Effect of Pretreatment on Cu/ZnO-HT in MTC Reaction and Its In-situ XANES

Ting C. Hsiao (蕭鼎洲) and Shawn D. Lin (林昇佃)

Department of Chemical Engineering and Material Science, Yuan Ze University, Chungli, Taiwan

Most research which use methanol as feedstock to form carbon-bond growth products focused on MTH (methanol-to-hydrocarbon, including MTO- methanol to olefin and MTG- methanol to gasoline). Their mechanism are considered as that two methanol molecules dehydrate to di-methyl ether, and then continue to dehydrate and condense into higher oxygenates, leading to shirt-chain light olefins. These light olefins may condense further to aromatics, paraffins, cycloparaffins, or C_{6+} olefins.

Zeolites, such as ZSM-5, H-SAPO-34, Ga_2O_3/H-ZSM-5…etc., are used at high temperatures (633 - 773K) for traditional MTH processes. This type of catalysts was found to deactivate by the coke formation. This research intends to reduce the reaction temperature and also to develop new Cu catalysts for the reaction. Lower temperature (e.g., 523 K) may preserve more oxygen on the long-chain product and consequently shift the selectivity toward oxygenates. This study intends to change the operating condition such as pretreatment, space velocity, composition of catalys to control conversion and selectivity of carbon-chain growth products.

Our previously study shows that Cu/ZnO/HT (hydrotalcite) catalyst was found to have good potential for this reacton at around 500 K but the catalyst is very sensitive to pretreatment. Table 1 illustrates the pretreatment effect in the reaction results. At 773K-calcination condition, low methanol conversion and no formation of C_{2+} product are obserbed, in which CO, CO_2, DME, and MF are the main products. With increasing reduction temperature, the methanol conversion increased and the MF disappeared from product stream. CO is still the main product. Most importantly, the selectivity to C_{2+} shows maximum at 523K-reduction. Higher reduction temperature decreased S_{C2+}. The catalyst structure after different pretreatment is obviously affecting the C_{2+} formation and, therefore, XANES is applied to analyze the structure changed during different pretreated conditions. In-situ XANES (X-ray Absorption Near-Edge Structure) analysis during a TPO of fresh Cu/ZnO-HT is shown in Fig. 1. XRD analysis shows that the intial $Cu(OH)_2$ is converted to CuO, which is also shown in Cu-edge XANES. The corresponding Zn edge (Fig.1 (b)) show unusual change as the while line is lower with increasing calcination temperature. This suggests a partial reducton in Zn during TPO. No explantion to this phonomen is available and it awaits more detailed analysis. Our previous TPR profile of the calnied catalyst shows two reduction peaks from 323 to 823K. Fig.2 shows that Cu is reduced as the temperature increased, but 589K-reduction condition did not totally reduce the catalyst. During the TPR, Zn edge shows almost the same shape of curve. This suggests Zn formed a stable structure after calcination. As memtioned previously, the type of structure has significant fator for the MTH reaction. The interplay between Cu, Zn and hydrotalcite can be expected but is not inderstood yet. Futher EXAFS experiment may help to elucidate the active structure.

Table1 The pretreatment effect in MTH on Cu/ZnO/HT at 523K (WHSV= 0.2 h^{-1}, P_{MeOH}= 200 torr)

Pretreat.	X	S_{CO2}	S_{CO}	S_{MF}	S_{DME}	S_{C2+}
773K,C	38.3	38.6	39.8	7.8	13.8	0
473K,R	56.4	18.9	47.59	2.4	15.8	15.4
523K,R	65.4	14.6	49.8	0	14.0	20.1
550K,R	68.2	13.9	65.7	0	16.2	4.2
773K,R	70.3	14.3	72.3	0	13.4	0

773K,C: calcined at 773K for 1hr; 473K,R: reduced at 473K for 30 min; X:conversion (%); S:selectivity; MF: methyl formate; DME: di-methyl ester; C_{2+}: higher compounds

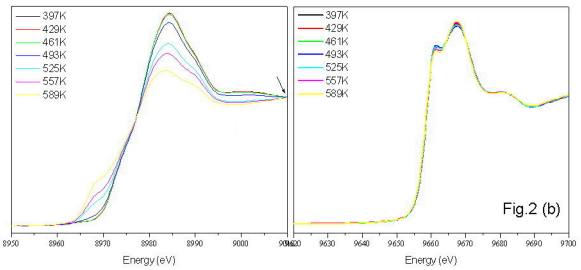

Figure 1. In-Situ TPO XANES Spectrum of fresh Cu/ZnO/HT: (a) Cu edge, and (b) Zn edge, flow rate of O_2= 50 sccm

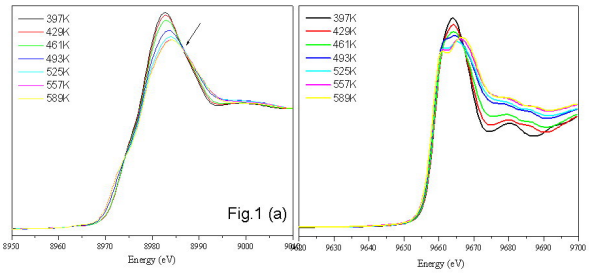

Figure 2. In-Situ TPR XANES Spectrum of calcined Cu/ ZnO/HT: (a) Cu edge, and (b) Zn edge, flow rate of H_2= 50 sccm