

# Bimetallic catalysis: CO hydrogenation over palladium–cobalt catalysts prepared by sol/gel method

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## Abstract

Silica supported cobalt, palladium and cobalt–palladium bimetallic catalysts prepared by sol/gel technique and characterized by X-ray photoelectron spectroscopy, have been investigated in the CO hydrogenation reaction at 1 bar pressure in the temperature range between 200 and 300°C. It has been established that palladium facilitates reduction of cobalt which segregates to the catalyst surface to some extent. In the catalytic hydrogenation of CO over a catalyst with the ratio of Co/Pd = 2 a synergism is observed, while over cobalt and palladium catalysts alone much lower activities are measured. Over the pure cobalt sample which has a limited reducibility, only short chain hydrocarbons, mainly alkenes, are formed, whereas when palladium sites activating hydrogen, are introduced the amount of alkanes is enhanced and the chain length increases up to C<sub>8</sub>–C<sub>9</sub>. The limited reducibility of the cobalt is explained by the small particle size due to the preparation technique. Palladium acts in the bimetallic system not only as a component which helps cobalt reduction, but as sites activating hydrogen participating in the reaction and causes synergism. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Co–Pd bimetallic particles; Sol/gel method in sample preparation; Cooperative palladium; Cobalt sites

## 1. Introduction

Bimetallic catalysts have been the subject of numerous studies during the last three decades [1–5]. Particularly, it has been extremely interesting when the metal itself active in a catalytic reaction, was modified or promoted with a second metal which also had activity in the same reaction. One of the frequently used metals has been cobalt being an active component in the

CO hydrogenation to produce higher hydrocarbons [6]. On the other hand, palladium has also been found to be an active metal for the formation of oxygenated hydrocarbons [7–10]. Even to summarize the major relevant articles that have been published, several books would be needed to accommodate all information. Here, we, therefore, wish to quote only those papers which have dealt with the catalytic activity and selectivity of these two metal combinations [11–17] complemented by some other metals like platinum [18–24] and ruthenium [25–29].

Studies on the palladium–cobalt catalysts prepared on SiO<sub>2</sub> by incipient wetness method

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have normally showed an enrichment in palladium after reduction in a stream of hydrogen indicated by XPS [11–14]. Size of the particles was rather small (about 3–4 nm) and XRD showed also an alloy formation in agreement with TPR data. The change in the selectivity in various hydrocarbon reactions also indicated palladium enrichment on the surface. Selective hydrogenation of 1,3-butadiene, however, showed a somewhat different picture [15,16]. First, a surface enrichment was found in cobalt or in palladium depending on the surface treatment by oxygen or by hydrogen, respectively. Alloy particles were also observed by TPR measurements, however, the hydrogen adsorption was found to be activated in contrast to what Juszcik et al. observed [13,14]. Nevertheless, the authors agreed that cobalt could be reduced in the presence of palladium. In the selective hydrogenation a synergism was observed in the rate [15] and the selectivity in *trans/cis*-butene-2 ratio never reached the value characteristic of pure cobalt, even in the case of 0.1 wt.% Pd 5 wt.% Co composition [16].

Cobalt reduction was also measured in other bimetallic combinations regardless whether the samples were supported on inorganic support or inserted into NaY zeolite supercages [18–23]. Moreover, the cobalt was fully reduced in the presence of platinum when NaY zeolite was applied in place of alumina support [24]. Reduction and synergism were also observed in combination of cobalt with ruthenium deposited on NaY [25] and on other inorganic oxides like TiO<sub>2</sub> [26,27], respectively. Significant promoter effect has been observed also on alumina supported cobalt Fischer–Tropsch catalysts in the CO/H<sub>2</sub> reaction [28,29].

From these works it has appeared that, while facilitating the reduction of cobalt ions by palladium, platinum and ruthenium was a common feature for the cobalt based bimetallic catalysts, considerable disagreements still exist in the further effect of the second metal. In the present work, we are concerned with the effect of new preparation method using sol/gel technique in

which both the metal and support have small particle size and supposedly the small particles of metal and bimetallic system are stabilized. The samples are characterized by XPS technique and CO hydrogenation as test reaction are employed to investigate the properties of the bimetallic catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

The palladium and cobalt samples denoted as 1R to 5R contain only cobalt and only palladium (1R and 5R, respectively) and 2R to 4R cobalt and palladium in various atomic ratios (Pd/Co for 2R, 3R and 4R are 1:2, 1:1 and 2:1, respectively). The total metal loading is 5 wt.%. Sample 5R was prepared in the following way. Dinitro–diamminopalladium, Pd(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>, (0.002 mole) was dissolved in 22 g of ethyleneglycol containing acetylacetone, CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub> (0.016 mole), at 80°C. After stirring for 10 min, 14.8 g of tetraethylorthosilicate, Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, was added to the solution and mixed at 80°C for 2 h to give homogeneous reddish transparent solution. To the reddish transparent solution, 5.12 g of water was added and stirred at 80°C for 8 h to give transparent monolythic gel. The gel was dried at 80°C under reduced pressure, powdered and activated in a hydrogen stream of 6 l/h at 400°C for 4 h. For the preparation of the samples 4R to 2R, before the addition of Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, the ethanol solution of cobalt nitrate hexahydrate Co(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to the ethyleneglycol solution containing Pd(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> and CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>. The procedures after this were the same as described above. Sample 1R was prepared by adding first the ethanol solution of Co(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O to ethyleneglycol and mixing it with Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. The residual procedures were the same as in the case of 5R. Here, acetylacetone was not used because sample 1R did not contain Pd, that is, it was not necessary to stabilize Pd

complex in order to prevent the deposition of Pd black. Characterization of the samples was carried out by means of XRD. The particle size of Pd in 5 wt.% Pd/SiO<sub>2</sub> prepared was found to be 5 nm by TEM.

## 2.2. Sample characterizations

The samples were characterized by means of temperature programmed reduction (TPR) type SORBSTAR equipped with thermal conductivity detector (TCD) and quadrupole mass spectrometer, using 1 vol.% hydrogen/argon mixture with 20°C min<sup>-1</sup> ramp rate. As after preparation the samples were already reduced at 400°C for 4 h and passivated, the TPR experiments give information only about the composition of the outer skin of the catalyst grains.

XPS studies were performed on the reduced catalyst samples using an XSAM800 cpi photoelectron spectrometer manufactured by KRATOS. AlK<sub>α</sub> and MgK<sub>α</sub> characteristic X-ray lines with 80 eV pass energy were applied to measure the cobalt and palladium spectra, respectively. The use of two different sources was necessary because for cobalt the oxygen Auger peak is overlapping the Co 2p binding energy region when MgK<sub>α</sub> source is employed. On the other hand, when AlK<sub>α</sub> is applied to measure the palladium peak the cross talk originating from Si 2p is disturbing. In situ cell was used for the post-treatment of the catalyst samples [25]. Thus, it was possible to measure surface composition of palladium and cobalt as well as the valence state of the component in the samples in the as received state, after reduction at 400°C for 2 h, after oxidation at 300°C for 2 h and finally after second reduction at 400°C for 2 h. The Si 2p line at 103.3 eV binding energy was used as internal reference for the binding energy scale. The raw spectra presented are plotted after subtraction of the background spectra of the metal free support. In the original spectra the Co peak intensities were about 10<sup>4</sup> counts above 1.6 10<sup>5</sup> background counts. Peak position was determined by peak synthesis technique. For the Co

2p spin doublet range the separation was constrained.

## 2.3. Catalytic reaction

CO hydrogenation was measured in a plug flow reactor at 1 bar pressure and with a 2:1 mixture of H<sub>2</sub>/CO using a mass flow rate in the range between 5.1 and 15 cm<sup>3</sup> min<sup>-1</sup>. The catalysts were in situ reduced before the reaction for 2 h at 400°C, then cooled to the reaction temperature (around 250°C). After having reached the reaction temperature, the catalyst samples were treated in the reaction mixture overnight to stabilize the activity and then the catalyst performance was measured (product distribution, selectivity, activity and energy of activation). For product analysis a Packard 9000 type gas chromatograph was used equipped with a FID detector and a 50 m long 0.53 mm ID wide bore CP-Al<sub>2</sub>O<sub>3</sub>/KCl plot fused silica column (type 7518). Only the hydrocarbon products were measured and the rate as well as the conversion were calculated for these products.

## 3. Results and discussion

The catalysts prepared by sol/gel technique were always reduced before use (all samples were reduced in hydrogen at 400°C for 4 h after preparation and stored after passivation performed at room temperature by exposing the sample to air). Temperature programmed reduction was performed on all passivated samples and the results obtained for 1R, 2R, 3R 4R and 5R are presented in Fig. 1. Reduction of the pure cobalt and pure palladium samples (curves A and E, respectively) have TPR peaks at considerably different temperatures (450°C and 150°C, respectively) in the post-reduction procedure. The very wide peak in the case of the pure cobalt reduction is indicative of the presence of the highly dispersed particles containing cobalt. At the intermediate compositions various peak structures were monitored. With addition

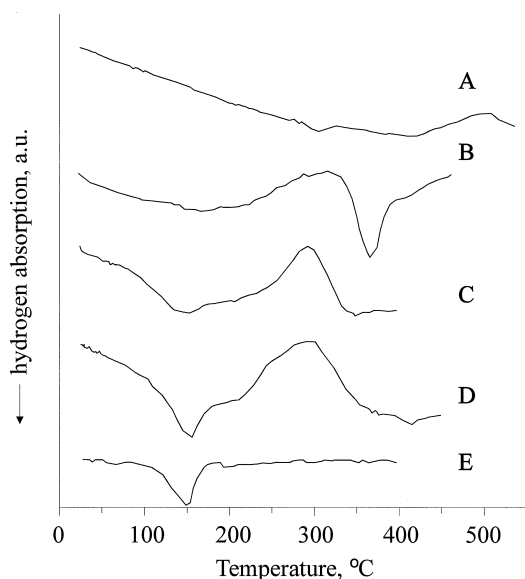


Fig. 1. Temperature programmed reduction of Pd–Co/SiO<sub>2</sub> samples. Curve (A): sample 1R; (B): sample 2R; (C): sample 3R; (D): sample 4R and (E): sample 5R. The hydrogen uptake is indicated by the trace moving downward. For notation see text.

of the small amount of palladium to cobalt (sample B, Co/Pd<sub>bulk</sub> = 2) the temperature of the cobalt reduction is shifted from 450°C to 375°C and a very wide peak appears at 150°C indicating that palladium is also dispersed in the presence of cobalt. Increasing the amount of palladium, the high temperature cobalt TPR peak shifts to 350°C and at 220°C a shoulder is

developed (see curves C and D in Fig. 1) which could be attributed to the presence of bimetallic particles. The peak at 375°C which corresponds to cobalt, is also shifted to lower temperature.

Further characterization was carried out by X-ray photoelectron spectroscopy. Cobalt alone (sample 1R), without palladium is not reducible as shown in Table 1 (rows 1 and 2), consequently, the surface of pure cobalt is oxidized in the ‘as received’ state and cannot be reduced into metallic cobalt after hydrogen treatment at 400°C for 2 h and its activity is likely developed during the reaction (see later). This is in contradiction with earlier results [13,14,16] indicating an entirely new structure of the present system prepared by sol/gel technique.

In Fig. 2 the XPS spectra of Co–Pd/SiO<sub>2</sub> sample (sample 2R) are presented (upper and lower sets of curves are for Co 2p and Pd 3d lines, respectively). The numbering of (1) to (4) means the ‘as received’ state (1) in which the sample is reduced and passivated, reduction in H<sub>2</sub> for 2h (2), oxidation in O<sub>2</sub> at 300°C for 2 h (3), and repeated reduction in H<sub>2</sub> at 400°C for 2 h (4). The presence of bimetallic particles suggested by the TPR results is supported by the reversible oxidation/reduction of cobalt. (see also Table 1 rows 3–6). This means that the bimetallic particles formed are not segregated under oxidative treatment and keep their inti-

Table 1  
XPS results measured on 1R to 5R samples at various treatments

Sample	Treatment	Composition	Co/Pd <sub>(bulk)</sub>	Co 2p, BE in eV ± 0.3	Pd 3d, BE in eV ± 0.3	Co/Si	Pd/Si	Co/Pd <sub>(surf)</sub>
1R	as received	Co100		781.3		0.042		
	H <sub>2</sub> /400°C			781.5		0.040		
2R	as received	Pd33Co67	2	781.0	336.5	0.017	0.009	1.9
	H <sub>2</sub> /400°C			778.1	334.2	0.041	0.018	2.3
	O <sub>2</sub> /300°C			780.0	336.3	0.037	0.011	3.4
	H <sub>2</sub> /400°C			777.4	334.2	0.037	0.014	2.6
3R	H <sub>2</sub> /400°C	Pd50Co50	1	778.4	334.8	0.041	0.015	2.7
4R	H <sub>2</sub> /400°C	Pd67Co33	0.5	778.4	334.8	0.037	0.018	2.0
5R	as received	Pd100			335.1		0.011	
	H <sub>2</sub> /400°C				333.2		0.011	
	O <sub>2</sub> /300°C				336.4		0.013	
	H <sub>2</sub> /400°C				334.4		0.012	

Note: reference is Si 2p: 103.3 eV B.E.; Pd and Co were measured using MgK<sub>α</sub> and AlK<sub>α</sub> excitation sources, respectively.

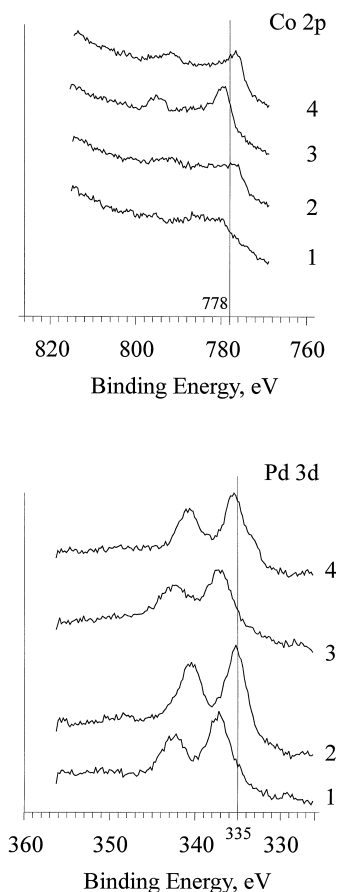


Fig. 2. Co 2p (upper curves) and Pd 3d (lower curves) XPS lines measured for sample 2R. Treatments: (1): as received; (2): reduction in  $H_2$  at  $400^\circ C$  for 2 h; (3): oxidation at  $300^\circ C$  for 2 h; (4): reduction in  $H_2$  at  $400^\circ C$  for 2 h.

mate contact in the cobalt–palladium catalysts (compare upper and lower sets of curves in Fig. 2 for cobalt 2p and palladium 3d core level lines, respectively). A slight enhancement can be observed in the  $(Co/Pd)_{surf.}$  ratio as the sample is oxidized, but palladium is repeatedly enriched at the surface after reduction in a stream of hydrogen.

All palladium containing cobalt samples can be reduced at  $400^\circ C$  as indicated in Fig. 3 (compare curves (a) for pure cobalt (1R) and (b) to (d) for samples 2R, 3R and 4R, respectively, and also rows 2, 4, 7 and 8, respectively, in Table 1). The surface cobalt/palladium ratio ( $(Co/Pd)_{surf.}$ ) is higher than that in the bulk for

both 3R and 4R samples (compare the corresponding values for samples 3R and 4R in column 7). It is, however, not fully understood why the surface cobalt to palladium ratio in the samples 3R and 4R shown in Table 1 (rows 7 and 8) considerably deviates from the bulk ratio (bulk cobalt/palladium ratio is 1 and 0.5, respectively). That is, while the bulk Co/Si ratio is significantly lower for sample 4R than that for sample 2R, the  $(Co/Pd)_{surf.}$  ratio (see column 9) measured by XPS is still high and  $(Co/Pd)_{surf.}$  ratio more or less the same for 2R to 4R samples.

The XPS results on sample 5R containing pure palladium is not surprising because the shift in the 3d binding energy follows the treatment: by oxidizing environment it is oxidized and then reduced under hydrogen treatment (see Fig. 4 and Table 2 rows 9–12).

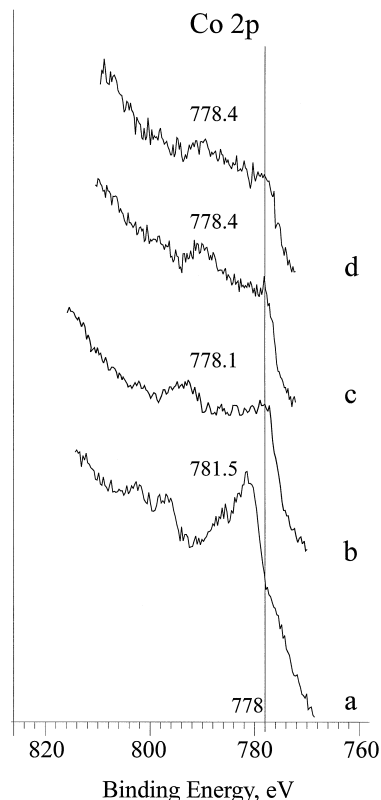


Fig. 3. Co 2p XPS spectra for the samples after reduction in  $H_2$  at  $400^\circ C$  for 2 h. (a): sample 1R; (b): sample 2R; (c): sample 3R; (d): sample 4R.



face of the bimetallic catalysts is enriched in cobalt regardless of the bulk composition. Although the Co2p/Si2p ratio on the surface can be considered more or less constant, palladium is also present. This is supported by the fact that, apart from 1R sample, the Pd–Co samples are reversibly oxidized/reduced as indicated by the binding energy of the Co2p line being 778 eV. Since the reducibility of the 1R sample (pure cobalt on silica) is questionable, at least after reduction at 400°C, the rate of CO hydrogenation under the same condition as used for

the palladium containing catalysts, has a lower value. The striking effect is the high selectivity in alkenes and the short chain hydrocarbons produced (after C<sub>4</sub> no higher molecular weight hydrocarbons are formed).

When palladium is added to cobalt, the amount of cobalt reduced and located at the surface is enhanced and the rate of the CO hydrogenation significantly increases. Here we have to note that our data cannot be referred to the number of surface atoms, because its determination is very uncertain. However, the total

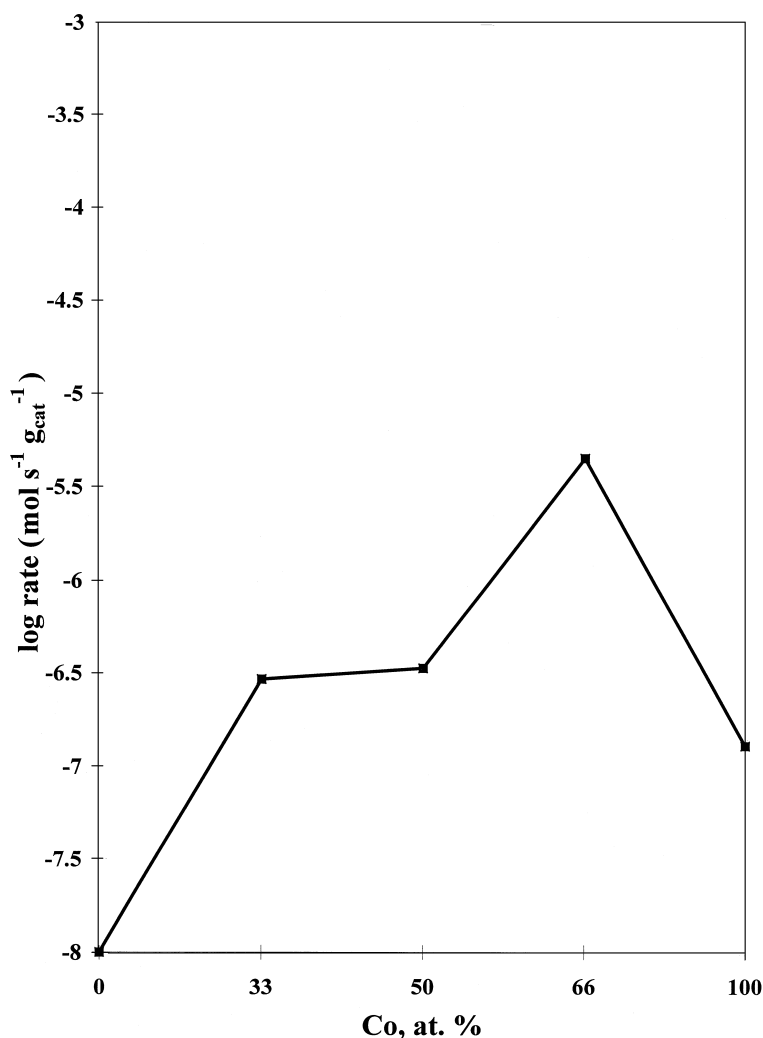


Fig. 6. Rates (in mole s<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>) vs. bulk composition of the bimetallic catalysts. H<sub>2</sub>/CO = 2, flow rate: 10.7 cm<sup>3</sup> min<sup>-1</sup>, temperature: 255°C.

amount of metal loading (weight percent) does not change, thus the activity is referred to the 1 g of catalyst. Simultaneously, the chain length increases and the amount of alkenes related to the alkanes decreases. Similar trend is valid for the other palladium containing catalysts, except pure palladium whose activity is negligible under similar conditions.

For explanation it is assumed that the working active site is related to the cobalt atoms exposed to the surface whose reduction is facilitated by palladium, but furthermore, its presence increases the hydrogenation activity of the number of active sites. This is supported by the increased amount of alkanes among the  $C_{2+}$  hydrocarbons and the increased chain length. On the other hand, for the pure cobalt catalyst—due to the sol/gel technique—on the small cobalt particles the hydrogen chemisorption is activated, i. e. the system is working under hydrogen deficient condition, thus, the alkenes are not easily hydrogenated which causes an accelerated deactivation which stops chain growing.

The rate passes through a maximum as the nominal bulk Co/Pd ratio decreases as shown in Fig. 6. The synergism, as was also demonstrated in the selective hydrogenation [16], is similar to those that was also observed in Co–Ru system [26–29]. However, it is not fully understood why the catalyst with similar surface Co/Pd ratio has much lower activity (compare e. g. 2R and 3R). We may speculate that, although the cobalt ions are mostly reduced, the cobalt particles are embedded into palladium matrix in the case of 3R and 4R and ionic interaction between palladium and cobalt is operative as indicated by the binding energy changes both for Co 2p and Pd 3d lines shown in Table 1 (compare columns 5 and 6. for Co 2p and Pd 3d, respectively). This is supported by the binding energy shifts for palladium and for cobalt being from 333.2 to 334.8 eV and from 778.1 to 778.4 eV, respectively.

The working site is suggested to be the surface cobalt atoms modified by the palladium,

whereas the palladium itself is not an active catalyst for the CO hydrogenation under the present condition. This statement is supported by the Anderson–Schulz–Flory distribution which is presented in Fig. 7 for 1R to 4R catalysts. The  $\alpha$ -values are similar and vary in the range between 0.65 and 0.78 for the samples 2R to 4R (see column 8 in Table 2) and only slightly change with temperature. On pure cobalt catalyst sample  $\alpha$ -value is significantly lower than that measured on the Pd–Co samples. This is in contrast to what have been reported [6,30,31]. We assume that the nano-scale cobalt particles present as a result of the sol/gel technique can be deactivated by carbonaceous deposits much faster than on Co–Pd catalysts prepared by conventional incipient wetness method and thus chain propagation on the surface is terminated at much shorter chains.

The anomalous behavior in the Anderson–Schulz–Flory distribution observed earlier for Ru/SiO<sub>2</sub> catalysts prepared by sol/gel technique [32], is not operative in the present system. This can probably be ascribed to the apriori properties of the metal itself and not to the preparation method.

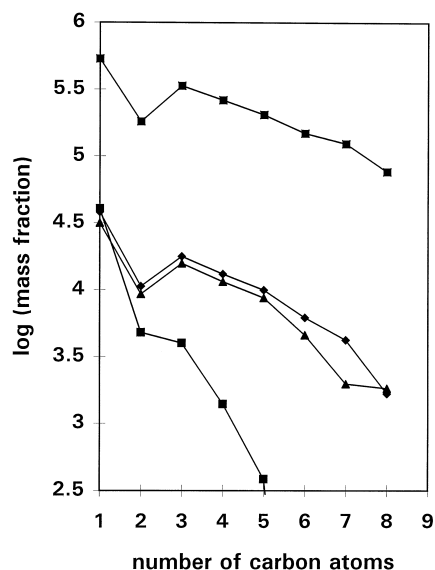


Fig. 7. Anderson–Schulz–Flory plot for various catalysts from 1R to 4R. Symbols and conditions: see Fig. 5.



In summary, the Co–Pd samples are fully reducible and form bimetallic particles which can be reversibly oxidized/reduced. CO hydrogenation takes place in the range of 200–300°C producing mainly alkenes on pure cobalt catalyst with short chains, while on the Pd–Co samples the chain length increases and  $\alpha$ -values increase and the amount alkane formation is considerably enhanced. Synergism on the addition of small amount of palladium to cobalt is observed and the rate of the CO hydrogenation significantly increases.

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