Microwave synthesis of thermally stable TUD-1 materials

Sang-Eon Park*, Sung-Min Jeong and Nanzhe Jiang
Laboratory of Nano-Green Catalysis and Nano Center for Fine Chemicals Fusion Technology, Dept. of Chemistry, Inha University, Incheon, 402-751, Korea
*separk@inha.ac.kr

Introduction

TUD-1 with 3-D sponge like mesoporous structure is a potentially important silica material in the catalytic applications, especially as catalytic supportant [1]. The general gelation and crystallization method is suitable to incorporate various metals in to silica framework and give good catalytic activities [2]. This is also a unique approach to prepare mesoporous zeolite composites with interconnecting meso and micropores which have shown higher catalytic performance than zeolite nanoparticles in the cracking of hexane [3]. However, the TUD-1 was synthesized via two step processes of gelation and crystallization step with hydrothermal process, which took long time and rather hard to control of water contents during synthesis especially in the drying step.

The microwave technique has been regarded as a novel synthesis tool due to some beneficial advantages such as homogeneous nucleation to give smaller and uniform crystals having rather larger external surfaces, rapid rates in the synthesis times, phase controlled synthesis, facile morphology control, greener synthesis as an energy efficient way and so on [4]. Besides them application of the microwave technique for the synthesis of nanoporous materials can allow rather facile incorporation of heteroatoms onto the zeolitic frameworks, more hydrophobicity and higher thermal stability than those of hydrothermally synthesized materials. The microwave synthesized microporous materials showed superior catalytic performances to those of the conventional hydrothermal synthesized samples [5].

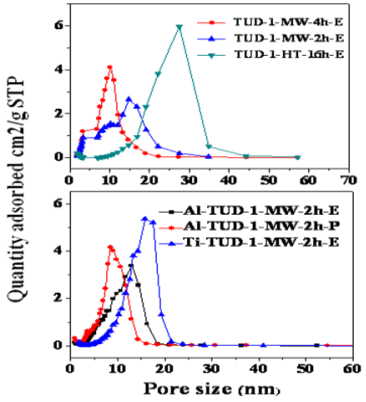
In the present work, applying TUD method, we synthesized pure silica, metal incorporated silica, metal oxides containing silica materials, metal oxides and mixed metal oxides by using microwave heating. The process of TUD method was simplified by without drying process and decreasing the synthetic time at 180 °C.

Materials and Methods

TUD materials with different compositions were synthesized by adding appropriate amounts of water and TEA (97%, ACROS) to the alkoxides (or mixture of alkoxides). After stirring for a few minutes, a solution of quarternary ammonium hydroxide was added as a mineraliser under vigorous stirring. This mixture with a molar ratio of $SiO_2/xZrO_2/(0.3\text{-}0.5)TEAOH/(0.5\text{-}1)TEA/(10\text{-}20)H_2O$ was aged at room temperature for 12-24 h, and dried at 100 °C for 12 h or directly followed by microwave treatment in a Teflon vessel at 180 °C for 1-2 h and finally calcined in the presence of air at 600 °C for 10 h.

Results and Discussion

The pure silica TUD materials were prepared by microwave without drying process and the pore size was simply controlled. The pore size decreased through the increasing of microwave irradiation time. But all of samples showed smaller pore size then hydrothermal synthesized one. Instead of TEAOH, TPAOH was also applied as mineralize agent in the preparation of Al containing TUD-1. The samples without drying process gave the dramatically increased pore volume but with the slight bigger pore size. In the case of microwave prepared Ti-TUD-1, we obtained homogeneous mesopores with tetragonally incorporated Ti species in the wall.



Samples	S_{BET}, m^2/g	V_{meso}, cm^3/g
TUD-1-HT	388	1.28
TUD-1-MW-2h-E	543	1.1
TUD-1-MW-4h-1-E	607	1.08
Al-TUD-1-MW-2h-E	442	1.1
Al-TUD-1-MW-2h-P	642	1.28
Ti-TUD-1-MW-2h-E	493	1.18
Ti-TUD-1-HT[6]	628	1.1

Figure 1. Pore size distribution of TUD-1 synthesized by MW with TEAOH (-E) and TPAOH (-P); all samples prepared without drying

Significance

The general two step gelation and crystallization method was simplified in MW synthesis. And both pore size and pore volume were controllable by simply control the microwave irradiation time. Also, MW Synthesis could work in both cases with or without drying process within relatively short time.

References

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