In situ studies of structural changes in DME synthesis catalyst with synchrotron powder diffraction

Kazi Bayzid Kabir [a], Helen E. Maynard-Casely [b,1], Sankar Bhattacharya [a,*]

[a] Department of Chemical Engineering, Monash University, Clayton, Victoria -3800, Australia
[b] Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria -3168, Australia

ABSTRACT

Structural changes in a bi-functional dimethyl ether synthesis catalyst (CuO-ZnO-Al_2O_3-MgO + γ-Al_2O_3, BFC), a methanol synthesis catalyst (CuO-ZnO-Al_2O_3-MgO, MSC) and a methanol dehydration catalyst (γ-Al_2O_3, MDC), were studied using X-ray synchrotron powder diffraction. The catalysts were first reduced in 10% H_2/He and then treated in a gas containing CO, H_2 and CO_2. Measurements were taken at temperatures between 50 °C and 500 °C. These measurements were complemented by ex-situ techniques—thermogravimetry (TG) and scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS). The X-ray diffraction (XRD) results showed that the copper oxide phase, present in methanol synthesis and bi-functional catalysts, reduced to form Cu^0 after reduction. No further chemical changes were observed for these catalysts. γ-Al_2O_3 was resistant to structural and chemical changes. The copper crystallite sizes of the methanol and bi-functional catalysts were found to increase with temperature. The extent of deactivation was higher for CuO-ZnO-Al_2O_3-MgO + γ-Al_2O_3 compared to CuO-ZnO-Al_2O_3-MgO.

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1. Introduction

Single-step conversion of syngas to dimethyl ether (DME) has received significant attention in the synthetic fuel research area since 1991 [1]. Conventional two-step synthesis involves production of methanol from syngas, purification of methanol and then dehydration of methanol in a separate reactor to produce DME. The single-step process eliminates the intermediate step, by incorporating both the reactions in the same reactor. This process also has higher yield than the conventional process, since it removes the thermodynamic limitation of CO-hydrogenation [2] by in situ dehydration of methanol to DME. A hydrogenation catalyst (usually copper based [2]) and a dehydration catalyst (usually γ-Al_2O_3 [3]) placed in a single reactor are responsible for one-step conversion of syngas to DME. Copper-based catalysts have various industrial applications (i.e. methanol synthesis, water-gas shift, methanol reforming) and hence extensively studied over the years [4–9]. Meanwhile, a wide range of solid acids (e.g. alumina, silica-alumina, zeolites) have also been studied as methanol dehydration

catalyst [10]. A combination of these two catalysts, usually called a bi-functional catalyst [11], is a relatively new concept and merits extensive investigation for optimal integration of the two conventional steps.

The properties of the catalyst under reaction conditions can be different from ambient conditions. Therefore, ex situ characterisation of catalysts does not always provide useful data on how the catalyst would perform in realistic reaction conditions. The high-flux of synchrotron based radiation sources (10^1 to 10^{10} times brighter than conventional laboratory X-ray sources [12]) enables the study of solid catalysts in situ within high-pressure and high-temperature environment [13].

Advantageous features of synchrotron radiation (SR), such as beam stability and continuous tunability, have resulted in immense progress in the application of SR based techniques for catalyst characterisation over the past 20 years [12]. Combination of different techniques also enables acquisition of complementary data from the same set of experiments. Conversion of aurichalcite precursor to copper catalyst (for reverse water gas shift) was studied by recording diffraction and absorption sequentially with a very short time delay [14]. Time-resolved XRD was combined with Raman and mass spectroscopy to investigate the behaviour of SAPO-34 under methanol-to-olefin (MTO) condition [15]. XRD identified the chemical and structural changes in the catalyst. The nature of coke formed during the MTO condition was observed in the Raman
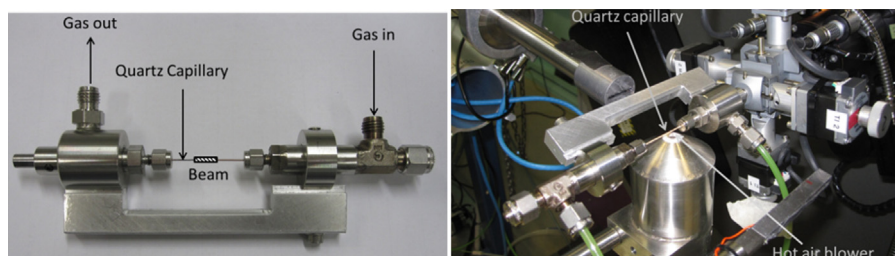
Fig. 1. (a) Flow cell with sample inside the quartz capillary, (b) flow cell-hot air blower configuration.

Table 1
Bulk composition of the MSC and MDC catalysts (wt%).

	CuO	ZnO	Al_2O_3	MgO	C
CuO-ZnO-Al_2O_3-MgO	63.6	24.8	10.3	1.30	–
γ-Al_2O_3	–	–	96.5	–	3.50

spectra while mass spectra provided information regarding the gaseous product [15]. XRD study of hydrothermally synthesised nickel succinate was also studied for dehydration–rehydration (40–200 °C) and decomposition (up to 600 °C) [16].

Changes in phase structures of binary (Cu, Zn) and ternary (Cu, Zn, Al) catalysts were studied in situ using a reactor-X-ray powder diffraction (XRD) cell during activation and synthesis conditions [17]. The CuO phase present in the catalyst reduced to Cu^0. The activity also steadily decreased with on-stream time. This investigation was further developed using a combination of XRD and X-ray absorption fine structure spectroscopy (XAFS) [18]. Alloying of Cu and Zn was observed when the catalysts were heated to 300 °C or above.

The focus of the current study is on dimethyl ether synthesis catalyst. Study on the effect of the addition of the dehydration component to the methanol synthesis catalyst using in situ techniques has not been reported in the literature. Therefore, in this study dynamic changes in the structure of the bi-functional catalyst for DME synthesis during activation and synthesis reaction were investigated using in situ synchrotron XRD. Studies only on the methanol synthesis catalyst and dehydration catalyst were also performed to examine the effect of the dehydration component on the performance of methanol synthesis catalyst. Complementary analysis was undertaken using thermogravimetry (TG) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS).

2. Materials and methods

2.1. Materials

A commercial methanol synthesis catalyst (CuO-ZnO-Al_2O_3-MgO) and a commercial methanol dehydration catalyst (γ-Al_2O_3), were used in the current study. The samples will be called MSC and MDC from here onwards. Bulk compositions of the catalysts are shown in Table 1. The bi-functional catalyst for syngas to DME synthesis was prepared by physically mixing the commercial catalysts. The ratio of the MSC to MDC in the bi-functional catalyst was 3–1 (mass basis). Two gas mixtures (10% H_2 in He; CO 40%, H_2 40% and CO_2 20%) were also used during the XRD measurements.

2.2. Methods

The catalysts were studied by the powder diffraction beam line end station (10-BM-1) at the Australian Synchrotron [19,20]. In a typical experiment, ca. 50 mg of catalyst was loaded into 0.7 mm OD (0.5 mm ID) quartz capillary. The catalyst loaded quartz
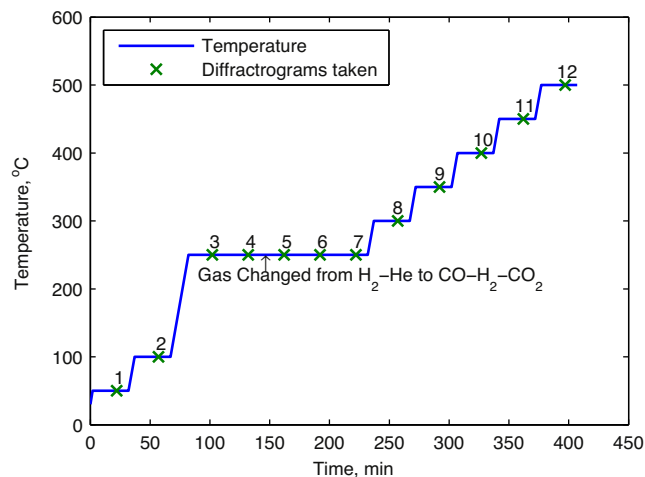
Fig. 2. Temperature profile for XRD measurements (measurement times are indicated by x).

capillary was then inserted into the flow cell, as shown in Fig. 1 (a). The flow cell was then installed on to the beamline end station, as shown in Fig. 1(b). The beam size at the sample was 1 mm (horizontal) × 1.2 mm (vertical). The beam was focused at the centre of the quartz capillary. The catalyst was reduced by flowing 10% H_2 in He gas through the flow cell from room temperature to 250 °C using a gas manifold. The sample holder and the flow cell were allowed to oscillate by 10 degrees to ensure maximum interaction between the bulk sample and the X-ray source. A Cyberstar hot air blower was used to heat up the sample inside the capillary at a heating rate of 10 °C/min. Diffraction patterns from the capillary were collected with the MYTHEN-II strip detector [21] at a wavelength of 0.7743 Å (approximately 16,000 keV). The wavelength was determined from the refinement of a NIST LaB$_6$-660b standard. Before collecting the diffraction patterns the catalyst was held at a given temperature for 20 min. At 250 °C the gas was changed from H_2-He mixture to CO-H_2-CO_2 mixture. Fig. 2 shows the temperature profile and times for the 12 diffraction spectra collected during the course of the experiment. Each diffractogram was collected for 10 min. No further analysis of the exhaust gas from the flow cell was performed.

Structural parameters of the crystalline copper were obtained after Reitveld refinement of the XRD data using TOPAS [22]. Copper crystallite size in (1 1 1) direction was calculated using the Scherrer equation [23]:

$$L = \frac{K\lambda}{B \cos\theta}$$

where B is the full width at half maximum (FWHM) of the peak profile, L is the volume average of crystal thickness in direction normal to the reflection plane, K is the constant of proportionality, θ is the angle of the reflection and λ is the wavelength.