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Hydrogenation of acetylene into ethane–ethene mixtures over modified Pd–alumina catalysts

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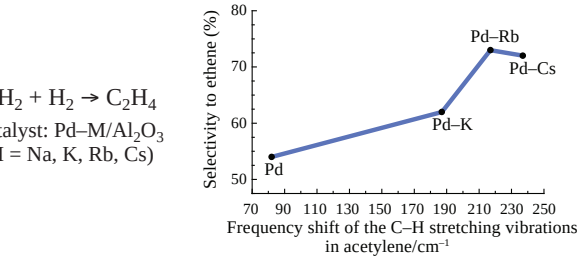
The diffuse-reflectance IR spectroscopic data using acetylene as a probe molecule showed the strengthening of basic properties of γ-Al_2O_3 modified with alkali metals in the sequence Al_2O_3 < Na/Al_2O_3 < K/Al_2O_3 < Rb/Al_2O_3 < Cs/Al_2O_3. The increase in the basicity of the support of Pd–alumina catalysts had a positive effect on the ethene selectivity in hydrogenation of acetylene in an ethane–ethene mixture.



Keywords: acetylene, ethene, hydrogenation, palladium, modification of the support, diffuse reflectance FTIR spectroscopy, DRIFT, acid–base properties.

The process of selective hydrogenation of acetylenic and dienic hydrocarbons is of significant industrial importance. The light olefins C_2 and C_3 containing up to a few percent of acetylenes are usually produced by steam cracking of naphtha or liquefied petroleum gas. The presence of even trace amounts of acetylene in ethylene deteriorates the properties of the polymers produced from these olefinic materials. The fine purification of ethane–ethene mixtures from acetylene in the industrial scale is achieved by catalytic hydrogenation on supported Pd catalysts. Some excellent reviews on this topic (hydrogenation of acetylene in ethene-rich streams) have been published in the last 15 years.[1–5] The effect of promoters and additives on the activity and selectivity of Pd-containing catalysts was considered. The mechanisms of acetylene hydrogenation were proposed on the basis of concise physicochemical studies.[1,6] Over the last decade, this hydrogenation process has become a starting point for the study of semi-hydrogenation of more complex molecules containing C≡C triple bonds[7] (for example, arylacetylenes[8,9]). Normally, supported Pd-containing catalysts for selective hydrogenation are not employed without any promoter, namely, metals of group IB (Cu, Ag, Au), *sp* metals and semi-metals (Pb, Sn, Bi, Ga) are used most often.[10] The most studied bimetallic catalysts for selective alkyne hydrogenation are PdAg/Al_2O_3 compositions used industrially since 1980s.[5,10] Alkali metals have been proposed as promoters in selective hydrogenation catalysts in a number of patents.[11–13] At the same time, only a few reports of potassium-promoted catalysts were published.[14–16] The promoting effect of potassium manifested as an increase in the rate of acetylene hydrogenation and ethene selectivity was attributed to the electron transfer from the modified support to Pd.[15] The support could play an important role in the catalytic performance for achieving the high conversion and better selectivity to the desired products.[5] Nevertheless, there is no clear understanding of the role of acid–base properties of the oxide supports on the activity and selectivity of the relevant Pd catalysts in partial hydrogenation of acetylene.

The goal of this work was to study the dependence of the catalytic properties of Pd–alumina catalysts[†] modified with alkali metal salts in selective hydrogenation of acetylene in ethane–ethene mixtures on the basicity of the support. Alumina modified with alkali metals was prepared by calcination of Al_2O_3 impregnated with carbonates of Na, K, and Cs and nitrate of Rb at 500 °C. According to published data on the example of K/Al_2O_3, the interaction of the alkali metal (potassium) species with a support proceeds as follows.[18–20] Initially hydroxyaluminocarbonate $KAl(OH)_2CO_3$ is formed by the reaction between potassium carbonate and the alumina support. Further hydroxyaluminocarbonate decomposes to a mixed oxide of aluminum and potassium ($KAlO_2$ or spinel $K_2Al_2O_4$). The latter process occurs at temperatures below 500 °C . Also the formation of Al–O–K groups takes place as a result of replacement of isolated hydroxyl groups with K^+ ions[19,20] or/and as interaction of K_2O formed by K_2CO_3 decomposition (possible only at a higher temperature) with the support.[18] Alumina modified with other alkali metals is less studied,[20] but it can be assumed that the transformations are similar.

[†] The γ-Al_2O_3 support (S_{BET} of 220 m^2 g^{-1}) was used both in the unmodified form and after modification with carbonates or nitrates of alkali metals. Spherical alumina granules of 3–5 mm were crushed, and a fraction with a particle size of 0.25–0.5 mm was selected. Further the alumina was calcined in a flow of dry air at 500 °C. Alkaline additives (10 wt%) were introduced by incipient wetness impregnation from aqueous solutions of Na_2CO_3, K_2CO_3, $RbNO_3$ and Cs_2CO_3 (Aldrich, 99.9%). The impregnated samples were dried at 120 °C and annealed in a flow of dry air at 500 °C for 2 h. Palladium was further introduced by incipient wetness impregnation using an aqueous solution of H_2PdCl_4. The content of palladium in the samples was 0.04 wt%. Allyl alcohol was used as a reducing agent.[17]

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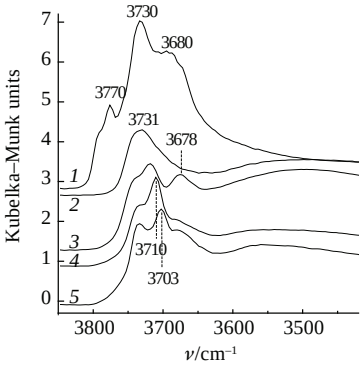


Figure 1 DRIFT spectra of OH groups of alumina carriers: (*1*) Al_2O_3, (*2*) Na/Al_2O_3, (*3*) K/Al_2O_3, (*4*) Rb/Al_2O_3 and (*5*) Cs/Al_2O_3.

Acid–base properties of the starting γ-Al_2O_3 support and the carriers modified with alkaline additives were studied by diffuse-reflectance FTIR spectroscopy (DRIFT).‡ The IR spectrum of the initial Al_2O_3 (Figure 1) exhibits absorption bands at 3770, 3730 and 3680 cm^{-1} in the region of stretching vibrations of OH groups. They belong to terminal and bridged OH groups containing 1, 2 and 3 Al atoms in their structure, respectively.[21] Introduction of alkali cations results in the changes of the spectral pattern. The terminal OH groups (3770 cm^{-1}) vanish and the intensities of the bands of the bridged OH groups (3730 and 3680 cm^{-1}) decrease. Simultaneously new OH groups appear with the O–H stretching frequencies 3703 (Cs), 3710 (Rb), 3717 (K) and 3731 cm^{-1} (Na). The positions of the bands at 3731 cm^{-1} for Na/Al_2O_3 and at 3717 cm^{-1} for K/Al_2O_3 are similar to previously reported for Na- and K-added Al_2O_3.[22–24]

It was shown[25,26] that acetylene having a weakly acidic proton can be used as a suitable IR probe molecule to study the basicity of oxides. The positions of the C–H bond stretching vibrations in weakly adsorbed complexes and C≡C bond stretching vibrations in strongly adsorbed π-complexes can be used for the characterization of oxide basicity and presence of coordinating metal ions. The information on the basicity of oxides was obtained at an acetylene pressure of 20 Torr. Upon acetylene adsorption on the modified γ-Al_2O_3 (Figure 2), adsorption complexes formed are characterized by the C–H stretching vibrations at 3200–3000 cm^{-1} and C≡C stretching vibrations at 1940 cm^{-1}, they are destroyed by evacuation of the samples. The shift of the frequency of the C–H stretching vibrations towards lower frequencies (relative to the frequency of 3287 cm^{-1} in the gas phase) provides evidence for the

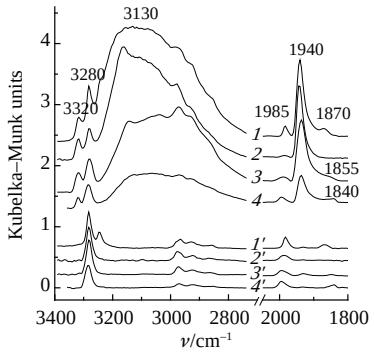


Figure 2 DRIFT spectra of acetylene adsorbed on modified alumina carriers: (*1*) Na/Al_2O_3, (*2*) K/Al_2O_3, (*3*) Rb/Al_2O_3 and (*4*) Cs/Al_2O_3; at 20 Torr and after evacuation at room temperature for 15 min (*1′*–*4′*).

‡ The spectra were recorded at room temperature using a Nicolet Protégé 460 spectrometer supplied with a diffuse-reflectance unit in the frequency range of 6000–1500 cm^{-1} at the resolution of 4 cm^{-1}. Before the spectroscopic measurements the samples were evacuated at 500 °C for 2 h, the heating rate was 10 K min^{-1}. Adsorption of acetylene was performed at room temperature and partial acetylene pressure of 20 Torr.

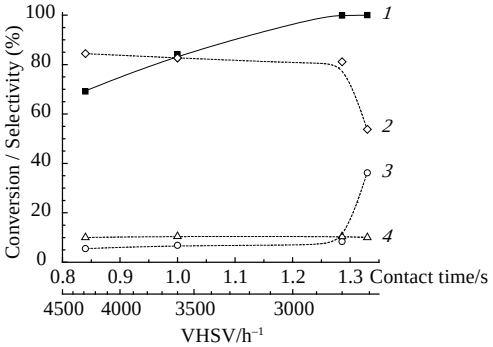
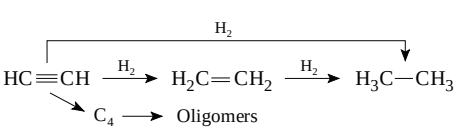


Figure 3 (*1*) Acetylene conversion and selectivities to (*2*) C_2H_4, (*3*) C_2H_6 and (*4*) C_4 in hydrogenation of acetylene into the ethane–ethene mixture on Pd/γ-Al_2O_3.

progressive strengthening of basic properties of the carrier in passing from Na to Cs. The bands at 3320 cm^{-1} can be associated with the stretching vibrations of the C–H bond as a result of strong polarization of the adsorbed acetylene molecules. Several other adsorption complexes are observed with absorption bands at 3280, 1985 and 1850–1870 cm^{-1}. The bands at 3280 and 1985 cm^{-1} are attributed to a complex formed due to dissociative adsorption of acetylene on low-coordinated centers Al^{3+}–O^{2-}.[26] The bands at 1870 cm^{-1} (Na/Al_2O_3), 1855 cm^{-1} (Rb/Al_2O_3), 1840 cm^{-1} (Cs/Al_2O_3) can be assigned to acetylenides formed *via* interaction with alkali cations,[27] as far as such bands are not observed in the IR spectrum of acetylene adsorbed on Al_2O_3. The position of the broad band at about 3160–3050 cm^{-1} assigned to the C–H bond forming a hydrogen bond with surface oxygen species, which act as rather strong Lewis basic sites, is shifted from 3130 cm^{-1} in the case of Na-modified Al_2O_3 to 3100 cm^{-1} (modified with K), 3070 cm^{-1} (Rb/Al_2O_3) and finally to 3050 cm^{-1} (Cs/Al_2O_3). This shift reflects the strengthening of the basicity of the carriers from the Na-modified support to the Cs-modified carrier. The same band of C–H bond vibrations of acetylene adsorbed on Al_2O_3 was observed at 3205 cm^{-1} indicating weaker basic properties of unmodified alumina.[26] Thus, modification of γ-Al_2O_3 with alkali cations results in strengthening of basic properties in the order: $Al_2O_3 < Na/Al_2O_3 < K/Al_2O_3 < Rb/Al_2O_3 < Cs/Al_2O_3$.

The activity and selectivity of prepared Pd–alumina catalysts in selective hydrogenation of acetylene into ethane–ethene mixture were estimated in a flow-type fixed-bed quartz reactor at an atmospheric pressure and temperature of 80 °C.§ The overall process can be represented as outlined in Scheme 1.

Acetylene in an access of hydrogen is converted into ethene and ethane as main products. The final hydrogenation product, ethane, is supposed to be formed either as a result of the consecutive conversion of acetylene first into ethene then into ethane or straightforward hydrogenation of acetylene. In parallel with the main process, oligomerization of acetylene and/or ethene producing the so-called 'green' oil (C_{4+} oligomers)



Scheme 1

§ Reaction conditions: 80 °C, 1 atm, the volume hourly space velocity (VHSV) of 1000–4300 h^{-1}. The composition of the feed mixture was as follows: ethane (0.48 vol%), ethene (4.94 vol%), acetylene (1.25 vol%), hydrogen (2.5 vol%), the balance was He. The catalyst loading was 0.5 ml. Prior to the catalytic test, the catalysts were activated in a flow of dry hydrogen at 150 °C for 1 h. Analysis of products was performed by a gas chromatography equipped with FID using a packed column filled with $NaHCO_3/\gamma$-Al_2O_3.

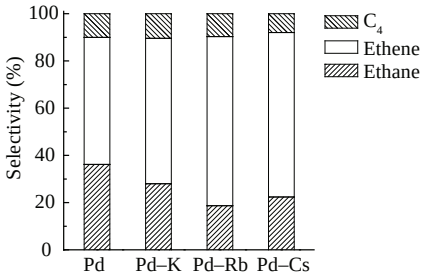


Figure 4 The selectivity to products in hydrogenation of acetylene into ethane–ethene mixture at 100% acetylene conversion on Pd/Al_2O_3, Pd–K/Al_2O_3, Pd–Rb/Al_2O_3 and Pd–Cs/Al_2O_3 catalysts.

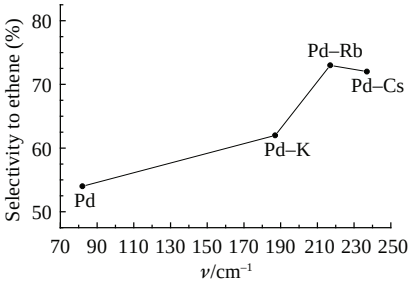


Figure 5 Dependence of the selectivity to ethene as a function of the support basicity of Pd/Al_2O_3, Pd–K/Al_2O_3, Pd–Rb/Al_2O_3 and Pd–Cs/Al_2O_3 catalysts determined as the frequency shift ν of the C–H stretching vibrations in the acetylene molecule.

occurs. The oligomers are strongly adsorbed on the catalyst surface and deactivate the catalyst.

The typical dependences observed in acetylene conversion in an ethane–ethene mixture on Pd catalysts are shown in Figure 3. The acetylene conversion in an access of ethene does not result in the consumption of the latter until the complete conversion of acetylene is observed. At a 100% acetylene conversion, an abrupt decrease of the yield of the target product, ethene, occurs as a result of its hydrogenation into ethane. The fraction of acetylene converted into C_4 hydrocarbons remains constant in the entire range of space velocities and is about 10% on Pd/Al_2O_3. These peculiarities are observed for all the studied catalytic systems.

The data on the selectivity to products over different modified catalysts in acetylene conversion are presented in Figure 4. These results correspond to a 100% conversion of acetylene.[¶] The Pd–Na/Al_2O_3 catalyst is not considered since the maximum conversion on it was only 70%. Hydrogenation of ethene to ethane as well as the formation of C_4 hydrocarbons are undesirable reactions reducing the selectivity of the process. One of the key tasks in design of an effective catalyst for the hydrogenation of acetylene is to achieve the highest selectivity to ethene formation at the complete conversion of acetylene. The lowest selectivity towards acetylene hydrogenation into ethene is found for the monometallic Pd/Al_2O_3. A noticeable change of the selectivity to ethene is observed for the catalysts modified with alkali metal cations. The spectroscopic data show that modification of the alumina carrier with alkali cations results in strengthening of the basicity of the catalyst from Na to K, Rb, and then Cs. It can be assumed that this increase in the basicity leads to the formation of partially negatively charged palladium particles[28] that are characterized by better hydrogen adsorption, including dissociative adsorption. Figure 5 depicts the dependence of the selectivity towards ethene as a function of the frequency shift of the stretching vibrations of the C–H bond in the acetylene molecule reflecting the strengthening of the basicity of the carrier. It is seen from this figure that the increase in the basicity of the support affects the selectivity to the target product in a positive manner. Also the lower selectivity to C_{4+} products on K, Rb and Cs-modified Pd–alumina catalysts (see Figure 4) compared to the monometallic system can be explained by suppressed acidity of the support, since C_{4+} oligomer products are known to be formed with participation of acid sites of the carrier.[3,5]

In conclusion, modification of Pd–alumina catalysts with alkaline additives produces a positive effect on ethene selectivity in acetylene hydrogenation in ethane–ethene mixtures. Nevertheless, the herein synthesized catalysts cannot be considered as competitors to the most active industrial bimetallic PdAg catalysts. More investigations of alkali metals as promoters to catalysts of semi-hydrogenation of acetylene in an ethene-rich stream are necessary, including optimization of the alkali metal loading and the effect of alkaline promotion on the activity, selectivity and long-term stability of catalysts (mono- and bimetallic) under more realistic industrial conditions.

[¶] Catalytic tests were carried out with a decrease in VHSV from 4300 to 1000 h^{-1}. The values of VHSV at a 100% conversion of acetylene were as follows: 2700 h^{-1} on Pd/Al_2O_3, 1600 h^{-1} on Pd–K/Al_2O_3, 1000 h^{-1} on Pd–Rb/Al_2O_3 and 2300 h^{-1} on Pd–Cs/Al_2O_3.

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