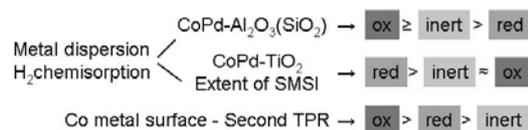# DETERMINATION OF METAL DISPERSION IN COBALT-PALLADIUM CATALYSTS

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Hydrogen chemisorption (HC) is used as a method for metal specific surface area determination in multi-component systems. HC is insufficient to distinguish the components when a catalyst contains several metallic ingredients. Application of this method to Co-Pd catalysts gives data about the particles size but suffers some ambiguity because the surface area of any metal is indistinguishable. Present work is an attempt to obtain comparative assessment about the relative part of the metals on the surface in supported $Co(Pd)/Al_2O_3$ (SiO_2, TiO_2) catalysts pretreated in various atmospheres. HC, TPR, XPS and IRS experiments performed with Al_2O_3 and SiO_2 supported samples showed that the relative part of metal exposed on the surface was affected by the type of applied pretreatment. The SMSI effect that was registered in the system $10\%Co+0.5\%Pd/TiO_2$ is influenced by the pretreatment following an order of magnitude (red)>(inert)≈(ox).

Metal dispersion / H_2 chemisorption

CoPd-Al₂O₃(SiO₂) → ox ≥ inert > red

CoPd-TiO₂ Extent of SMSI → red > inert ≈ ox

Co metal surface - Second TPR → ox > red > inert

INTRODUCTION

Hydrogen adsorption measured on supported monometallic catalysts is widely used for determination of metal specific surface area, metal dispersion, respectively, and metal particle size calculation as well. Hydrogen chemisorption as a selective method for metal specific surface area determination is applied also in case of multi-component systems such as supported metal catalysts since hydrogen is adsorbed mainly on the surface of the metal and the adsorption on the surface of the non-metallic component is relatively low.[1] However, hydrogen chemisorption is insufficient to distinguish the components when the studied catalyst contains several metallic ingredients. Such is the case of supported bimetallic cobalt-palladium catalysts. Application of hydrogen adsorption method with cobalt-palladium catalysts gives data about the amount of metal atoms exposed on the sample surface. Particle size calculation is speculative because in this case the surface area of both metals is indistinguishable, since hydrogen chemisorption is not selective for bimetallic cobalt-palladium catalysts. Attempts about evaluation of Co dispersion in bimetallic catalysts are done besides research the impact of the promoter on the rate and extent of cobalt oxides reduction and the state and local environment of the promoter itself using combination of methods as H_2 chemisorption, TPR, EXAFS, XANES, Scanning transmission X-ray spectroscopy.[2] Present work is an attempt to obtain comparative assessment about the relative metal particles size in supported cobalt-palladium catalysts using hydrogen chemisorption, TPR and XPS.

EXPERIMENTAL

The studied catalysts were obtained from precursors prepared using nonporous supports – SiO_2 (Cabosil M-5, $S_{BET} \approx 200$ m²/g), Al_2O_3 (Degussa-P 110 C1, $S_{BET} \approx 90$ m²/g, mixture of γ and δ modifications) and TiO_2 (Degussa-P 25 ca. 80% anatase and 20% rutile, $S_{BET} \approx 50$ m²/g,). The deposition of the metal salts was carried out by immersion of the support

into aqueous solutions of $Co(NO_3)_2.6H_2O$ and $Pd(NO_3)_2.2H_2O$. Systems were dried in rotary desiccator 24 h in vacuum at 60°C. The preparation aimed cobalt loading $\approx$ 10% and Pd $\approx$ 0.5%.

The precursors were preliminary thermally decomposed. The applied pretreatment procedure comprised heating in a gas flow consecutively at 100, 200 and 300°C, 1 h at each level. The temperature was raised by 100°C·h^{-1} between the levels. This pretreatment procedure allows smoother evaporation of water and destruction of the supported nitrates.[3] Hindrance of Co_2SiO_4 [4] and $CoAl_2O_4$ [5] formation is supposed at the used circumstances. During pretreatment three different types of media were used – air, hydrogen and argon. Thus prepared samples were noted as (ox), (red) and (inert), respectively, following the character of the used atmosphere. Described pretreatment procedure was realized in the measuring cells of the respective apparatuses directly before the very chemisorption and reduction (TPR) experiments.

The chemisorption of hydrogen was measured by the volumetric method in an all-glass device described in Ref. 6.[6] The chemisorption experiments were carried out on the samples after their reduction in hydrogen flow successively 1 h at 300°C, 1 h at 400°C and 2 h at 450°C. After reduction or hydrogen adsorption measurement, the samples were evacuated to $P < 1.10^{-5}$ Torr (1 Torr = 133.3 Pa) at the respective reduction temperature. Adsorption isotherms of H_2 were obtained in the pressures region 0–100 Torr at temperature $\approx$100°C because of the activated adsorption of hydrogen on cobalt [5,7] and to avoid significant absorption in the bulk of Pd.[8] We consider these conditions as more reliable for comparing the chemisorption properties of the mono- and bimetallic catalysts. The monolayer coverage was determined by extrapolation of the linear part of the isotherm to zero pressure and was used to calculate metal dispersion D_H (D_H = number of metal atoms on the surface of sample/total number of metal atoms in the sample).[1]

Temperature-programmed reduction (TPR) was carried out in a quartz reactor with 150 mg of each sample by a mixture 10% H_2 in Ar, flow rate 25 ml/min, heating up to 900°C by 10 deg/min. After cooling in Ar the reduced samples were oxidized in the same measuring cell with flowing air at room temperature. Second TPR was carried out at the described above conditions.

X-ray photoelectron spectroscopy (XPS) analyses were performed in the UHV chamber of an electron spectrometer ESCALAB-MkII (VG Scientific). The spectra were excited by unmonochromatized MgKα radiation (hv = 1253.6 eV). Total instrumental resolution was 1.5 eV (measured from the Ag5d$_{5/2}$ line width). Energy scale was calibrated by the C1s line (285 eV). XPS experiments were carried out with chosen samples *ex-situ* – registration of the spectra after exposing to air of the pretreated samples.

Diffuse-reflectance infrared spectra were recorded *in situ* by a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) using Collector II DRIFT accessory (Thermo Spectra-Tech, USA). High Temperature/Vacuum Chamber (Thermo Spectra-Tech, USA) with CaF$_2$ windows was installed into the used smart accessory in order to study samples in non-ambient gaseous environments. The spectra were collected in 1111–4000 cm^{-1} range.

RESULTS AND DISCUSSION

Metal dispersion calculated after measuring hydrogen chemisorption on mono- and bimetallic samples with various carriers obtained by preliminary treatment in different media is represented on Table 1.

Co dispersion in all alumina supported monometallic samples, irrespectively of the applied pretreatment, was very low after reduction at 300°C and increased with the reduction temperature. These properties could be due to formation of large particles of cobalt nitrate stabilized on the alumina surface giving rise to a low extent of cobalt reduction. As a whole, pretreatment in reductive atmosphere results in lowest values of metal dispersion. The presence of palladium in the catalyst resulted in an order of magnitude higher H_2 adsorption on all samples reduced at 300°C. However, metal dispersion in the bimetallic samples pretreated in oxidizing or inert conditions decreased with the increase of reduction temperature contrary to the behavior of prereduced Co-Pd/Al$_2$O$_3$ that demonstrated slight increase but dispersion remained the lowest one.

Table 1

Results from hydrogen chemisorption, second TPR and XPS measurements

Sample	D_H, %			Second TPR	XPS, SAR, 2h/450°C
	300°C	400°C	450°C	peak area	Co/Al,Si,Ti
10%Co/Al$_2$O$_3$ (inert)	0.5	1.7	3.2	1530	
10%Co+0.5%Pd/Al$_2$O$_3$ (inert)	3.3	2.8	2.5	1950	
10%Co/Al$_2$O$_3$ (ox)	0.3	1.6	2.5	1400	
10%Co+0.5%Pd/Al$_2$O$_3$ (ox)	3.4	3	2	3380	
10%Co/Al$_2$O$_3$ (red)	0.02	0.6	1	1180	
10%Co+0.5%Pd/Al$_2$O$_3$ (red)	0.6	1	0.8	2300	0.118
10%Co/SiO$_2$ (inert)	3.2	3.5	3	-	
10%Co+0.5%Pd/SiO$_2$ (inert)	4.5	3.4	2.6	-	
10%Co/SiO$_2$ (ox)	3.4	3.8	3.4	1090	
10%Co+0.5%Pd/SiO$_2$ (ox)	6	4.2	3.3	3300	
10%Co/SiO$_2$ (red)	2.5	3.4	3.5	870	
10%Co+0.5%Pd/SiO$_2$ (red)	2.2	2.4	3	3100	0.151
10%Co+0.5%Pd/TiO$_2$ (inert)	2.8	1	0.8	1530	
10%Co+0.5%Pd/TiO$_2$ (ox)	3.7	1.4	1.2	720	
10%Co+0.5%Pd/TiO$_2$ (red)	3.6	1.1	0.8	-	0.390

In the case of Co/SiO$_2$ samples metal dispersion is higher than that in Co/Al$_2$O$_3$ and relatively stable during reduction temperature increase. The most remarkable difference is observed with reductively pretreated samples. Obviously supported particles of nitrate on silica are of lower size and their reduction proceeds to a higher extent giving rise to, respectively, higher metal dispersion. As in the case of bimetallic alumina supported systems highest metal dispersion was observed with those on silica support after oxidative or inert pretreatment and reduction at 300ºC. Increase in the reduction temperature of these samples resulted in decrease of dispersion. 10%Co+0.5%Pd/SiO$_2$ (red) demonstrated higher dispersion than the respective sample on alumina and constant increase with the temperature of reduction.

Strong influence of reduction temperature on the adsorbed hydrogen amounts were registered with the bimetallic systems supported on TiO$_2$ independently on the type of the used pretreatment. Sharp decrease in hydrogen adsorption was registered after reduction at 400 and 450ºC. This samples behavior is due to the presence of well-pronounced effect of interaction between the support and deposited metal (SMSI) that appears about and above $T_{red} = 400$ºC.[9]

The results on metal dispersion presented on Table 1 allow us to claim that pretreatment of the bimetallic system 10%Co+0.5%Pd in an oxidative atmosphere leads to catalysts of higher metal dispersion. SiO$_2$ supported samples have as a whole higher average dispersion. Special attention should be paid to the results with prereduced samples because the low dispersion could not be explained only with a low extent of reduction of supported cobalt at 300ºC.[10] It is well known that presence of a precious metal like Pt or Pd results in higher extent of reduction of cobalt in the supported bimetallic catalysts.[11-22] This tendency is confirmed with our results with the samples pretreated in oxidizing and inert atmosphere. The temperature of 300ºC is sufficient to obtain almost complete reduction of deposited metals in thus pretreated samples. Treating the samples at higher temperatures resulted in decrease of metal dispersion. Obviously, the mechanism of metal particles formation in the bimetallic samples has some peculiarities in case of reductive pretreatment. Despite the low rate of temperature increase and the stepwise process, the reduction of palladium at applied conditions proceeds to a high extent on the surface of large particles of nitrates

deposited on the support. The almost pure palladium particles play the role of nuclei and supplier of hydrogen for further reduction of both palladium and cobalt (nitrate and/or oxide). Induced and facilitated cobalt reduction by hydrogen transfer from palladium results, however, in formation of bimetallic particles with surface enriched in cobalt. The surface of such particles is less effective in supplying active hydrogen and the process of cobalt oxide phase reduction is decelerated.[18,23,24] That is why slight increase in dispersion was registered after reduction of the bimetallic samples at 400ºC followed by decrease at 450ºC. At the latter conditions metal particles agglomeration determines the properties accompanied by continuous formation of bimetallic particles with enrichment of the surface in cobalt. When palladium particles have already been formed (during oxidative or inert pretreatment at temperatures up to 300ºC) acceleration to complete cobalt reduction is possible at 300ºC. The discussed mechanism of metal phase formation in bimetallic Co-Pd catalysts is additionally complicated by the effect of SMSI in case of titania used as support. Based on data from Table 1 we can state that SMSI has stronger influence on the loss of palladium atoms on the surface of metal particles than the process of enrichment in cobalt.

XPS spectra and data presented on Table 1 support the discussed mechanism. XPS study was performed with samples prepared by pretreatment in reductive medium and after measuring hydrogen adsorption following consecutive reduction at 300, 400 and 450ºC. Characteristic bands for the presence of Co^{2+} were registered in the spectra of samples (Fig. 1).[25,26] XPS spectra in the region Pd3d showed presence of palladium on the surface of 10%Co+ +0.5%Pd/TiO$_2$ (red) only (Fig. 1). Obviously, the surface of metal particles in silica and alumina supported samples is determined by formation of bimetallic phase with enrichment in cobalt [11,13,14,27] to high extent, whereas in the sample with TiO$_2$ support part of the metal surface is covered by reduced titania. Exposure to air of the reduced catalysts ("ex situ" experiment) results in formation of presumably thin CoO layer with low or no Pd presence on the surface of metal particles in silica and alumina supported samples but restores in part and oxidizes palladium atoms exposed on the surface in 10%Co+0.5%Pd/TiO$_2$ (red) registered as Pd^{2+} in the spectrum (Fig. 1).[28]
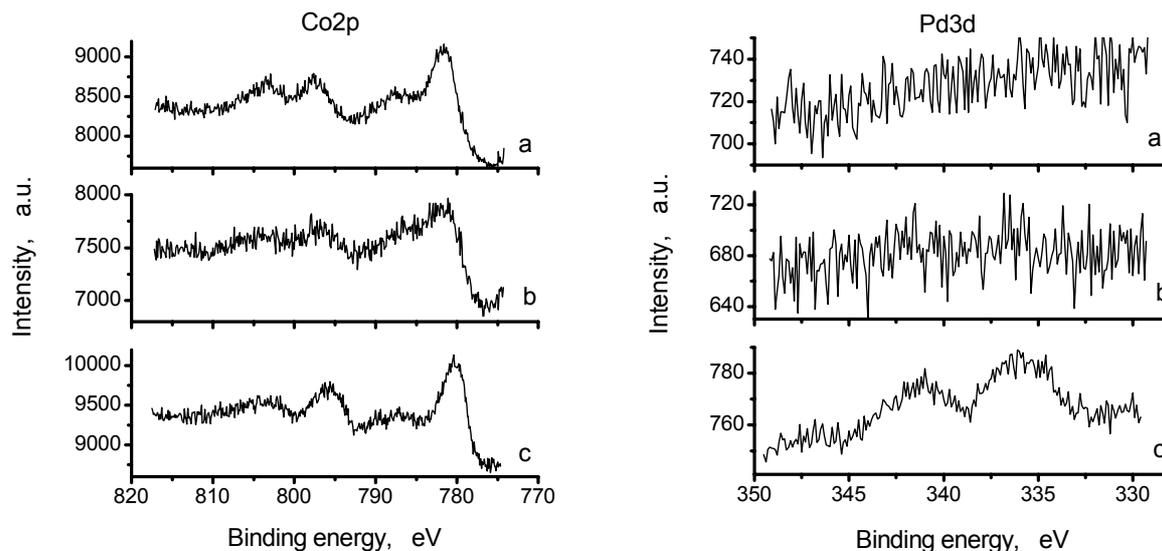
Fig. 1 – Detailed XPS spectra in Co2p and Pd3d regions:
a – 10%Co+0.5%Pd/Al$_2$O$_3$ (red),
b – 10%Co+0.5%Pd/SiO$_2$ (red),
c – 10%Co+0.5%Pd/TiO$_2$ (red).

Aiming to obtain additional information about the processes of metal phase formation in bimetallic catalysts other type of experiments was carried out. It allows certain evaluation of the surface properties of metal particles. The examination was conducted with samples after their reduction by TPR that were subjected to subsequent treatment in air at room temperature. Oxidation of the surface of cobalt or bimetallic particles is supposed in the course of this process. Second TPR was carried out after this procedure. One peak was registered for all samples at 210 < Tmax < 250ºC. The temperatures were lower with 100 deg or more than those registered during the first TPR. Fig. 2 gives illustration of the results. The profiles are consistent with a mechanism of oxygen interaction with the surface of metal particles without penetration deeper into the bulk and without formation of separate phase of Co$_3$O$_4$ or CoO.[29,30] If palladium atoms are exposed on the surface oxygen adsorbed on them is easily removed at room temperature in the first moments after switching from air to Ar+H$_2$ mixture for taking the second TPR. The peak area from the second TPR profiles represents the amount of hydrogen necessary to remove oxygen adsorbed on the surface cobalt atoms and could be used as a measure of the surface cobalt in the metal particles. These areas were calculated using an OriginPro program (ver. 8.6.0Sr3, OriginLab Corporation, Northampton, USA) and represented on Table 1.
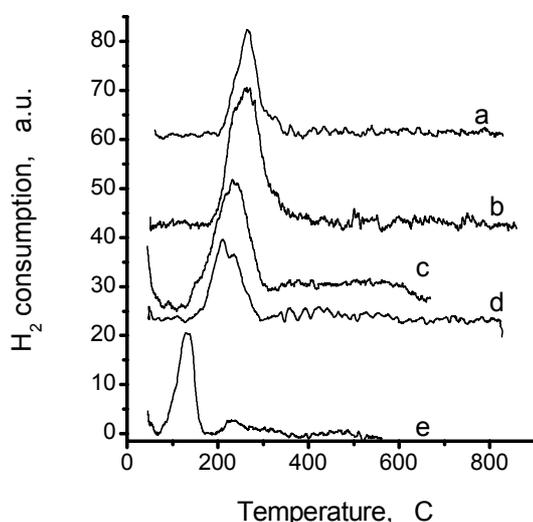

Fig. 2 – Second TPR spectra:
a – 10%Co/Al$_2$O$_3$ (red),
b – 10%Co+0.5%Pd/Al$_2$O$_3$ (red),
c – 10%Co+0.5%Pd/SiO$_2$ (ox),
d – 10%Co+0.5%Pd/TiO$_2$ (inert),
e – 10%Co/SiO$_2$ (ox).

The results from used method of second TPR are consistent with the conclusions already presented on the basis of chemisorption experiments for lower dispersion of cobalt in Al_2O_3 and SiO_2 supported monometallic samples than in the bimetallic ones. Comparison of hydrogen consumption from bimetallic samples applying the method of second TPR confirms that samples pretreated in oxidative medium are characterized by higher dispersion. Despite some coherence between the results obtained by hydrogen chemisorption and the method of second TPR related to metal dispersion it is worth to note a discrepancy. Second TPR data revealed better dispersion of cobalt supported on alumina than that on silica irrespectively of the pretreatment procedure. We could explain this difference with influence of the type of the support. Essential parameter in TPR experiments is the final level during the temperature rise. It was 900°C in our experiments. Taking into account that the interaction between the support and metal particles is negligible on SiO_2 [1,31] compared to Al_2O_3 the process of agglomeration of formed during TPR particles proceeds to a lower extent and determines better dispersion in Co/Al_2O_3 catalysts. Bimetallic systems of (ox)-type do not show differences in hydrogen consumption and, respectively, the metal in these samples is characterized with comparable particle size. Additional details in the mechanism concerning the interaction between cobalt oxide(s) phase(s) and the support during TPR should be verified for explanation of the better dispersion of metal in prereduced SiO_2 supported bimetallic sample.

Hydrogen consumption calculated from the second TPR experiment for TiO_2 supported samples showed less cobalt exposed on the surface of metal particles after the (ox) pretreatment in comparison with the size of metal surface formed in (inert) one (Table 1). Higher metal dispersion of (ox)-type sample that is determined by hydrogen adsorption is not in contradiction with the found by second TPR experiment. Adsorption measurements were carried out after reduction at Tred ≤ 450ºC. SMSI arises at about 400-450ºC and it is still not completely realized in this range. TPR was carried out up to 900ºC and the SMSI effect can become fully operating increasing Tred because it is temperature dependent. Thus, once again, the results obtained by the method of second TPR show the role of SMSI effect in characterizing the surface properties of bimetallic samples.

In situ DRIFT study was performed to obtain additional information about the metal particles surface composition of the sample 10%Co+ +0.5%Pd/TiO_2 (red). IR study was carried out after measuring its catalytic activity in the reaction of CO

hydrogenation. In the spectrum of the used catalyst bands at 1345, 1430, 1530 cm^{-1} were registered assigned to the presence of carbonates and hydrocarbonates at the surface.[32] Bands of physically adsorbed water and hydroxyl groups bound by H-bond were seen too, at ~1640 cm^{-1} and ~3400 cm^{-1}, respectively.[33] The sample surface was cleaned by consecutive flows of Ar and Ar+H_2 mixture at 200°C before CO adsorption.

Fig. 3a shows the spectra after CO adsorption at room temperature from a mixture (H_2+Ar +CO) at low CO partial pressure. The characteristic bands of gaseous CO in the cell are visible in the region 2050-2200 cm^{-1}.[33] The doublet at 2014 and 2032 cm^{-1} is assigned to linear adsorption of CO on the surface Co atoms.[34] These bands are characteristics for the presence of Co atoms in different coordination on the surface. The very week band at 1936 cm^{-1} is assigned to bridge form of CO adsorption on surface Pd atoms.[32]

Intensity of the bands characteristic for gas phase CO was decreased after keeping the cell isolated and full with the mixture at room temperature but that of carbonates, hydrocarbonates and adsorbed water increased (Fig. 3-b). The doublet for CO adsorbed on Co atoms disappeared but the band of CO on Pd is shifted to lower wavenumbers. The spectrum is clear proof that CO hydrogenation proceeds on the surface of 10%Co+0.5%Pd/TiO_2 (red) even at room temperature and the surface Co atoms are no more occupied by CO. The week band at 1936 cm^{-1} was shifted to 1908 cm^{-1} in conformity with a decreased CO coverage of Pd. Blowing the cell with Ar flow (Fig. 3-c) resulted in disappearance of the band of adsorbed water at 1635 cm^{-1} and those for gas phase CO.

The spectra after adsorption of CO at room temperature from a mixture (H_2:CO=3:1) at higher partial pressure gave additional characteristics of the system. Band positions of the doublet are not coverage dependent and this feature of the system needs further study. In contrast to CO on Co a shift of the band of bridge bonded CO on Pd to 1987 cm^{-1} and appearance of the very week band of linearly adsorbed CO on Pd at ~2089 cm^{-1} were registered. The latter band is better seen at decreasing CO partial pressure during blowing the cell at room temperature with Ar (Fig. 3e-f). The results of IR study are in conformity with mechanism of metal phase formation in bimetallic Co-Pd samples already discussed. Despite higher extent of bimetallic particles formation following reductive pretreatment and enrichment in Co of the metal surface, regions containing only Pd atoms are also presented. Catalytic activity of these catalysts is clearly influenced by the presence of palladium on the surface.
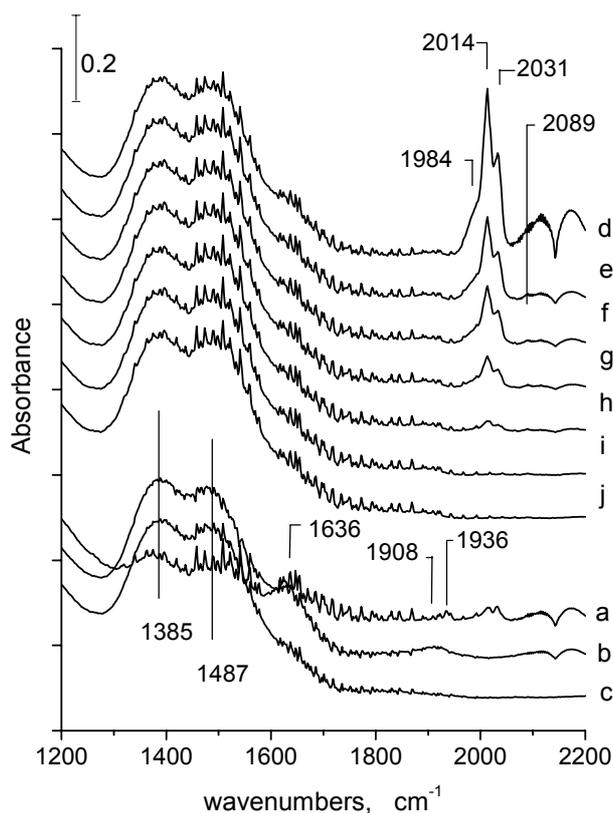
Fig. 3 – IR spectra of used in catalytic test sample 10%Co+0.5%Pd/TiO$_2$ (red):

at low partial pressure of CO
a – adsorption,
b – after stay in gas mixture at Troom,
c – after CO desorption;

at high partial pressure of CO
d – adsorption,
e–j – during CO desorption.

CONCLUSIONS

The surface of metal particles in Co-Pd bimetallic catalysts is determined by the type of the applied oxidative, reductive or inert gas pretreatment. Metal dispersion changed in the catalysts with Al$_2$O$_3$ and SiO$_2$ supports following the order (ox) ≥ (inert) > (red). A modified TPR experiments could help measuring the Co metal surface. This mode of TPR gave dependence of metal surface on the type of the pretreatment in the order (ox) > (red) > (inert).

SMSI effect with the samples of the system 10%Co+0.5%Pd/TiO$_2$ was confirmed to take place after reduction at T>300 °C. Its influence depended on the mode of pretreatment in the order (red) > (inert) ≈ (ox).

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