Bimetallic PtCo Catalyst for Selective Hydrogenation of Phenylacetylene

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Abstract. The semi-hydrogenation of phenylacetylene to styrene is one of the most important industrial reactions. However, achieving high styrene selectivity at high phenylacetylene conversion remains technically challenging, because over hydrogenation is kinetically preferable. Herein, silica-supported PtCo bimetallic catalyst was synthesized by glycol reduction method. A 75.2% selectivity towards the styrene was obtained at the phenylacetylene conversion of 93.6%. The excellent catalytic performance of the bimetallic catalyst in this reaction system could be attributed to the synergistic effect between Pt and Co. Due to the transfer of Co electrons to Pt, electron-rich Pt was formed. The weak π adsorption of alkenes was greatly promoted, which in return promoted phenylacetylene conversion and improved styrene selectivity. Our research is supposed to open up new opportunities for the development of high-efficiency alkyne-to-alkene conversion catalysts through the addition of coagents.

Keywords: Bimetallic PtCo Catalyst; Phenylacetylene; High-efficiency Alkyne-to-Alkene Conversion Catalysts.

1. Introduction

Styrene is an important monomer for the production of polystyrene, styrene-butadiene rubber, etc., and an important raw material for the production of coatings and dyes.[1-3]Phenylacetylene is a common impurity component in styrene raw materials, which can easily cause poisoning of catalysts in styrene polymerization, and also deteriorate polystyrene, thereby affecting the performance of polystyrene.[4] Therefore, it is very important to eliminate a small amount of phenylacetylene impurities in styrene.

For how to remove phenylacetylene in styrene, many domestic and foreign literatures and patents have discussed and selective hydrogenation (to styrene) is viewed as a viable process solution.[5-8] Since the hydrogenation of phenylacetylene is a tandem reaction,[9] when phenylacetylene is converted to styrene by catalytic hydrogenation, it is easy to over-hydrogenate to ethylbenzene. A number of metal catalysts have already been developed and applied to the phenylacetylene semi-hydrogenation reaction over the past few decades, including Pd,[10-12] Pt,[13-15] Ru,[16-18] Rh,[19, 20] Ni,[21-23] and Au.[24-26] Among them, Pt-based catalysts have been widely used, because of their high catalytic activities. However, low selectivity to the target products restricts their applications. At present, there are two main methods to improve the styrene selectivity: 1) adding some modifiers to the catalyst; 2) using the properties of the carrier such as dispersion force and electronic effect to improve the styrene selectivity.

In our work, we attempted to prepare a bimetallic $PtCo/SiO_2$ catalyst via glycol reduction method, and studied its performance for the hydrogenation of phenylacetylene. Various analytical techniques, including N_2 adsorption-desorption, inductively coupled plasma-atomic emission spectroscopy (ICP-AES), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) were performed to get an understanding of the microscopic morphology and electronic structure of the catalyst. The silica support synthesized by the hydrolysis method had a high specific surface area and a large number of pores, providing advantageous conditions for the loading of metal particles, so that the metal particles were uniformly and highly dispersed on the carrier. Furthermore, due to the addition of Co, the electronic structure of Pt was changed, making it more electron-rich. This favored the weaker π adsorption of alkenes on the catalyst.

Thus, a high styrene selectivity (75.2%) was obtained while maintaining a high conversion of phenylacetylene (93.6%).

2. Experimental

2.1 Materials

Ethanol (A.R.), ammonia (A.R.), tetraethyl orthosilicate (A.R.), ethylene glycol (A.R.) and deionized water were purchased from the Beijing Tongguang Fine Chemicals Company. N-[3-(trimethoxysilyl) propyl]ethylenediamine(99%), phenylacetylene (A.R.) and polyvinyl pyrrolidone(PVP) were purchased from Aladdin. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) (99%) and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$)(99%) were purchased from Macklin. All chemicals were used without further purification.

2.2 Materials Preparation

The bimetallic PtCo catalyst was prepared by ethylene glycol reduction method. Ethyl orthosilicate was hydrolyzed in alcohol solution to form silica. The alcohol solution was a mixed solution of ethanol, water and ammonia. The hydrolyzate was centrifuged, dried, and calcined at 600 °C for 2 h under static air to obtain SiO_2, which was then used as the support. Chloroplatinic acid hexahydrate($H_2PtCl_6 \cdot 6H_2O$) was used as the Pt precursor, and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) was used as the cobalt precursor. A slurry of SiO_2 in a polyvinyl pyrrolidone(PVP), chloroplatinic acid and cobalt nitrate ethylene glycol solution was stirred at 120℃ for 1 h. The resulting precipitates were dried at 80℃ overnight and ultimately calcined in argon at 200 °C for 2 h. In the bimetallic PtCo catalyst, the loadings of Pt and Co were both 1.5wt%. As comparisons, monometallic Pt catalyst with a metal content of 1.5wt% and monometallic Co catalyst with a metal content of 1.5wt% were prepared using the same procedures.

2.3 Materials Characterization

The specific surface area, total pore volume and mean pore diameter were measured by N_2 adsorption–desorption experiments on a Micromeritics Tristar ASAP 2020M instrument. The test temperature was 77.4K. Prior to the analysis, the samples were degassed at 300 °C for 4 h. Elemental analysis was performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using an Agilent ICPOES730 instrument. The powder samples were subjected to acid digestion before the testing. Transmission electron microscopy (TEM) images were carried out using a Tecnai G2 F20 instrument from FBI, USA. The TEM samples were prepared by dispersing the catalyst powders in ethanol for 5 min under ultrasonication, and then by dispersing the solution onto a carbon film on a copper grid. Power X-ray diffraction patterns were performed using a Bruker D8 ADVANCE diffractometer operating at 40 kV and 40 mA with Cu Kα (Kα= 1.5405 Å) radiation. 2θ scans were performed from 20°to 80°at a 4°/min speed. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific Escalab 250Xi. All binding energies were referred to the C1s peak at 284.6 eV of surface adventitious carbon.

2.4 General Procedure for Hydrogenation

The hydrogenation of phenylacetylene was carried out in a stainless-steel autoclave equipped with a pressure gauge and a magnetic stirrer. Typically, 10 mL of ethanol solvent, 40 ul of phenylacetylene, and 20 mg of catalyst were introduced into the reactor at room temperature. The air in the autoclave was purged with a vacuum pump. Then, the reactor was filled with 0.4 MPa of hydrogen. When the reaction temperature reached 70 °C, stirring (600 r/min) was started, and the reaction began. After the reaction, the solid catalyst was separated from the solution by centrifugation. The liquid reaction mixture (1 ml) was added to a gas chromatography vial along with a certain amount of external standard n-dodecane (20 ul) for further quantitative analysis. Conversion and selectivity

measurements were performed using a gas chromatograph (Huifen HF-900) with a flame ionization detector. Substrate conversion and product selectivity were calculated using appropriate calibration curves and response factors. For the recyclability test, in addition to using the recovered catalyst, the reaction were carried out under the same reaction conditions as described above. At the end of the catalytic reaction, the mixture was centrifuged and the solid was recovered, washed thoroughly with ethanol, and reused in the next run.

3. Results and Discussions

3.1 Characterization of the Catalyst

The basic characteristics of the catalysts are summarized in Table 1. The SiO_2 support exhibits a mesoporous structure with a specific surface area of 448.09m^2g^{-1}, total pore volume of 1.64 $cm^3\ g^{-1}$, and an average pore diameter of 15.08 nm. The surface area of the supports all reduced to varying degrees after loading with the metallic components, but pore size changed slightly, indicating that the SiO_2 was an excellent support for the PtCo catalyst. The decrease of the surface area compared to SiO_2 is attributed to pore blockage caused by the metallic components during catalyst preparation.

Table 1 also shows the metal contents of the samples measured by ICP. The amounts of Pt and Co in the catalysts measured by ICP are lower than the theoretical values, which may be due to the incomplete adsorption of Pt and Co metal ions onto the SiO_2 support. These phenomena are always observed in the catalysts preparation process.

Table 1. Structural and morphological properties of the catalysts and bare support

Sample	*Pt[a](wt%)*	*Co[a](wt%)*	*S_{BET}[b](m^2g^{-1})*	*Vp[b](cm^3g^{-1})*	*Dp[b](nm)*
SiO_2	-	-	448.09	1.64	15.08
Pt/ SiO_2	1.35	-	256.68	1.32	13.68
PtCo/SiO_2	1.34	1.39	238.32	1.18	11.74
Co/ SiO_2	-	1.41	240.68	1.27	12.62

[a]As determined by ICP. [b] BET surface area, total pore volume (Vp) and mean pore diameter (Dp) were measured from the N_2 adsorption–desorption isotherms.

The TEM investigations of the catalysts were conducted to study their morphological characteristics. The TEM and particle size distribution histograms of PtCo/SiO_2 are shown in Figure 1. It can be seen in the figure that the metal Pt particles were uniformly and densely dispersed on the silica support. The metal is present on the support in the form of spherical particles with an average particle size of about 2.09nm. The lattice spacing of Pt particles is about 0.215nm, which corresponds to the (111) plane of metallic Pt.[27]

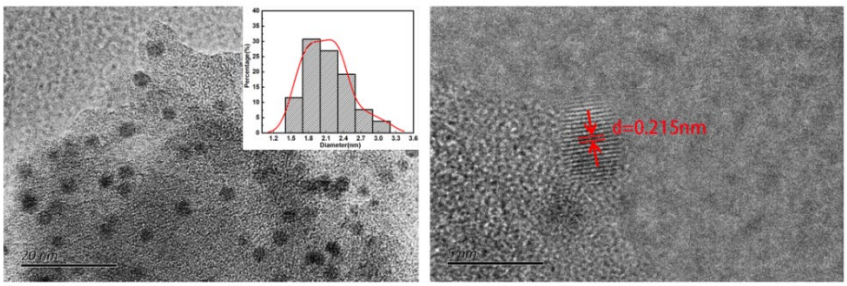


Figure 1. TEM and particle size distribution histograms of PtCo/SiO_2 catalyst

The XRD patterns of the SiO_2 support and the catalysts are shown in Figure 2. Compared with pure SiO_2, the XRD patterns of the mono-Pt, bimetallic PtCo and mono-Co samples only changed slightly, indicating that the mesoporous structure of SiO_2 was well retained after supporting with metal components. There were no any diffraction peaks of the Pt and Co metals in all these samples,

except the broad peak at 24° assigned to the amorphous silica,[28] indicating that the metal Pt particles were very small and highly dispersed on the surface of the carrier, which was consistent with the results obtained by TEM.

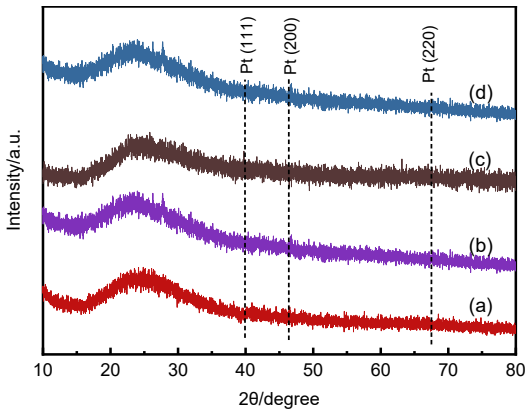


Figure 2. XRD patterns of (a) SiO_2, (b) Pt/SiO_2, (c) $PtCo/SiO_2$ and (d) Co/SiO_2

Surface chemical states of the catalysts were analyzed by means of X-ray photoelectron spectroscope (XPS). Figure 3 shows the XPS spectra of Pt/SiO_2, Co/SiO_2 and $PtCo/SiO_2$ catalysts. The Pt 4f $_{7/2}$ spectra and 4f $_{5/2}$ spectra both could be deconvoluted two peaks for all catalysts. The peaks at 71.14 and 74.52eV were assigned to Pt^0 $4f_{7/2}$ and Pt^0 $4f_{5/2}$, and the peaks at 72.30 and 75.42eV were assigned to Pt^{2+} $4f_{7/2}$ and Pt^{2+} $4f_{5/2}$ in $PtCo/SiO_2$. The peaks at 71.44 and 74.71eV were assigned to Pt^0 $4f_{7/2}$ and Pt^0 $4f_{5/2}$, and the peaks at 72.50 and 75.67 eV were assigned to Pt^{2+} $4f_{7/2}$ and Pt^{2+} $4f_{5/2}$ in Pt/SiO_2. The binding energies of the $PtCo/SiO_2$ were lower than those of the Pt/SiO_2, which suggested electron transferred from Co to Pt, which can be also identified by the binding energy shifts of Co.

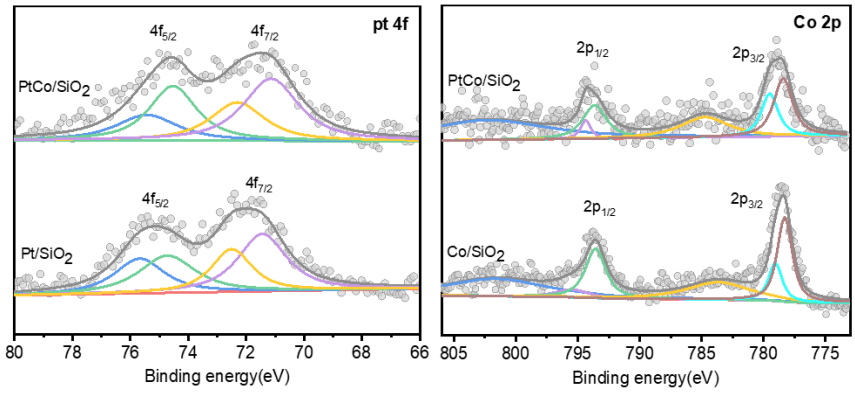


Figure 3. XPS spectra of Pt 4f and Co 2p for the catalysts

3.2 Catalytic Performance

The hydrogenation of phenylacetylene can yield the semi-hydrogenated product styrene and the fully hydrogenated product of phenylethane, as shown in Figure 4. Styrene is our target product because it is very important in industry.

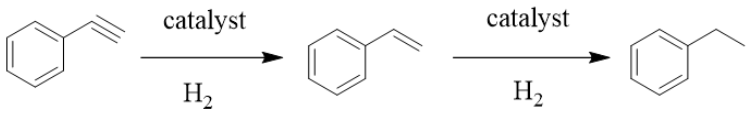


Figure 4. The hydrogenation pathways of phenylacetylene.

The catalytic performances of all catalysts under the given reaction conditions are shown in Table 2. As we can see, Pt/SiO_2 exhibits high activity under our given reaction condition, with a 90.3% conversion of phenylacetylene, but an extremely low selectivity to styrene of only 6.2%. On the other hand, Co/SiO_2 shows extremely low catalytic activity, and phenylacetylene basically does not react. Compared with the mon-Pt and mon-Co catalysts, it is obvious that the catalytic performance of PtCo bimetallic catalyst is significantly improved, indicating the promoting effect of Co on Pt. In particular, the $PtCo/SiO_2$ achieved 75.2% selectivity to styrene with 93.8% phenylacetylene conversion.

Table 2. The performance of all the catalysts for phenylacetylene hydrogenation[a]

Catalysts	*Conversion (%)*	*Selectivity (%)*
Pt/SiO_2	90.3	6.2
$PtCo/SiO_2$	93.8	75.2
Co/SiO_2	12.1	54.3

[a]Reaction conditions: catalysts: 0.1 g, H_2 pressure: 0.4 MPa, temperature: 70°C, reaction time: 1h

Cycling stability is an important parameter to evaluate catalyst performance. The cycle stability of the $PtCo/SiO_2$ for the selective hydrogenation of phenylacetylene was investigated, and the result was shown in Figure 5. The catalyst showed excellent stability, and after 5 cycles, the conversion rate decreased by only 2.9%, and the selectivity to styrene decreased by 3.5%.

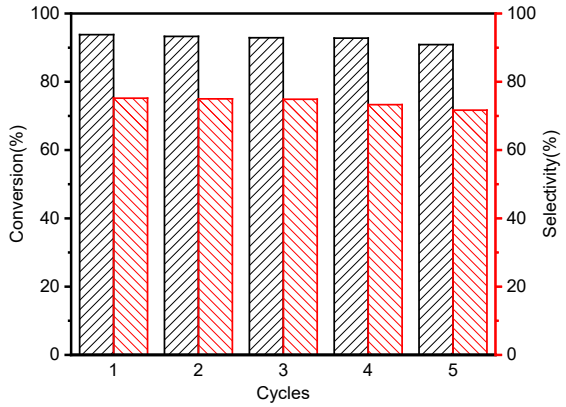


Figure 5. Recycle stability of $PtCo/SiO_2$ for the selective hydrogenation of phenylacetylene

Previous reports indicate that the key to obtain high styrene selectivity is to weaken the adsorption strength of the intermediate, i.e., alkene. [28] Semi-hydrogenated products (styrene) have strong σ bond adsorption patterns on pure Pt. As a result, the alkene groups are usually fully hydrogenated to alkanes, as observed in Pt/SiO_2. The weak π adsorption of alkenes is greatly promoted by the electron-riched Pt in the bimetallic $PtCo/SiO_2$ catalyst. Therefore, the desorption of alkenes is more favorable than complete hydrogenation to ethylbenzene. This is why $PtCo/SiO_2$ is highly selective for styrene. In addition, because Co/SiO_2 does not have the poor hydrogen overflow efficiency on Co, its hydrogenation activity is low.

4. Conclusion

In this paper, glycol reduction method was used to prepare bimetallic PtCo catalyst supported on silica for phenylacetylene hydrogenation. A 75.2% selectivity towards the styrene was obtained at the phenylacetylene conversion of 93.6%. The excellent catalytic performance of bimetallic catalyst in this reaction system can be attributed to the synergistic effect between Pt and Co. The results show the addition of Co to Pt catalyst can make a difference on the electronic properties of Pt atoms in catalysts. Therfore, the bimetallic PtCo catalyst are more effective to transfer electrons to the π molecular orbitals of phenylacetylene, which in return promotes phenylacetylene activation and improves catalytic reactivity. Our research is supposed to open up new opportunities for the

development of high-efficiency alkyne-to-alkene conversion catalysts through the addition of coagents.

References

[1] C.S. Wondergem, T. Hartman, B.M. Weckhuysen, In Situ Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy to Unravel Sequential Hydrogenation of Phenylacetylene over Platinum Nanoparticles, ACS Catalysis. 9(12) (2019) 10794-10802.

[2] C.-T. Kuo, Y. Lu, L. Kovarik, M. Engelhard, A.M. Karim, Structure Sensitivity of Acetylene Semi-Hydrogenation on Pt Single Atoms and Subnanometer Clusters, ACS Catalysis. 9(12) (2019) 11030-11041.

[3] Shakirov, M.P. Boronoev, N.A. Sinikova, E.A. Karakhanov, A.L. Maksimov, Selective Hydrogenation of Phenylacetylene on a Pd-Containing Catalyst Based on a Polymer Layered Substrate, Russian Journal of Applied Chemistry. 93(2) (2020) 258-267.

[4] M. Hu, S. Zhao, S. Liu, C. Chen, W. Chen, W. Zhu, C. Liang, W.C. Cheong, Y. Wang, Y. Yu, Q. Peng, K. Zhou, J. Li, Y. Li, MOF-Confined Sub-2 nm Atomically Ordered Intermetallic PdZn Nanoparticles as High-Performance Catalysts for Selective Hydrogenation of Acetylene, Adv Mater. (2018) e1801878.

[5] R.S.S.a.F.O. Danilov, Theoretical modeling of mechanisms of phenylacetylene and styrene hydrogenation on the Pd (100) surface, Russian Chemical Bulletin. 60(9) (2019) 656—1661.

[6] Marc Armbruster, Kirill Kovnir, Malte Behrens, Detre Teschner, Yuri Grin, and Robert Schlogl, Pd-Ga Intermetallic Compounds as Highly Selective Semihydrogenation Catalysts, JACS. 132 (2010) 3.

[7] G. Giannakakis, M. Flytzani-Stephanopoulos, E.C.H. Sykes, Single-Atom Alloys as a Reductionist Approach to the Rational Design of Heterogeneous Catalysts, Acc Chem Res. 52(1) (2019) 237-247.

[8] A.H. Al-ShaikhAli, A. Jedidi, D.H. Anjum, L. Cavallo, K. Takanabe, Kinetics on NiZn Bimetallic Catalysts for Hydrogen Evolution via Selective Dehydrogenation of Methylcyclohexane to Toluene, ACS Catalysis. 7(3) (2017) 1592-1600.

[9] J. Zhang, K. Gao, S. Wang, W. Li, Y. Han, Performance of bimetallic PdRu catalysts supported on gamma alumina for 2-ethylanthraquinone hydrogenation, RSC Advances. 7(11) (2017) 6447-6456.

[10] S.O. Ojwach, A.O. Ogweno, Neutral and cationic (pyrazolylmethyl)pyridine palladium (II) complexes: kinetics and chemoselectivity studies in hydrogenation of alkenes and alkynes, Transition Metal Chemistry. 41(5) (2016) 539-546.

[11] L. Shen, S. Mao, J. Li, M. Li, P. Chen, H. Li, Z. Chen, Y. Wang, PdZn intermetallic on a CN@ZnO hybrid as an efficient catalyst for the semihydrogenation of alkynols, Journal of Catalysis. 350 (2017) 13-20.

[12] Z. Wang, L. Yang, R. Zhang, L. Li, Z. Cheng, Z. Zhou, Selective hydrogenation of phenylacetylene over bimetallic Pd–Cu/Al2O3 and Pd–Zn/Al2O3 catalysts, Catalysis Today. 264 (2016) 37-43.

[13] M.Y. Byun, Y.E. Kim, J.H. Baek, J. Jae, M.S. Lee, Effect of surface properties of TiO2 on the performance of Pt/TiO2 catalysts for furfural hydrogenation, RSC Advances. 12(2) (2022) 860-868.

[14] B. Sheng, L. Hu, T. Yu, X. Cao, H. Gu, Highly-dispersed ultrafine Pt nanoparticles on graphene as effective hydrogenation catalysts, RSC Advances. 2(13) (2012).

[15] M. Hu, L. Jin, Y. Dang, S.L. Suib, J. He, B. Liu, Supported Pt Nanoparticles on Mesoporous Titania for Selective Hydrogenation of Phenylacetylene, Front Chem. 8 (2020) 581512.

[16] C. Li, Z. Shao, M. Pang, C.T. Williams, X. Zhang, C. Liang, Carbon Nanotubes Supported Mono- and Bimetallic Pt and Ru Catalysts for Selective Hydrogenation of Phenylacetylene, Industrial & Engineering Chemistry Research .51(13) (2012) 4934-4941.

[17] J.-Y. Ruzicka, D.P. Anderson, S. Gaw, V.B. Golovko, Platinum-Ruthenium Nanoparticles: Active and Selective Catalysts for Hydrogenation of Phenylacetylene, Australian Journal of Chemistry. 65(10) (2012).

[18] D. Duraczyńska, E.M. Serwicka, A. Drelinkiewicz, D. Rutkowska-Żbik, M. Witko, R. Socha, M. Zimowska, Z. Olejniczak, Nanospace constraints in mesoporous silica carriers—A factor of critical importance in promoting the catalytic activity of supported ruthenium (II) complex with hemilabile phosphine ligand, Applied Catalysis A: General. 427 (2012) 16-23.

[19] X.-Y. Quek, Y. Guan, E.J.M. Hensen, Structure sensitivity in the hydrogenation of unsaturated hydrocarbons over Rh nanoparticles, Catalysis Today. 183(1) (2012) 72-78.

[20] E. Leitmannová, J. Svoboda, J. Sedláček, J. Vohlídal, P. Kačer, L. Červený, Hydrogenation of phenylacetylene and 3-phenylpropyne using Rh(diene) complexes under homogeneous and heterogeneous conditions, Applied Catalysis A: General. 372(1) (2010) 34-39.

[21] X. Deng, R. Bai, Y. Chai, Z. Hu, N. Guan, L. Li, Homogeneous-like Alkyne Selective Hydrogenation Catalyzed by Cationic Nickel Confined in Zeolite, CCS Chemistry. 4(3) (2022) 949-962.

[22] M. Jian, J.X. Liu, W.X. Li, Hydroxyl improving the activity, selectivity and stability of supported Ni single atoms for selective semi-hydrogenation, Chem Sci. 12(30) (2021) 10290-10298.

[23] M.D. Navalikhina, N.E. Kavalerskaya, E.S. Lokteva, A.A. Peristyi, E.V. Golubina, V.V. Lunin, Selective hydrogenation of phenylacetylene on Ni and Ni-Pd catalysts modified with heteropoly compounds of the Keggin type, Russian Journal of Physical Chemistry A. 86(12) (2012) 1800-1807.

[24] X. Wang, M.A. Keane, Gas phase selective hydrogenation of phenylacetylene to styrene over Au/Al2O3, Journal of Chemical Technology & Biotechnology. 94(12) (2019) 3772-3779.

[25] X. Liu, C.-Y. Mou, S. Lee, Y. Li, J. Secrest, B.W.L. Jang, Room temperature O2 plasma treatment of SiO2 supported Au catalysts for selective hydrogenation of acetylene in the presence of large excess of ethylene, Journal of Catalysis. 285(1) (2012) 152-159.

[26] Lidong Shao, Detre Teschner, and Wei Zhang, Gold supported on graphene oxide: an active and selective catalyst for phenylacetylene hydrogenations at low temperatures, ACS Catalysis. 4 (2014) 2369-2373.

[27] H. Li, C. Xu, X.-L. Mu, P. Zhang, X.-M. Zhang, N. Zheng, Acetylene-Mediated Synthesis of Supported Pt Nanocatalyst for Selective Hydrogenation of Halonitrobenzene, ChemNanoMat. 4(5) (2018) 518-523.

[28] Y.S. Lin, N. Abadeer, K.R. Hurley, C.L. Haynes, Ultrastable, redispersible, small, and highly organomodified mesoporous silica nanotherapeutics, J Am Chem Soc. 133(50) (2011) 20444-57.