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CO-induced segregation as an efficient tool to control the surface composition and catalytic performance of $PdAg_3/Al_2O_3$ catalyst

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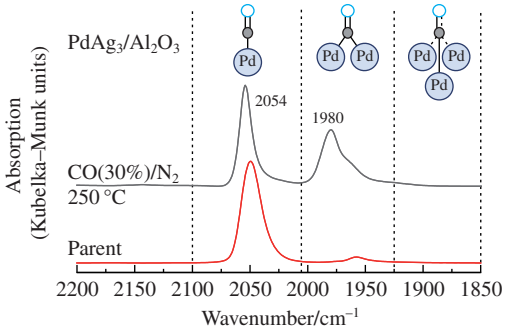
A treatment of $PdAg_3/Al_2O_3$ catalyst with CO at 250 °C enhanced its activity towards the selective C_2H_2 hydrogenation without any noticeable losses of C_2H_4 selectivity. The CO-DRIFTS and XPS data acquired *in situ* have indicated that the observed effect arises from Pd surface segregation induced by the CO adsorption and partial transformation of isolated surface Pd_1 active sites into Pd_2 dimers. The catalytic performance of $PdAg_3/Al_2O_3$ was found to be similar or even better as compared to the best reported catalysts.



A selective removal of trace amounts of acetylene impurities in the ethylene feed is an important step in the industrial production of polyethylene.[1,2] Supported palladium-based bimetallic catalytic systems possess a high activity in the selective hydrogenation of acetylenic bonds, showing improved selectivity and resistance to coke formation.[3–5] Thus, the surface structure of bimetallic nanoparticles is currently of considerable interest since it is crucial for their catalytic performance and the development of specific methods to control the structure of surface active sites.[6]

An adsorption-induced segregation may be a convenient technique to tune the surface structure of bi- and polymetallic catalytic systems. The segregation phenomenon arises from the difference in the atomic sizes and surface energies of constituent elements, which causes a preferential migration to the surface of the components characterized by a lower surface energy.[7] The adsorbtion-induced segregation, wherein one metal binds to an adsorbate more strongly than the other one, occurs under the influence of different adsorbate molecules (O_2, CO, NO, carbohydrate species, *etc.*). In the case of metal surfaces, CO is one of the most common adsorbates, and its adsorption strength varies appreciably from one metal to another.[8] This segregation is applied in both theoretical and experimental investigations of bimetallic compounds such as Pd–Au,[9–11] Cu–Ni,[12] and Pt–Cu.[13] Impressive results were achieved for Pd–Cu systems with different Pd/Cu ratios.[14] FTIR-CO data indicated an increase in the Pd surface concentration, which might proceed in two steps. Thus, the segregation increases the concentration of isolated surface Pd_1 sites and is followed by the formation of Pd–Pd dimers. This process also depends on the Cu/Pd ratio. An existing correlation of catalyst activity/selectivity for the acetylene hydrogenation with a surface composition indicated that the increased surface concentration of isolated surface Pd_1 sites could enhance the activity in the selective acetylene hydrogenation without sacrificing the selectivity.[14]

The structural and catalytic properties of bimetallic palladium–silver phases are similar to those of Pd–Cu systems.[15] Thus, the Pd–Ag bimetallic composition is an effecient catalyst for the selective hydrogenation of terminal and internal alkynes.[16] Numerous reports have been dedicated to the design of these catalysts as highly selective systems for the purification of ethylene streams produced from naphtha cracking.[17–21] Our previous works have also confirmed the efficiency of Pd–Ag catalysts towards the selective liquid-phase hydrogenation of phenylacetylene and diphenylacetylene.[22,23] It is remarkable that Pd–Ag alloy is capable of forming isolated Pd_1 sites on its surface, which provides the superior alkene selectivity and stability.[24,25] The single-atom structure, where Pd atoms are separated from each other by atoms of other (usually inactive) metal, can be obtained *via* a simple method of the incipient wetness co-impregnation.[26,27]

Many theoretical and experimental studies explored the stability of Pd–Ag systems and changes in their surface characteristics as a response to the treatment with various adsorbates (O_2, CO, and C_2H_2).[28,29] However, spectroscopic and catalytic investigations into the controlled modification of the catalytic properties of Pd–Ag alloys are still limited. The possibility to tune their catalytic performance in the selective hydrogenation of acetylene *via*

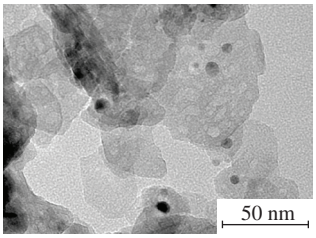


Figure 1 TEM image of $PdAg_3/Al_2O_3$ catalyst.

CO-induced segregation has earlier been demonstrated for Pd–Cu systems,[14] however such data on Pd–Ag catalysts are absent. The present work was aimed at the investigation of opportunity to control the surface structure of Pd–Ag bimetallic system *via* the approach of CO-induced segregation, thus tailoring its catalytic performance. We have employed CO-DRIFTS and XPS techniques in order to correlate the spectroscopic and catalytic characteristics of the $PdAg_3/Al_2O_3$ catalyst (the Ag : Pd molar ratio was 3 : 1)† and to acquire a detailed information on its surface structure and usability in the gas-phase selective hydrogenation of C_2H_2.

A representative TEM micrograph of $PdAg_3/Al_2O_3$ catalyst reduced under H_2/Ar flow revealed the presence of contrast virtually spherical cubo-octahedral particles (Figure 1). The mean diameters of nanoparticles are in the range of 5–8 nm. After the treatment with CO, there were no significant detectable changes in the particle sizes.

Figure 2 shows the DRIFT spectra of CO adsorbed on the surface of $PdAg_3/Al_2O_3$ sample after its reduction with H_2 and treatment with CO at elevated temperatures. Three types of CO adsorption on the surface of monometallic palladium are known: the linear-bound (2200–2000 cm^{-1}), bridged (2000–1900 cm^{-1}) and hollow (~1900–1800 cm^{-1}) forms of CO.[30] We have previously demonstrated[31] that the addition of silver to a Pd/Al_2O_3 sample leads to a drastic increase in the proportion of linear-bound CO relative to the multiple-coordinated forms due to the formation of bimetallic PdAg solid solution. As one can see from Figure 2, the spectrum of freshly reduced $PdAg_3/Al_2O_3$ catalyst (curve *1*) contains only one intense absorption band (maximum at 2050 cm^{-1}) corresponding to the linear-bound CO. The almost total absence of any absorption bands at 2000–1800 cm^{-1} indicates the formation of ordered 'single-atom' structure, wherein the each Pd atom is exclusively surrounded by atoms of the other metal.[31–33]

The treatment of $PdAg_3/Al_2O_3$ sample under CO(30%)/N_2 flow at the elevated temperature (250 °C) led to an appearance of another absorption band (the maximum at 1980 cm^{-1} and shoulder at ~1964 cm^{-1}). This signal corresponds to the bridged CO, suggesting that neighboring Pd–Pd pairs ('palladium dimers') have been formed on the surface upon the treatment with CO. The formation of strong Pd–CO bonds leads presumably to the surface segregation of Pd atoms and transformation of isolated Pd_1 sites into polyatomic Pd_n centers.[14] On the other hand, there is no adsorption band observed at a wavenumber lower than 1920 cm^{-1}, which suggests the absence of 3-fold-hollow form of bonded CO. This indicates that the formation of large palladium ensembles (Pd_n, where $n > 2$) is not favorable under these conditions.

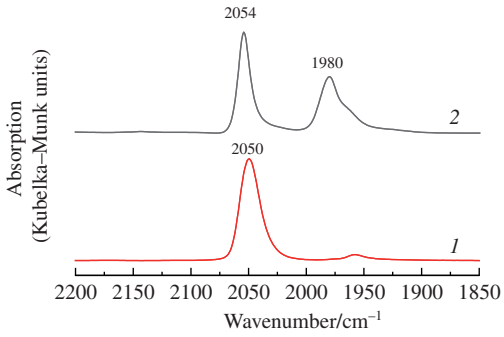


Figure 2 CO-DRIFT spectra of (*1*) freshly reduced and (*2*) CO-treated $PdAg_3/Al_2O_3$ catalyst.

† According to the ICP-AES data, the synthesized catalyst contained 2.1 and 6.3 wt% of Pd and Ag, respectively. The inductively coupled plasma atomic emission spectra were recorded on a Baird Plasma Spectrovac PS-6 instrument.

Table 1 XPS data for the freshly reduced and CO-treated $PdAg_3/Al_2O_3$ catalysts.

Treatment	$I_{Pd\ MVV}/I_{Ag\ MVV}$	Treatment	$I_{Pd\ MVV}/I_{Ag\ MVV}$
H_2, 300 mbar, 450 °C	0.36	CO, 130 mbar, 100 °C	0.40
CO, 130 mbar, 20 °C	0.40	CO, 130 mbar, 200 °C	0.41

An enrichment of the surface with Pd was confirmed by XPS data. Integral intensities of the Auger lines of silver and palladium (Ag MNN and Pd MNN, respectively) were employed for the estimation of redistribution of atoms on the surface of bimetallic particles due to a higher surface sensitivity as compared to intensities of the core levels (Ag 3*d* and Pd 3*d*). The depth of analyses was ~2 and ~5 nm, respectively (Table 1). In the case of sample reduced under H_2 atmosphere at 450 °C, its treatment with CO even at 20 °C increased the $I_{Pd\ MVV}/I_{Ag\ MVV}$ ratio up to 0.4. The subsequent treatments with CO at 100 and 200 °C did not cause any significant changes in the ratio of intensities. Thus, the acquired XPS results allowed us to conclude that the CO-induced segregation of Pd begins at room temperature and promotes an enrichment of the surface with Pd, which is also consistent with the CO-DRIFTS data.

The catalytic performance of $PdAg_3/Al_2O_3$ was estimated in the selective gas-phase acetylene hydrogenation (Table S1, see Online Supplementary Materials). Figure 3(*a*) compares the C_2H_2 conversion as functions of temperature for freshly reduced and CO-treated catalysts. These data show clearly that the treatment with CO leads to the significantly increased catalytic activity. The full conversion of C_2H_2 was achieved at ~156 and 133 °C for the freshly reduced and CO-treated catalysts, respectively, indicating a significantly higher catalytic activity of the latter. Remarkably, the selectivity towards C_2H_4 was similar in both cases [Figure 3(*b*)]. This indicates that the activity of Pd–Ag catalyst can be improved by CO-induced segregation along with avoiding any considerable negative effects on the C_2H_4 selectivity. These results are in a good agreement with the data reported previously for Pd–Cu catalysts.[14] For instance, a $CuPd/Al_2O_3$ catalyst possessing the optimal Cu : Pd ratio (50 : 1) allows one to considerably increase the activity (20 K temperature reduction to achieve 100% conversion) using CO-induced segregation whilst only marginally affecting the C_2H_4 selectivity.

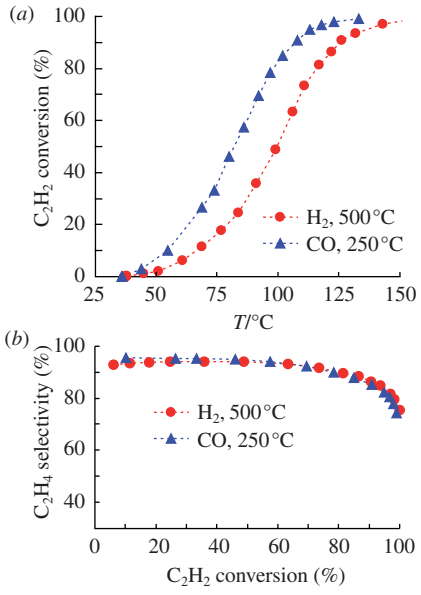


Figure 3 Catalytic performance of freshly reduced with H_2 and CO-treated $PdAg_3/Al_2O_3$ catalysts in the acetylene hydrogenation as the dependences of (*a*) C_2H_2 conversion on the reaction temperature and (*b*) C_2H_4 selectivity on the C_2H_2 conversion.

It is worth to compare the acquired catalytic data with those of the state-of-the-art materials reported on the selective C_2H_4 hydrogenation (Table S2).[26] Such a comparison has revealed that the catalytic performance of designed $PdAg_3/Al_2O_3$ is similar or even better as compared to the best known catalysts. At lower reaction temperatures (60–95 °C), all the catalysts demonstrated poorer characteristics of activity and/or selectivity in comparison with our results. The selectivity towards the C_2H_4 formation does not exceed 80% at the C_2H_2 conversion of ~90%. A higher activity observed by other authors at reaction temperatures higher (> 150 °C) than in our case results in the poorer selectivity (especially for $AuPd_{0.025}/SiO_2$ catalyst, see Table S2).

The correlation of catalytic data with the XPS and CO-DRFTS results allows us to conclude that the observed enhancement of catalytic activity arises from the enrichment of catalyst surface with Pd during the CO-induced segregation and from a partial transformation of isolated Pd_1 centers into Pd–Pd dimers (Pd_2 sites). This CO-induced segregation increases the surface concentration of Pd active sites, avoiding any formation of multinuclear Pd surface ensembles (Pd_n, $n > 2$), which are responsible for the significantly reduced C_2H_4 selectivity. The absence of multiatomic Pd_n sites was confirmed by the CO-FTIR, no CO absorption bands being observed at a wavenumber < 1920 cm^{-1} even after an extended treatment of the catalyst with CO. Therefore, the improved catalytic activity of $PdAg_3/Al_2O_3$ was attained without any noticeable losses of C_2H_4 selectivity.

In conclusion, the results presented herein and acquired in our previous work on the $PdAg_2/Al_2O_3$ catalyst in the liquid-phase hydrogenation of diphenylacetylene[22] have clearly demonstrated that the CO-induced segregation can be efficiently applied to the fine tuning of surface structure and catalytic performance of bimetallic PdAg catalysts employed in liquid- and gas-phase reactions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.023.

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