The study of oxidative carbonylation of methanol to dimethyl carbonate on Cu/ST catalysts

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1. Introduction

Dimethyl carbonate (DMC) is an environmental benign chemical compound and unique intermediate with versatile chemical reactivity which may contribute to "Green Chemistry" replacing toxic or high waste technology. Furthermore, DMC has gained interest as dipolar aprotic solvent and as fuel additive improving the octane number and replacing more toxic or less biodegradable additives [1]. Among several phosgene-free approaches for DMC production, the direct oxidative carbonylation of methanol with CO and O_2 in a liquid-phase slurry reactor has shown to be one of the most promising processes for the production of DMC [2].

In this paper, a series of Cu(I) supported catalysts were prepared by solid-state ion exchange. The catalytic activity to synthesize DMC was studied in a slurry reactor. The catalysts have been characterized by XRD analytical methods and well discussed. Cu/TS catalysts revealed a very excellent activity in oxidative carbonylation of methanol. The MeOH conversion and DMC selectivity reached 7.82％and 86.85.0％ respectively over Cu/TS10 with the reaction condition T=413K, P=2.4MPa, CO/O2=2; The preparation temperature took a dominant role both in the structure and reactivity for Cu/TS catalysts in this reaction.

2. Experiment

2.1 Catalyst preparation

Preparation of Si-Ti oxides suppots

Various Si-Ti mixed oxides were prepared by an acid catalyzed sol–gel process in analogy to the following procedure ST: TEOS (tetraethyl orthosilicate) was dissolved in ethanol and stirred in a 250ml PP-beaker for 15 min, then CH_3COOH and H_2O was added, then stirred till to change to Si-based sol. $Ti(OiPr)_4$ was dissolved in ethanol and stirred in a 250 ml PP-beaker for 15 min, then CH_3COOH was added in turn stirred to Ti-base sol. Then the two sols were mixed stirred, the beaker was covered with parafilm and stored overnight under stirring until the sol converted into a Si-Ti mixed gel. After drying, the gel were calcined according to the temperature program:

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$$RT \xrightarrow{0.5K/\min} 338K(180\min) \xrightarrow{0.5K/\min} 823K(180\min) \xrightarrow{2K/\min} RT$$

The support was marked STx, such as ST3, which meaned the ratio of Si to Ti atom was 3.

Preparation of Cu/ST catalyst

CuCl and ST supports were mixed and grinded in a ball grinder, then calcining in a tube oven under N_2 atmosphere for 3 hours then cooling to room temperature.

2.2 Catalytic activity test

The catalytic reaction was performed in a batch reactor with 50ml of methanol and 2 g of catalyst. The initial pressure is 2.4MPa and the molar ratio of CO to O_2 was fixed at 2. The reaction products were collected and analyzed with a gas chromatograph (Agilent 6890) equipped with a FID detector, using a 0.25mm×15m capillary column HP-PLOT/Al_2O_3 "M" Deactivated.

2.3 Catalyst characterization

The crystal structures of the catalysts were determined using a Rigaku D/max 2500 X-ray powder diffractometer with monochromated Cu Kα (40kV/100mA) radiation.

3. Results and discussion

3.1. The effect of supports on the activitys

The effect of support on MeOH conversion and selectivity to DMC over Cu/ST catalysts are shown in figure 1. It was clear that the composition of supports has a strong influence on the catalytic activity, MeOH conversion increases with the increase of Si content and reached the

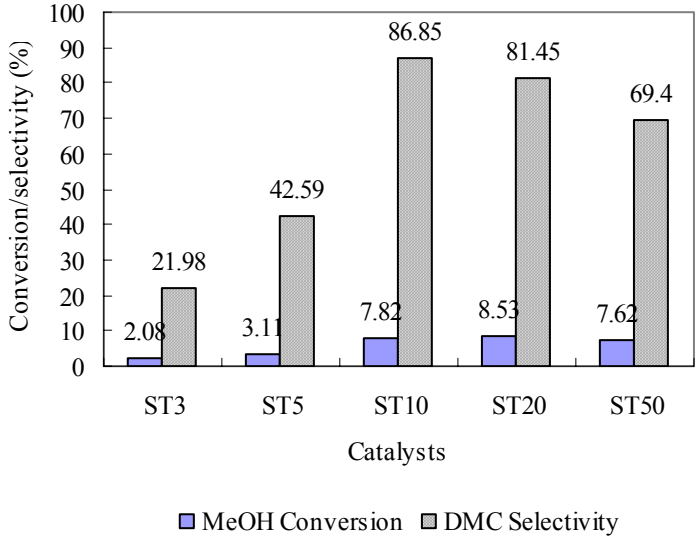

Figure 1 The effect of support on MeOH conversion and selectivity to DMC

highest value when the ration of Si to Ti reaches to 20, and further increase of Si content led to a decrease of MeOH conversion. Additionally, the highest selectivity (86.85%) to DMC is also

observed with Cu/ST10, an excess of Si content in support is harmful to both MeOH conversion and DMC selectivity. In all cases, the best support for Cu/ST catalysts is ST10.

3.2. The effect of calcined temperature on the activitys

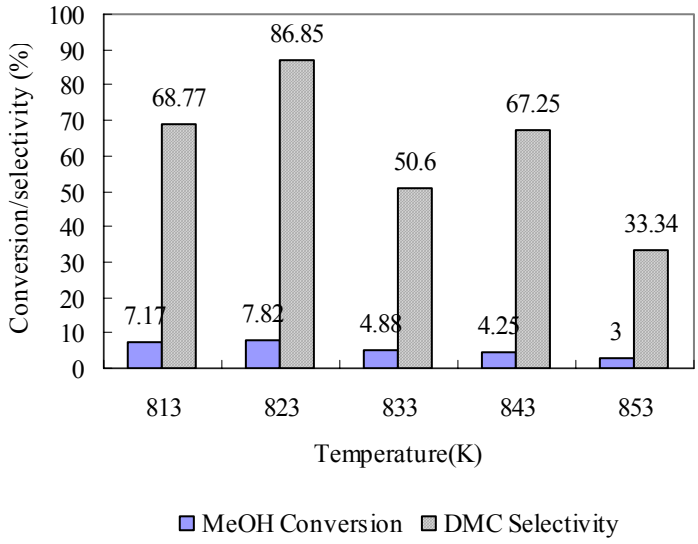

Figure 2 The effect of calcined temperature of Cu/ST10 on MeOH conversion and selectivity to DMC

Figure 2 gives results of the effect of calcining temperature on MeOH conversion and selectivity to DMC. We can see that MeOH conversion and selectivity to DMC increases with the calcined temperature increases from 813K to 823K, then declines with the temperature further increasing.

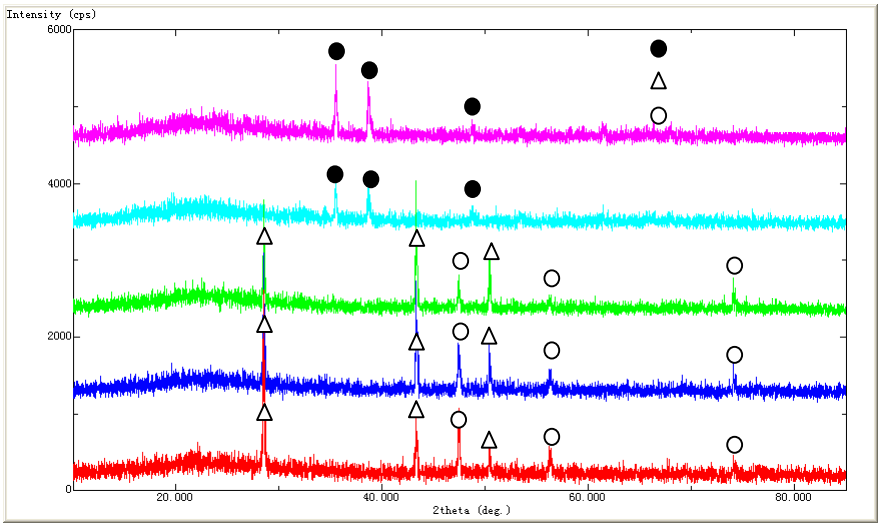

Figure 3 XRD pattern of Cu/ST10 catalysts on different calcined temperature

In our study, Cu/ST10 was calcined on various temperature in N_2 atmosphere for 3 hours, XRD pattern of which is presented in figure 3. All catalysts gave no diffraction peaks of

titania, which proves that titanium species were highly dispersed in SiO_2 amorphous support and the support is stable on the temperature investigated. From 813K to 833K, the height of diffraction peaks of CuCl decreases with the increasing of calcined temperature, due to CuCl decomposes in the course of calcined which is shown in reaction (1):

$$2CuCl \rightarrow 2Cu + Cl_2 \uparrow \quad (1)$$

However, the diffraction peaks of both CuCl and Cu disappear on 843K and 853K, simultaneity, the diffraction peaks of CuO appear and enhances with the increasing of temperature, which proved harmful for the DMC creation. Due to the catalysts were calcined under the atmosphere of N_2, we think that CuCl decomposes to Cu and Cl_2 completely on 843K, then Cu changes to CuO by the oxidation of the lattice oxygen (O*) in bulk of ST mixed oxides support:

$$Cu + O^* \rightarrow CuO \quad (2)$$

According to above result, the suitable calcined temperature for Cu/ST10 is 833K, and further investigation are necessary in the future.

4. Conclusions

Si-Ti mixed-oxides support catalyst Cu/ST prepared by an acid-catalyzed sol-gel method is effective for the oxidative carbonylation of methanol to DMC, the favorite composition of support is about ST10, and the suitable calcined temperatue is at 833K.

5. Acknowledgements

The authors are grateful for the financial support of Shanxi Province Science Foundation, P. R. China No. 20051008 and No. 20031022, Shanxi Returned scholarship No. 20030031 as well as Taiyuan Science and Technology Foundation No.22099740.

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