

Report regarding the work done at BM23 according to the proposal (CH3954)

Exploring the co-component influence on the state of Pd in the gas-phase toluene acetoxylation: A combine study of XANES (Pd L_{2,3}-edge) and EXAFS (Pd K-edge) to reveal the geometric and electronic effects

Proposal Summary:

The goal of the present study is to find the geometric effect (often structural) and electronic state of Pd, which can be merely influenced by the presence of co-component and, in turn, affects the catalytic behavior in the gas phase acetoxylation of toluene. To capture the geometric and electronic effects, XAS measurements at ambient conditions, while activating the samples at 300 °C in air, and more importantly, under the pulse exchange conditions (toluene and acetic acid) could be promising. For these current investigations Pd K-edge EXAFS at BM23 and Pd L_{2,3}-edges XANES at ID12 are proposed. From EXAFS the geometric affects such as either alloying or incorporation of elements into Pd bulk lattice, metal-metal bond coordination/distances can be explored, whereas from XANES the local changes in the electronic structure like the oxidation state of Pd or d-orbital occupancy could be anticipated. Supporting information from the conventional characterization methods like XRD/XPS/TG-DTA can provide more insights for the present investigation. Additionally, FT-IR surface adsorption experiments with toluene and/or acetic acid were already performed in our laboratory. Besides, the adsorption and activation energies for dissociation of reactant molecules over Pd(111) surface was elucidated with density functional theory (DFT) methods.

Proposal Summary is accepted to perform the work only at BM23

Experiment description

Activation conditions

Catalyst amount	- 50 mg
Activation temperature	- 300 °C for 1 h
10 % O ₂ /He flow	- 23 ml / min

Reaction conditions

Reaction pressure	- 2 bar
Reaction temperature	- 210 °C
10 % O ₂ / He flow	- 18 ml / min

Saturator contains single reactant

- 18 ml / min of 10 % O₂ was bubbled through saturator which contain either Toluene or Acetic acid
- The expected amount of Toluene taken by the gas is 29.8 ml/h (1.33 mmol) in gas phase
- The expected amount of Acetic acid taken by the gas is 17.1 ml/h (0.76 mmol) in gas phase

Saturator contains mixed reactants (Toluene and Acetic acid)

- 18 ml / min of 10 % O₂ was bubbled through saturator which contain 1:4 ratio of Toluene and Acetic acid

Pd K edge EXAFS performed under following conditions

Catalysts	Tol+O ₂	Tol+He	AcOH+O ₂	AcOH+He	Tol+AcOH+O ₂	Tol+AcOH+He
10 wt % Pd - 8 wt % Mn/TiO ₂	5 h	5 h	5 h	5 h	3 h	3 h
10 wt % Pd - 8 wt % Sb/TiO ₂	5 h	5 h	5 h	5 h	3 h	3 h

Results and discussion

Quick EXAFS at PdK edge for PdSb/TiO₂ catalyst under Toluene and O₂

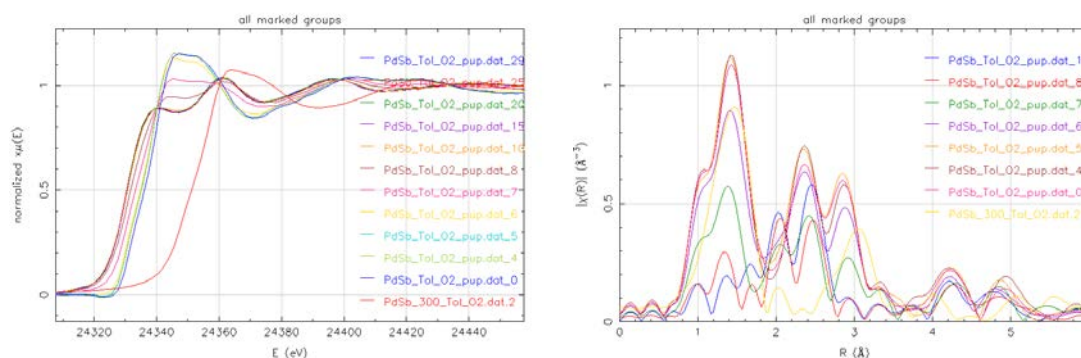


Fig. 1 a) Normalized Pd K EXAFS, b) K² weighted Fourier transform of the PdSb/TiO₂ catalysts under toluene and molecular oxygen.

Initially, PdSb/TiO₂ catalyst is activated in presence of air at 300 °C for 2h. Quartz capillary reactor system was used for the XAS measurements. To check influence of the individual reactants and the gas medium on the structure of the Pd, initially toluene along with the O₂ is passed on to the sample. Quick EXAFS at PdK edge measurements were performed for 30 min while increase in the reaction pressure from 1 bar to 2 bar. The XANES results along with the K² weighted Fourier transforms are presented in Fig. 1. It is remarkable to know that the PdCl₂ (the precursor in the catalyst) is restructured to metallic Pd within 30 min of the toluene exposure; on further (6 h) no appreciable change to the structure is noticed. We supposed that the structural modifications are happening to the catalyst under 5 h of reaction stream. But the current XAS investigation gave a clear hint for the formation metallic Pd in the PdSb/TiO₂ especially under Toluene flow. On the other hand, similar experiment was performed for similar catalyst but consists of Mn instead of Sb (PdMn/TiO₂). The results are presented in Fig. 2. It is surprisingly to know that the structure of PdCl₂ modified to metallic Pd and PdO. It indicates the fact that the co-component vicinity to the Pd plays also a major

role on the reducibility of the Pd atoms. Clearly, Sb in presence of toluene stabilizing the metallic Pd, whereas Mn modified the metallic Pd to PdO.

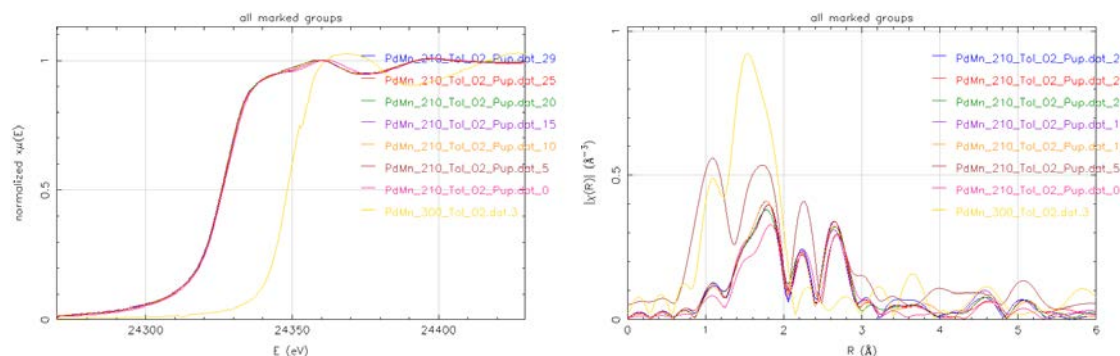


Fig. 2 a) Normalized Pd K EXAFS, b) K^2 weighted Fourier transform of the PdMn/TiO₂ catalysts under toluene and molecular oxygen.

Quick EXAFS at PdK edge for PdSb/TiO₂ catalyst under Acetic acid and O₂

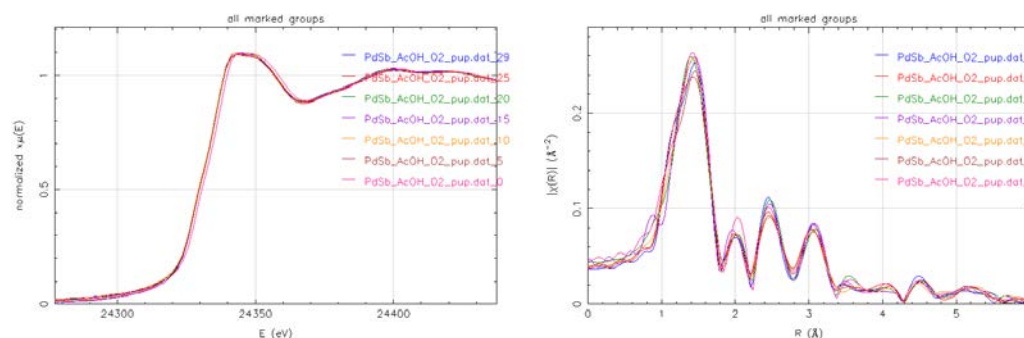


Fig. 3 a) Normalized Pd K EXAFS, b) K^2 weighted Fourier transform of the PdSb/TiO₂ catalysts under Acetic acid and molecular oxygen.

Secondly, to check influence of the acetic acid besides toluene, Quick EXAFS at PdK edge measurements for PdSb/TiO₂ were performed while increase in the reaction pressure from 1 bar to 2 bar. The XANES results along with the K^2 weighted Fourier transforms are presented in Fig. 3. In contrast to results obtained under the influence of toluene, here, there is no apparent change to the PdCl₂ structure is noticed. Hence, the formation of metallic Pd is clearly avoided. From the current result, we can say that acetic acid or Sb are incapable to direct the formation of metallic Pd from PdCl₂. Besides, similar experiments at PdMn/TiO₂ showed interesting feature, which are presented in Fig. 3. To our surprise, the PdCl₂ modified to metallic Pd within 30 min of exposure of acetic acid. It shows that Mn plays a major role

on the reducibility of the Pd from PdCl₂ but further promoting the oxidation of formed metallic Pd.

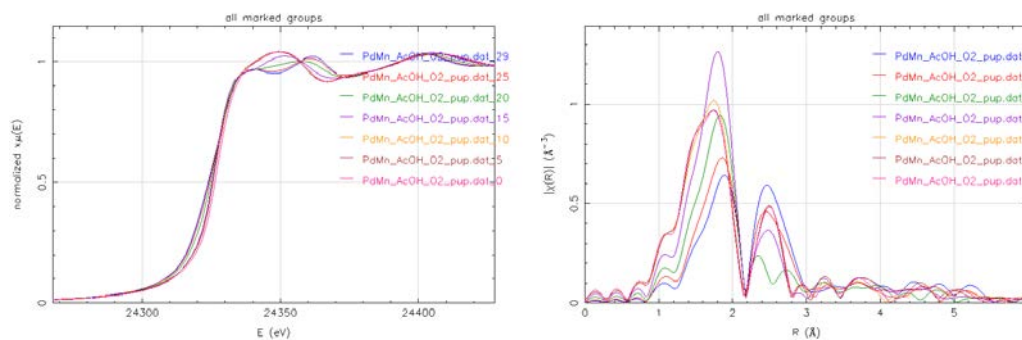


Fig. 4 a) Normalized Pd K EXAFS, b) K² weighted Fourier transform of the PdMn/TiO₂ catalysts under Acetic acid and molecular oxygen

Conclusions

Pd K edge QEXAFS at PdSb/TiO₂:

Toluene is found to be effective reducing agent and Sb is stabilizing the formed metallic Pd particles. Acetic acid had not great role on the reducibility of the catalysts

Pd K edge QEXAFS at PdMn/TiO₂:

Mn played an important role for the formation of metallic Pd phase from PdCl₂. Further, Mn promoting the oxidation of metallic Pd