

## Research Article

# Comparison of the Effects of Fluidized-Bed and Fixed-Bed Reactors in Microwave-Assisted Catalytic Decomposition of TCE by Hydrogen

Lili Ren and Jin Zhang

*School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China*

Correspondence should be addressed to Lili Ren, renlily@126.com

Received 13 June 2012; Revised 6 August 2012; Accepted 6 August 2012

Academic Editor: Wen-Hua Sun

Copyright © 2012 L. Ren and J. Zhang. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Trichloroethylene (TCE) decomposition by hydrogen with microwave heating under different reaction systems was investigated. The activities of a series of catalysts for microwave-assisted TCE hydrodechlorination were tested through the fixed-bed and the fluidized-bed reactor systems. This study found that the different reaction system is suitable for different catalyst type. And there is an interactive relationship between the catalyst type and the reaction bed type.

## 1. Introduction

Chlorinated organic compounds like trichloroethylene (TCE), which are widely distributed pollutants due to their extensive use for metal degreasing or textile cleaning, are very harmful to human beings from an environmental point of view [1, 2]. Methods for safe and environmentally acceptable destruction of recovered wastes or stocks of TCE are imminently needed. Conventionally, abatement of the TCE involves destructive technologies like thermal degradation, which often leads to the formation of carcinogenic byproducts [3]. It is well known that the incineration process is a well-established and expedient method for the elimination of chlorinated organic wastes, while highly energy-demanding and toxic heterocyclic organic compounds led by incomplete combustion still need solve [4]. Thus, safe conversion of TCE into value added products is still an intriguing goal of research. Because of its simplicity and effectiveness, hydrodechlorination (HDC) of chlorinated organics is an attractive alternative to incineration from both economic and environmental points of view. Moreover it enables the conversion of industrial byproducts to valuable chemical feedstock or environmentally friendly products [5–8]. High reaction temperature (excess of 773 K for non-catalytic [9, 10]), expensive precious metal catalysts (Pd, Pt, Rh and so forth [11]), and low hydrogen utilization are the main

problems that need to be solved for HDC of chlorinated organics [12]. Recently the use of microwave irradiation to accelerate the catalytic reactions has given some remarkable results [13–15]. With the employing of the microwave irradiation, the selectivity of the products distinctly increased [16]. We also introduced microwave technology into TCE HDC reaction and found that the addition of microwave does well to the TCE decomposition ratio [13, 16].

The HDC reaction is usually performed with the fixed bed (Figure 1, left). During the experiment, the local hot spots near the reactor wall have been detected, which resulted in the incomplete decomposition [17, 18]. Fluidization is the process by which solid particles attain a fluid-like state through suspension in a flowing gas or liquid [19]. Thus the fluidized bed reactor provides a close idealization in gas-solid contactors for high heat transfer rates, which is needed to ensure isothermal operation in a reactor [20]. The advantages of fluidized bed have been embodied in many heterogeneous catalytic reactions [21–25]. The combination of microwave with fluidized bed for the drying process of fruits and crops has shown significant improvement in operation cost and quality of products [26–28]. The microwave-assisted HDC of TCE is also a gas-solid phase reaction; herein the solid catalysts as internal heat carriers will provide a more homogeneous temperature distribution and offer the opportunity for high decomposition rates in

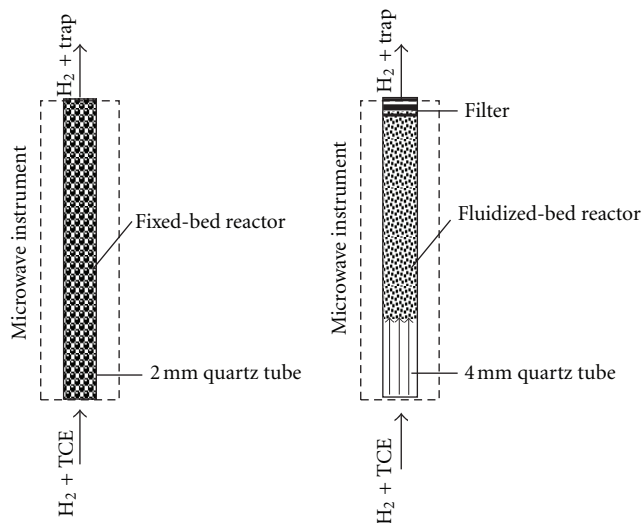


FIGURE 1: The schematic diagram comparing the fixed bed system with the fluidized bed system.

a small reactor space. Thus, in this paper, we investigated the effect of the reaction bed (the fluidized bed and the fixed bed) on the microwave-assisted HDC of TCE.

## 2. Experimental

**2.1. Catalysts Preparation.** A series catalyst has been prepared. All of the supported catalysts prepared through impregnation method. First  $\gamma\text{-Al}_2\text{O}_3$  (supplied by Shanghai Wusi Chemical Reagent Co., Ltd., China) or  $\text{SiO}_2$  (supplied by Shanghai Xingao Chemical Reagent Co., Ltd., China) was impregnated by aqueous solution of metal nitrate and stirred at  $80^\circ\text{C}$  for 4 h. Then the samples were dried at  $120^\circ\text{C}$  overnight and subsequently reduced by hydrogen at  $300^\circ\text{C}$  for 6 h. The components of all the catalysts presented in this paper are denoted as weight ratios.

**2.2. Catalytic Reaction.** Figure 1 is a schematic diagram comparing salient features of our old fixed-bed reactor with the new fluidized-bed reactor. The two setups are identical except for larger reactor diameter (for high gas flow rate required for fluidization). Using a bubbler for TCE supply, the amount of evaporated TCE corresponding to the weight loss of the bubbler was measured before and after the reaction. Nonreacted TCE can be completely trapped in a cold trap operated with liquid nitrogen. The flow ratio of  $\text{H}_2$  and TCE was adjusted approximately to 15:1. The production of HCl was trapped in a water bubbler and quantified very accurately by adding a pH indicator so as to calculate the decomposition rate. The detailed operation condition for the fixed bed can be seen in [16]. By increasing the hydrogen flow rate from 100 mL/min to  $\gtrsim 200$  mL/min, the reactor mode can be varied from fixed bed to fluidized-bed. For all fluidized-bed reactor experiments, 1 gram of as prepared catalyst was used at the reactor. To achieve good fluidization, the catalyst particle size was kept between 70 and 120 microns.

TABLE 1: TCE decomposing results over different catalysts and different reactor modes.

Catalyst	Reaction system	TCE decomposition ratio
Ni	Fixed bed	1.7%
	Fluidized bed	18.0%
10% Ni/ $\text{Al}_2\text{O}_3$	Fixed bed	30.0%
	Fluidized bed	6.2%
10% Ni/ $\text{SiO}_2$	Fixed bed	10.4%
	Fluidized bed	0.6%
Fe	Fixed bed	0.5%
	Fluidized bed	1.0%
10% Fe/ $\text{Al}_2\text{O}_3$	Fixed bed	0.4%
	Fluidized bed	0.1%
10% Fe/ $\text{SiO}_2$	Fixed bed	0
	Fluidized bed	0
Co	Fixed bed	0.6%
	Fluidized bed	2.0%
10% Co/ $\text{Al}_2\text{O}_3$	Fixed bed	13.3%
	Fluidized bed	1.6%
10% Co/ $\text{SiO}_2$	Fixed bed	0
	Fluidized bed	0

The MW absorption capability of the catalyst was determined by placing a quartz tube (4 mm ID), filled with the catalyst, into a cylindrical MW source. The hydrogen flow rate kept on  $100\text{ mL}\cdot\text{min}^{-1}$  for 2 hours under 120 W microwave irradiation. For microwave experimental, the detected method of temperature can be seen in [13].

## 3. Results and Discussion

Table 1 is to compare the catalytic activity for different catalysts with fixed bed and fluidized bed, respectively. From Table 1, we can see that not all pure metal catalysts show high TCE decomposition ratios under microwave conditions. And Ni is the most active metal catalyst compared with others. For loaded catalysts, Ni/ $\text{Al}_2\text{O}_3$  has the highest decomposition ability for fixed-bed experimental. The catalyst, which that is no activity with the fixed bed under microwave conditions, that is no activity either with the fluidized bed, such as 10% Fe/ $\text{SiO}_2$  and 10% Co/ $\text{SiO}_2$  catalysts.

There was another interesting phenomenon that could be observed when the reaction bed was changed from the fixed bed to the fluidized bed. First we could divide the catalysts into the supported catalysts and the pure metal catalysts. Then the following results can be easily concluded. For the pure metal catalysts, the activity with the fluidized bed is obviously higher than that with the fixed bed (see the activity of Ni, Fe, and Co). On the contrary, for all the supported catalysts, the activity with the fixed bed is higher than that with the fluidized bed, which, is completely different from our intuition.

As is well known, comparing with the fixed bed, fluidized bed has better internal heat transfer and allows for efficient



FIGURE 2: The picture of NiO/Al<sub>2</sub>O<sub>3</sub> (a) and Ni/Al<sub>2</sub>O<sub>3</sub> (b) after experiment.

temperature control. But why did there appear totally opposite results for pure metal catalysts and supported catalysts with the same reaction system and operation conditions?

10% NiO/Al<sub>2</sub>O<sub>3</sub> and 10% Ni/Al<sub>2</sub>O<sub>3</sub> have been chosen as the comparison to investigate the microwave distributing state in the microwave cavity. The whole reactor filled with the catalysts. The reduction treatment had been performed using MW irradiation for NiO/Al<sub>2</sub>O<sub>3</sub> while for Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, microwave-assisted HDC of TCE experimental was performed. Figure 2 shows the picture of the above two catalysts after test. The results demonstrated impressively that the heating was not uniform for the whole reaction bed. From the color of the catalysts we can easily deduce that there exists strong absorbing region and weak absorbing region. The hot area of microwave-heated region focuses on a 5 cm long region located the side of the reactor exit. When we carried out the test in the fixed bed reactor, the catalyst bed usually located at the strong absorbing region. Adequate adsorbing microwave time ensures the higher reaction temperature. While for the fluidized-bed test, the heat is transported by the moving particles themselves. It is well known that catalyst particles are carried by the streaming gas and move around in a restless and chaotic way for fluidized bed. Because the strong absorbing microwave zone is limited, the time when running particles are located at strong absorbing zone is uncertain. This would hardly ensure the enough time for particles to absorb the microwave for heating up. So for the fluidized bed, catalyst was to be asked to have strong MW absorption ability to heat up speedy to the reaction temperature. Comparing the absorbing capacity of the two type materials, pure metal catalyst particles are clearly greater than the supported catalyst particles because the supports we chose were Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, which have very low ability to absorb microwave [18]. For the pure metal catalysts, the decomposition ratio increased as the reaction system changed from the fixed bed to the fluidized bed, because of the better internal heat and mass transfer ability for fluidized bed. While for the supported catalysts, the temperature of catalyst bed is hardly as high as the fixed bed, which prevents the superiority of the fluidized bed to be embodied. In order to improve the TCE decomposition ratio, the catalyst with strong absorbing microwave ability is needed, which need us to design and prepare the new catalyst combined with the microwave knowledge. Another problem that should be urgently solved is uniform heating of the microwave irradiation. Recently we are trying to add extension to make MW-adsorbed area focus on the center of the reactor. These are the focus of our research.

#### 4. Conclusions

In conclusion, microwave-heating-assisted decomposition of TCE by hydrogen with the fixed bed and the fluidized bed

has been investigated, respectively. Compared with the other active metals we investigated, whether it is a pure metal or supported catalyst, Ni showed the best HDC activity under microwave conditions. At the same time, within the scope of our study, the supported catalysts fit for the fixed bed, while for the fluidized bed, the pure metal catalysts showed the higher decomposition ability.

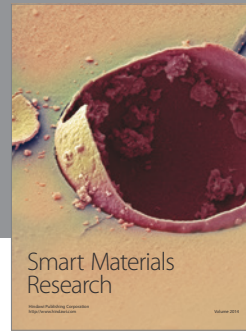
#### Acknowledgments

This research was supported by the Project of Chinese Ministry of Education (Grant no. 11YJ CZH139) and the Preliminary National Natural Science Foundation of Southeast University of China (Grant no. 9207040021).

#### References

- [1] R. E. Doherty, "A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1, 1, 1-trichloroethane in the United States: Part 2-Trichloroethylene and 1, 1, 1-trichloroethane," *Environmental Forensics*, vol. 1, no. 2, pp. 83–93, 2000.
- [2] A. L. Hines, T. K. Ghosh, S. K. Loyalka, and R. C. Warder, *Indoor Air Quality and Control*, Prentice Hall, Englewood Cliffs, NJ, USA, 1993.
- [3] N. S. Babu, N. Lingaiah, and P. S. S. Prasad, "Characterization and reactivity of Al<sub>2</sub>O<sub>3</sub> supported Pd-Ni bimetallic catalysts for hydrodechlorination of chlorobenzene," *Applied Catalysis B*, vol. 111-112, pp. 309–3316, 2012.
- [4] A. Musialik-Piotrowska, "Destruction of trichloroethylene (TCE) and trichloromethane (TCM) in the presence of selected VOCs over Pt-Pd-based catalyst," *Catalysis Today*, vol. 119, no. 1–4, pp. 301–304, 2007.
- [5] F. D. Kopinke, D. Angeles-Wedler, D. Fritsch, and K. Mackenzie, "Pd-catalyzed hydrodechlorination of chlorinated aromatics in contaminated waters-effects of surfactants, organic matter and catalyst protection by silicone coating," *Applied Catalysis B*, vol. 96, no. 3-4, pp. 323–328, 2010.
- [6] T. Zhou, Y. Li, and T. Lim, "Catalytic hydrodechlorination of chlorophenols by Pd/Fe nanoparticles: comparisons with other bimetallic systems, kinetics and mechanism," *Separation and Purification Technology*, vol. 76, pp. 206–214, 2010.
- [7] R. Cheng, W. Zhou, J. Wang et al., "Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: role of nano-Ni and its size effect," *Journal of Hazardous Materials*, vol. 180, pp. 79–785, 2010.
- [8] S. Ordóñez, E. Díaz, R. F. Bueres, E. Asedegbega-Nieto, and H. Sastre, "Carbon nanofibre-supported palladium catalysts as model hydrodechlorination catalysts," *Journal of Catalysis*, vol. 272, no. 1, pp. 158–168, 2010.
- [9] J. A. Manion, P. Mulder, and R. Louw, "Gas-phase hydrogenolysis of polychlorobiphenyls," *Environmental Science and Technology*, vol. 19, no. 3, pp. 280–282, 1985.
- [10] R. Louw, J. W. Rothuizen, and R. C. C. Wegman, "Vapour phase chemistry of arenes. Part II. Thermolysis of chlorobenzene and reactions with aryl radicals and chlorine and hydrogen atoms at 500°," *Journal of the Chemical Society*, no. 12, pp. 1635–1640, 1973.
- [11] C. Amorim and M. A. Keane, "Catalytic hydrodechlorination of chloroaromatic gas streams promoted by Pd and Ni: the role of hydrogen spillover," *Journal of Hazardous Materials*, vol. 211-212, pp. 208–217, 2012.

- [12] T. N. Kalnes and R. B. James, "Hydrogenation and recycle of organic waste streams," *Environmental Progress*, vol. 7, pp. 185–191, 1988.
- [13] H. Takashima, L. Ren, and Y. Kanno, "Catalytic decomposition of TCE under microwave," *Catalysis Communications*, vol. 5, pp. 317–319, 2004.
- [14] H. Takashima, M. Karches, and Y. Kanno, "Catalytic decomposition of trichloroethylene over Pt-/Ni-catalyst under microwave heating," *Applied Surface Science*, vol. 254, no. 7, pp. 2023–2030, 2008.
- [15] R. Varma, D. Sheu, B. J. Wood, and G. N. Krishnan, "Dctoxification of trichloroethylene," EPRI Project Report RP8000-45, 1990.
- [16] L. Ren and X. Pan, "Catalysts used for microwave-assisted TCE decomposition by hydrogen," *Catalysis Communications*, vol. 12, pp. 1366–1369, 2011.
- [17] N. Barrabes, D. Cornado, K. Foettinger et al., "Hydrodechlorination of trichloroethylene on noble metal promoted Cu-hydrotalcite-derived catalysts," *Journal of Catalysis*, vol. 263, no. 2, pp. 239–246, 2009.
- [18] D. M. P. Mingos and D. R. Baghurst, "Tilden Lecture. Applications of microwave dielectric heating effects to synthetic problems in chemistry," *Chemical Society Reviews*, vol. 20, pp. 1–47, 1991.
- [19] J. R. Thomas Jr. and F. Faucher, "Thermal modeling of microwave heated packed and fluidized bed catalytic reactors," *Journal of Microwave Power and Electromagnetic Energy*, vol. 35, pp. 165–174, 2000.
- [20] K. Takehira and T. Shishido, "Autothermal reforming of CH<sub>4</sub> over supported Ni catalysts prepared from Mg–Al hydrotalcite-like anionic clay," *Journal of Catalysis*, vol. 221, pp. 43–54, 2004.
- [21] Q. Jing, H. Lou, L. Mo, and X. Zheng, "Comparative study between fluidized bed and fixed bed reactors in methane reforming with CO<sub>2</sub> and O<sub>2</sub> to produce syngas," *Energy Conversion and Management*, vol. 47, pp. 459–469, 2006.
- [22] S. Ma, Y. Wang, N. Shah, and G. P. Huffman, "Catalytic methane decomposition using a fluidized bed reactor for hydrogen production," *Preprints of Papers—American Chemical Society, Division of Fuel Chemistry*, vol. 50, no. 2, pp. 636–637, 2005.
- [23] C. Lin, T. Peng, and W. Wang, "Effect of particle size distribution on agglomeration/defluidization during fluidized bed combustion," *Powder Technology*, vol. 207, pp. 290–295, 2011.
- [24] S. Jašo, H. Arellano-Garcia, and G. Wozny, "Oxidative coupling of methane in a fluidized bed reactor: influence of feeding policy, hydrodynamics, and reactor geometry," *Chemical Engineering Journal*, vol. 171, no. 1, pp. 255–271, 2011.
- [25] P. Subramanian, A. Sampathrajan, and P. Venkatachalam, "Fluidized bed gasification of select granular biomaterials," *Bioresource Technology*, vol. 102, no. 2, pp. 1914–1920, 2011.
- [26] E. I. Goksu, G. Sumnu, and A. Esin, "Effect of microwave on fluidized bed drying of macaroni beads," *Journal of Food Engineering*, vol. 66, no. 4, pp. 463–468, 2005.
- [27] J. Varith, P. Dijknarakukul, A. Acharyaviriya, and S. Acharyaviriya, "Combined microwave-hot air drying of peeled longan," *Journal of Food Engineering*, vol. 81, no. 2, pp. 459–468, 2007.
- [28] C. Sangdao and M. Krairiksh, "Analysis of a continuous fluidised-bed microwave rice kernel drying system," *Maejo Ational Journal of Science and Technology*, vol. 1, pp. 61–71, 2008.



# Hindawi

Submit your manuscripts at  
<http://www.hindawi.com>

