Direct and versatile synthesis of metal-containing mesoporous silica nanoparticles for heterogeneous catalysis

Chia-Min Yang,[a]* **Nien-Chu Lai,**[a] **Ming-Chieh Tsai**[a]

[a]*Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan*

**Corresponding author: +886-3-5165521, cmyang@mx.nthu.edu.tw*

Abstract: A "pH-jump" synthesis was developed to prepare metal-containing mesoporous silica nanoparticles. Materials containing highly dispersed Cu or Cu/Zn were prepared and exhibited superior catalytic activity and stability for the selective oxidation of propylene with O_2 to produce acrolein. The synthetic strategy could be applied to prepare materials containing other metals using ammonia or suitable amine-type stabilizing ligands for other catalytic reactions.

Keywords: metal-containing mesoporous material, direct synthesis, heterogeneous catalysis.

1. Introduction

Supported catalysts containing highly dispersed metals generally exhibit high activity in heterogeneous catalysis. Their preparation remains challenging,[1] and low metal dispersion is often a problem when metals being deposited on mesoporous or high-surface-area supports.[1] Herein a simple and direct synthetic strategy to prepare metal-containing mesoporous silica nanoparticles (MSNs) is reported and demonstrated by copper-containing MSNs for oxidation reactions.[2] It is based on the "pH-jump" synthesis of MCM-41-type MSNs[3] with the ammonia complex of Cu(II) as metal precursor. After reduction, the copper-containing MSNs contained nanosized metallic particles and exhibited superior catalytic activity and stability for the selective oxidation of propylene with O_2 to produce acrolein. The strategy could be easily applied to synthesize MSNs containing other metals using ammonia or suitable amine-type stabilizing ligands. MSNs containing both Cu and Zn were also prepared and the influence of ZnO on the catalytic performance of the selective oxidation of propylene was studied.

2. Experimental

The synthesis of Cu- and Cu/Zn-containing MSNs were prepared by following similar procedure reported previously for the pure-silica MSNs[3] using the ammonia complexes of Cu(II) and Zn(II) as metal precursors and ethyl acetate as a pH modifier. The surfactant in the Cu-containing samples was removed by calcination or by solvent extraction, resulting in samples with varied Cu/Si ratio of x% denoted as xCu-C and xCu-E, respectively. A reference calcined sample with Cu/Si=3% prepared by impregnation was denoted as 3Cu-IC. For the catalytic studies, a catalyst was pretreated online with H_2 at 350 °C for 1 h and the reaction gas (5% propylene, 5% O_2 in He, space velocity: 30,000 $cm^3\ h^{-1}\ g_{cat}^{-1}$) was flowed over the catalyst. The gas leaving the reactor was analyzed by GC equipped with TCD and FID.

3. Results and discussion

The ammonia complex of Cu(II) was stable under the alkaline synthesis conditions, and all the copper species were precipitated in the solids, as confirmed by ICP-MS and EDX. The ordered mesostructure, high mesoporosity and particle morphology were confirmed by PXRD, N_2 physisorption and SEM. The process of solvent extraction did not cause metal leaching, and the Cu/Si ratios for the calcined and solvent-extracted samples were nearly identical. H_2-TPR and N_2O-oxidation/H_2-TPR analyses revealed high metal dispersion of the samples (> 50%), and the estimated particle sizes for 3Cu-C and 3Cu-E (~1.6 nm and 2.0 nm, respectively) were consistent with derived from XAS.

The reduced catalysts were used for the oxidation of propylene with O_2 at 180-260 °C. All catalysts predominantly produced acrolein and CO_2, with ethanal and trace amounts of other C2 and C3 molecules as byproducts (cf. Table 1). Acrolein yield was found strongly associated to metal dispersion, and the increase in propylene conversion as increasing temperature was accompanied by a drop in the acrolein selectivity and

Table 1. Steady-state catalytic performance of the H_2-reduced Cu-containing MSNs.

Catalyst	T (°C)	Conversion (%)		Selectivity (%)				Acrolein yield (%)	Formation rate ($mmol_{acro}g_{Cu}^{-1}h^{-1}$)	TOF (h^{-1})
		O_2	C_3H_6	acrolein	CO_2	ethanal	others			
3Cu-C	180	1.6	0.7	58	31	8	3	0.4	8	1.4
	220	9.4	3.9	51	42	6	1	2.0	39	7.7
	260	33.9	13.9	50	41	4	5	6.9	136	27.3
3Cu-E	180	3.4	1.7	56	37	6	1	1.0	19	4.1
	220	26.0	9.8	51	45	3	1	5.0	98	23.4
	260	64.5	25.1	48	42	3	7	12.1	236	60.0
3Cu-IC	180	0.2	0.1	59	29	8	4	0.1	1	1.0
	220	0.7	0.4	54	35	8	3	0.2	4	5.0
	260	3.2	1.6	46	43	6	5	0.7	14	19.0
3Cu-EM	180	1.1	0.5	63	26	8	3	0.3	6	0.2
	220	3.2	1.9	69	22	7	2	1.3	25	0.7
	260	7.8	5.2	70	17	6	7	3.6	69	1.9

slightly increase in the CO_2 selectivity. The catalytic activity was also influenced by the surface properties of silica support, as evidenced by the poor performance of the surface-passivated sample 3Cu-EM. In-situ XAS and DRIFT indicated that the Cu(0) species were immediately oxidized to Cu(I) at room temperature, and the Cu(I) species together with the silanol nests present in 3Cu-E contributed to the adsorption of propylene, thereby resulting in the high catalytic activity of the sample.

When Zn was co-precipitated, the resulting Cu/Zn-containing MSNs (Cu/Zn-MSNs) showed broader H_2-TPR peaks that were shifted toward higher temperature, indicating lower reducibility of copper in the presence of ZnO. A volcano relationship between the amount of ZnO and the catalytic activity for the selective oxidation of propylene with O_2. In-situ XAS and other analyses suggested that the presence of ZnO made CuO_x smaller in size before reduction and promoted larger fraction of copper to remain at 1+ oxidation state after reduction and during the catalytic reaction. The Cu/Zn-containing MSNs exhibited stable catalytic activity with acrolein and CO_2 as major products (Fig. 1). The optimized sample contained 0.65 wt% of Zn and showed propylene conversion of 8.2% and 22.1% and acrolein yield of 4.3% and 12.6% at 220 °C and 260 °C, respectively.

The synthetic strategy could be easily applied to incorporate first-row transition metals and noble metals into MSNs using suitable stabilizing ligands, Catalytic studies of the resulting materials on CO_2 reduction (Ni-MSNs), biodiesel fuel production (Ti-MSNs) and methane oxidation (Fe-MSNs) were discussed.

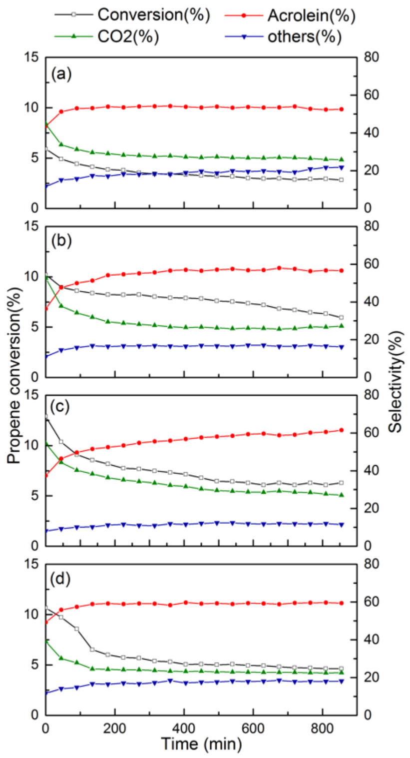

Figure 1. Changes in propylene conversion and product selectivities with on-stream time for Cu/Zn-MSNs with Zn loading of (from a to d) 0%, 0.32%, 0.65% and 1.12%.

4. Conclusions

Cu- and Cu/Zn-containing MSNs were synthesized by the "pH-jump" method and showed high catalytic activity for the selective oxidation of propylene with O_2 to acrolein. The synthetic strategy can be applied to prepare MSNs containing other metals.

References

1. M. D. Gawande, A. Goswami, F. X. Felpin, T. Asefa, X. Huang, R. Silva, X. Zou, R. Zboril, R. S. Varma, Chem. Rev. 116 (2016) 3722.
2. C. H. Liu, N. C. Lai, J. F. Lee, C. S. Chen, C. M. Yang, J. Catal. 316 (2014) 231.
3. N. C. Lai, C. J. Lin, W. C. Huang, C. M. Yang, Microporous Mesoporous Mater. 190 (2014) 67.