Comparative investigation of (10%Co+0.5%Pd)/TiO₂(Al₂O₃) catalysts in CO hydrogenation at low and high pressure

Maya Shopska¹,⁎, Alfonso Caballero², Silviya Todorova¹, Katerina Aleksieva¹, Krassimir Tenchev¹, Hristo Kolev¹, Martin Fabian³, Georgi Kadinov¹

¹ Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria; shopska@ic.bas.bg
² Inorganic Chemistry Department, Materials Science Institute (CSIC-US), Seville, Spain
³ Institute of Geotechnics, Slovak Academy of Sciences, Kosice, Slovakia; fabianm@saske.sk

⁎ Correspondence: shopska@ic.bas.bg; Tel.: 00359-2-979-39-18


Abstract: Surface properties of prereduced (Co+Pd)/Al₂O₃ and (Co+Pd)/TiO₂ catalysts were studied. Metal dispersion was 1-3%. CoPdA demonstrated high temperature H₂ desorption and firmly held CO and carbonate species on the surface. SMSI operated on CoPdT even after contact with H₂O and air. Metal surface reconstruction and increased formation of CH₄ groups occurred during catalysis. At low pressure, CoPdT was more active whereas CoPdA had higher CH₄ selectivity. At high pressure, catalysis on CoPdA revealed dependence on Tₛₑₜ, synthesis of CO₂, hydrocarbons, decreased CO₂ production, and higher CH₄/CO₂ ratio. CO conversion decreased with time due to difficulties in surface diffusion of reagents/intermediates/products and metal particle agglomeration.

Keywords: CO hydrogenation; cobalt-palladium catalysts; DRIFTS; low and high pressure

1. Introduction

CO hydrogenation in synthesis gas is an environmentally friendly process, which is alternative to oil refinement [1]. Obtained products are of low or without content of nitrogen and sulphur [1,2]. The main products of the CO hydrogenation process are CH₄, CO₂, and light and heavy hydrocarbons. CH₄ and CO₂ are considered unwanted products [3,4].

Co-Pd catalysts are active in the process of CO hydrogenation [5-8]. Many factors affect their activity and selectivity [1,2,9-11]. Product distribution is influenced directly by some process parameters but others affect it indirectly through their effect on the conversion [10]. The CO hydrogenation reaction is thermodynamically favoured by increasing pressure. Since the reaction mechanism is very complex involving separate hydrogenation and polymerization routes [12], investigations at low and high pressure have been carried out to get detailed information about the reasons and ways of product distribution change. Generally, the effect of increased pressure results in enhanced CO conversion, a decrease in light hydrocarbon synthesis, and an increase of C₃⁺ compound quota [2,6,9-18]. Comparative analyses at different pressures in the interval of 0.33–40 atm have been done [2,6,9,10,12-18]. A 10 atm pressure has been accepted as an optimum as a result of investigations on combined influence of process parameters as pressure, temperature, H₂/CO ratio, flow rate, and conversion [12,14].

The present study discusses surface properties of alumina- and titania-supported (10%Co+0.5%Pd) catalysts and selectivity in CO hydrogenation at low and high pressure. The aim is a better understanding the specific role of the support.
2. Materials and Methods

Bimetallic catalysts with 10%Co and 0.5%Pd were prepared by deposition of metal nitrate salts from aqueous solution on non-porous TiO$_2$ and Al$_2$O$_3$ supports. The precursors were reduced in H$_2$ flow applying two modes: (i) for studies at P = 1 atm - heating at 100 and 200 °C for 1 h, and 2 h at 300 °C; (ii) for studies at P = 10 atm - heating at 260 or 400 °C for 15 h. Catalytic activity measurements were carried out at P = 1 atm and T$_{\text{react}}$ = 150–365 °C or P = 10 atm and 260 °C. Samples of both groups of catalysts were studied by a number of methods. Chemisorption of H$_2$ (at 100 °C) and CO (at 25 °C) was measured by volumetric method [19-21]. Irreversibly adsorbed CO was determined as a difference between total and reversible adsorption [22]. Particle size distribution was derived by photon cross-correlation spectroscopy (PCCS). Electron paramagnetic resonance (EPR) spectra were recorded at 25 °C in X-band. X-ray photoelectron spectra (XPS) were recorded using AlK$_\alpha$ X-ray source. The spectra were processed according to Refs. 23 and 24. Temperature-programmed desorption (TPD) of H$_2$ (T$_{\text{des}}$=100 °C) and CO (T$_{\text{des}}$ = 25 and 200 °C) was studied by differential scanning calorimeter. CO hydrogenation at 1 atm was studied in situ by diffuse-reflection infrared spectroscopy (DRIFTS) in a high temperature vacuum chamber. PCCS, EPR, XPS, TPD, and DRIFTS measurements were made with catalyst samples after a CO hydrogenation test at 1 atm.

3. Results and Discussion

Two main reactions are running in our investigations at the chosen reaction conditions: (i) CO + 3H$_2$ = CH$_4$ + H$_2$O and (ii) CO + H$_2$O = CO$_2$ + H$_2$ [25]. T$_{\text{red}}$ and T$_{\text{react}}$ effect on the catalytic behaviour of the synthesized materials was examined at 1 atm in the temperature intervals 300–450 °C and 130–375 °C, respectively. A T$_{\text{red}}$ over 300 °C led to a decrease in CO conversion and CH$_4$ and CO$_2$ yields. A definitely sharp decrease was found in the case of Al$_2$O$_3$-supported system. The observed dependences were due to metal particle agglomeration. The increase of T$_{\text{react}}$ resulted in an increase in CO conversion and CH$_4$ and CO$_2$ yields [6] and a decrease in the CH$_4$/CO$_2$ selectivity ratio. Values within 2–19 of the CH$_4$/CO$_2$ ratio were registered on TiO$_2$-supported samples in the interval T$_{\text{react}}$ = 285–335 °C and 3–24 for Al$_2$O$_3$-supported samples in the range 315–365 °C. These results showed that water gas-shift reaction (WGSR) was favoured to a significant extent by the temperature. (Co+Pd)/TiO$_2$ samples were more active and the highest activity exhibited one reduced at 300 °C (CoPdT). (Co+Pd)/Al$_2$O$_3$ samples had lower activity but demonstrated higher selectivity to CH$_4$ if particularly reduced at 400 °C (CoPdT).

The properties of two samples were compared, namely the most active CoPdT one reduced at 300 °C and the most selective CoPdT entity reduced at 400 °C. At the initial stage of the catalytic test H/CO ratio values of 2.9 and 2.8, respectively, were determined. Metal dispersion was calculated based on H$_2$ chemisorption and it was estimated to be very low as 3.61 and 1% for CoPdT and CoPdA, respectively. The data showed presence of large metal particles and a very small part of the supported metal was accessible to contact with reagents. The reasons can be related to low BET area of the titania and due to processes during decomposition of the cobalt nitrate in reductive medium followed by metal particle agglomeration facilitated by the subsequent reduction at 400 °C. In the case of CoPdA, the surface Pd atoms are highly diluted in the bimetallic particles.

In order to reveal why titania-supported catalysts were more active and those on alumina produced more CH$_4$, samples of both of them were studied after the catalytic tests. We considered that samples selected after catalysis would manifest surface properties that do not change or change insignificantly during subsequent studies.

A different number of peaks corresponding to particle hydrodynamic radii and representing particle size distribution in both materials characterized correlation functions obtained by PCCS. Values of the hydrodynamic radii showed that 100% of the CoPdT catalyst particles were of 40–120-nm size. For CoPdA catalyst, the result was in-
indicative about bimodal particle size distribution of 90-102 nm (58%) and 7.5-10 μm (42%). Thus, in both cases the catalyst particles were found as agglomerates.

EPR registered spectra with g factor of 2.2551±0.005, which was representative of tetrahedrally coordinated Co²⁺ ions [26]. Concerning their amount, it was found that CoPdT > CoPdA is valid. Perhaps, pretreatment mode and Al₂O₃ support gave rise to large amount of cobalt in diamagnetic state (Co, CoPd alloy particles and/or Co³⁺) after reduction at 400 °C. XPS revealed also Co⁰, metallic Pd, and Pd²⁰. Most probably ion presence was due to the ex-situ measurements, where oxygen adsorption and oxidation of the particle surface layer proceeded without penetration into the bulk while exposing to air [27,28], and/or owing to presence of unreduced phases. (Co+Pd)/support ratio of CoPdA catalyst was lower than that for CoPdT. This peculiarity was attributed to lower TiO₂ surface area, which presumed that all the metal was on the carrier grains but not in the bulk. EPR and XPS data could be assigned to higher extent of metal particle agglomeration and alloying in the CoPdA sample. On the surface of this sample, smaller amounts of carbon were registered. Deconvolution of the C1s peaks revealed that about 20% and 50% carbon with CoPdT and CoPdA, respectively, at the surface was in the form of carbonates indicating that alumina exposed stronger adsorption sites [29]. Deconvolution of the O1s spectra of CoPdT showed a composition of three sub-peaks [30] and Ti/O>0.5, which is below the stoichiometry and presupposes oxygen deficit (TiO₂⁻). Thus, strong metal-support interaction (SMSI) has been invoked to occur during sample reduction that is preserved after catalytic runs and exposition to air.

In situ DRIFTS studies of CO hydrogenation were performed at T_{\text{react}} = 50–250 °C. Registered bands, band maxima, and shoulders of the adsorbed species were ascribed as follows: 1767 cm⁻¹ – CO multiple (bridge) bonded on Co⁰; 1864 cm⁻¹ – CO multiple bonded on Pd⁰; 1934-90 cm⁻¹ – CO bridge bonded on Pd⁰ and/or linear bonded on Co⁰; 2000-36 cm⁻¹ – CO linear bonded on Co⁰; 2040-60 cm⁻¹ – CO linear bonded on Co⁰⁺; 2050/60 cm⁻¹ – hydrocarbonyl (H-Co-CO); and 2073-100 cm⁻¹ – CO linear bonded on Pd⁰ [31-35]. Registration of many bands due to one type of adsorbed CO species was assigned to existence of various sites on the metal particles with differences in nature, coordination of atoms, electronic state, and bond energy with adsorbates. Comparative analysis of the spectra during reaction showed modification of CO adsorption forms/sites with temperature change [15]. The spectral changes indicated: (i) facile CO interaction with hydrogen even at room temperature, which concerned preferably linear species; (ii) formation of new sites on CoPdT due to SMSI destruction/reduction because of synthesized H₂O reaction product [37] and because of partial oxidation of surface Co atoms by water molecules and/or reduction of residual oxide phases with formation of new adsorption centres in close contact with the support (CoPdT, CoPdA) [38,39]; and (iii) cobalt hydrocarbonyl species could contribute to some band broadening and intensity increase. When the T_{\text{react}} was around 250 °C the bands in the CoPdT spectra decreased significantly in intensity to (almost) complete disappearance, particularly those of bridge bonded CO on Pd, thus displaying acceleration of the hydrogenation process [34] as a result of predominant dissociative adsorption of both CO and H₂ favouring formation of CH₃ intermediates and CH₄ [5]. The spectra of CoPdA demonstrated significant stability of the CO adsorption on the surface via irreversibly adsorbed CO that is considered a precondition which further favours the hydrogenation process to methane [34,38].

Bands characteristic of hydrocarbon species were distinguished by vibrations of a CH₃ group at 1370-93, 1420-52, and 2957 cm⁻¹, a CH₂ group at 1461, 2851, and 2926 cm⁻¹, and a CH group at 1356 cm⁻¹ (Fig. 4, a, b) [40,41]. With all bands, an increase of intensity was registered at T_{\text{react}} ≥ 175 °C for CoPdA and 150 °C for CoPdT samples. This mostly concerned the band of CH₃ groups at 2926 cm⁻¹. With CoPdT the I_{CH₃}/I_{CO} intensity ratio was 1.2-2 in the range 175-250 °C, which showed availability of sites for steady adsorption of CH₃ intermediates [42,43]. Synthesized CH₄ (1303-05, 3013-16, 3099 cm⁻¹) [40,41] became perceptible at 200 and 225 °C in the spectra of CoPdT and CoPdA, respectively. Band intensities increased with T_{\text{react}} much more with CoPdT sample in the range 225-250
°C where a 3.7-fold increase of the 3015-cm⁻¹ band intensity was detected. This particularity shows that both catalysts have potential to produce higher hydrocarbons than CH₄ even at 1 atm.

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** In situ DRIFTS spectra recorded at different temperatures during CO hydrogenation at 1 atm in presence of: (a) CoPdA sample; (b) CoPdT sample.

Bidentate (1245-68, 1566-80, 1616-18, 1640 cm⁻¹) and monodentate (1320-75, 1472, 1521-22 cm⁻¹) carbonate and formate species (1341-90, 1566-80, 1616-18 cm⁻¹) were registered on the surface of catalysts [41]. Bidentate carbonates are classified as weakly held carbonates [44] whereas desorption of formate and monodentate carbonate species takes place at higher temperatures. It can be supposed that a release of small CO₂ amounts registered with CoPdA at T_{\text{vac}} ≥ 125 °C was due to desorption of bidentate carbonates. Thus, the results suppose existence of sites for strong adsorption of formate and carbonate species on the surface. CO₂ formation was suppressed and the catalyst gets more selective to CH₄. In the case of CoPdT the increase of T_{\text{vac}} over 150 °C facilitated the transformation of carbonate-like intermediate species to increase the amount of CO₂ in the gaseous phase. The catalyst manifested high activity but poor selectivity.

TPD studies showed two regions of desorption of H₂ and CO. From CoPdT sample the main amount of H₂ was desorbed at low temperatures while the situation was opposite with CoPdA. High temperature desorption of H₂ (T>360 °C) from CoPdA displayed presence of low reactive and low mobile adsorption form, which could not participate in the formation of formates and CH₄. The presence of such H₂ species can cause diminished contact of the CO with catalytically active sites, a lower number of adsorbed CO species, and increased H/CO ratio on sites generating CH₄ formation. On comparing CO species adsorbed at 25 °C and at 200 °C by TPD we observed that with CoPdT the amount of CO species desorbed at a low temperature (below ~200 °C, two types) increased with T_{\text{ads}} at the expense of those desorbed at a high temperature. Considering CoPdA the CO species desorbing at a low temperature changed only their share upon T_{\text{ads}} increase. High temperature species represented a significant part of the adsorbed CO on CoPdT at both used T_{\text{ads}}. Based on DRIFTS results, the CO desorbed at a low temperature occurs from linear and bridge bonded species whereas CO desorbed at a high temperature originates from carbonate-like species. Depending on T_{\text{ads}} and support, the linear CO species prevailed over the bridge forms to a different extent. All desorption peaks independent of adsorbed gas and T_{\text{ads}} fall into common temperature intervals that supposes surface species of close bonding energies and a similar structure of adsorption sites. This facilitates interaction between the species to form hydrocarbon(s) and CO₂, the latter being result of carbonate-like intermediate decomposition. Comparative analyses of CO₂=TPD and CO₂=TPD together with DRIFTS data supposed facilitated partial destruction of carbonate species, most probably those of bidentate type. Since desorption from CoPdA catalyst in the high temperature region was negligible compared to that from CoPdT, it could be assumed that the surface possesses a peculiar set of homogeneity of intermediates that contributes to a higher selectivity of the CoPdA catalyst.

Catalytic tests at 10 atm showed that the CO conversion and selectivity depended on T_{\text{red}} (Fig. 2). Methane was still the main hydrocarbon product and the CH₄/CO₂ selectivity
ratio was CoPdA > CoPdT, taking into account that the CO₂ amount produced by the CoPdT catalyst was 1.5-1.6 times higher. The CO conversion over CoPdT decreased faster with time on stream (1.4 times) after both T_red (260 and 400 °C), in contrast to CoPdA, which was obviously more stable especially after reduction at 400 °C.

![Figure 2. CO conversion at P=10 atm over the studied samples after reduction at different temperatures. Inset: Product distribution.](image)

Selectivity was generally preserved with some changes after T_red = 400 °C: decreased C₅⁻ and CO₂ amounts while the share of CH₄ and C₂-C₃ compounds slightly increased. The decrease in CO conversion was assigned to higher carbon deposition on the surface, difficult diffusion of reagents/intermediates/products due to synthesis of C₅⁻ hydrocarbons [6,18], consumption of reagents in metal oxide reduction, and metal particle agglomeration. Reduction at 400 °C supposed higher extent of metal reduction favouring a decrease in CO₂ formation through WGSR since the number of active sites for this case as Co⁰ decreased. CoPdT preserved higher CO₂ production most probably because of better dispersion and SMSI providing active sites. The agglomeration renders different effect on the conversion depending on carrier material. CO conversion over CoPdA was more stable due to improved resistance of the metal particles to agglomeration. In the case of CoPdT the agglomeration and SMSI (see XPS data) led to diminished CO conversion by lowering dispersion and number of active sites. By increasing metal particle size selectivity of both catalysts to different hydrocarbons is changed because the formation and homogenization of the bimetallic particle surface is facilitated. Modified properties of the surface cobalt atoms and larger particle size favoured CO dissociation over cobalt [15,36]. Together with the effect of increased pressure, the probability for polymerization and carbon chain growth is augmented. However, increased P_H₂ enriched the surface in CH₅ species [1,9,11] and helped to divide bigger intermediates into smaller segments and thus decreased chain growth to some extent in situation of slightly enhanced CO dissociation [9]. In the case of CoPdA catalyst, the increased P_H₂ could contribute to stable CO conversion avoiding deactivation of metal by oxidation during the process [15].

4. Conclusions

Co-Pd catalysts with alumina support pretreated in H₂ were more selective toward methane and produced lower CO₂ amount during CO hydrogenation at 1 atm compared to catalysts with titania. The properties were preserved in the reaction at 10 atm due to strong metal-support interaction in CoPdT, which was not reduced by contact with H₂O and air, thus determining sites for carbonate species formation and CO₂ production. CoPdT produced a lower C₅⁻ amount because of stable adsorption of CH₅ intermediates.

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References

3. Schmidt-Rohr, K. Why combustions are always exothermic, yielding about 418 kJ per mole of O2. J. Chem. Education 2015, 92, 2094-2099, DOI: 10.1021/acs.jchemed.5b00333


