Influence of Pd-Al Bimetallic Interaction on CO Adsorption Properties of Pd/Al Systems: XPS, TDS and Static SIMS Studies

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The metal-substrate and metal-metal interactions (MSI, MMI), which play an important role in the field of heterogeneous catalysis, can affect electronic structure, morphology and surface structure of supported and/or multilayer systems as well as their adsorption properties. CO adsorption properties of Pd/Al systems have been studied using X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS) and static secondary ion mass spectroscopy (SSIMS) under UHV conditions. Measured XPS and TPD spectra were compared to the ones of clean bulk metals (Pd, Al). Pd ad-layers, prepared by vacuum evaporation onto pure Al substrate surfaces, exhibited strong interaction with Al atoms resulting in the formation of Pd-Al alloy of noble metal-like electronic structure. The shifts of Pd 3d core levels and of the Pd 4d-band centre toward higher binding energies due to formation of bimetallic bond were observed. The CO TPD spectra consisted of two desorption peaks, both lying lower than those from Pd foil, indicating a distinct weakening of the Pd-CO chemisorption bond. CO dissociation on Pd/Al surface during adsorption/desorption cycles, accompanied by the CO2, H2O and CH4 production, was observed. The CO dissociation on Pd/Al surface caused creation of chemical bonds to carbon and oxygen species, respectively, and consequently the weakening of Pd-Al bimetallic bond.

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The steadily decrease of total CO adsorption capacity of Pd/Al sample was accompanied by a production of CO₂ and H₂O as result of surface reactions: 2 CO → CO₂ + C, CO + H₂ → H₂O + C. An example of CO₂ and H₂O production as an evidence of partial CO dissociation on Pd/Al system during desorption experiment is presented in Fig. 2. Note that channel of H₂O formation on Pd/Al was more preferred. The remaining carbon poisoning the surface was partially reacted-off in the form of CH₄ molecules, as indicated by TDS. The hydrogen atoms originated probably from residual atmosphere of UHV apparatus. Similar behaviour of CO₂, H₂O and CH₄ production were observed in the case of bulk PdAl alloy surface.\textsuperscript{17}

In order to monitor surface structural changes of Pd/Al system during CO adsorption/desorption cycles, SIMS experiments followed each CO exposure and TDS measurement. Analysing obtained SIMS mass spectra, SIMS relative intensities of ionic clusters of PdAl\textsuperscript{+}, PdC\textsuperscript{+}, AlO\textsuperscript{+} and AlOH\textsuperscript{+} were plotted in Fig. 3. One can see steady increases of PdC\textsuperscript{+}, Pd\textsuperscript{+} and AlO\textsuperscript{+}/Al\textsuperscript{+} signal intensities, due to the CO dissociation activity of Pd/Al surface accompanied by a formation of chemical bonds of Pd and Al atoms to carbon and oxygen species. We observed the behaviour...
Influence of gas interaction with Pd/Al systems was investigated by means of XPS. Two similar Pd/Al systems were prepared independently into XPS, and TDS and SIMS UHV systems, respectively. After Pd deposition onto Al substrates, one of them was in situ studied by means of XPS technique. Second one, prepared into TDS and SIMS apparatus, was exposed by the air, transported to the XPS system and after ex situ characterised by XPS. The results are presented in Figs. 4 and 5, where valence bands and Pd 3d core levels structures of in situ and ex situ prepared Pd/Al systems, respectively, are compared with the ones of pure Pd foil.

In situ prepared and characterised Pd/Al sample exhibited typical shapes of bimetallic system - noble metal-like electronic structure, clearly different from that of bulk Pd. The Pd 4d-band maximum was located at 4.5 eV below the Fermi level and had a relatively narrow profile. The Pd 3d core levels shift of 1.8 eV towards higher binding energies, relative to the bulk values was observed.

Contrary, splitting of Pd 3d doublets (see Fig. 5) due to simultaneous presence of both the metal Pd and Pd-Al alloy states and/or considerable extinction of Pd-Al states were observed always after Pd/Al sample transport across the air. On the base of these results, we can conclude that gas (CO, O2,...) interaction with the Pd/Al systems tend to the important weakening and/or total breaking of the bimetallic bond.
Summary

The CO interaction with Pd/Al bimetallic systems was investigated by means of XPS, TDS and SSIMS techniques. The electronic structure of the Pd/Al was affected by the strong bimetallic bonding between Pd and Al. The weakening of CO bond to the Pd/Al alloys compared to pure Pd was observed. CO dissociation on Pd/Al surface during adsorption/desorption cycles, accompanying by the CO₂, H₂O and CH₄ production, was observed. The presence of CO on Pd/Al surface and its CO dissociation activity caused creation of chemical bonds to carbon and oxygen species, respectively, and consequently weakening of Pd-Al bimetallic bond.

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References