

Pd-Zn Containing Catalysts for Ethanol Conversion Towards Hydrocarbons

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Development of the alternative hydrocarbon fuel sources is an urgent task in the current energy field. Ethanol can be considered as alternative basis for hydrocarbon fuel production. In this work we studied ethanol conversion into alkanes-olefines and alkane-aromatic hydrocarbons over palladium and zinc containing catalysts supported on alumina or MFI/alumina and mentioned catalysts structure, to give a reasonable explanation of the catalysts action mechanism. The catalyst based on MFI/alumina showed high stability to coking and stable productivity for over 48 hours. The total yield of the target fraction of C₃-C₁₂ hydrocarbons achieves 95 wt.% based on carbon. Among the obtained alkanes branched structures predominate.

1. Introduction

Currently the annual ethanol production is over 80 billion liters and up to 160 billion liters is expected in close time as Demirbas (2008) has reported. Hence, great amount of manufactured ethanol can be considered as alternative basis for hydrocarbon fuel production. The reaction in focus is the ethanol conversion into hydrocarbons. Over the last few years, some features of this reaction were studied and reported by Karim et al. (2006). The reaction is efficiently catalyzed by metal nanoparticles supported on acidic γ -alumina. Pd-Zn catalytic systems are well-known as polyfunctional catalysts for steam conversion of methanol (Fukuhara et al., 2007), selective acetylene hydrogenation into ethylene for polyethylene production (Mashkovskii et al., 2009) etc. In many cases, there was direct evidence that nano-sized PdZn alloy formation was responsible for the unique catalytic properties: activity and selectivity (Dagle, 2007). Thus the goal of this work is to investigate the Pd-Zn systems behavior in the mentioned reaction, to observe corresponding structural changes and to give a reasonable explanation of the catalysts deactivation mechanism.

2. Experimental

We used pilot samples of Pd-Zn/MFI/alumina catalyst containing 0.6 wt.% Pd and 1 wt.% Zn; Si/Al ratio was 30 (Slivinskiy et al., 2003). The Pd-Zn/ γ -alumina catalyst was prepared by impregnation of technical γ -alumina with methanol solution of Pd(μ -OOCMe)₄Zn(OH₂) complex (Kozitsyna et al., 2006). Sample contained 0.7 wt% Pd and 0.4 wt% Zn. After impregnation sample was calcined at 500°C in Ar atmosphere for 5 hours and then activated at 450°C in H₂ flow for 10 hours. Both gaseous and liquid organic products in aqueous and organic phases were identified by GC-MS. The charge state and the local structure of metal-containing active components were investigated by XAFS spectroscopy and XRD analysis at the Structural Materials Science end-station of the National Research Centre "Kurchatov Institute" (Chernyshov et al., 2009).

3. Results and Discussion

In the presence of the studied PdZn catalysts supported on $\gamma\text{-Al}_2\text{O}_3$, ethanol converted to alkanes and olefins up to C₈, carbon oxides, liquid oxygenates and water (Figure 1, 3). It was found that the maximum yield of aliphatic hydrocarbons C₃-C₈ fraction about 50 wt.% was achieved over catalysis PdZn - containing system obtained by the impregnation of a bimetallic complex PdZn(OAc)₄•H₂O on $\gamma\text{-Al}_2\text{O}_3$. When using monometallic systems containing Pd and Zn, with a concentration of the active ingredients equivalent concentration in a bimetallic system (0.6 wt.%Pd and 0.4 wt.% Zn), the desired fraction yield reduced down 25% and 10% respectively (Figure 1).

Among the reaction products of ethanol conversion over Pd-catalyst alkanes dominated, while at the Zn-containing catalyst aim fraction consists of 70% of the olefins and only 30% of alkanes (Figure 1). In case of Pd-Zn catalyst (prepared from bimetallic complex) one may observe that total yield of aim fraction increased in comparison with monometallic catalysts and ratio alkanes/olefins close to 45/55. Obtained data allow to suggest a co-catalytic effect of Pd and Zn. Comparison of Pd-Zn catalyst based on bimetallic complex with one based on monometallic Pd and Zn acetates showed the aim fraction of hydrocarbons to be higher in case of catalyst prepared from bimetallic complex. The reason of the phenomena might be short distances between Pd and Zn in Pd($\mu\text{-OOCMe}$)₄Zn(OH₂) complex that are similar to sum of metals atomic radiuses. These interatomic distances stay constant after complex impregnation and calcinations of catalyst.

Application of Pd-Zn/MFI/ γ -alumina catalyst in the same reaction leads to almost exhaustive conversion of ethanol to C₃₊ products. The catalyst showed a significant increase in the yield of the hydrocarbon fraction. The main products in this case are alkanes and aromatics. Hydrocarbons yield achieved 95 wt.% calculated on the carbon converted ethanol (Fig. 1, 2). A large amount of aromatic compounds in products can be explained by the hydrocarbon pool mechanism of the ethanol conversion over MFI-type catalyst in the Ethanol-to-gasoline and Ethanol-to-hydrocarbons processes (Johansson et al., 2009). Life test showed Pd-Zn/MFI/ γ -alumina stable works during 50 hours on stream (Fig. 4). Found that only γ -alumina based catalysts have very short lifetime. The activity drops down by an order of magnitude after only 3 hours of operation. To explain this difference one should use structural data concerning with genesis of Pd-Zn species.

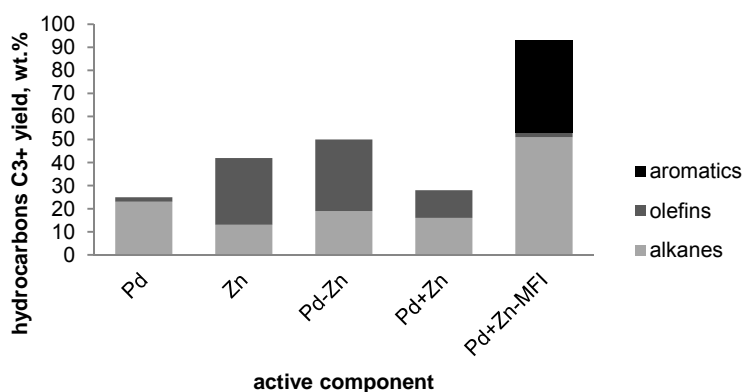


Figure1: Fraction of C₃₊ hydrocarbons yield during ethanol conversion over PdZn containing catalysts* supported on $\gamma\text{-Al}_2\text{O}_3$ and MFI/ $\gamma\text{-Al}_2\text{O}_3$.

* - "Pd-Zn" – catalyst modified with bimetallic complex Pd($\mu\text{-OOCMe}$)₄Zn(OH₂); "Pd+Zn" – catalyst modified with monometallic complexes.

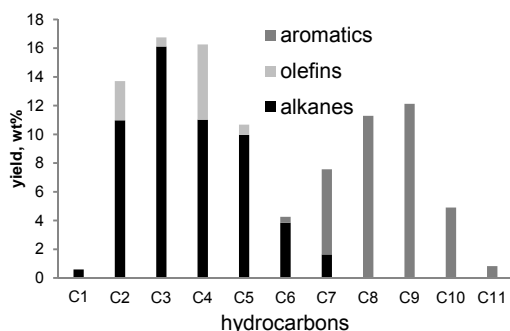


Figure 2: Composition of C₃-C₁₁ hydrocarbons fraction obtained during ethanol conversion over Pd+Zn/MFI/γ-Al₂O₃ catalyst.

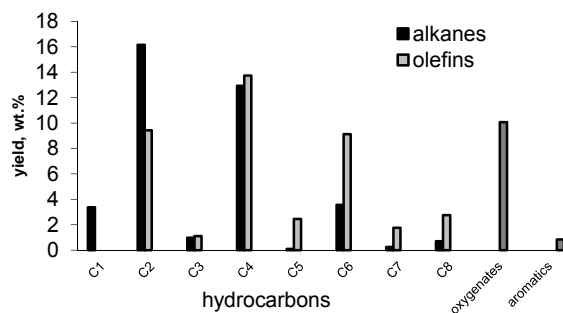


Figure 3: Composition of C₃-C₁₁ hydrocarbons fraction obtained during ethanol conversion over Pd-Zn/γ-Al₂O₃ catalyst.

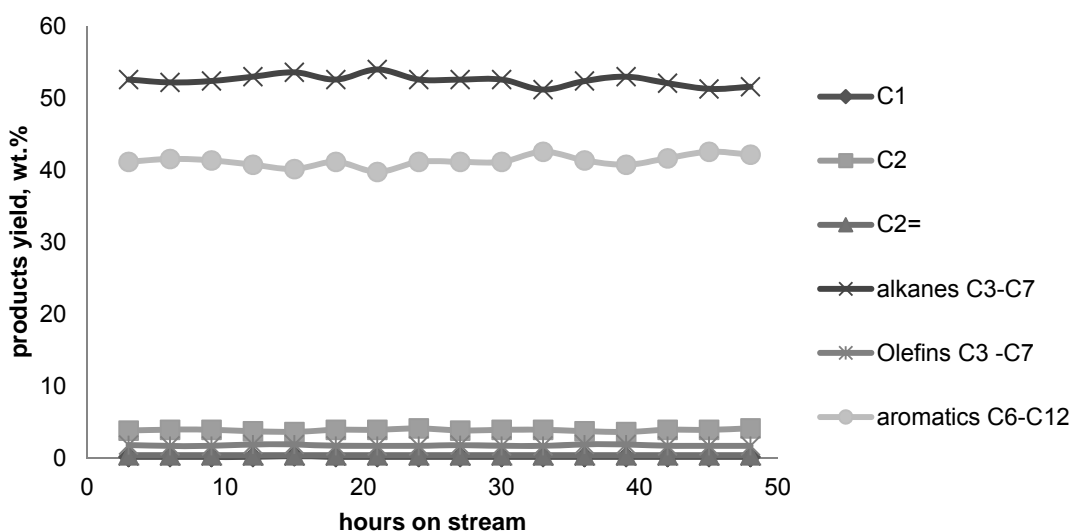


Figure 4: Hydrocarbons yield obtained during ethanol conversion over Pd+Zn/MFI/γ-Al₂O₃ catalyst.

Structural properties of the materials under study were investigated by XRD (Figure 5) and XAFS (Figure 6) techniques. XANES spectra obtained for the initial PdZn/MFI/γ-alumina and PdZn/γ-alumina catalysts showed that palladium is presented as PdO phase (Figure 6), while the zinc state can be described as a mixture of bulk ZnO and ZnO dissolved in the γ-alumina binder. Most probable, distorted structure of the spinel type is formed. The FTs derived from EXAFS spectra show that Zn has the oxygen environment but no distinct second metal-metal sphere is observed that is indicative of poor short-range ordering (Figure 6).

Both catalysts undergo significant structural changes during and after the catalytic experiment. In particular, Pd (II) turns into Pd (0), which is manifested in a characteristic energy shift of the absorption edge in the XANES spectrum (Fig. 6). Noteworthy, the general shape of the XANES curve gives evidence that Pd is not in the pure metallic state but rather forms a solid substitution alloy, in which Pd atoms are statistically replaced with Zn. Metallic Pd phase has the (111) reflection at 40.1°. Since the atomic radius of zinc is close to palladium (0.135 and 0.140 nm, respectively) (Slater, 1964), the formation of such substitution alloy should cause contraction of the lattice and a shift in the diffraction peak position toward higher angles. The XRD pattern of the catalyst after the experiment contains a peak at 41.4° that better corresponds to PdZn alloy rather than to Pd in the pure metallic state (Figure 5).

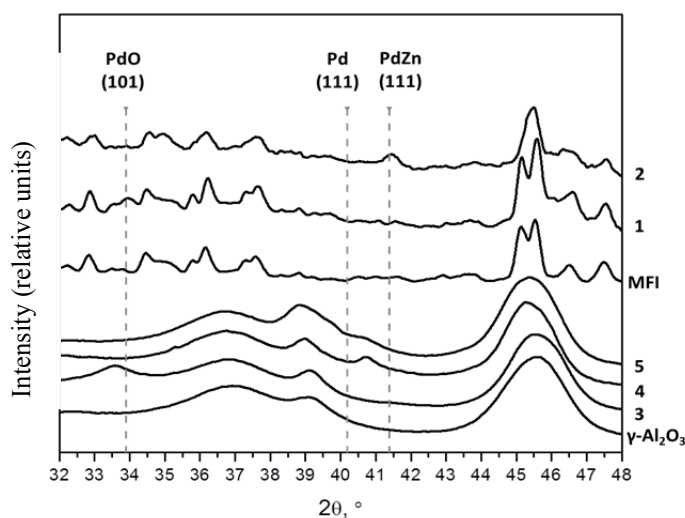


Figure 5: Diffractograms of PdZn catalytic systems.

* - Data are presented for the initial (1) and after catalytic tests (2) PdZn/MFI/ γ -alumina catalyst, and for the original (3), reduced (4) and after catalytic tests (5) PdZn/MFI/ γ -alumina catalyst.

** - For comparison, the diffractograms of supports are presented.

EXAFS data measured at the Pd K-edge (Figure 6) further confirms the formation of PdZn alloy on the surface of both catalysts. It should be noted that X-ray absorption spectroscopy techniques are integral and can detect only averaged state of an element in a sample. Thus, it is difficult to distinguish the contribution of alloy phase against the background of ZnO, because the content of mixed ZnO + Al₂O₃ phase significantly exceeds that of the PdZn alloy phase. However, XANES data measured at the Zn K-edge for the PdZn/MFI/ γ -Al₂O₃ catalyst after the experiment (Figure 6) make it possible to distinguish the characteristic inflection corresponding to the partial reduction of zinc.

TEM images (Figure 7) give some visual representation of the problem in focus. It is not easy to compare structure in PdZn/alumina and PdZn/MFI/alumina because of their different origin. But some patterns can be revealed. The alloy particles in PdZn/alumina catalyst after reduction (Fig. 7) have broader size distribution and less zinc content (Pd/Zn ratio is approximately 1:0.6) due to partial zinc migration into the vacant alumina structure. While the alloy particles in PdZn/MFI/alumina catalyst have Pd/Zn ratio equal to 1 and smaller size (Fig. 7). The larger zinc content in the bulk material gives more stable structure and composition. Zinc in its oxide form can act like glue to the PdZn alloy nanoparticles stopping aggregation process.

Comparing XRD data for both catalysts after reaction (Figure 5) one can observe the main difference between them in the 39-41° region where (111) plane reflection of Pd takes place. While PdZn/MFI/ γ -Al₂O₃ has a smaller lattice parameter for the PdZn alloy than in the bulk Pd and peak position at 41.4° the PdZn/ γ -alumina catalyst has a larger lattice parameter and corresponding peak position at 39°. This can be explained by expanding of the Pd lattice due to intercalation of light elements that have high diffusion probabilities. There are two phases that can have such a structure: palladium hydride (Grunwaldt et al., 2006) and palladium carbide (Tew et al., 2011). The palladium hydride phase is only stable in hydrogen atmosphere (Grunwaldt et al., 2006). Thus, most probably the diffraction peak indicates Pd carbide formation. This can explain low operation stability of the PdZn/ γ -alumina catalyst.

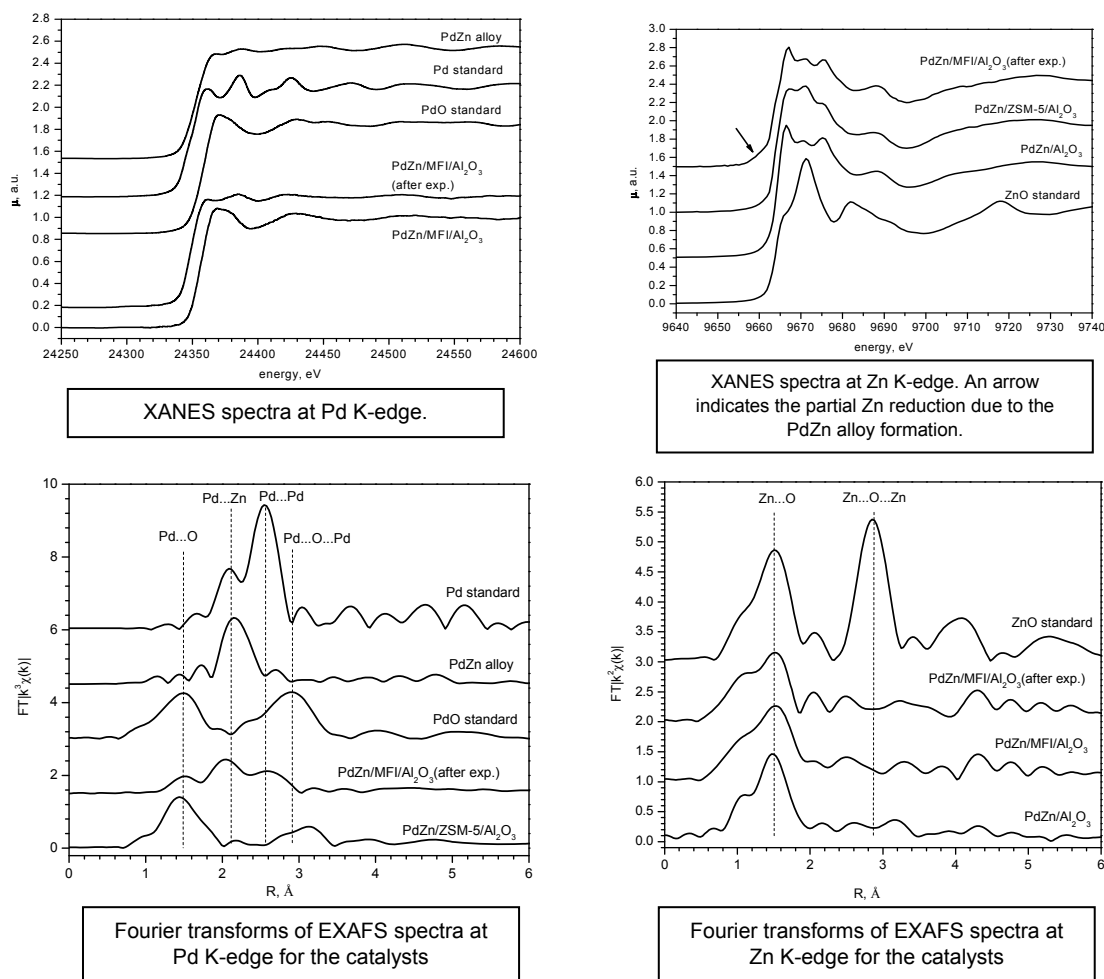


Figure 6: XANES and EXAFS data for PdZn catalysts

* - For comparison spectra for some reference systems are presented.

** - The arrow shows a partial recovery of zinc to nulvalentnogo condition associated with the formation of the alloy.

Conclusions

The regularities of ethanol conversion towards hydrocarbons over PdZn containing catalysts were investigated. Our study showed that the selectivity of alcohols conversion into aliphatic hydrocarbons depends on the structure of catalyst precursor, supports nature and the topology and size factor of the active components. Found that in a hydrogen atmosphere during pretreatment nanoparticles of PdZn alloy were forming on the catalysts surface. During thermal treatments Zn partially migrates into the support phase resulting in zinc-aluminum spinel formation. This process is much more pronounced in PdZn/Al₂O₃ catalyst. This leads to the formation of alloy particles depleted with zinc of composition PdZn_{0.6}, while in PdZn/MFI/Al₂O₃ catalyst composition characterized by the ratio of Pd and Zn as 1:1. PdZn/Al₂O₃ selectivity after a few experiments in the ethanol conversion reaction to hydrocarbons got similar to one over the Pd/Al₂O₃ catalyst. This fact shows that the selectivity of the process depends on the zinc content in the alloy.

PdZn alloy particles formed on the zeolite, remain resistant to agglomeration. At the same time, on γ -Al₂O₃ PdZn particles rapidly destructs via Zn diffusion in γ -alumina. Metal-state Pd (0) particles agglomerates and undergo carbidization. This leads to a rapid loss of activity of the PdZn/Al₂O₃ system.

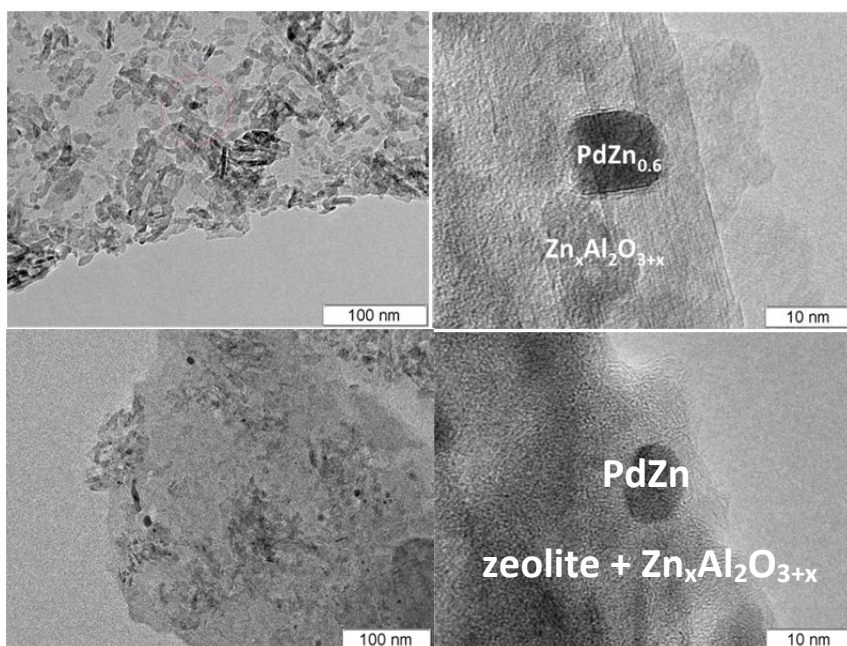


Figure 7: HRTEM images of PdZn/Al₂O₃ (on the top) u PdZn/MFI/Al₂O₃ (on the bottom).

Acknowledgements

Authors thank for financial support RFBR (grants 12-03-00489, 12-03-33062) and Council on Grants of the President of the Russian Federation for the Support of Young Scientists MK-2151.2012.3 and leading scientific schools, grant no. NSh_65264_2010.3.

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