

Preparation and characterization of $H_3PW_{12}O_{40}/ZrO_2$ catalyst for carbonation of methanol into dimethyl carbonate

Chao Lung Chiang¹ · Kuen Song Lin¹ · Ssu-Han Yu¹

Received: 8 September 2016/Accepted: 20 February 2017 © Springer Science+Business Media B.V., part of Springer Nature 2018

Abstract A $H_3PW_{12}O_{40}/ZrO_2$ catalyst for effective dimethyl carbonate (DMC) formation via methanol carbonation was prepared using the sol-gel method. X-ray photoelectron spectra showed that reactive and dominant (63%) W(VI) species, in WO_3 or H_2WO_4 , enhanced the catalytic performances of the supported ZrO_2 . The mesoporous structure of H₃PW₁₂O₄₀/ZrO₂ was identified by nitrogen adsorptiondesorption isotherms. In particular, partial sintering of catalyst particles in the duration of methanol carbonation caused a decrease in the Brunauer-Emmett-Teller surface area of the catalyst from 39 to 19 m²/g. The strong acidity of $H_3PW_{12}O_{40}/$ ZrO₂ was confirmed by the desorption peak observed at 415 °C in NH₃ temperatureprogrammed desorption curve. At various reaction temperatures (T = 110, 170, and220 °C) and CO₂/N₂ volumetric flow rate ratios (CO₂/N₂ = 1/4, 1/7, and 1/9), the calculated catalytic performances showed that the optimal methanol conversion, DMC selectivity, and DMC yield were 4.45, 89.93, and 4.00%, respectively, when T = 170 °C and CO₂/N₂ = 1/7. Furthermore, linear regression of the pseudo-firstorder model and Arrhenius equation deduced the optimal rate constant $(4.24 \times 10^{-3} \text{ min}^{-1})$ and activation energy ($E_a = 15.54 \text{ kJ/mol}$) at 170 °C with $CO_2/N_2 = 1/7$ which were favorable for DMC formation.

Keywords Carbon dioxide \cdot Methanol \cdot Carbonation \cdot Dimethyl carbonate \cdot H₃PW₁₂O₄₀/ZrO₂ catalyst \cdot Greenhouse effect gas

Kuen Song Lin kslin@saturn.yzu.edu.tw

¹ Department of Chemical Engineering and Materials Science/Environmental Technology Research Center, Yuan Ze University, Chungli District, Taoyuan City 32003, Taiwan, ROC

Introduction

In recent decades, natural gas, coal, and petroleum have provided more than 85% of the energy used by industry globally. The growing demand for energy raises CO₂ emissions yearly, causing serious global warming and climate change [1]. In order to reduce CO₂ emissions, several solutions have been proposed, including improving energy utilization efficiency, replacement with renewable energy, CO₂ storage/capture, and CO₂ conversion [1–3]. For the purpose of CO₂ reutilization, CO₂ conversion is the most appropriate solution, since it results in an appreciable profit for chemical and petrochemical industries [4–7]. In chemical and petrochemical industrial processes, tons of CO₂ can be directly converted to valuable hydrocarbons, such as urea, salicylic acid, dimethyl carbonate (DMC), cyclic carbonates, and polycarbonates via chemical conversions [8]. Notably, in comparison with other traditional agents used in carbonation, methanation, and esterification processes, such as methyl iodide, dimethyl sulfate, phosgene, and chloromethane, DMC is considered a low-toxicity biodegradable green chemical [9–11].

DMC has previously been produced from phosgene [12], esters [13, 14], CO_2 [15–18], and methanol [19], respectively. However, DMC production by CO₂ conversion is exothermic and non-spontaneous with negative enthalpy/entropy, and a high Gibbs energy, which restrict its application [20]. To remove the limitations of CO_2 conversion, several catalysts have been prepared to raise the reaction entropy and lower the Gibbs energy. Aymes et al. [21] prepared unsupported SnO₂ and ZrO₂ with highly effective active sites that were favorable for methanol carbonation. In addition, ZrO_2 can also act as a catalyst for interactions involving CO, H_2 , CH_4 , water, and CO₂ due to its flexible lattice structure and excellent redox properties [22, 23]. Tomishige et al. [15] prepared a ZrO₂ catalyst at different calcination temperatures to carbonate methanol into DMC at 5 MPa and 463 K. The mechanisms of DMC formation via methanol carbonation on ZrO₂ surfaces with tetragonal and monoclinic structures have been well studied [16]. It reveals that an increase in Brønsted basicity of hydroxyl groups and Lewis acid/base pairs may improve the catalytic performance of ZrO₂. On this basis, Jiang et al. [17] synthesized $H_3PW_{12}O_{40}/ZrO_2$ using the sol-gel method, which showed nine times the catalytic performance of ZrO₂ due to its raised Brønsted basicity. Moreover, the catalytic activation of ZrO₂ can be improved by adding $H_3PW_{12}O_{40}$ or $Ce_rTi_{1-x}O_2$ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0) as a precursor during catalyst preparation [18, 24]. The H₃PW₁₂O₄₀ could also be incorporated on the exfoliated montmorillonite for the production of alcohol, ketone, and oxime from cyclic aromatic hydrocarbons substrates, such as cyclohexanol [25].

Therefore, the crystal structures, morphologies, chemical compositions, and catalytic activities of $H_3PW_{12}O_{40}/ZrO_2$ prepared via the sol-gel method were investigated in present study. DMC formation in a fixed-bed reactor at various reaction temperatures (T = 110, 170, and 220 °C) and CO_2/N_2 volumetric flow rate ratios ($CO_2/N_2 = 1/4, 1/7, \text{ and } 1/9$) was analyzed by on-line Fourier-transform infrared spectroscopy (FTIR) and gas chromatography (GC). Based on the results,

the optimal methanol conversion, DMC selectivity, and DMC yield were calculated and obtained. The rate constant (k) and activation energy (E_a) of methanol carbonation were evaluated by linear regression of the pseudo-first-order model and Arrhenius equation, respectively. The dependence of DMC formation on temperature and CO₂/N₂ volumetric flow rate ratio have also been discussed.

Experimental

Catalyst preparation via sol-gel method

The catalyst precursor was prepared by dissolving ZrOCl₂·8H₂O and H₃PW₁₂·O₄₀·12H₂O in a 1:1 molar ratio in ethanol (12.5 mL) at 70 °C with stirring for complete dissolving, and then cooling slowly to room temperature. High-concentration NH₃OH solution was added dropwise to adjust the pH to 7.0 \pm 0.2, followed by stirring for 30 min. Pure gels were obtained by filtering, drying, and then washing with hot water until Cl anions were completely removed. Eventually, H₃PW₁₂O₄₀/ZrO₂ powder was afforded after calcining at 500 °C in a flowing airstream for 4 h.

Catalyst characterization

X-ray diffraction (XRD) patterns of the catalyst samples were recorded at a scan rate of $4^{\circ}(2\theta)$ /min using monochromatic Cu K_{α} radiation (MXP18; MAC Science) at 30 kV and 20 mA. The recorded specific peak intensities and 2θ values were further identified using an electronic database system (JCPDS). The morphologies, microstructures, and particle sizes of fresh and used H₃PW₁₂O₄₀/ZrO₂ were investigated by field-emission scanning electron microscopy (FE-SEM; S-4700 Type II; Hitachi). The chemical compositions of fresh and used H₃PW₁₂O₄₀/ZrO₂ were determined by X-ray photoelectron spectroscopy (XPS; ESCA PHI 1600; Physical Electronic) at the excitation energy of Al K_{α} (1486.6 eV). The C 1s (284.5 eV) peak was used as a calibration standard for tungsten and zirconium species (e.g., WO₃, H₂WO₄, WCl₂, ZrOCl₂, and ZrO₂) and their wide-region spectra. XPS signals of the above species were recorded using a cylindrical mirror analyzer. Specific surface areas and pore diameters were obtained from nitrogen adsorption-desorption isotherms (ASAP 2020; Micromeritics) using the Brunauer-Emmett-Teller (BET) equation. In addition, the acidity of H₃PW₁₂O₄₀/ZrO₂ was investigated by NH₃ temperature-programmed desorption (TPD; ChemiSorb 2750; Micromeritics) at 25-700 °C.

Catalytic performance calculation

The catalytic activity of these as-synthesized $H_3PW_{12}O_{40}/ZrO_2$ catalysts were evaluated in a fixed-bed stainless steel column reactor (CatRea2 v.1.02; JNP Tech.) with an inner diameter of 10 mm (catalyst loading: 1.0–1.5 g). Operating conditions, including the temperature/pressure in the fixed-bed reactor, and the flow rates of inlet gases, were controlled by a computer (with instilled LabVIEW software) connected to the above reactor. Methanol (0.05 mL/min) and CO_2/N_2 gas mixtures [volumetric flow rate ratio (CO_2/N_2) = 1/3, 1/7, and 1/9] were supplied to the fixed-bed zone at 40.0 mL/min and 50 bar under various reaction temperatures (110, 170, and 220 °C) for 10 h. FTIR was conducted on a Nicolet Magna-IR 830 spectrometer using the attenuated total reflectance method; 32 scans were collected to produce a spectrum, and background noise correction was performed. A GC–TCD (China Chromatography 9800) instrument connected to the FTIR spectrometer was used to measure the concentrations of unreacted methanol, DMC, and other byproducts. Ultimately, methanol conversion and DMC selectivity/yield using as-synthesized H₃PW₁₂O₄₀/ZrO₂ were calculated using Eqs. (1)–(3), which have been modified from related literature [20, 26, 27]:

Methanol conversion (C) =
$$\frac{[\text{MeOH}]_0 - [\text{MeOH}]}{[\text{MeOH}]_0} \times 100(\%)$$
(1)

DMC selectivity (S) =
$$\frac{[DMC]}{[DMC] + [H_2O]} \times 100 \ (\%)$$
(2)

DMC yield $(Y) = C \times S(\%)$ (3)

Kinetic analysis

The experimental equilibrium constant (k) and activation energy (E_a) were evaluated stepwise using Eqs. (4) and (5). In order to obtain k, we used a fixed methanol flow rate, allowing the methanol concentration to be considered constant, and thus simplifying and integrating the consumption rate of CO₂ to Eq. (4). It is called the pseudo-first-order model and is used for the simple analysis of reactant consumption rate [28, 29]. The activation energy of methanol carbonation was calculated using the linear form of the Arrhenius equation [Eq. (5)].

$$\ln \frac{[CO_2]_0}{[CO_2]} = \ln \frac{C_0}{C} = k(t - t_0)$$
(4)

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A \tag{5}$$

Results and discussion

Crystal structures and morphologies of H₃PW₁₂O₄₀/ZrO₂

The effects of methanol carbonation on the crystal structure of $H_3PW_{12}O_{40}/ZrO_2$ are displayed in Fig. 1. Diffraction peaks of ZrO_2 ($2\theta = 30.2^\circ$, 34.6° and 50.0°) and WO_3 ($2\theta = 60.0^\circ$) were confirmed using the JCPDS database. The existence of



Fig. 1 XRD patterns and FE–SEM microphotos of **a** fresh and **b** used $H_3PW_{12}O_{40}/ZrO_2$ for DMC formation via methanol carbonation

 WO_3 was attributed to the oxidization of $H_3PW_{12}O_{40}$ on the catalyst surface during the calcination procedure. The position and intensity of diffraction peaks in XRD patterns of fresh and used $H_3PW_{12}O_{40}/ZrO_2$ catalysts were unchanged. Based on the morphology of $H_3PW_{12}O_{40}/ZrO_2$, the particle size was observed and it increased from 194 to 270 nm due to the slight sintering of catalyst particles during DMC formation.

Chemical composition on H₃PW₁₂O₄₀/ZrO₂ surface

The chemical composition of as-synthesized $H_3PW_{12}O_{40}/ZrO_2$, measured by using XPS, is shown in Fig. 2. The signals for the Zr, W, and O elements in Fig. 2a indicate their existence on the catalyst surface. For W species, the valences were identified as W(VI) and W(II), as shown in Fig. 2b. WO₃ and H_2WO_4 were produced from $H_3PW_{12}O_{40}$ ·12H₂O, while WCl₂ was formed by the combination of W cations and residual Cl anions. Most importantly, the total integrated peak area percentage of W(VI) was 66.3%. It infers that it was the dominant species can induce methanol carbonation. Furthermore, the Zr species were 38.9 and 61.1%, respectively. The XPS spectra of W and Zr species showed that the percentage of reactive W species was over 60%, and residual Cl anions lowered the ratio of reactive W species.

Nitrogen isotherms and NH₃-TPD measurement of H₃PW₁₂O₄₀/ZrO₂

As shown in Fig. 3a, nitrogen isotherms of fresh and used $H_3PW_{12}O_{40}/ZrO_2$ are recognized as Type IV-H3 (mesopore with slit arrangement) according to the standard isotherms of the International Union of Pure and Applied Chemistry [30].





The BET surface area (pore volume) of $H_3PW_{12}O_{40}/ZrO_2$ decreased from 39 m²/g (0.24 cm³/g) to 19 m²/g (0.04 cm³/g), as shown in Table 1. It can be seen that the mesopore percentage in the catalyst decreased from 89.4 to 82.2% with an



Fig. 3 a Nitrogen isotherms and b NH3-TPD curve of fresh and used H3PW12O40/ZrO2

Table 1 Pore textural properties of as-synthesized H₃PW₁₂O₄₀/ZrO₂

Sample (H ₃ PW ₁₂ O ₄₀ / ZrO ₂)	BET surface area (m ² /g)	Langmuir surface area (m ² / g)	Pore volume ^a (cm ³ /g)	Saturated nitrogen adsorbed amount (cm ³ /g)—77 K	Pore size distribution ^a		
					V _{mirco} (%)	V _{meso} (%)	V _{marco} (%)
Fresh	39	64	0.24	154	1.9	89.4	8.7
Used	19	30	0.04	28	14.5	82.2	3.3

^aAverage pore volume and pore size were measured by the BJH desorption method

increasing micropore percentage. This indicated that the catalyst particles were partially sintered, such that the pore size became smaller for DMC formation via methanol carbonation. The acid characteristic of the as-synthesized $H_3PW_{12}O_{40}/ZrO_2$ was analyzed by NH₃-TPD, as shown in Fig. 3b. Generally, desorption temperatures of NH₃ peaks are proportional to the acidity [31], and the integrated peak area of NH₃ desorption is related to the amount of acidic sites on the catalyst surface. A single large NH₃ desorption peak appeared at 415 °C, indicating a strongly acidic surface. Thus, the activities of acidic sites on the catalyst surface favored DMC formation via methanol carbonation.

Catalytic performances of H₃PW₁₂O₄₀/ZrO₂

During DMC formation via methanol carbonation, the gaseous products were analyzed by in situ FTIR, as shown in Fig. 4. The intensities of specific absorption peaks for DMC (1705, 687 cm⁻¹), methanol (2974, 1053 cm⁻¹), and CO₂ (3730, 2345 cm⁻¹) increased markedly with reaction time, suggesting the formation of DMC. Especially, the absorption peak of water was undetected in the FTIR spectra because of the lower feeding rate of methanol. This implied that DMC formation may occur continuously toward the positive direction. The DMC yield was likely to exceed the equilibrium conversion of methanol, which was attributed to the effective prevention of water formation. Apart from the kinds of products, the effects of reaction temperature and CO₂/N₂ volumetric flow rate ratio on methanol conversion, DMC selectivity, and DMC yield were also studied. As shown in Fig. 5a–c, the optimal temperature and CO₂/N₂ volumetric flow rate ratio for methanol conversion (4.45%). At CO₂/N₂ = 1/4 with a fixed methanol flow rate, the



Fig. 4 Online FTIR spectra during DMC formation by using H₃PW₁₂O₄₀/ZrO₂ for 10 h



Fig. 5 Methanol conversions at various temperatures in CO_2/N_2 volumetric flow rate ratios of **a** 1/4, **b** 1/7, and **c** 1/9, for DMC formation via methanol carbonation with $H_3PW_{12}O_{40}/ZrO_2$

methanol conversion became stable after 420 min (Fig. 5a), revealing that the methanol had been totally consumed as a limiting reagent (Eq. 6).

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \tag{6}$$

At the ratio of $CO_2/N_2 = 1/9$, the CO_2 concentration was too low (limiting agent) and was insufficient for DMC formation. Therefore, it may reduce the final methanol conversion. In similar, the dependence on temperature, CO₂/N₂ ratio, and DMC selectivity is displayed in Fig. 6a-c. For example, the optimal temperature and CO₂/N₂ volumetric flow rate ratio for DMC selectivity were 170 °C and 1/7, respectively, giving the highest DMC selectivity (89.93%). It shows that most of the methanol feedstock was converted to DMC. Finally, DMC yields at various temperatures and CO₂/N₂ volumetric flow rate ratios (Fig. 7a-c) were consistent with the catalytic performances in methanol conversion and DMC selectivity, showing that the highest DMC yield (4.00%) was obtained at 170 °C and $CO_2/N_2 = 1/7$. Based on these calculations, it is likely that the reaction temperature and CO_2/N_2 volumetric flow rate ratio were dominant factors in the catalytic performance of H₃PW₁₂O₄₀/ZrO₂. Furthermore, DMC formation was seen to occur in the positive direction at a medium CO_2/N_2 volumetric flow rate ratio (1/7), thus increasing the final catalytic performance according to Le Chatelier's principle [28, 29, 32, 33]. However, variety tendencies of these catalytic performances were confirmed that corresponds to the results of kinetic analyses.

Kinetics analysis of DMC formation via methanol carbonation

According to Eq. (4), the slope of the linear regression lines increased with the rate constant (k) of methanol carbonation, as shown in Fig. 8a-c and Table 2. At various CO_2/N_2 volumetric flow rate ratios, it is apparent that the slope of linear regression lines at 170 °C was larger than those at 110 or 220 °C. The results of linear regression for the pseudo-first-order model revealed that the rate constant (k) at 170 °C was higher than those at 110 or 220 °C. Notably, CO₂/N₂ volumetric flow rate ratios also affected the k value. In the duration of DMC formation, a relative high CO₂ concentration led to methanol carbonation occurring in the positive direction until an equilibrium state was reached. Afterwards, carbon from the reduction of CO₂ was deposited on the catalyst surface, causing catalyst deactivation. For instance, the rate constant at 110 °C using $CO_2/N_2 = 1/7$ was 3.25×10^{-3} min⁻¹, which is larger than that for CO₂/N₂ = 1/4 (k = 3.03 × 10⁻³) min⁻¹) and 1/9 ($k = 2.51 \times 10^{-3} \text{ min}^{-1}$), as shown in Table 2. The linear regression data of the pseudo-first-order model for the rate constant corresponded with the previously calculated catalytic performances. Similarly, the slope of linear regression of Arrhenius equation also increased with the activation energy (E_a) of methanol carbonation, as shown in Fig. 8d-f and Table 2. Table 2 displays that the activation energy in $CO_2/N_2 = 1/7$ ($E_a = 15.54$ kJ/mol) was lower than those in $CO_2/N_2 = 1/4$ ($E_a = 20.56$ kJ/mol) and 1/9 ($E_a = 28.17$ kJ/mol). This indicated that the optimal reaction temperature and CO2/N2 volumetric flow rate ratio for DMC formation were 170 °C and 1/7, respectively, giving optimal k (4.24 × 10⁻³ min⁻¹)



Fig. 6 DMC selectivities at various temperatures in CO_2/N_2 volumetric flow rate ratios of **a** 1/4, **b** 1/7, and **c** 1/9 for DMC formation via methanol carbonation with $H_3PW_{12}O_{40}/ZrO_2$



Fig. 7 DMC yields at various temperatures in CO_2/N_2 volumetric flow rate ratios of **a** 1/4, **b** 1/7, and **c** 1/9 for DMC formation via methanol carbonation with $H_3PW_{12}O_{40}/ZrO_2$



Fig. 8 Linear regression of **a**–**c** pseudo–first-order reaction and **d**–**f** Arrhenius equations at various temperatures in CO_2/N_2 volumetric flow rate ratios of 1/4, 1/7, and 1/9, for DMC formation via methanol carbonation with $H_3PW_{12}O_{40}/ZrO_2$

and E_a (15.54 kJ/mol) values. In comparison of these linear regressions and catalytic performances, it implies that DMC formation via methanol carbonation was preferred at a medium CO₂/N₂ volumetric flow rate ratio (1/7) and reaction temperature (170°C). At these reaction conditions, it allows the reaction to readily proceed in the positive direction until equilibrium was reached. After that, the catalyst particles were slightly sintered until the reactive W species was totally poisoned, causing the rate constant to decrease with larger E_a . In summary, the catalytic performances of H₃PW₁₂O₄₀/ZrO₂ at reaction temperature (110°C) and CO₂/N₂ feeding ratio (1/9) were the lowest one due to the lower CO₂ concentration

CO ₂ /N ₂ volumetric flow rate ratio	Pseudo-first-o	order model	Arrhenius equation		
	Temp (°C)	Rate constant $(k \times 10^3, \min^{-1})$	R^2 value	Activation energy $(E_{\rm a}, \text{ kJ/mol})$	R^2 value
1/4	110	3.03	0.995	20.56	0.997
	170	3.49	0.999		
	220	1.98	0.995		
1/7	110	3.25	0.964	15.54	0.999
	170	4.24	0.974		
	220	2.38	0.970		
1/9	110	2.51	0.999	28.17	0.999
	170	2.90	0.999		
	220	1.97	0.997		

Table 2 Kinetic analysis for DMC formation using $H_3PW_{12}O_{40}/ZrO_2$ at various temperatures with CO₂/ N₂ volumetric flow rate ratios of 1/4, 1/7, and 1/9

and insufficient heat supply. On the other hand, the high reaction temperature (220°C) and CO_2/N_2 feeding ratio (1/4) might cause the sintering of $H_3PW_{12}O_{40}/ZrO_2$ catalyst particles and the deposition of carbon over the surface, thus reducing its catalytic performances. The slight sintering of catalyst particles can also be seen by FE-SEM microphotos in Fig. 1. According to some related literature [34–37], the carbon deposition had the possibility to be removed by low-temperature burning with a flowing O_2 or O_3 stream. The deposited carbon should be oxidized to CO_2 following Eqs. (7) and (8). This method may provide the possible solution to regenerate the used catalyst by removing the deposited carbon.

$$\mathbf{C} + \mathbf{O}_2 \to \mathbf{CO}_2 \tag{7}$$

$$3C + 2O_3 \rightarrow 3CO_2$$
 (8)

Conclusions

The existence of reactive W species in H₃PW₁₂O₄₀/ZrO₂ prepared via the sol–gel method was well characterized by XRD and XPS. The acidic strength of H₃PW₁₂O₄₀/ZrO₂ was also shown by NH₃-TPD measurement. Additionally, DMC formation was demonstrated and confirmed by its specific absorption peak at 1705 cm⁻¹ in online FTIR spectra for 1–10 h. In particular, the formation of water was effectively prevented by minimizing the feeding rate of methanol, which could enhance the DMC yield. Optimal reaction temperature and CO₂/N₂ volumetric flow rate ratio for DMC formation via methanol carbonation were 170 °C and 1/7, respectively, giving the highest methanol conversion (4.45%), selectivity (89.93%), and yield (4.00%) of DMC. The optimal rate constant ($k = 4.24 \times 10^{-3} \text{ min}^{-1}$) and activation energy ($E_a = 15.54 \text{ kJ/mol}$), evaluated from linear regression of the pseudo-first-order model and Arrhenius equation, respectively, were also obtained at 170 °C and CO₂/N₂ = 1/7. These analytical

results of linear regression were in agreement with the practical catalytic performance. In summary, $H_3PW_{12}O_{40}/ZrO_2$ was demonstrated to be an effective catalyst for DMC formation via methanol carbonation. It has the possibility to extend the application of methanol for CO_2 reutilization and global warming reduction.

Acknowledgements The financial support of the Ministry of Science and Technology (MOST), Taiwan (MOST 105–3113–E–008–003) is gratefully acknowledged. We also thank Prof. Y. W. Yang, Dr. J. F. Lee, and M. L. Lu of the National Synchrotron Radiation Research Center (NSRRC) for their helps in the EXAFS experiments.

References

- 1. A. Demirbas, Energy Source Part A 30, 70 (2008)
- R.A. Dagle, J. Hu, S.B. Jones, W. Wilcox, J.G. Frye, J.F. White, J. Jiang, Y. Wang, J. Energy Chem. 22, 368 (2013)
- 3. A. Dibenedetto, A. Angelini, P. Stufano, J. Chem. Technol. Biotechnol. 89, 334 (2013)
- 4. N.A.M. Razali, K.T. Lee, S. Bhatia, R. Mohamed, Renew. Sust. Energy Rev. 16, 4951 (2012)
- 5. J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei, Y. Sun, Catal. Today 148, 221 (2009)
- 6. N. Yang, R. Wang, J. Clean. Prod. 103, 784 (2015)
- 7. C.L. Chiang, K.S. Lin, Nanosci. Nanotechnol. Lett. 8, 1072 (2016)
- 8. H. Arakawa, Chem. Rev. 101, 953 (2001)
- 9. C. Li, X. Zhang, S. Zhang, Chem. Eng. Res. Des. 84, 1 (2006)
- 10. Y. Ono, Pure Appl. Chem. 68, 367 (2006)
- 11. W.L. Dai, S.L. Luo, S.F. Yin, C.T. Au, Appl. Catal. A Gen. 366, 2 (2009)
- 12. H. Babad, A.G. Zeiler, Chem. Rev. 73, 75 (1973)
- 13. S.R. Jagtap, M.D. Bhor, B.M. Bhanage, Catal. Commun. 9, 1928 (2008)
- 14. Y. Zhao, L.N. He, Y.Y. Zhuang, Chin. Chem. Lett. 19, 286 (2008)
- 15. K. Tomishige, Y. Ikeda, T. Sakaihori, J. Catal. 192, 355 (2000)
- 16. T.J. Kyeong, T.B. Alexis, Top. Catal. 20, 97 (2002)
- 17. C. Jiang, Y. Guo, C. Wang, C. Hu, Y. Wu, E. Wang, Appl. Catal. A Gen. 256, 203 (2003)
- 18. K.W. La, I.K. Song, React. Kinet. Catal. Lett. 89, 303 (2006)
- 19. U. Romano, R. Tesel, M.M. Marri, Ind. Eng. Chem. Prod. Res. Dev. 19, 396 (2000)
- 20. C.V. Miguel, M.A. Soria, A. Mendes, L.M. Madeira, J. Nat. Gas Sci. Eng. 22, 1 (2015)
- D. Aymes, D. Ballivet-Tkatchenko, K. Jeyalakshmi, L. Saviot, S. Vasireddy, Catal. Today 147, 62 (2009)
- 22. E.I. Kauppi, K. Honkala, A.O.I. Krause, J.M. Kanervo, L. Lefferts, Top. Catal. 59, 823 (2016)
- 23. M. Anpo, S.C. Moon, Res. Chem. Intermed. 25, 1 (1999)
- 24. K.W. La, J.C. Jung, H. Kim, S.H. Baeck, I.K. Song, J. Mol. Catal. A Chem. 269, 41 (2007)
- 25. H. Wang, L. Zhang, Y. Yang, L. Fang, Y. Wang, Catal. Commun. 87, 27 (2016)
- B.A.V. Santos, C.S.M. Pereira, V.M.T.M. Silva, J.M. Loureiro, A.E. Rodrigues, Appl. Catal. A Gen. 455, 219 (2013)
- 27. K. Kobl, S. Thomas, Y. Zimmermann, K. Parkhomenko, A.C. Roger, Catal. Today 270, 31 (2016)
- 28. Q. Yang, H. Wang, X. Ding, X. Yang, Y. Wang, Res. Chem. Intermed. 41, 4101 (2015)
- 29. Z. Li, P. Liu, F. He, M. Wang, E.N. Pistikopoulos, Comput. Chem. Eng. 35, 1857 (2011)
- 30. F. Rouquerol, J. Rouquerol, K. Sing, Academic Press 124, 234 (1999)
- 31. J. Bian, M. Xiao, S. Wang, Y. Lu, Y. Meng, Catal. Commun. 10, 1142 (2009)
- 32. I. Novak, J. Chem. Educ. 82, 1190 (2005)
- 33. H.J. Hofmann, A. Brandner, P. Claus, Chem. Eng. Technol. 35, 2140 (2012)
- 34. C.H. Bartholomew, Catal. Rev. 24, 67 (1982)
- 35. T.N. Angelidis, V.G. Papadakis, Appl. Catal. B Environ. 12, 193 (1997)
- E.S. Lokteva, A.E. Lazhko, E.V. Golubina, V.V. Timofeev, A.V. Naumkin, T.V. Yagodovskaya, V.V. Lunin, J. Supercrit. Fluids 58, 263 (2011)
- S.B. Rasmussen, A. Kustov, J. Due-Hansen, B. Siret, F. Tabaries, R. Fehrmann, Appl. Catal. B Environ. 69, 10 (2006)