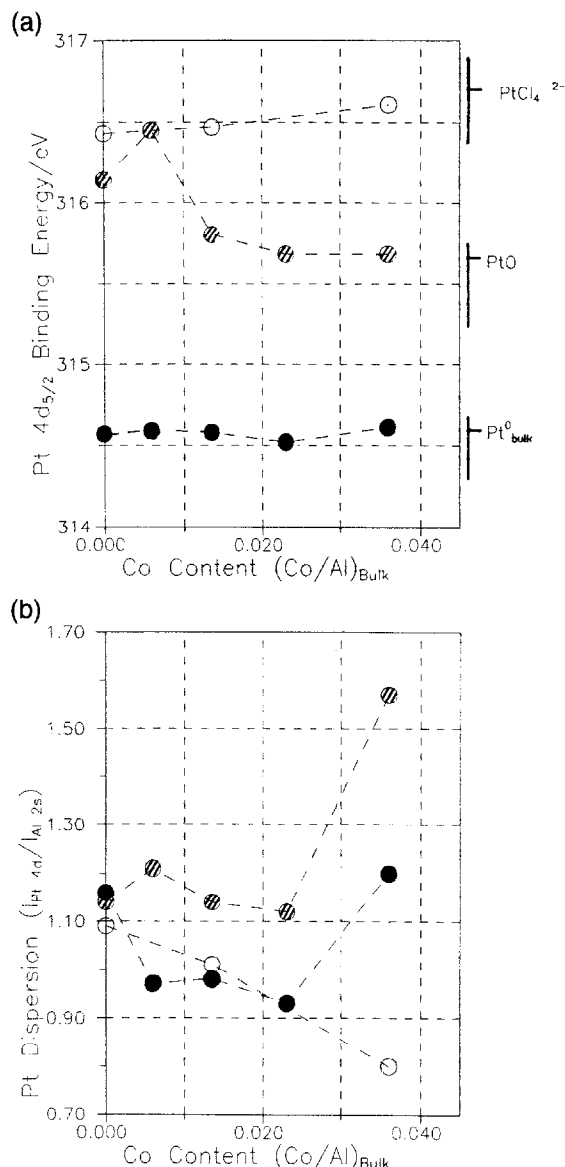


Fig. 1. (a) Binding energy of the Pt  $4d_{5/2}$  XPS transition vs. the sample cobalt content in the  $\text{PtCo}_x/\text{Al}_2\text{O}_3$  catalysts after different pretreatments (○: dried; shaded ○: calcined; ●: +reduced). (b) Dispersion of the platinum containing phase ( $D_{\text{Pt}}$ ) as determined by XPS vs. the sample cobalt content in the  $\text{PtCo}_x/\text{Al}_2\text{O}_3$  catalysts after different pretreatments (symbols as in Fig. 1a).

XPS and other methods is due to sensibility of the  $[\text{Pt(IV)Cl}_6]^{2-}$  complex to the X-ray radiation, since under the effect of X-ray source the complex is transformed into  $[\text{Pt(II)Cl}_4]^{2-}$  as was verified by our earlier experiments with

pure  $K_2[Pt(IV)Cl_6]$  and also by literature data [8]. Nevertheless, after drying the impregnated samples, platinum is present in a chloro-complex irrespective of the cobalt content, which indicates the lack of any chemical interaction between cobalt and platinum in the state of impregnation.

Before considering the changes in platinum dispersion ( $D_{Pt}$ ), the homogenous distribution of the components must be discussed. Here the term of Pt dispersion is not the same as used in chemisorption ( $D = Pt_{surf}/Pt_{tot}$ ), but proportional to that. Taking into account the specific surface area of the alumina support, the metal coverage is estimated to be lower than one monolayer even at the highest metal content. Here we refer to earlier works [4] where at similar sample compositions a value lower than the monolayer coverage was obtained calculated from the Kerkhof–Moulijn model.

The change in  $D_{Pt}$  in the as prepared state is, however, affected by the presence of cobalt. As shown in Fig. 1b,  $D_{Pt}$  decreases with increasing cobalt content. The decrease in the Pt 4d/Al 2s ratio in the as prepared state is an obvious proof against the peripheral deposition of Pt and Co ions on the support. This can be explained either by partial covering the platinum crystallites by the cobalt ions deposited at the same nucleation site on alumina, or by a competitive nucleation of the platinum and cobalt species. The latter process may not be effective because the solvated ions containing platinum and cobalt in the impregnating solution have opposite charge. Therefore, the decrease observed for both  $D_{Pt}$  and  $D_{Co}$  shown in Fig. 1b and Fig. 2b, respectively, is attributed to the deposition of cobalt within or over the platinum chloro-complex (co-deposition). This is a further proof for the random and uniform distribution of both components because the  $D_{Pt}/D_{Co}$  ratio being proportional to the XPS area ratios of Pt/Co, does not change with increasing Co content.

The high BE of Co  $2p_{3/2}$  transition shown in Fig. 2a and the presence of the N 1s peak at 406.1 eV B.E. in the X-ray photoelectron spec-

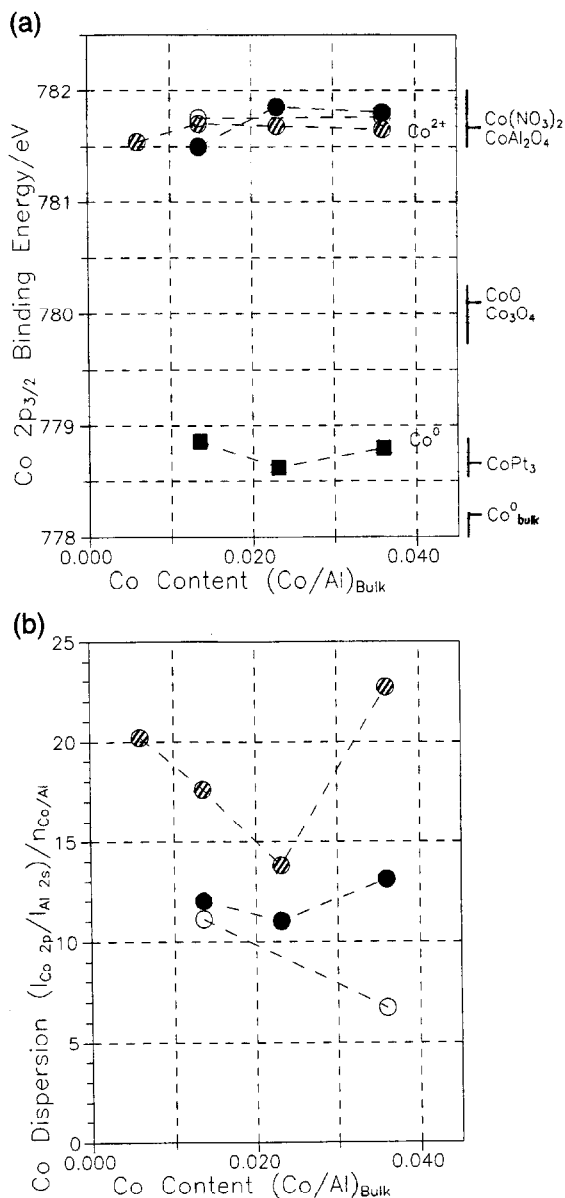


Fig. 2. (a) Binding energy of the Co  $2p_{3/2}$  XPS transition vs. the sample cobalt content in the  $PtCo_x/Al_2O_3$  catalysts after different pretreatments. Symbols: for  $Co^{2+}$ : ○: dried; shaded ○: calcined; ●: +reduced, for  $Co^0$ : ■. (b) Dispersion of the cobalt containing phase ( $D_{Co_m}$ ) as determined by XPS vs. the sample cobalt content in the  $PtCo_x/Al_2O_3$  catalysts after different pretreatments (symbols as in Fig. 1a).

tra indicates that after drying the sample in as prepared state contains cobalt nitrate [4].

After calcination in oxygen at 570 K the BE of the Pt  $4d_{5/2}$  transition does not change significantly in the samples containing no, or the

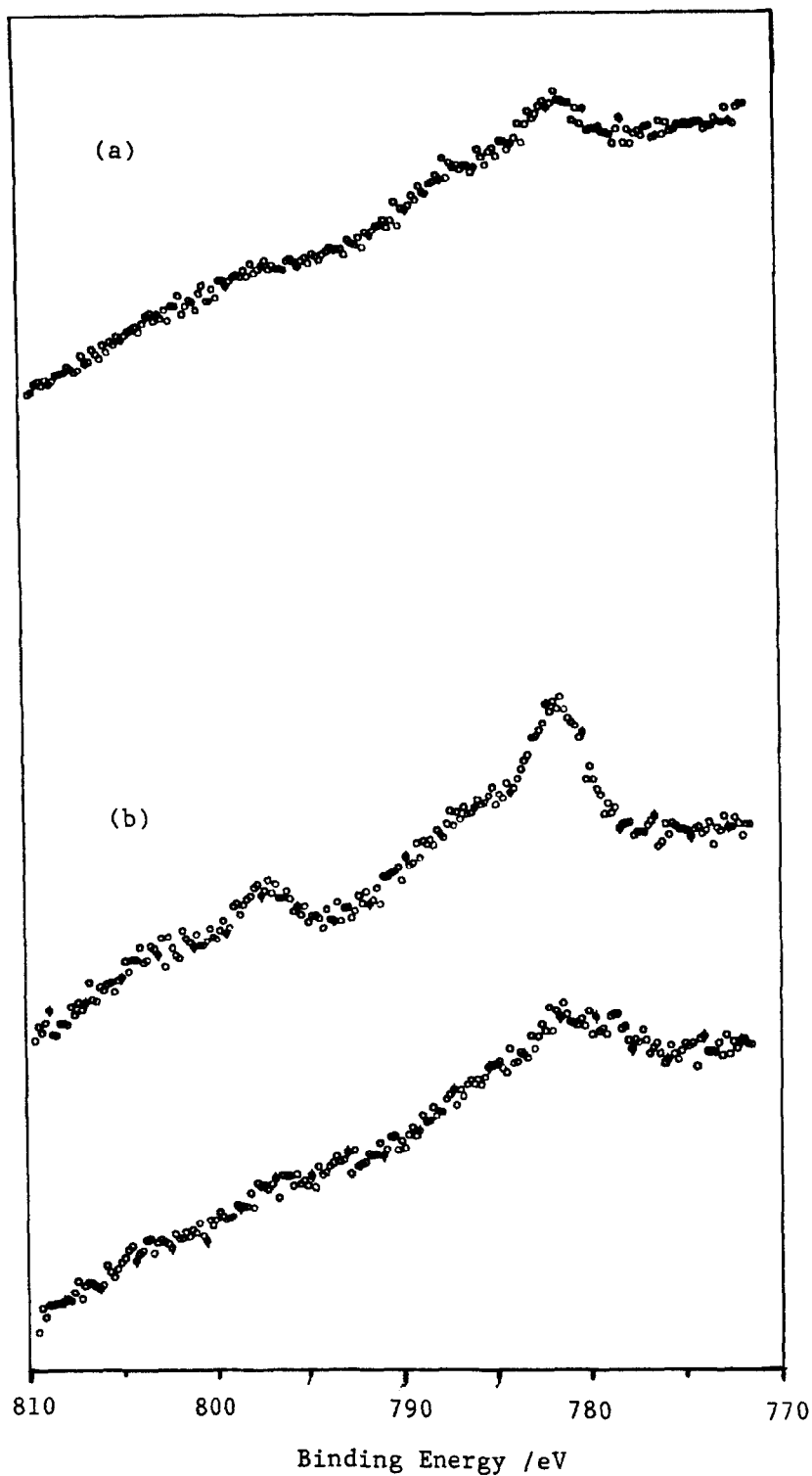


Fig. 3. Co 2p XPS regions recorded over calcined (upper) and reduced (bottom)  $\text{PtCo}_{1/9}/\text{Al}_2\text{O}_3$  (a),  $\text{PtCo}_{1/4}/\text{Al}_2\text{O}_3$  (b),  $\text{PtCo}_{3/7}/\text{Al}_2\text{O}_3$  (c) and  $\text{PtCo}_{2/3}/\text{Al}_2\text{O}_3$  (d) catalysts. Note: reduced spectrum in (a) is not available due to bad statistics.

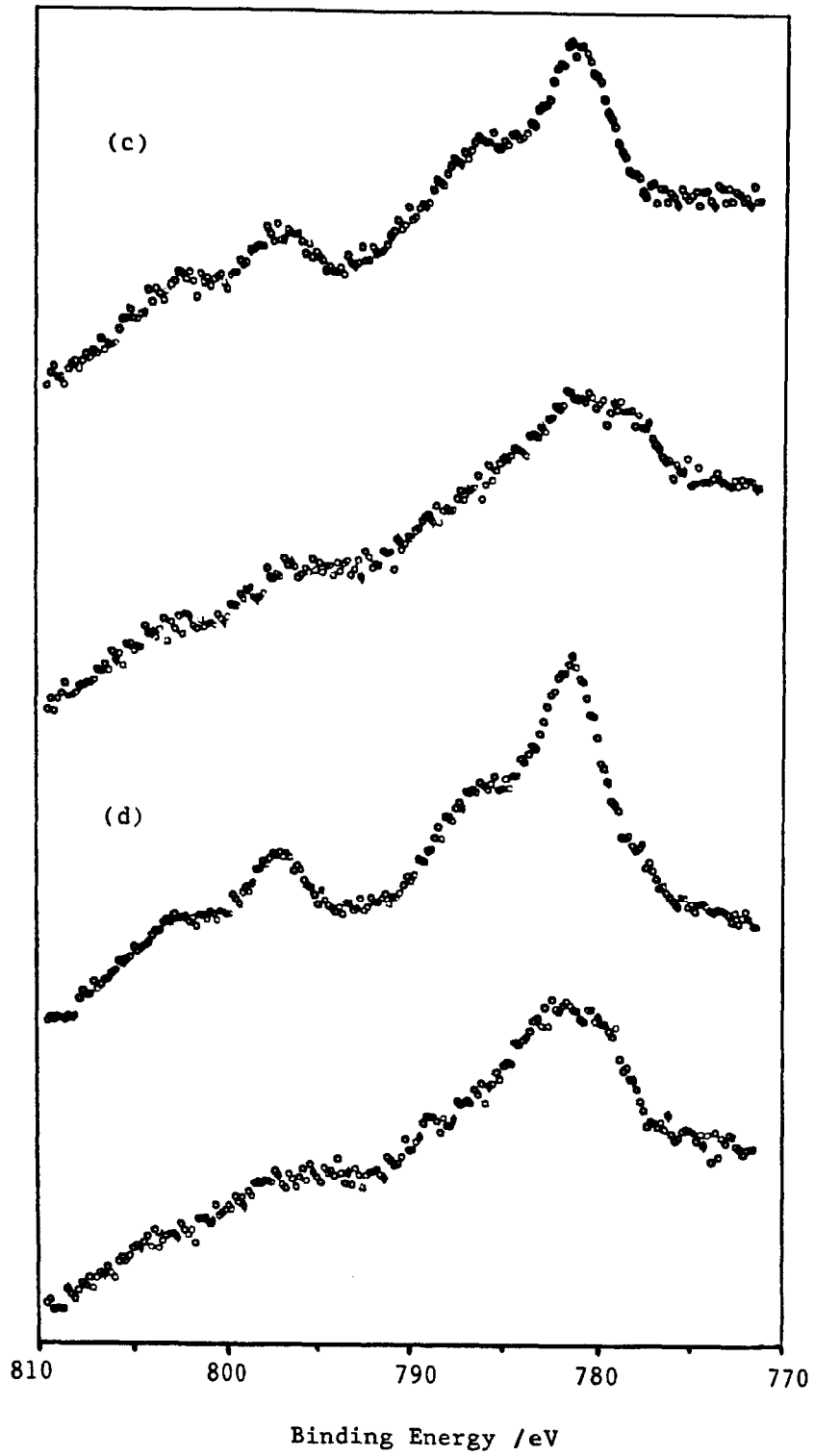
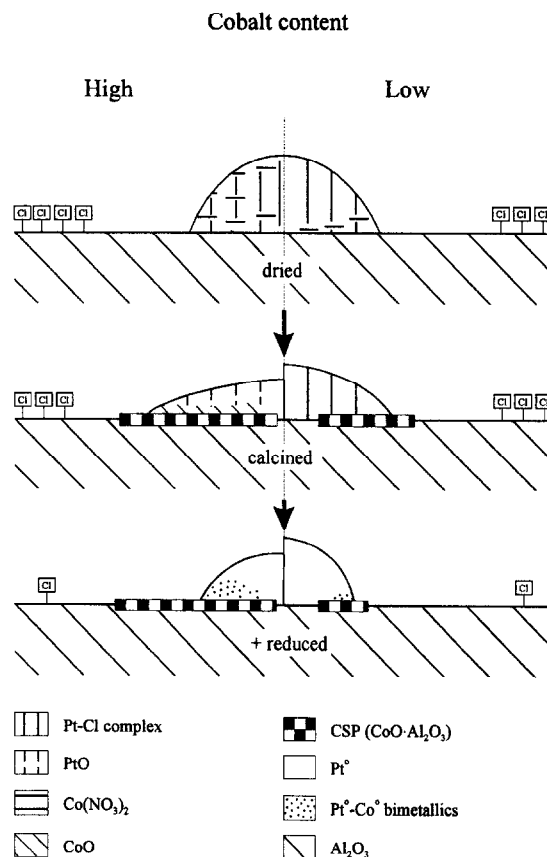


Fig. 3 (continued).

least amount of cobalt (Fig. 1a). In agreement with previous results obtained for platinum on alumina catalysts [9], most of the chloride ligands are retained after calcination. However, with increasing cobalt content a decrease in Pt  $4d_{5/2}$  BE indicates the exchange of chloride ligands for oxygen [4] with the simultaneous formation PtO. The exchange induced by cobalt, confirms that platinum and cobalt are co-deposited onto alumina support because the enhanced oxidation can likely be due to  $\text{NO}_2$  evolving during the decomposition of  $\text{Co}(\text{NO}_3)_2$  in the vicinity of the platinum complex. A similar phenomenon was observed during decomposition of  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  complex and  $\text{Fe}(\text{NO}_3)_3$  deposited on Cab-O-Sil surface when the large amount of  $\text{N}_2$  and  $\text{N}_2\text{O}$  evolved during decomposition, was the product of surface reaction between  $\text{NH}_3$  and  $\text{NO}_3$  [10].

The corresponding changes in  $D_{\text{Pt}}$  are shown in Fig. 1b. Here, in comparison with the as prepared state, platinum dispersion does not change for the monometallic sample. After cobalt addition the difference between  $D_{\text{Pt}}$  determined in the as prepared and calcined states increases with increasing cobalt content. Here  $D_{\text{Co}}$  is also higher than that in the as prepared state as shown in Fig. 2b. The BE of the Co  $2p_{3/2}$  transitions measured after calcination remains high as shown in Fig. 2a. As nitrogen could no longer be detected, the high BE value is attributed to the presence of cobalt surface phase (CSP) [4] containing  $\text{Co}^{2+}$  ions, whose typical shake-up satellite structure is shown in Fig. 3.

The suggested surface transformations caused by calcination are illustrated in Scheme 1. In the monometallic catalyst calcination has no significant effect on the surface structure involving Pt–O–Al bonds in a crystallite/support interface of  $\text{Pt}(\text{IV})\text{Cl}_4(\text{OAl})_2$  species [4], i.e. the chloro-platinum complex remains unchanged. In the cobalt containing samples,  $\text{Co}(\text{NO}_3)_2$  is decomposed into  $\text{NO}_2$  and  $\text{CoO}$ .  $\text{NO}_2$  assists the removal of chlorine in the  $\text{Cl}^- \rightarrow \text{O}^{2-}$  ligand exchange in the surrounding platinum



Scheme 1.

complex formed by co-deposition. Simultaneously,  $\text{CoO}$  is anchored by the alumina surface with formation of the CSP of high stability. With increasing amount of cobalt, CSP spreads along the alumina surface and forms interface between the platinum oxide and alumina. Thus, in bimetallic catalysts Pt–O–Al bonds are not formed and the  $\text{PtO}$  particles easily moves on top of the CSP layer as shown in Scheme 1. On the samples with higher cobalt content  $\text{CoO}$  is in excess in the  $\text{PtO}$  particles, hence the main result of calcination is the CSP formation as an interface between alumina and Pt–Co containing particles.

Subsequent reduction in a stream of hydrogen at 570 K results in diminished BE of the Pt  $4d_{5/2}$  peaks similar to that of bulk metal [4] (see Fig. 1a). However, this result cannot give information about the formation of Pt–Co inter-

metallic species since if platinum is the major component, no BE shift in its photoelectron peaks is observed in Pt–Co alloys [4,11,12].

In the Co 2p regions presented in Fig. 3 a new peak component appears at around 778.7 eV BE. In order to explain this BE position the following considerations must be taken into account. If no electrical (metallic) contact existed between the two metallic phases, i.e. separate  $\text{Co}^0$  and  $\text{Pt}^0$  particles were present on the surface after reduction, the measured BE would have shown a positive shift of nearly 1.0 eV referred to that of bulk cobalt metal [13] indicating presence of the cobalt particles in a highly dispersed phase (small particles). Consequently, increase in the cobalt concentration in the sample would have resulted in the formation of larger  $\text{Co}^0$  particles and in a gradual decrease in the value of Co 2p<sub>3/2</sub> BE, which cannot be observed in Fig. 2a. On the other hand, assuming that the metallic platinum and cobalt particles are in electrical contact, the BE measured for  $\text{Co}^0$  shows a +0.6 eV BE shift referred to bulk cobalt metal. Due to the presence of relatively large  $\text{Pt}^0$  particles, this shift cannot originate from the size effect (final state effect), it must be evaluated as a real chemical shift. The same BE shift was established for cobalt in  $\text{CoPt}_3$  [14]. Consequently, over the samples with higher cobalt content the formation of Pt–Co intermetallics is established.

In Fig. 1b changes in the  $D_{\text{Pt}}$  measured after reduction are also shown. Since over Pt/ $\text{Al}_2\text{O}_3$  sample no significant change in the  $D_{\text{Pt}}$  is measured after any stages (drying, calcination and reduction) of the sample preparation, the change in surface morphology is not associated with chemical transformation of platinum, i.e., the metal/support interface (Pt–O–Al) remains unchanged during the different pretreatments. However, adding cobalt to the system, a novel modified support (CSP) interface is formed after calcination. In  $D_{\text{Pt}}$  after calcination and reduction an overall increase and decrease, respectively, are detected as a result of the change between the respective species formed in calci-

nation and in reduction and the modified interface. Thus, in the calcined bimetallic samples the enhanced interaction (adhesion) between the interface (CSP) and the particulate metal oxide leads to the increase of  $D_{\text{Pt}}$ . Its decrease after  $\text{H}_2$  treatment is attributed to the diminished adhesion between CSP and the metallic particles, as compared to the monometallic catalyst in which the  $\text{Pt}^0$ –Pt–O–Al interaction is predominant. As a consequence of the effect of cobalt, reduction results in the appearance of a minimum in  $D_{\text{Pt}}$  as is shown in Fig. 1b. The location of minimum is uncertain due to the uncertainty in XPS measurements ( $\pm 0.07$ ).

As is shown in Fig. 2b reduction of the samples results also in the decrease in  $D_{\text{Co}_{\text{tot}}}$  with respect to those measured for the calcined samples. It may be attributed mainly to the zerovalent cobalt formed by reduction whose dispersion is lower than the phase containing cobalt ions after calcination (under reductive conditions platinum segregates to the surface in Pt–Co bimetallics [12]). This may also confirm formation of the Pt–Co intermetallic in relatively large particles. In the samples with the lowest cobalt content the decrease in  $D_{\text{Co}_{\text{tot}}}$  (to below the XPS detection limit of cobalt) can likely be due to similar surface transformations. In this case, however, zerovalent cobalt might be formed by the partial reduction of the stable CSP as illustrated in Scheme 1.

The  $\text{PtCo}_x/\text{Al}_2\text{O}_3$  samples were tested by CO hydrogenation at 523 K at 1 bar pressure. The reaction rates measured after 80 min on stream and plotted vs. cobalt content (Fig. 4), passes through a minimum curve just as was previously found by XPS for the platinum dispersion over the reduced samples. This trend is similar to that observed for the shallow minimum in Pt dispersion vs. Co content which turned out to be a function of the surface structure developed during the sequential pretreatment steps. Thereby, it can be established that the catalytic activity is mainly controlled by the surface platinum atoms in the bimetallic system.

In Table 1, the product selectivity support the



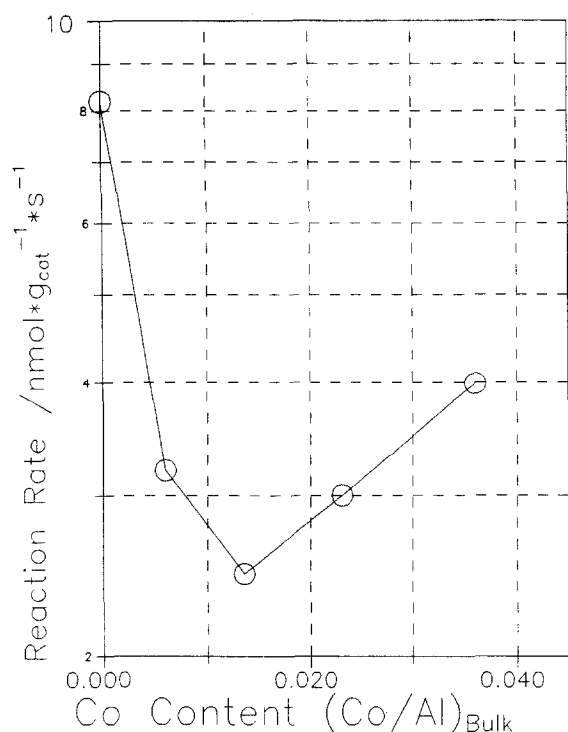


Fig. 4. Rate of CO + H<sub>2</sub> reaction (in  $\mu\text{mol g}^{-1} \text{s}^{-1}$ ) at 523 K and 1 bar pressure obtained after about 80 min on the stream over reduced PtCo<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts vs. the cobalt content.

previous statement since the corresponding values on cobalt are different [15]. The reaction products like CH<sub>3</sub>Cl, CH<sub>3</sub>OH requires the participation of support surface. The diminishing selectivity in CH<sub>3</sub>OH with increasing cobalt content clearly indicates that lesser number of

Lewis centres around the active Pt sites are available as a consequence of the predominance of CoO-modified surface [16]. CH<sub>3</sub>Cl selectivity also decreases with increasing cobalt content in the bimetallic samples. It is accompanied by a simultaneous increase in methane production which proves that the mechanism of CH<sub>3</sub>Cl formation involves the metal–support interface. The increasing extent of hindering this interfacial reaction route is obviously due to the expansion of Co-modified support surface (CSP) around the active metallic particles.

The slight change of the hydrocarbon selectivity with increasing cobalt content is ascribed to the catalytic effect of zerovalent cobalt incorporated into the Pt<sup>0</sup> particles.

#### 4. Conclusion

Evolution of the surface structure of PtCo<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> samples was determined step by step after different pretreatments around the active metallic particles by means of X-ray photoelectron spectroscopy. In order to follow the distinct changes occurring on adding cobalt, the platinum content of the samples was kept constant.

On the effect of cobalt, the following changes occur in Pt–Co/Al<sub>2</sub>O<sub>3</sub> samples:

- (i) With increasing Co content CoO forms

Table 1

Product selectivity (mol%) obtained in the CO + H<sub>2</sub> reaction over pretreated PtCo<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts

Sample	MeH	MeCl	MeOH <sup>a</sup>	C <sub>1</sub> <sup>b</sup>	C <sub>2</sub>	C=
Pt	65.9	24.8	6.3	97.0	3.0	19.5
PtCo <sub>1/9</sub>	63.4	33.8	–	97.2	2.8	34.0
PtCo <sub>1/4</sub>	83.5	12.9	–	96.4	3.6	27.4
PtCo <sub>3/7</sub>	86.0	9.8	–	95.8	4.2	21.7
PtCo <sub>2/3</sub>	88.3	4.1	–	92.4	7.6	23.3
Co <sub>S</sub> <sup>c</sup>	79.3	–	–	79.3	20.7	91.0
Co <sub>L</sub> <sup>c</sup>	87.5	–	–	87.5	12.5	60.0

<sup>a</sup> Including DME (0.3%).

<sup>b</sup> C<sub>1</sub> = MeH + MeCl + MeOH + DME.

<sup>c</sup> Measured over small (Co<sub>S</sub>) and large (Co<sub>L</sub>) Co<sup>0</sup> particles in 10% Co/Al<sub>2</sub>O<sub>3</sub> catalyst [15].

cobalt surface phase (CSP), which makes interface between PtO (Pt) and alumina below and around the metal containing particles.

(ii) Unlike monometallic platinum sample, in presence of cobalt the dispersion of the platinum phase varied during the pretreatments. After reduction the platinum dispersion first decreased then increased with increasing cobalt content. This shallow minimum in  $D_{\text{Pt}}$  is also indicative of the change in the surface structure induced by cobalt. The same trend obtained for the catalytic activity of the samples in the CO + H<sub>2</sub> reaction. The genesis of the surface structure, therefore, helps us to elucidate the correlation between reaction mechanism and surface structure.

### Acknowledgements

The work was carried out in the framework of the scientific exchange program between C.N.R.S. (France) and the Hungarian Academy of Sciences. The authors are greatly indebted to C.N.R.S. (France) and the French M.R.T. for providing financial support to the research.

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