Experimental Study on Microwave–SiC-assisted Catalytic Hydrogenation of Phenol

Jing Sun, Zhenyu Jiang, Ke Wang, Faqi Li, Zhanlong Song^{*}, Wenlong Wang^{*},

Xiqiang Zhao and Yanpeng Mao

National Engineering Laboratory for Coal-Fired Pollutants Emission Reduction, Shandong Provincial Key Lab of Energy Carbon Reduction and Resource Utilization, Shandong University, Jinan 250061, China

Supporting Information

2. Materials and experimental design

2.2 Catalyst preparation and characterization

2.2.1 Catalyst Synthesis

The ZrO_2 , CeO_2 , and $ZrCeO_2$ supports were synthesized by means of a coprecipitation method.

A solution of 2 mol/L ZrO(NO₃)₂·2H₂O was firstly dissolved in dilute nitric acid, and then slowly added to a 4 mol/L NH₄OH solution, followed by vigorous stirring for 30 min at ambient temperature. The resultant precipitate was filtered and washed with deionized water until the pH reached 7, and then dried at 110 °C for 12 h. Thereafter, the as-obtained precursor was heated at 500 °C for 6 h at 10 °C/min in air atmosphere to create the ZrO₂ support.

The synthesis of the CeO₂ support was similar to that of the ZrO_2 , with a 2 mol/L (NH₄)₂Ce(NO₃)₆ solution used instead of $ZrO(NO_3)_2 \cdot 2H_2O$.

The ZrCeO₂ support was synthesized by dissolving a 2 mol/L ZrO(NO₃)₂·2H₂O solution and 2 mol/L (NH₄)₂Ce(NO₃)₆ solution in dilute nitric acid with a Zr/Ce molar ratio of 1:1, and then adding the mixture to a 4 mol/L NH₄OH solution, followed by stirring for 60 min at room temperature. The following washing, drying, and calcination steps were the same as those of the ZrO₂ support detailed above.

The calcined ZrO₂, CeO₂, and ZrCeO₂ supports were loaded with 2 wt % Pd by equal impregnation. An aqueous solution of Pd(NO₃)₂ containing 2 wt % Pd was mixed with the support, stirred continuously for 30 min, and dried at room temperature for 12h. Finally, the powder was heated at 400 °C for 180 min in air atmosphere. Following the calcination, the fresh catalyst was reduced with H₂ purging at a flow rate of 60 ml/min at 300 °C for 1h. Therefore, Pd/ZrO₂, Pd/CeO₂, and Pd/ZrCeO₂ catalysts of 2 wt % were obtained.

2.2.2 Catalyst Characterization

The structure of the samples (non-Pd and Pd based catalysts) were determined by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation at 45 kV and 40 mA with a step size of 0.04° in the range of 10°–90°.

The mass fraction of Pd in the Pd based catalysts was tested using an inductively coupled plasma optical emission spectroscopy (ICP–OES, Agilent 5110, USA).

The energy-dispersive X-ray (EDX) elemental mapping images of the samples were taken to illustrate the distribution of Pd, O, Zr and Ce elements using a scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (EDS).

The surface properties of the catalysts were detected by NH₃ temperature-

programmed desorption (NH₃-TPD, AutoChem II 2920, U.S.A.) and CO₂ temperatureprogrammed desorption (CO₂-TPD, AutoChem II 2920, U.S.A.). In these TPD experiments, all samples were first treated in He at 500 °C for 1 h and cooled to 50 °C. And then exposed to 20% NH₃ (or CO₂, 50 mL/min, He in balance) for 30 min, purged in He for 1 h at 100 °C and heated linearly at 10 °C/min to 600 °C in 50 mL/min He. NH₃ or CO₂ in effluent was recorded continuously as functions of temperature.



(c) Pd/ZrCeO₂

Figure S1 The elemental mapping images of Pd based catalysts:

(a) Pd/ZrO₂, (b) Pd/CeO₂ and (c) Pd/ZrCeO₂.

3. Results and discussions

3.2 Microwave-induced catalytic hydrogenation of phenol

Besides the condensable liquid products, CH_4 , CO and CO_2 were detected in the gas products via Gas Chromatography. The overall yield as well as the composition of gas products on basis of relative volume percentage at H₂ flow rate of 100 and 200 ml/L respectively was illustrated in **Figure S2**. Even though the relative proportion varied among the different catalyst supports, the selectivity of CH_4 was higher at low H₂ flow rate while the selectivity of CO_2 was higher at high H₂ flow rate, and the selectivity of CO was relatively low for all scenarios, indicating side reactions such as decomposition occurred in the hydrogenation process.



Figure S2 Overall yield and relative content proportion of the gas products for three different catalysts at H₂ flow rate of (a) 100 mL/min and (b) 200 mL/min

3.4 Reaction mechanism of microwave-induced catalytic hydrogenation of phenol

As the H[•] radical plays an important role in the hydrogenation process, specific experiments were designed in this work to validate the formation of H[•] radicals with a fiber spectrometer (FX2000-EX, *ideaoptics*, China). When microwave irradiation was imposed on a mixture of H₂ and argon (where argon was used as inert carrier gas) with and without SiC particles, the emission spectra were collected with the characteristic spectral lines being interpreted, as illustrated in **Figure S3**. Obviously, the plasma phenomenon could not be triggered when microwave radiation was exposed only on the given gas mixture without introducing any conductor or semiconductor like SiC particles. In contrast, characteristic spectral lines were detected when the H_2 and argon gas mixture passed through a SiC-particle bed under microwave radiation.

As shown in Figure S3, the characteristic spectral lines were mainly concentrated in the 550-966 nm visible near infrared regions with a few lines in the 200-550 nm ultraviolet and visible regions. The characteristic spectral lines in the microwave-SiCinduced plasma were mainly divided into two main categories: dielectric materials (SiC) and atomic hydrogen/argon. According to NIST Atomic Spectra Database (available on https://physics.nist.gov/asd, National Institute of Standards and Technology, Gaithersburg, MD.) and our previous study, most spectral lines concentrated in the 388-924 nm region, with relatively high intensity, are produced by atomic transitions of hydrogen and argon, as illustrated in Figure S3. According to Table S1, it can be deduced that the presence of SiC particles enables the generation of excited electrons under the microwave radiation. The excited-state electrons collide with the surrounding hydrogen or argon atoms, and the resulting energy transfer can stimulate hydrogen atoms to generate H' radicals (plasma) which gives rise to the characteristic hydrogen spectral lines (H I) observed when they return to the ground state. Additionally, there is also the SiC-stimulated spectrum showing peaks at 251.99, 288.29 and 309.75 nm, much lower than those of hydrogen/argon, which can be attributed to their high lattice

energy in solid phase.



Figure S3 The spectrum captured during the microwave interaction with and without SiC particles at H_2/Ar atmosphere

interaction at H ₂ /Ar atmosphere				
	Observed	Ritz	Transition	
Species	Wavelength	Wavelength ^a	Probabilities ^a /	Transition path ^a
	(nm)	(nm)	A_{ki} (s ⁻¹)	
Si (I)	251.99	251.92	5.49×10^{7}	$3s^23p^2 \rightarrow 3s^23p4s$
Si (I)	288.29	288.16	2.17×10^{8}	$3s^23p^2 \rightarrow 3s^23p4s$
Si (I)	309.75	302.00	3.30×10^{3}	$3s^23p^2 \rightarrow 3s3p^3$
C (I)	358.86	359.51	n/a	$2s^2 2p3s \rightarrow 2s^2 2p(^2P^{\circ}_{1/2})11p$
H (I)	388.41	388.90	2.21×10^{5}	2p→8d
H (I)	415.67	410.18	4.90×10^{5}	2p→6s
H (I)	656.95	656.27	5.39×10^{7}	2p→3d
H (I)	827.03	827.19	n/a	3→33
H (I)	843.38	843.80	2.58×10^{3}	3→18
H (I)	853.01	854.54	6.49×10^3	3→15
H (I)	923.35	922.90	8.91×10^{4}	3→9

Table S1 Most intense emission lines detected in axial spectra of the MW-SiC interaction at H_2/Ar atmosphere

a. These data are based on the NIST Atomic Spectra Database (version 5.7.1). Available online: <u>https://physics.nist.gov/asd</u>. National Institute of Standards and

Technology, Gaithersburg, MD. DOI: <u>https://doi.org/10.18434/T4W30F</u>