

Activity and selectivity of Co-Pd/TiO₂ catalysts in CO hydrogenation

M. G. Shopska*, I. Zh. Shtereva, H. G. Kolev, K. I. Aleksieva, S. Zh. Todorova, G. B. Kadinov

Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

Dedicated to the 80th anniversary of Professor Lachezar Petrov, DSc,
Corresponding Member of the Bulgarian Academy of Sciences

Received: November 29, 2019; Revised: December 27, 2019

Activity and selectivity of the (10%Co+0.5%Pd)/TiO₂ system in CO hydrogenation were studied in dependence of pretreatment mode and reduction and reaction temperature. The investigation was directed to evaluate information about influence of surface species and sites on catalyst performance. Samples were preliminary treated in air, hydrogen, or argon and studied by chemisorption of H₂ and CO, TPR, XPS, EPR, *in situ* DRIFTS, and catalytic measurements. Dependences of pretreatment mode and reduction temperature on catalyst activity in CO conversion and selectivity to CH₄ were found. Pretreatment in hydrogen resulted in an active catalyst characterized by bridged CO species on the metal surface with weakened C-O bonds that facilitated cleavage at lower temperatures and sites of medium strength on the support where bidentate carbonate species was formed. This catalyst produced methane at a lower temperature but the selectivity was low due to high CO₂ formation. A selective catalyst was prepared by pretreatment in air and distinguished by dominance of formate and monodentate carbonate species formed on strong adsorption sites of the support. Thus, methane production started at higher temperatures but at a higher CH₄/CO₂ ratio. Being a reducible support of weak Lewis acidity TiO₂ contributed to CO₂ formation because of its intrinsic activity in the water-gas shift reaction. Contribution of the support depended on preliminary treatment mode and the effect of the latter was supposed stronger in the case of active catalyst preparation.

Keywords: CO hydrogenation, Co-Pd catalysts, TiO₂ carrier, DRIFTS, selectivity, H₂ and CO chemisorption

INTRODUCTION

Catalysis is an instrument of the so-called green chemistry to overcome disadvantages and challenges in chemical production. A diversity of chemical processes poses different tasks to catalysis in order to achieve the green chemistry requirements to become ecology friendly. Catalysts meeting the green chemistry 12 postulates should be highly selective, characterized by a decreased variety of intermediates to avoid unnecessary by-product synthesis and thus allowing reagent complete inclusion into target products [1].

The CO hydrogenation process takes place in presence of cobalt and cobalt-palladium supported catalysts. Their surface may be composed by various compounds. The adsorption sites on the surface of metal particles differ in property and vary in concentration ratio: Co and Pd sites with modified properties exist parallel to typical Co and Pd adsorption sites. The influence of the latter on hydrogen and CO adsorption is of great significance determining the heterogeneous catalytic process mechanism.

Main reactions of the CO hydrogenation process are synthesis of CH₄/hydrocarbons (HCs) and water-gas shift reaction (WGSR).

In the related literature the explanation of reaction mechanism, products formation, and catalyst selectivity during the CO hydrogenation process are not generally accepted because of contradiction among obtained data in many cases. Methanation (HCs synthesis) takes part on Co and Pd atoms. There are different ideas about CH₄ formation on cobalt and they have developed in two directions [2, 3]: (i) CO adsorption (CO_{ads}), C-O bond cleavage with formation of surface carbon (C_{ads}) that is distinguished from metal carbide, and C_{ads} hydrogenation; (ii) CO adsorption and hydrogenation of CO_{ads} species to CH_xO_{ads}. It has been established that C_{ads} hydrogenation occurs very easily while that of CO_{ads} requires an increased temperature, which indicates a lower reaction rate. HCs synthesis, i.e. formation of C-C bonds, is explained by creation of CH_x intermediates, condensation of CH_xO entities, and CO insertion. Different surface species of CO have been registered on the catalyst surface. However, another type of O-containing intermediates, different from the aforementioned, has not been found. In spite of that there are investigations reporting results about CH_xO species on Co [4] and Pd [5, 6]. In a great number of studies, it is supposed that a predominant pathway for CH₄ formation is through CO dissociation.

* To whom all correspondence should be sent:

E-mail: shopska@ic.bas.bg

WGS proceeds in presence of eighth-group metals independent of whether they are in reduced or oxidized state, however, in the latter case the rate is much higher [7]. There are different hypotheses about the reaction mechanism: (i) formate; (ii) redox; and (iii) carboxylate [8]. Carboxyl species is shorter-lived than formate one. It has been established that the reaction goes through formation of surface formic acid intermediate [CO-OH] and the rate-determining step is assigned to decomposition into hydrogen and CO₂ [9, 10]. A reaction intermediate for the redox route has not been proved experimentally [8]. Amongst alumina supported catalysts based on eighth-group metals, a reduced Co/Al₂O₃ sample has been characterized by the highest activity [7].

The present paper deals with the activity and selectivity of (10%Co+0.5%Pd)/TiO₂ catalysts depending on factors like pretreatment, reduction temperature, and reaction temperature. The paper is also aimed at putting forward some additional information about how the variety of surface species and sites affects the performance of obtained bimetallic systems. Variance of the above-mentioned factors may lead to an increase in activity. However, activity is not an isolated property of the catalyst since it is accompanied by kind of selectivity in work. It is necessary to vary purposefully the factors and regulate the effect of their influence at creation of catalysts so that a higher activity is accompanied by improved selectivity.

EXPERIMENTAL

Bimetallic Co-Pd catalysts were prepared by depositing metal nitrate salts from aqueous solution on non-porous TiO₂ (Degussa P-25, 50 m²/g) support. The suspension was dried in a vacuum rotary desiccator at 60 °C for 24 h. The procedure was aimed at preparing ~10% cobalt and ~0.5% palladium loading.

Preliminary treatment of the precursors comprised consecutive heating in a gas flow at 100, 200, and 300 °C for 1 h at each level (heating rate of 100 deg/h). Air, hydrogen, and argon were used for oxidative, reductive, and inert gas pretreatment atmosphere, respectively. Selected pretreatment mode was carried out *in situ* in the measuring cell of the respective device before each kind of study. The prepared samples were denoted as 'ox', 'red', and 'inert' in order to distinguish used pretreatment medium.

Chemisorption of hydrogen and carbon monoxide was measured by the volumetric method in a glass device. The experiments were performed with samples successively reduced in hydrogen flow

at 300 °C for 1 h, at 400 °C for 1 h, and at 450 °C for 2 h. After reduction, as well as after each hydrogen adsorption measurement the samples were evacuated to $P < 1.33 \times 10^{-3}$ Pa at the temperature of reduction. Adsorption isotherms of hydrogen were obtained in the pressure range 0–13.3 kPa at a temperature of ca. 100 °C in order to minimize absorption in the bulk of palladium [11] and to activate hydrogen adsorption on cobalt [12, 13]. Monolayer coverage was determined by extrapolation of the linear part of the isotherm to zero pressure.

Carbon monoxide chemisorption was measured at room temperature. The term 'total adsorption' is used to designate the amount of all kinds of adsorbed CO species on various sites. Strongly (irreversibly) adsorbed CO species determine the reaction mechanism in the CO hydrogenation process. For a quantitative analysis of the metal surface, it is necessary to measure and eliminate the share of weakly bonded CO to Co and Pd ions and other sites on the support.

Experimentally, the strongly adsorbed species of CO (CO_s) was determined in the following sequence: (i) total CO adsorption measurement; (ii) evacuation of the sample at room temperature to $P < 1.33 \times 10^{-3}$ Pa; (iii) second measurement of isotherm to determine weak (reversible) adsorption (CO_w). Strongly bonded CO was estimated as a difference between 'total' and 'weak' adsorption [14].

Catalytic activity measurements in the process of CO hydrogenation were carried out in a flow-type glass reactor at atmospheric pressure in the temperature range of 150–360 °C. Catalyst loading was 140 mg (fraction 0.63–0.8 mm). The measurements were carried out with reduced samples at three temperatures following the procedure mentioned above. Before each test, the catalyst was cooled in a hydrogen flow to the selected initial reaction temperature. A H₂/CO reaction mixture of 4/1 at a flow rate of 25 ml/min was used. At reactor outlet the mixture was analyzed by gas chromatography (Varian 3700 with thermal conductivity detector, 2 m Porapak Q column working at room temperature, hydrogen carrier gas 20 ml/min).

In situ diffuse-reflectance IR spectroscopy (DRIFTS) was used to monitor the catalytic measurements of CO hydrogenation (H₂/CO = 4/1, 8 ml/min, T ≤ 250°C). Spectra were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation, USA) equipped with Collector II accessory where a High Temperature/Vacuum Chamber (Thermo Spectra-Tech, USA) was mounted. CaF₂ windows limited the working

spectral range to 1111–4000 cm⁻¹, and the spectra were collected at 100 scans, 1.928 cm⁻¹ date spacing. Temperature-programmed reduction (TPR) was carried out in a quartz reactor with 150 mg of sample charge. 10% H₂ in Ar at a total flow rate of 25 ml/min was used as reducing agent. The temperature was raised by 10 deg/min up to 900 °C. Recorded TPR profiles were used for graphical calculation of the peak area at temperatures higher than the applied T_{red}. This area is proportional to the amount of unreduced metal (URM) and could help in determining metal dispersion of the studied samples.

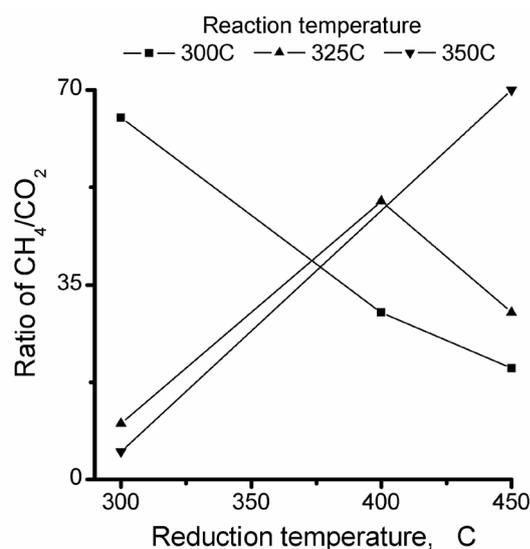


Fig. 1. Selectivity ratio dependence on reduction and reaction temperature for (10%Co+0.5%Pd)/TiO₂(ox) sample.

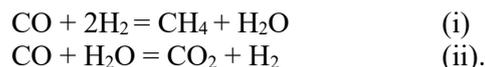
X-ray photoelectron spectroscopy (XPS) was used for *ex-situ* study of sample surface after the catalytic measurements. The analyses were carried out by an ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5×10^{-10} mbar (during measurements 1×10^{-8} mbar) using AlK α X-ray source (excitation energy $h\nu = 1486.6$ eV). The pass energy of the hemispherical analyzer was 20 eV, 6 mm slit widths (entrance/exit). The instrumental resolution measured as the full width at a half maximum (FWHM) of the Ag3d_{5/2} photoelectron peak was 1 eV. The energy scale was corrected depending on the Ti2p peak maximum at 458.8 eV. Processing of the measured spectra included subtraction of X-ray satellites and Shirley-type background [15]. The peak positions and areas were evaluated by a symmetrical Gaussian-Lorentzian curve fitting. The relative concentrations of the different chemical species were determined based on normalization of the peak areas to their photoionization cross-sections as calculated by Scofield [16].

Ex-situ spectra based on electron paramagnetic resonance (EPR) phenomenon were recorded on a JEOL JES-FA 100 EPR spectrometer operating in X-band with standard TE011 cylindrical resonator. An ES-DVT4 Varied Temperature Controller provided spectra detection at a temperature of -150 °C. The desired low temperature was achieved by a cooling gas (liquid nitrogen) system, which was controlled by the spectrometer computer.

RESULTS AND DISCUSSION

Metal dispersion was determined based on hydrogen chemisorption experiments for all studied samples. An average value of about 3.4% was obtained after reduction at 300 °C, which decreased to ~1.8% after reduction at the higher temperature (400/450 °C) studied.

All catalysts were tested in the CO hydrogenation process at atmospheric pressure. Under the selected reaction condition, CH₄ was produced as the sole hydrocarbon [17]. Two main reactions were running in this investigation:



The results showed a different type of change of CO conversion and of hydrocarbon production with reaction temperature.

The CH₄/CO₂ ratio was low and almost constant independent of reduction and reaction temperature for a hydrogen-pretreated (prereduced) sample and for a sample pretreated in an inert gas flow. The change of reduction temperature from 300 to 450 °C affected the behaviour of these samples by decreasing both conversion and selectivity. There was not a clear dependence of the CH₄/CO₂ ratio on reduction or reaction temperature in the case of (10%Co+0.5%Pd)/TiO₂(ox). However, a somewhat similar effect was found on the selectivity ratio upon combination between reduction and reaction temperature in the region of 300 – 450 °C (Fig. 1).

Comparative analysis showed that depending on precursor treatment mode (oxidative, inert, or reductive medium) and reduction temperature the catalysts ranged in different rows of activity in CO conversion and selectivity to CH₄ formation. Information, parameters, and properties derived using different methods are shown in Table 1 featuring the most active sample in CO conversion and that of the highest selectivity to CH₄ amongst all studied samples. For comparative purpose, data collected at a reaction temperature of 300 °C are taken as reference. Figures 4 – 7 illustrate some of the discussed sample properties.

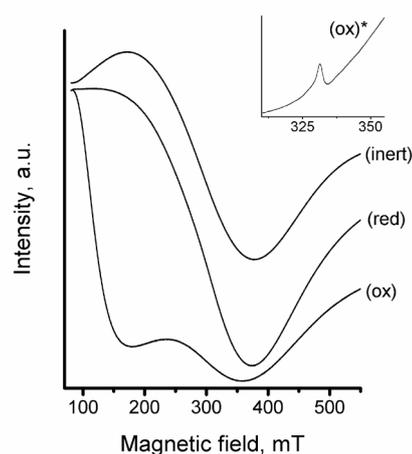
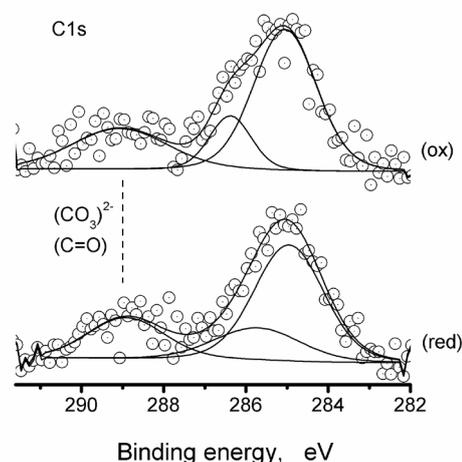
Table 1. Data derived from TPR, XPS, chemisorption and catalytic measurements about the catalyst system (10%Co+0.5%Pd)/TiO₂.

Parameter	Active	Selective
Pretreatment	(red)	(ox)
T _{red} , (°C)	300	300
Co states (TPR)	Co ⁰ , Co ⁿ⁺	Co ⁰ , Co ⁿ⁺
R _{URM}	0.2	
Total carbon, (at.%)	9.53	8.71
CO ₃ , (%)	20	26
CH ₄ /CO ₂	3	65
D _{H100C} , (%)	3.6	3.7
H _{100C} /CO _s	2.9	2
CO _s /CO _w	0.8	1
	(22/28)	(32.8/31.8)

Legend: CO₃ – percentage of deposited surface carbon corresponding to carbonate(s); R_{URM} - unreduced metal ratio ($R_{URM} = URM_a:URM_s$), H_{100C} – sample capacity for monolayer hydrogen adsorption measured at 100 °C after reduction at a respective T_{red}; CO_w - sample capacity for weak (reversible) CO adsorption measured at room temperature after reduction at a respective T_{red}; Co_s – calculated sample capacity for strong (irreversible) CO adsorption; D_{H100C} - metal dispersion based on H_{100C} and determined after reduction at a respective temperature.

After performing the catalytic tests, all the samples were investigated by XPS and EPR. Results obtained by EPR spectroscopy (Fig. 2) show that at room temperature a broad singlet line with a g factor of 2.2551 ± 0.005 was detected in samples pretreated in reductive and inert flow, which is due to tetrahedrally coupled Co²⁺ ions [18]. It can be supposed that the line is significantly broadened due to additional deformation of the Co²⁺ tetrahedra or superposition of metallic Pd because the studied catalysts were bimetallic [19]. Another possible reason for this line broadening is dipole-dipole interaction between the particles, since cobalt concentration is 10%, high enough for EPR measurements. Preliminary treated catalyst in air (denoted as ‘ox’) has a signal of g factor 5.4552, which can be assigned to isolated octahedrally coordinated Co²⁺ ions with some tetragonal and trigonal distortions [20]. In addition, a weak signal with a g factor of 1.9751 due to Ti³⁺ was recorded at a temperature of –150 °C (Fig. 2, inset) [21]. Co²⁺ and Co³⁺ on the surface of the tested samples were also registered by XPS measurements, as well as metallic Pd and Pd²⁺ [22]. The presence of these ions in the used (already reduced) samples is due to available unreduced oxide phase(s) and/or to the ‘*ex-situ*’ measurements where oxygen adsorption and oxidation of the particle surface layer proceeds without penetration into the bulk during exposition to air [23, 24]. Additionally, 8.71–10.06 at. % carbon

were registered by XPS (Table 1, Fig. 3).

**Fig. 2.** EPR spectra of samples measured at room temperature and –150 °C (inset) after catalytic test.**Fig. 3.** C1s high-resolution XP spectra of samples from different systems tested in CO hydrogenation and classified correspondingly as selective or active catalysts.

Carbon deposition due to XPS measurement itself was not observed. So, the registered amounts of HCs were assigned to surface HCs species formed along with methane and remained adsorbed on the catalyst and/or because of contamination upon sample preparatory procedure of grinding. The shape of the C1s peak exhibited a shoulder corresponding to carbon in a typical surrounding of carbonates [22]. Deconvolution of the high-resolution C1s peaks revealed that about 20–26% of the surface carbon was in the form of carbonates.

The TiO₂ support is not entirely inert. A strong metal-support interaction (SMSI) phenomenon is frequently observed after reduction of the catalysts and during reactions under reductive conditions. This phenomenon includes several features: Ti⁴⁺→Ti³⁺ reduction; anatase→rutile transition; acceleration of both transformations in presence of metals capable of hydrogen dissociative adsorption

(e.g. Co, Pd); metal surface decoration by partially reduced titania; and CoTiO₃ formation [14, 25–29]. Temperature-programmed desorption from TiO₂ revealed the CO₂ origin from bidentate carbonate species on sites of medium strength in the interval 190–230 °C and from monodentate species on strong adsorption sites at about 320 °C [30]. Evidence for SMSI in the studied samples was proved by a sharp decrease of metal dispersion found through hydrogen chemisorption, while presence of Ti³⁺ ions was confirmed by EPR.

XPS data about carbonate species retained on the surface are consistent with presence of adsorption sites of significant strength.

The amount of unreduced Co in the samples was evaluated by the area under the TPR profile above the reduction temperature of the respective sample (Fig. 4, grey area).

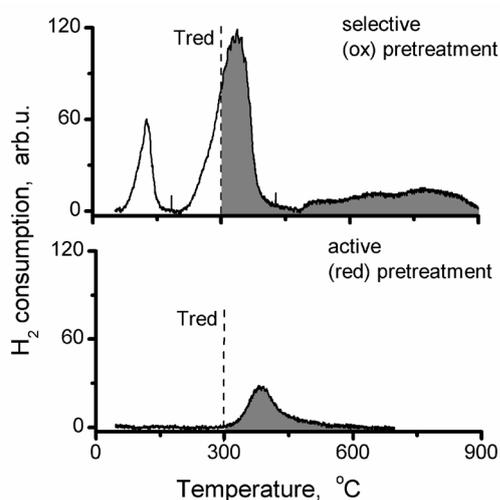


Fig. 4. TPR profiles of differently pretreated (10%Co+0.5%Pd)/TiO₂ samples.

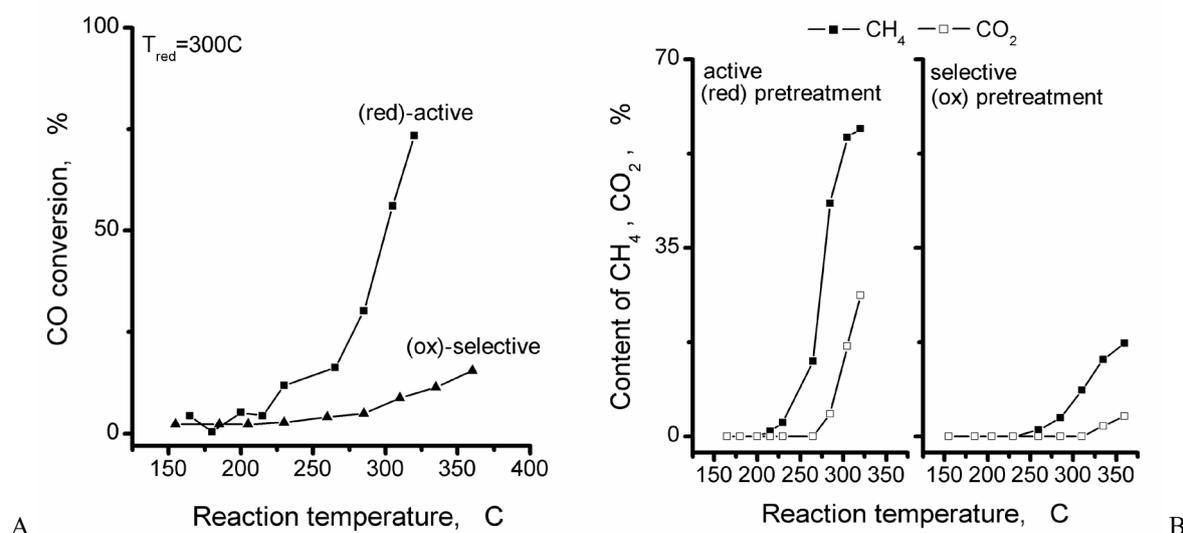


Fig. 5. Catalytic behaviour in CO hydrogenation of differently pretreated (10%Co+0.5%Pd)/TiO₂ catalysts: A - CO conversion, B - products distribution.

The ratio of active sample area (URM_a) to selective sample (URM_s) area (R_{URM}, Table 1) was regarded as an additional feature to evaluate the role of unreduced metal.

The TPR study showed that cobalt occurred in metallic and ionic state in both samples independent of T_{red} and preliminary treatment. The amount of Coⁿ⁺ predominated in the selective (10% Co + 0.5% Pd)/TiO₂(ox) sample (R_{URM} = 0.2). These results imply that most probably after ‘oxidative’ pretreatment unreduced cobalt is in the form of Co₃O₄ and CoTiO₃, whereas after ‘reductive’ pretreatment it is, presumably, in the form of unreduced CoO [31–37].

The catalytic activity measurements revealed that the more active catalyst was prepared by ‘reductive’ pretreatment and final reduction at 300 °C, both procedures being carried out by pure hydrogen (Fig. 5). Such a pretreatment implies the appearance of Ti³⁺ sites and O²⁻ vacancies [14, 25, 26].

The measurements of CO and hydrogen chemisorption indicated: (i) nearly the same metal dispersion of both samples; (ii) a higher H/CO_s ratio of 2.9 for the catalyst after ‘reductive’ pretreatment; (iii) the CO_s/CO_w ratio was almost the same for both catalysts (0.8 and 1), however, CO amount adsorbed on the surface was higher with the selective (10% Co+0.5% Pd)/TiO₂(ox) catalyst. Acquired data can be assigned to a large quota of CO adsorbed on metal ions, a larger share of bridge-bonded CO, a lot of separate Co and Pd particles in the active catalyst. Accordingly, the active sample was also characterized by bimetallic particles, Ti⁴⁺, Coⁿ⁺, and lack or lower level SMSI.

The selective catalyst was prepared by pretreatment in air and TiO₂ was stabilized in relation to phase transformations. Thus, on the surface of this sample there existed sites of different nature/character and strength for CO adsorption. The latter include Co, Pd and highly diluted Pd atoms on the surface of bimetallic particles, Ti³⁺ ions and O²⁻ vacancies of relatively lower amount, Ti⁴⁺ ions, many unreduced Co²⁺ ions (very low $R_{URM} = 0.2$). At the same time, the surface of the metal particles is partially covered by reduced titania due to SMSI. The low activity of this sample could be assigned to SMSI since the metal dispersion was almost preserved (Table 1).

Formation of carbonate species on the samples/support could proceed by two distinct mechanisms: (i) a contact of CO with surface defects followed by interaction with OH groups or (ii) direct interaction between CO and surface hydroxyls [30]. The probability to realize these ways is different depending on the preliminary treatment of the catalyst. Both mechanisms could be equally operative in the case of an active sample, because of surface site diversity characterized by more ions capable of CO adsorption and conversion. The latter mechanism is most probable in the case of selective catalyst taking into account a narrower site distribution.

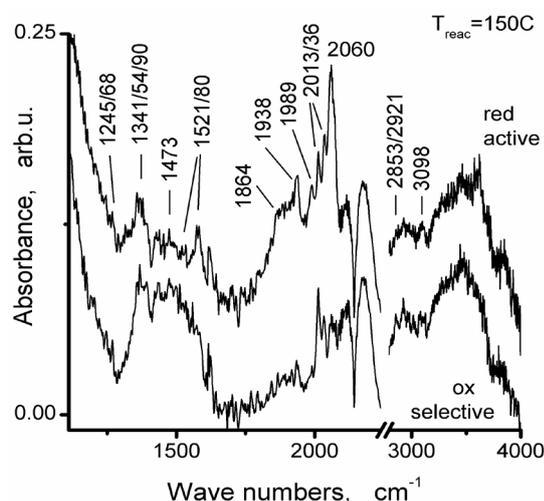


Fig. 6. *In situ* DRIFTS during CO hydrogenation.

Figure 6 shows the results obtained by *in situ* DRIFTS during CO hydrogenation. The doublet centered at 2142 cm⁻¹ is characteristic of gaseous CO. Bands of CO species adsorbed on the metal surface appeared at 2013, 2036, and 2060 cm⁻¹ for linearly adsorbed CO on cobalt particles; 1936 and 1989 cm⁻¹ for bridge-bonded CO on Pd; 1864 cm⁻¹ for multicenter bonded CO on Pd (Pd (111) facets on the surface of palladium particles) [32, 38].

Bidentate (1245/68, 1580, 1618, 1640 cm⁻¹) and

monodentate (1341/54, 1472, 1521 cm⁻¹) carbonate and formate species (1341/54/90, 1580, 1618 cm⁻¹) were registered on the catalyst surface [38]. Bands of monodentate carbonate and formate species were of higher intensity in the spectrum of the selective sample. This observation allows to state that the selective catalyst had larger amounts of the aforementioned surface species. They were relatively stable since reaction temperatures over 150 °C were necessary to initiate their transformation compared to the spectra of active sample. In addition, the bands were clearly visible to exhibit higher intensity even at 250 °C. Bands characteristic of hydrocarbon species (1390, 2853, 2921 cm⁻¹) were better resolved in the spectrum of the selective catalyst [38]. A band of the CH₄ reaction product at 3098 cm⁻¹ was recorded in both cases [38]. These observations concerning carbonate and hydrocarbon species retained on the selective sample surface are in agreement with XPS findings.

Figure 7 presents the changes of 2013 and 2036 cm⁻¹ band intensities in dependence of the reaction temperature. A general feature of the changes is concerned with decreasing band intensity. However, in the case of active sample (open symbols), some increase in intensity appeared in the interval of 150–225 °C.

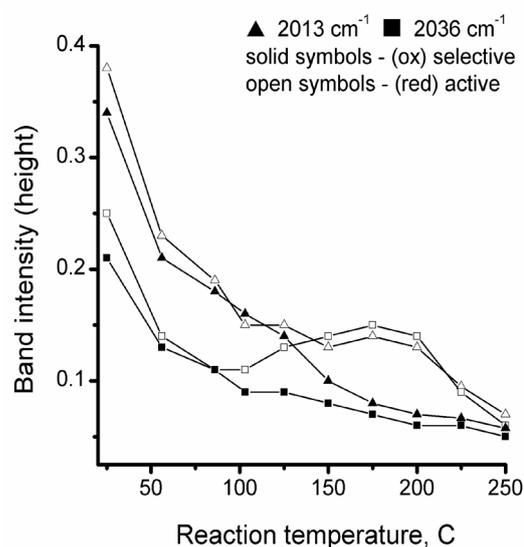


Fig. 7. Dependence of some infrared band intensities on reaction temperature.

The latter was accompanied by appearance and increasing intensity of bands characteristic of CO adsorbed as different species on palladium atoms. The observed feature could be attributed to synergism mode, surface reorganization, and a decrease in SMSI effect. The CH₄/CO₂ product ratio at the reaction temperature of 300 °C for the active and the selective catalysts was 3 and 65, respectively (Table 1). The XPS study revealed higher carbon

deposition on the surface of the active sample but a larger amount of carbonates on the surface of the selective sample. The results could be explained by (i) domination of sites for strong CO adsorption on the metal surface and for monodentate carbonates on the support in the selective catalyst that determine CO₂ formation at higher temperatures during the catalytic process; (ii) adsorption sites of medium strength for bidentate carbonate species, which prevail on the surface of the active catalyst; (iii) possibility for a varying ratio of linear to bridged CO species on the surface of metal particles in the active catalyst where weakened C-O bonding in bridge-bonded species facilitate cleavage at lower reaction temperatures. It is known that carriers with acid surface and those, which can be partially reduced, are suitable for WGS catalysts [39]. TiO₂ meets both requirements, namely, it is a weak acid support mainly with Lewis acid properties and in presence of metals (like Co and Pd) can be partially reduced to form oxygen vacancies. Even more, it has been found that Pd/TiO₂ (so as Pt, Rh, or Ru on TiO₂) is very effective in WGS and the catalytic activity is in proportion with SMSI [39]. Therefore, such a property should be taken into account together with the other factors mentioned above on discussing catalytic performance of the active catalyst.

CONCLUSIONS

Comparative analysis showed that the synthesis of (10%Co+0.5%Pd)/TiO₂ catalysts by applying different pretreatment and reduction sets could result in an active catalyst in the process of CO conversion to CH₄ and CO₂ or a selective one to higher yields of CH₄ and hydrocarbons. Since CO hydrogenation on bimetallic catalysts is dependent on Co state, amount of unreduced metal, bimetallic Pd-Co particle formation, and support features for CO and CO₂ adsorption, then the H_{100C}/CO_s and CO_s/CO_w ratios become apparent as important criteria for catalyst performance.

Acknowledgement: The financial support by the Bulgarian National Science Fund through contract KP-06-H29-9/14.12.2018 is gratefully acknowledged.

REFERENCES

1. P. T. Anastas, M. M. Kirchhoff, T. C. Williamson, *Appl. Catal. A-Gen.*, **221**, 3 (2001).
2. J. A. Rabo, A. P. Risch, M. L. Poutsma, *J. Catal.*, **53**, 295 (1978).
3. P. Biloen, J. N. Helle, W. M. H. Sachtler, *J. Catal.*, **58**, 95 (1979).
4. G. Blyholder, D. Shihabi, W. V. Wyatt, R. Bartlett, *J. Catal.*, **43**, 122 (1976).
5. M. L. Poutsma, L. F. Elek, P. A. Ibarbia, A. P. Risch, J. A. Rabo, *J. Catal.*, **52**, 157 (1978).
6. M. A. Vannice, R. L. Garten, *Ind. Eng. Chem. Prod. Res. Dev.*, **18**, 186 (1979).
7. D. C. Grenoble, M. M. Estadt, D. F. Ollis, *J. Catal.*, **67**, 90 (1981).
8. C. Ratnasamy, J. P. Wagner, *Catal. Rev.*, **51**, 325 (2009).
9. M. Masuda, K. Miyahara, *Bull. Chem. Soc. Japan*, **47**, 1058 (1974).
10. M. Masuda, *J. Res. Inst. Catal., Hokkaido Univ.*, **24**, 83 (1976).
11. P. C. Aben, *J. Catal.*, **10**, 224 (1968).
12. R. C. Reuel, C. H. Bartholomew, *J. Catal.*, **85**, 63 (1984).
13. J. M. Zowtiak, C. H. Bartholomew, *J. Catal.*, **83**, 107 (1983).
14. J. R. Anderson, Structure of metallic catalysts, Mir, Moscow, 1978 (in Russian).
15. D. Shirley, *Phys. Rev. B*, **5**, 4709 (1972).
16. J. H. Scofield, *J. Electron Spectrosc.*, **8**, 129 (1976).
17. S. Zheng, Y. Liu, J. Li, B. Shi, *Appl. Catal. A-Gen.*, **330**, 63 (2007).
18. N. Guskos, J. Typek, M. Maryniak, G. Żolnierkiewicz, M. Podsiadly, W. Arabczyk, Z. Lendzion-Bielun, U. Narkiewicz, *Mater. Sci. Poland*, **24**, 4 (2006).
19. P. Stefanov, S. Todorova, A. Naydenov, B. Tzaneva, H. Kolev, G. Atanasova, D. Stoyanova, Y. Karakirova, K. Aleksieva, *Chem. Eng. J.*, **266**, 329 (2015).
20. E. V. Makshina, N. S. Nesterenko, S. Siffert, E. A. Zhilinskaya, A. Aboukais, B. V. Romanovsky, *Catal. Today*, **131**, 427 (2008).
21. P. Claus, S. Schimpf, R. Schodel, P. Kraak, W. Morke, D. Honicke, *Appl. Catal. A-Gen.*, **165**, 429 (1997).
22. J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Minnesota, 1992.
23. N. M. Popova, L. V. Babenkova, G. A. Saveleva, Adsorption and interaction of simple gases with VIII group metals, Nauka, KazSSR, Alma-Ata, 1979 (in Russian).
24. D. Potoczna-Petru, J. M. Jablonski, J. Okal, L. Krajczyk, *Appl. Catal. A-Gen.*, **175**, 113 (1998).
25. C. N. Satterfield, Heterogeneous Catalysis in Industrial Practice, 2nd edn., McGraw-Hill Inc., 1980 (© 1991).
26. A. Nobile, Jr., M. W. Davis, Jr., *J. Catal.*, **116**, 383 (1989).
27. K. I. Hadjiivanov, D. G. Klissurski, *Chem. Soc. Rev.*, **25**, 61 (1996).
28. R. Riva, H. Miessner, G. Del Piero, D. Rebours, M. Roy, *Stud. Surf. Sci. Catal. (Natural gas conversion V)*, **119**, 203 (1998).
29. M. Voß, D. Borgmann, G. Wedler, *J. Catal.*, **212**, 10 (2002).
30. C. Weilach, C. Spiel, K. Föttinger, G. Rupprechter, *Surf. Sci.*, **605**, 1503 (2011).
31. S. Zh. Todorova, G. B. Kadinov, *Bulg. Chem. Commun.*, **34**, 232 (2002).
32. G. B. Kadinov, Ch. Bonev, S. Todorova, A. Palazov,

- J. Chem. Soc. Faraday Trans.*, **94**, 3027 (1998).
33. M. G. Shopska, I. Zh. Shtereva, G. B. Kadinov, *Bulg. Chem. Commun.*, **34**, 476 (2002).
34. M. G. Shopska, G. B. Kadinov, *Asian Chem. Lett.*, **14**, 111 (2010).
35. M. G. Shopska, G. B. Kadinov, I. Zh. Stereva, *Oxid. Commun.*, **34**, 85 (2011).
36. M. Shopska, G. Kadinov, I. Shtereva, *Rev. Roum. Chim.*, **59**, 219 (2014).
37. S. Todorova, A. Ganguly, A. Naydenov, H. Kolev, I. Yordanova, M. Shopska, S. Mondal, G. Kadinov, S. Saha, A. K. Ganguli, *Bulg. Chem. Commun.*, **47(C)**, 42 (2015).
38. L. H. Little, *Infrared spectra of adsorbed species*. Academic Press Inc., London, New York, 1966.
39. L. E. Oi, M.-Y. Choo, H. V. Lee, H. C. Ong, S. B. A. Hamid, J. C. Juan, *RSC Adv.*, **6**, 108741 (2016).