The extraction of methanol via the partial oxidation of methane over a hierarchical Co/ZSM-5 catalyst

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Abstract. Methanol is one of the main products obtained from the partial oxidation of methane over a mesoporous Co/ZSM-5 catalyst. The cobalt species are present as cobalt oxides. Issues associated with the extraction of methanol from the zeolite surface include the carbon imbalance caused by the transformation of methane in the catalyst pores as well as low extraction efficiency. The developed extraction method involved the use of a dry solvent and a mixture of the solvent with water for the reliable quantitative measurement and enhancement of product recovery. Furthermore, extraction parameters such as solvent type and volume, extraction time, and number of extraction cycles were investigated. A mixture of 1:1 ethanol and water afforded a methanol recovery of 94.2%. Optimum extraction was achieved using 1 mL of solvent/0.15 g of catalyst, an extraction time of 30 min, and three extraction cycles. As reuse was crucial for catalyst performance, Fourier transform infrared spectra revealed that the extraction solvent did not significantly affect the catalyst structure.

Keywords: hierarchical Co-ZSM5, partial oxidation of methane, methanol recovery, solvent extraction

1. Introduction
It is desirable to develop a method for the direct conversion of methane to methanol owing to environmental issues. Heterogeneous catalysts (ZSM-5) are promising support materials for examining the oxidation of methane to other products [1–6]. Bezniz et al. [1] have reported the low-temperature partial oxidation of methane to methanol and formaldehyde over Co–ZSM-5 agglomerates. The catalytic activity as well as the product selectivity for methane conversion depend on cobalt species that is impregnated into the catalyst. Hence, it is crucial to modify the ZSM-5 pores by the double-template method because of the high pore volume distribution and large crystal size [7]. Furthermore, Krisnandi et al. [8] and Karim et al. [9] have successfully reported the high conversion for methanol as the product obtained from the partial oxidation of methane over a heterogeneous catalyst (Co/ZSM-5). The results indicated that the zeolite porosity and Co loading method affect the yield of the partial oxidation reaction.

Previous studies have reported certain issues associated with the quantitative measurement of methanol as the conversion product [3,5,10]. The main issue is that the methanol recovery is not as high as the theoretical value, thereby indicating that inefficient extraction is a crucial factor in catalysis. Extraction involves the transfer of the target component from one phase to another second phase. Some factors affecting extraction include the extraction solvent, extractant composition, temperature, extraction time, and extraction cycle number.

Sobolev et al. [10] have reported the extraction of methanol by the partial oxidation of methane. Water and an acetonitrile–water mixture were used as solvents. After four extraction cycles, 80% of
Table 1. Extraction parameters

| Type of solvent      | Solvent volume (mL) | Extraction time (min) | Extraction cycle |
|----------------------|---------------------|-----------------------|------------------|
| Ethanol              | 0.5; 1.0; 1.5       | 15; 30; 45            | 1-5              |
| Propanol             |                     |                       |                  |
| Water                |                     |                       |                  |
| Ethanol:propanol v/v (1:1) |                 |                       |                  |
| Ethanol:water v/v (1:1) |                   |                       |                  |

methanol is recovered [10]. Knops-Gerrits and Goddard [3] have reported the preference of water over the acetonitrile–water mixture during extraction, whereas the reaction between methanol and water releases heat, which tends to facilitate the release of any extraneous dissolved air as bubbles. Starokon et al. [5] have compared methods for the extraction of methanol over an Fe/ZSM-5 surface using dry solvent as well as a mixture of organic solvents with water. Seventy-five percent of methane is recovered; however, the complete extraction of the reaction products is not achieved [5].

In this study, the recovery of methanol over Co/ZSM-5 was examined. In addition, the extraction method was modified. Furthermore, the products were quantitatively analyzed on account of the additional experiments conducted for the catalytic performance of zeolites.

2. Materials and methods

2.1. Materials

NaAlO₂, tetrapropylammonium hydroxide (TPAOH, 25 wt%), tetraethyl orthosilicate (TEOS), dimethyl diallyl ammonium chloride acrylamide copolymer (PDDA, 10 wt%), NaOH (Merck, >99%), pellet and an ammonia aqueous solution (Merck, 29%), HCl aqueous solution (Merck, 36%), Co(NO₃)₂.6H₂O (Aldrich, 98%), CH₄ gas (99.99%, BOC), N₂ gas (UHP), methanol (99.8%, Merck), ethanol (99.8%, Merck), propanol (99.9%, Merck), and distilled water were used.

2.2.2. Regeneration of the Co/ZSM-5 catalyst. The synthesis of the Co-ZSM-5 catalyst and its reaction with methane in a pressurized batch reactor have been reported elsewhere [8]. The catalyst was calcined at 550 °C for 2 h prior to regeneration.

2.2.2. Product extraction from Co/ZSM-5. First, 0.15 g of the regenerated catalyst was mixed with 0.05 mL of methanol, followed by transfer into a vial (2 mL). Second, the corresponding solvent (volumes: 0.5, 1.0 and 1.5 mL) was added into the vial. Afterward, the vial was sealed and placed in a shaker at 200 rpm for 30 min to ensure appropriate mixing. After extraction, the vial was subjected to centrifugation at 7500 rpm for 10 min for the separation of the solvent from catalyst particles. Extraction parameters such as solvent type and volume, extraction time, and extraction cycle number are summarized in table 1. The ethanol content was analyzed by gas chromatography (GC-FID Shimadzu 2010), and the catalyst was characterized by FTIR spectroscopy (Shimadzu Prestige 21).

3. Results and discussion

The double-template method was employed to synthesize the catalyst. TPAOH was used as the directing agent in the microporous MFI zeolite structure, and mesoscale cationic PDDA was used as the mesoporous template. Cobalt species was impregnated into the hierarchical ZSM-5 catalyst. The partial oxidation of methane was affected by the cobalt species. Cobalt oxide (CoO and CoO) is selective to methanol production, while Co(II) affords formaldehyde [1]. As the product (methanol) is strongly attached on the catalyst surface and only being released with solvent extraction, modified extraction parameters, i.e., solvent type and volume, extraction time, and extraction cycle number, were utilized to increase the extraction efficiency. This experiment was carried out using the regenerated catalyst. The characteristics of the catalyst used in this experiment have been described previously [8].
After regeneration, FTIR spectra were recorded to examine whether methanol and other products were still adsorbed onto the Co/ZSM-5 at room temperature. The infrared spectrum of the methanol adsorbed on the Co species is shown in figure 1. C–H symmetric stretching and C–H asymmetric stretching bands were observed at 2855 cm$^{-1}$ and 2958 cm$^{-1}$, respectively. Starokon et al. [11] have reported that methanol molecules are adsorbed on the catalyst surface. Oxygen atoms from methanol and cobalt species exhibited electrostatic interactions (i.e., dipole–dipole interaction).

### 3.1. Solvent type

Solvents were selected on the basis of their physical and chemical properties, such as dielectric constant, polarity, and solubility. Two organic solvents, their mixtures, and a mixture of water with the solvents were compared. The percentage recovery of methanol as a function of solvent type is shown in figure 2.

The use of ethanol afforded a high methanol recovery (87.0%), while the use of propanol afforded the lowest methanol recovery (43.8%). This result is related to solvent polarity, which plays a key role in increasing methanol recovery. Furthermore, methanol is formed by the substitution of methoxy groups by ethoxy groups [5]. A mixture of these solvents with water afforded higher methanol recoveries of 87.5% (1:1 v/v of water/ethanol) and of 53.3% (1:1 v/v water/propanol). This result can be explained by the fact that the interaction between methanol and the solvent is affected by the formation of hydrogen bonds between oxygen atoms from methanol and hydrogen atoms from water. Thus, methanol is released from the catalyst surface. During partial oxidation, methoxy species are initially formed from the chemisorption of methane on the oxide species, leading to the strong absorption observed for the product on the catalyst surface [1]. The hydrolysis of methoxy groups assisted by water led to the high recovery of methanol.

FTIR spectra were recorded to observe the effect of solvent on the catalyst structure. Five solvents were compared. An additional peak corresponding to Co/ZSM-5 was not observed during extraction using ethanol, water, and their mixtures, while extraction using propanol and 1:1 ethanol:propanol revealed differences (figure 3). C–H stretching peaks were observed at 2960–2850 cm$^{-1}$ in the FTIR spectra of these solvents. Propanol is still thought to be present within the catalyst pores because of its molecular size and boiling point. Hence, regeneration (i.e., heating at 550°C) leads to the evaporation of the remaining solvent. Hence, the solvent used herein does not significantly affect the catalyst structure.

### 3.2. Extraction time

The effect of extraction time on methanol recovery was investigated using ethanol as the solvent. From figure 4, the extraction time (15, 30, and 45 min) affects methanol recovery. The methanol
Figure 3. FTIR spectra of Co/ZSM 5 after extraction using different solvents.

Figure 4. Effect of extraction time on the methanol recovery from the Co/ZSM-5 surface.

Figure 5. (a) effects of extraction volume and (b) extraction cycle number on the recovery of methanol from the Co/ZSM-5 surface.

content increased with time, i.e., for extraction times of 0.5 and 1 min, methanol recoveries of 80.5% and 91% were obtained, respectively. Based on the product composition, a longer extraction time of 45 min led to decreased methanol recovery (82%). The increase in the extraction time leads to the increase in solvent evaporation. Hence, it is recommended to utilize an extraction time of less than 1 min for methanol.

3.3 Volume and extraction cycle number
The ethanol volume did not significantly affect the methanol recovery. As figure 5 shows, 1 mL of ethanol led to a methanol recovery of 73%. In addition, the effect of the extraction cycle number using ethanol as the solvent was investigated under the above-mentioned optimum conditions. The first extraction cycle recovered a majority of the methanol from Co/ZSM-5, while some methanol was
recovered from the second extraction cycle. Moreover, the third and fourth extraction cycles led to the recovery of low amounts of methanol. Furthermore, methanol was not obtained from the 5th cycle. In total, 94% of methanol was recovered from Co/ZSM-5. Notably, the extraction efficiency was obtained using a low volume of solvent and three extraction cycles.

4. Conclusions
Methanol, which was the main product obtained from the partial oxidation of methane, was extracted from the Co/ZSM-5 catalyst surface. An extraction method was developed herein. A high methanol recovery was achieved using a 1:1 v/v of ethanol:water as the solvent. An appropriate reaction time, solvent volume, and extraction cycle led to a high extraction efficiency. Despite the extraction conditions, Co/ZSM-5 demonstrated potential for reuse in the partial oxidation of methane to methanol as the extraction solvent did not alter its structure.

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