Supporting information

Selective hydrogenation of acetylene to ethylene by alkali-metal palladium complex hydrides

Qing Guo,[a,b] Chao Qin,[a] Jianping Guo,*[a,b] and Ping Chen[a,b]

[a]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China;

[b]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China;

E-mail: guojianping@dicp.ac.cn.

Chemical reagents

Palladium metal particle (Pd, 150 μm) was purchased from Shanghai Tuosi Chemical Co., Ltd. and reduced by H_2 at 200 °C for 3 hours before use. $PdCl_2$ (Pd 59-60%), KH (30% in mineral oil), Na metal (99.7%), and K metal (99%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Li metal (99.9%) was purchased from Alfa Aesar. KH was washed with cyclohexane for several times to remove the mineral oil before use. MgO nanosphere with the size of 50 nm was purchased from Beijing InnoChem Science & Technology Co., Ltd. H_2 (99.999%), Ar (99.999%), C_2H_2 (2.5% balanced by Ar) and simulated industrial feed gas (1% C_2H_2, 10% H_2 and 20% C_2H_4 balanced by Ar) were purchased from Dalian Guangming special gas Co., Ltd.

Because some of the chemical reagents and samples are sensitive to air and moisture, all sample manipulations were performed in an argon-filled glove box (O_2, $H_2O < 1$ ppm).

Material synthesis

1) Preparation of K_3PdH_3.

The K_3PdH_3 sample was prepared by carefully ball milling KH with palladium metal powders under argon atmosphere. Typically, Pd particles (300 mg) and KH (450 mg) were mixed in a stainless steel pot in glove box filled with argon. The molar ratio of Pd to KH is about 1:4. Then, the mixture was ball milled on a Retsch planetary ball mill (PM 400) at 200 revolutions per minute (ppm) for 20 hours under argon. After that, the yellow solid residue was collected and stored in glove box for further characterizations or activity test.

2) Preparation of Pd/MgO catalyst.

The Pd/MgO catalysts were prepared by impregnating MgO with H_2PdCl_4 solution followed by reduction in a H_2 flow. In a typical synthesis, 1 g MgO was dispersed in 15 ml ethyl alcohol in a 100 mL round-bottom flask, and the mixture was ultrasonically treated to get a homogeneous suspension. After that, 0.188 mL H_2PdCl_4 (1 mol L^{-1}) was diluted into 5 mL ethyl alcohol and introduced into the MgO suspension under magnetic stirring at room temperature. After stirring for 2 hours, the solvent was removed under vacuum at 60 °C in water bath. The solid residue was reduced at 50 °C for 2 hours under hydrogen and then treated at 400 °C for 4 hours under argon. After that, the sample was retreated by hydrogen at 50 °C for 2 hours. Pd loading was 2 wt% for Pd/MgO catalysts.

3) Preparation of A-Pd-H/MgO catalysts.

The A-Pd-H/MgO (A: Li, Na or K) catalysts were prepared by impregnating Pd/MgO catalysts in the respective alkali-ammonia solution. In a typical process, a mixture of Pd/MgO catalysts (100 mg) and the alkali metal with a molar ratio of A to Pd (10:1) were loaded into a stainless steel reactor in the glove box. The reactor was placed in a liquid nitrogen bath for 2 minutes and liquid ammonia was then introduced until the solid sample was immersed in it. The alkali metal was converted to respective alkali metal amide in the presence of Pd. After that, ammonia was removed and the solid residue was hydrogenated at 300 °C for 5 hours in a H_2 flow to convert amides to respective alkali hydrides. The catalysts obtained using Li, Na, and K from that process were denoted as Li-Pd-H/MgO, Na-Pd-H/MgO, and K-Pd-H/MgO, respectively.

4) Preparation of K-Pd-H/MgO-Air catalyst.

The K-Pd-H/MgO-Air sample was prepared by exposing K-Pd-H/MgO to air at room temperature for 3 days. And the sample was then reduced under a flow of H_2 at 80°C for 3 hours.

X-ray diffraction (XRD) characterizations

Powder X-ray diffraction (PXRD) patterns were recorded on a PANalytical X'pert diffractometer in a homemade sample cell sealed by KAPTON film to avoid air and moisture corrosion.

Temperature-programmed decomposition-mass spectrometry (TPD-MS) characterization of K_3PdH_3 and K-Pd-H/MgO

The TPD-MS experiment was conducted on a homemade reactor coupling with an on-line mass spectrometer to investigate the thermal stability of K-Pd-H/MgO and

K_3PdH_3. Typically, 50 mg K_3PdH_3 was loaded in a sealed stainless steel reactor and then heated from room temperature to 350 °C with a ramping rate of 1 °C min^{-1} under vacuum (10^{-8} Pa). The H_2 signal (m/z=2) was continuously recorded during the TPD-MS process.

Diffuse reflectance infrared fourier transform (DRIFT) characterization

The DRIFT spectra were acquired by using a Bruker Tensor II spectrometer with a resolution of 4 cm^{-1}.

HAADF-STEM and EDX characterization of K-Pd-H/MgO

The aberration corrected high angle annular dark filed scanning transmission electron microscopy (HAADF-STEM) images and corresponding elements mapping were obtained by using a JEM-ARM200F of JEOL.

Activity test

1) Acetylene hydrogenation without the presence of ethylene.

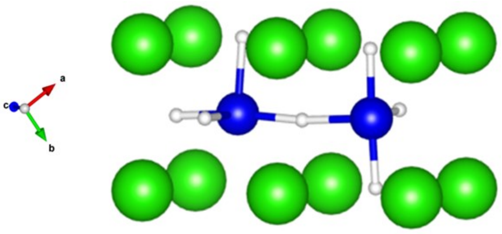
The activity tests of catalysts were performed in a fixed-bed flow reactor at atmospheric pressure, and the reactants were purified by Na/NaCl to decrease oxygen and water content to ppm level. Typically, catalysts were loaded into the reactor, and the mixture gas with given flow rates was then introduced followed by ascending temperature testing. The conditions of product analysis and the calculation methods for acetylene conversion and ethylene selectivity were the same with our previous work[1].

2) Acetylene hydrogenation under simulated industrial condition.

As for K-Pd-H/MgO catalyzed acetylene hydrogenation with large excess amount of ethylene, catalyst weight was 50 mg and the flow rate of mixture gas (1 vol % C_2H_2, 10 vol % H_2, 20 vol % C_2H_4 in argon) was 35 mL min^{-1}. Other test conditions were similar with the case of acetylene hydrogenation without ethylene. Acetylene conversion and ethylene selectivity with excess ethylene were calculated based on the formula proposed by Ma et al.[2]:

$$C_2H_2\ \text{Conversion} = \frac{C2H2(in) - C2H2(out)}{C2H2(in)} \times 100\% \qquad (1)$$

$$C_2H_4\ \text{Selectivity} = \{1 - \frac{C2H6(out) - C2H6(in) + 2C4(out)}{C2H2(in) - C2H2(out)}\} \times 100\% \qquad (2)$$



Pd-Pd 3.66 (Å)

Figure S1. The crystal structure and Pd-Pd distance of $CaPdH_2$.[1]

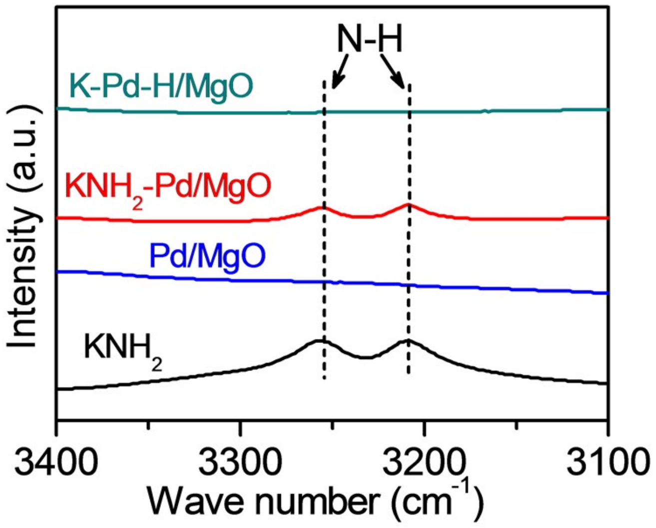


Figure S2. FT-IR spectra of the samples prepared by impregnating K and Pd/MgO in liquid ammonia (noted as KNH_2-Pd/MgO) and further hydrogenation (noted as K-Pd-H/MgO). The absence of N-H vibration adsorption indicated KNH_2 was hydrogenated into K-Pd-H.

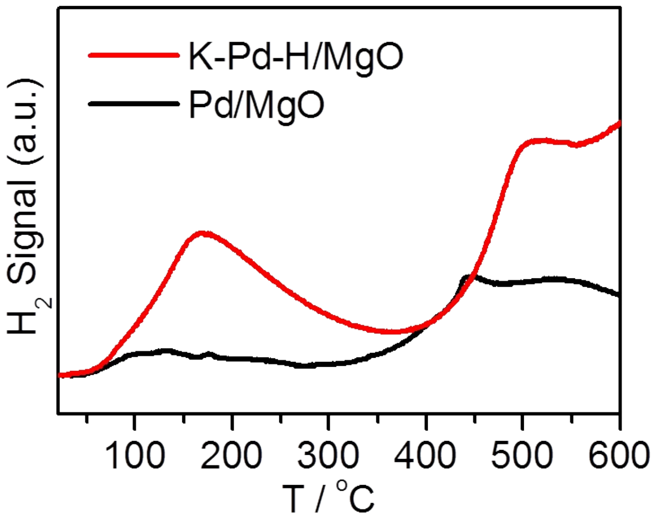


Figure S3. TPD-MS profiles of the as-prepared K-Pd-H/MgO and Pd/MgO samples. Compared with Pd/MgO, the H_2 intensity and peak area of K-Pd-H/MgO is significantly higher, indicating H presents in the prepared K-Pd-H/MgO sample. The relative low temperature peak of K-Pd-H/MgO compared with bulk K_3PdH_3 may be due to the nanosized potassium palladium hydride supported on MgO surface, as reference results indicate decreasing the particle size of metal hydride material will promote H_2 release at low temperature.[3]

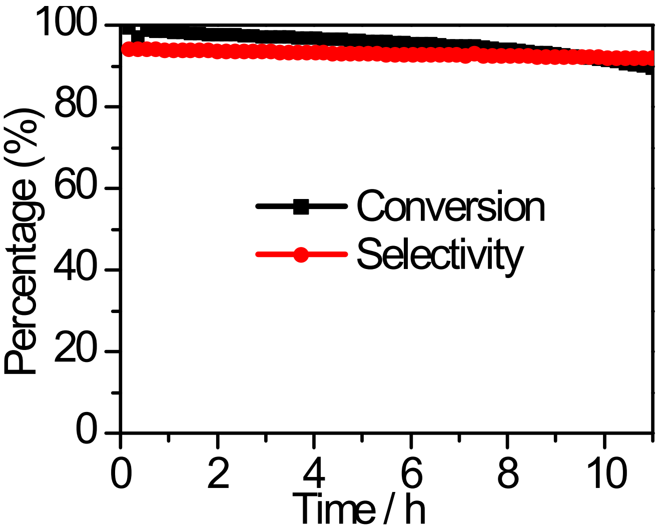


Figure S4. Stability test of K-Pd-H/MgO for acetylene hydrogenation under simulated industrial condition at 120°C. Black line: acetylene conversion; Red line: ethylene selectivity. (Reaction condition: 1% C_2H_2, 10% H_2, 20% C_2H_4, balanced by Ar, GHSV=42000 h^{-1})

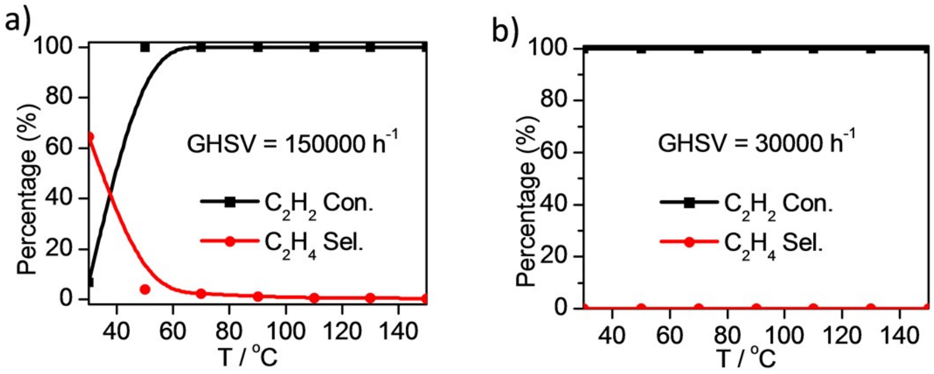


Figure S5. Temperature-dependent acetylene hydrogenation performance catalyzed by Pd/MgO under different GHSV. (Reaction conditions: 1% C_2H_2, 10% H_2 in argon; the GHSV is (a) 150000 h^{-1} and (b) 30000 h^{-1})

Table S1 Comparison of acetylene hydrogenation performance of K-Pd-H/MgO with the catalysts reported in the references.

Catalyst	**C_2H_2:H_2:C_2H_4**	**T (^oC)**	**C_2H_2 Conversion**	**C_2H_4 Selectivity**	**Reference**
$CaPdH_2$	1:10:0	120	100%	85%	[1]
Cu_1/ND@G	1:10:20	200	95%	98%	[2]
Na-Ni@CHA	0.5:8:50	170	100%	90%	[4]
Pd_1/ND@G	1:10:20	180	100%	90%	[5]
Pd-In/Al_2O_3	0.87:3.1:73	120	100%	81%	[6]
Pd_1/N-graphene	1:20:20	125	100%	93.5%	[7]
PdZn	2:20:40	80	100%	90%	[8]
Pd@SOD	1:20:9	150	100%	85%	[9]
In_2O_3	2.5:75:10	350	100%	85%	[10]
Pd_1/Cu(111)+Cu(100)	1:20:20	75	98.8%	95.6%	[11]
NiGa	1:10:20	220	90%	82%	[12]
Pd_1-Fe/Fe_2O_3(012)	1:10:20	120	100%	94.7%	[13]
Ni_1Cu_2/g-C_3N_4	0.5:5:25	170	100%	90%	[14]
K-Pd-H/MgO	1:10:20	120	100%	94%	This work

References

[1] Q. Guo, R. Chen, J. Guo, C. Qin, Z. Xiong, H. Yan, W. Gao, Q. Pei, A. Wu and P. Chen, *J. Am. Chem. Soc.*, 2021, **143**, 20891-20897.

[2] F. Huang, Y. Deng, Y. Chen, X. Cai, M. Peng, Z. Jia, J. Xie, D. Xiao, X. Wen, N. Wang, Z. Jiang, H. Liu and D. Ma, *Nat. Commun.*, 2019, **10**. 1-7.

[3] X. Zhang, Y. Liu, Z. Ren, X. Zhang, J. Hu, Z. Huang, Y. Lu, M. Gao, and H. Pan, *Energy Environ. Sci.*, 2021, **14**, 2302.

[4] Y. Chai, G. Wu, X. Liu, Y. Ren, W. Dai, C. Wang, Z. Xie, N. Guan and L. Li, *J. Am. Chem. Soc.*, 2019, **141**, 9920-9927.

[5] F. Huang, Y. Deng, Y. Chen, X. Cai, M. Peng, Z. Jia, P. Ren, D. Xiao, X. Wen, N. Wang, H. Liu and D. Ma, *J. Am. Chem. Soc.*, 2018, **140**, 13142-13146.

[6] Y. Cao, Z. Sui, Y. Zhu, X. Zhou and D. Chen, *Acs Catalysis*, 2017, **7**, 7835-7846.

[7] S. Zhou, L. Shang, Y. Zhao, R. Shi, G. I. Waterhouse, Y. C. Huang, L. Zheng and T. Zhang, *Adv. Mater.*, 2019, **31**, 1900509.

[8] H. Zhou, X. Yang, L. Li, X. Liu, Y. Huang, X. Pan, A. Wang, J. Li and T. Zhang, *Acs Catalysis*, 2016, **6**, 1054-1061.

[9] S. Wang, Z.-J. Zhao, X. Chang, J. Zhao, H. Tian, C. Yang, M. Li, Q. Fu, R. Mu and J. Gong, *Angew. Chem. Int. Ed.*, 2019, **58**, 7668-7672.

[10] D. Albani, M. Capdevila-Cortada, G. Vile, S. Mitchell, O. Martin, N. Lopez and J. Perez-Ramirez, *Angew. Chem.*, 2017, **56**, 10755-10760.

[11] L. Jiang, K. Liu, S.-F. Hung, L. Zhou, R. Qin, Q. Zhang, P. Liu, L. Gu, H. M. Chen, G. Fu and N. Zheng, *Nat. Nanotechnol.*, 2020, **15**, 848-853.

[12] Y. Cao, H. Zhang, S. Ji, Z. Sui, Z. Jiang, D. Wang, F. Zaera, X. Zhou, X. Duan and Y. Li, *Angew. Chem. Int. Ed.*, 2020, **59**, 11647-11652.

[13] R. Gao, J. Xu, J. Wang, J. Lim, C. Peng, L. Pan, X. Zhang, H. Yang and J.-J. Zou, *J. Am. Chem. Soc.*, 2021, **144**, 573-581.

[14] J. Gu, M. Jian, L. Huang, Z. Sun, A. Li, Y. Pan, J. Yang, W. Wen, W. Zhou, Y. Lin, H.-J. Wang, X. Liu, L. Wang, X. Shi, X. Huang, L. Cao, S. Chen, X. Zheng, H. Pan, J. Zhu, S. Wei, W.-X. Li and J. Lu, *Nat. Nanotechnol.*, 2021, **16**, 1141-1149.