

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

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Dedicated to the 80th anniversary of Professor Lachezar Petrov, DSc,
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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.

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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.

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