Effect of hard template's residues of the nanocasted mesoporous $LaFeO_3$ perovskite with the extremely high surface areas on methyl chloride oxidation

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Introduction

Silica-base mesoporous molecular sieves are always used as hard template (HT) to prepared some metal or multi-metal oxides through hard template method[1]. These HTs are usually removed by 2M NaOH solution. Many reports have noted that there were still a little amount of silica HT left in the final materials no matter how many times the samples were treated, especially in the multi-metal oxides[2]. However, to our knowledge, none of them showed the effect of the Si-residue content on the catalyst microstructure and the related catalytic behaviors.

In this work, silica-base mesoporous molecular sieve (SBA-15) was adopted as HT, by one-step-infiltration method to fill the mesoporous channels of HT with $LaFeO_3$ perovskite precursors. Continuously, HT was leached by NaOH solution. An attempt to obtain different Si-residue-content samples by controlling the leaching time, as well as NaOH concentration, and evaluate their catalytic activities in methyl chloride (CH_3Cl) oxidation has been done.

Materials and Methods

The mesoporous $LaFeO_3$ perovskite catalysts were prepared using a similar method of ref [3]. Samples with different Si-contents which were respectively noted as $LaFeO_3$/SBA-15, H-Si, M-Si and Meso-LaFe were obtained by controlling the leaching time of 2M NaOH solution, while L-Si was treated by high concentration of NaOH solution (10M). The traditional one (Tra-LaFe) was also prepared for comparing. The experiments were run in a fixed-bed quartz micro-catalytic flow reactor at atmospheric pressure. They were conducted at a 1500 ppm of methyl chloride, 10% of O_2, a GHSV = 15,000 h^{-1} and 200-600 °C.

Results and Discussion

Results of N_2 adsorption/desorption analysis and Si-contents are given in **Table 1**.

Table 1. Results of N_2 adsorption/desorption analysis and Si-contents for the prepared samples

Sample	Si content / *wt*.%	S_{BET}/ m^2g^{-1}	Pore volume / cm^3g^{-1}	Pore size/ nm
SBA-15	46.7	872	1.15	6.4
$LaFeO_3$/SBA-15	19.6	86	0.11	5.6
H-Si	13.6	90	0.16	6.0
M-Si	10.4	104	0.19	6.1
Meso-LaFe	5.4	158	0.26	6.0
L-Si	1.9	69	0.09	-
Tra-LaFe	0	19	0.02	-

With the decrease of Si content, the BET surface area was increasing, except sample L-Si which has be confirmed by XRD (not show here) that the perovskite structure has collapsed. This result demonstrates that the residue of Si has an adverse effect on the sample in term of the BET surface area. The phenomenon of L-Si indicated that super-low Si content sample could be obtained through treating by high concentration NaOH solution, but, the treatment may lead to the destruction of perovskite structure. In other word, some HT left may facilitate the stabilization of perovskite structure and mesoporous of catalysts.

Figure 1 shows (a) CH_3Cl conversion; (b) HCl selectivity in the $CH_3Cl + O_2$ reaction over the aforesaid catalysts except sample L-Si because $LaFeO_3$ was not the only species for it. Observe carefully, one can find that sample with higher BET surface area has a better activity in methyl chloride conversion and HCl selectivity. The curves shapes of H-Si, M-Si and Meso-LaFe are also different from that of $LaFeO_3$/SBA-15 and Tra-LaFe in HCl selectivity(Fig1b). This demonstrates that , in general, the residue of Si has an adverse effect on the catalyst morphology & pore structure and catalytic activity.

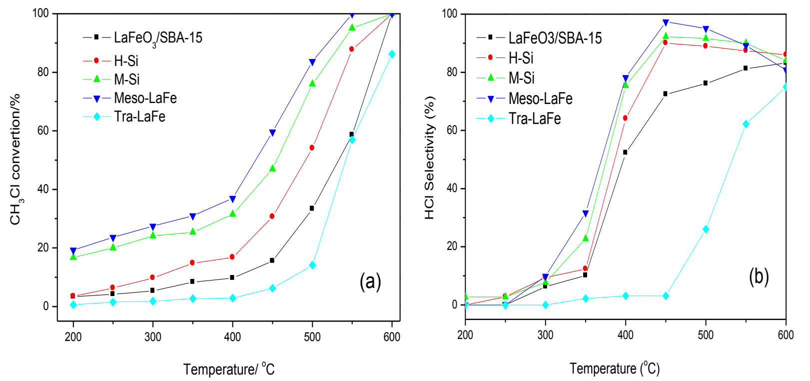

Figure 1. (a) CH_3Cl conversion; (b) HCl selectivity in the $CH_3Cl + O_2$ reaction over the catalysts

Significance

Massive left of HT is adverse for the mesoporous $LaFeO_3$ perovskite catalyst in the oxidation of methyl chloride. Within limits, the less HT left, the better catalytic activity and HCl selectivity.

References

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