Full Length Article

Dimethyl ether-to-olefins over aluminum rich ZSM-5: The role of Ca and La as modifiers

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ABSTRACT

Dimethyl ether (DME) has a strategic role both as an alternative fuel and a feedstock for petrochemicals. Aluminum rich H-ZSM-5 modified with Ca and La species were investigated in the conversion of Dimethyl ether (DME) to olefins. The crystallinity and morphology of Ca-ZSM-5, La-ZSM-5 and Ca-La-ZSM-5 were similar to the parent H-ZSM-5 as observed in XRD and FE-SEM analysis. The addition of both Ca and La ions, and their co-impregnation affects the acidity of parent H-ZSM-5 zeolite. In addition, Ca and La ions also induced the formation of basic sites in the zeolite framework. DME conversion of over 97% was observed over all catalyst systems during the 2 h time on stream. Ca-ZSM-5 showed the highest selectivity to light olefins especially propylene due to the presence of weak and medium acid sites.

1. Introduction

Light olefins ($C2^=$ to $C4^=$) especially ethylene and propylene are very important chemical compounds that are in high demand in the petrochemical industry. Researchers and scientists over the decade have developed so many technologies for the production of light olefins. Such technologies include: steam catalytic cracking [1,2], catalytic cracking of light naphtha [3,4], oxidative dehydrogenation of light alkanes [5–7], and methanol to olefins [8,9] to mention but few.

The dimethyl ether DME to olefin process is a more recent process. It enjoys the advantage of being sourced from both the natural gas and biomass routes in similitude to the MTO process. However, the lower energy requirement, equipment cost and H_2/CO required for the production of DME, makes the DME process more advantageous than the MTO process [10].

Since the DME to olefin (DTO) process is relatively new, preparation of highly efficient catalysts and suitable reaction condition are areas of concern that requires more scrutiny. Zeolites have been one the most active catalyst for the DTO process [11,12]. Among zeolites, ZSM-5 has been highly studied due to its stability and good selectively to light olefins in the DTO process. However, it is worth mentioning that controlled acidity is a key factor required for good selectivity to light olefins in the DTO process. Variation of SiO_2/Al_2O_3 content [10], alkaline and acid treatment [13] and the addition of metal oxide species [14] are among the techniques used to control zeolite acidity. Al-

Dughaither et al. [10] studied the catalytic activity of ZSM-5 with different SiO_2/Al_2O_3 in the DTO process. In their study, they observed a trade-off between conversion and selectivity as SiO_2/Al_2O_3 was varied. ZSM-5 zeolite with lower SiO_2/Al_2O_3 ratio gave higher initial conversion and low selectivity to light olefins, while ZSM-5 zeolite with high SiO_2/Al_2O_3 showed lower conversion and high selectivity to light olefins. Since the optimum desire in any given petrochemical process is to simultaneously maximize conversion and selectivity, the addition of metal oxide to zeolite might be a more viable option. However, the choice and concentration of metal oxide are underlining factors that will affect the acidity and overall activity of the developed metal oxide incorporated zeolite catalyst.

Here, we report the effect of Ca and La as an intended promoter for Al-rich ZSM-5 zeolite in the DTO process. The effect of Ca, La as well as possible synergy between both metals or possible species formed on ZSM-5 zeolite were systematically studied by X-ray analysis, N_2 physisorption measurements, X-ray photoelectron spectroscopy (XPS), NH_3 and CO_2 temperature program reduction and catalytic activity test.

2. Experimental

2.1. Catalyst preparation

The ZSM-5 catalyst used in this study was prepared from commercial ammonium form ZSM-5 supplied by Alfa aesar with $SiO_2/$

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Al_2O_3 ratios of 23. Lanthanum nitrate hexahydrate and calcium nitrate tetrahydrate supplied by Sigma Aldrich and Alfa Aesar respectively were used as metal oxide precursor for impregnation without further purification.

Before the impregnation protocol, the ammonium ZSM-5 was calcined at 823 K for 12 h to get H-ZSM-5. Metal promoted ZSM-5 were prepared by the impregnation technique. Ca and La impregnated H-ZSM-5 zeolite were referred to as Ca-ZSM-5 and La-ZSM-5 respectively. H-ZSM-5 co-impregnated with both metals was referred to as Ca-La-ZSM-5.

Ca-ZSM-5 and La-ZSM-5 were prepared by dissolving calculated amount of respectively salts that is equivalent to 3 wt% of each metal in 10 ml ethanol. Thereafter, 1 g of H-ZSM-5 catalyst was added to the solution. The resulting mix was allowed to air dry overnight and was later dried and calcined at 343 K and 823 K for 9 h and 5 h respectively. The Ca-La-ZSM-5 was prepared by co-impregnation using the respective salts of Ca and La. An amount equal to 1.5 wt% of each metal was used during the impregnation process.

2.2. Catalyst characterization

The properties of the parent H-ZSM-5 and the metal oxide promoted Ca-ZSM-5, La-ZSM-5 and La-Ca-ZSM-5 were systematically studied to give a better understanding of their physicochemical properties.

2.2.1. X-ray diffraction (XRD)

The XRD patterns of H-ZSM-5 and metal oxide promoted ZSM-5 zeolites were carried out on a Rigaku Miniflex diffractometer equipped with Cu K_α radiation (λ = 0.15406 nm). XRD analysis was performed with a step size of 0.03° and a scan speed of 3°/min in the 2θ range of 5–50°.

2.2.2. Temperature program desorption

NH_3 and CO_2 temperature program desorption of zeolite samples were done in a chemisorb 2750 micrometrics chemisorption analyzer. Approximately 0.15 g of zeolite was used for both the NH_3 and CO_2TPD procedures. Zeolite sample pre-treatment was carried out under a He flow of 25 ml/min at 823 K for 1 h. Subsequently, the sample was cooled down to adsorption temperature of 373 K for NH_3 and 320 K for CO_2. For the NH_3 TPD process, 10%NH_3 in He mixture was introduced at flow rate of 30 ml/min for 30 minsuntilNH_3 saturation was achieved. In the case of the CO_2 TPD process, 99.99% CO_2 gas was also introduced for 30 min. Thereafter, the physisorbed ammonia or carbon dioxide gas was removed by purging the sample with He for 1 h. Finally, the process temperature was ramped at10 K/min up to 990 K and 550 K for NH_3 and CO_2 respectively and the amount of desorbed gas was recorded every 0.5 s on a TCD detector.

2.2.3. Morphology and elemental composition

The morphology and elemental composition of parent and metal oxide modified zeolites were analysed using a field-emission scanning electron microscopes (FE-SEM, LYRA 3 Dual Beam, Tescan) equipped with Energy Dispersive X-ray Spectrometry (EDX, Oxford Instruments). In addition, we have also examined the dispersion of metal oxide species on the surface of zeolite samples by mapping analysis. Furthermore, X-ray photoelectron spectroscopy (XPS) analysis was done on samples to identify the chemical species after modification.

2.2.4. Pyridine FTIR analysis

NH_3-TPD technique cannot discriminate the types of constituent acidity (Brønsted (B) and Lewis (L) sites) in zeolites. Hence, we have employed FTIR spectroscopy to discern the states of hydroxyl groups and to identify the types of acid sites present in our zeolite samples. Hence, combining pyridine FTIR with NH_3-TPD technique will give a detailed explanation of acid sites and distribution in parent and modified ZSM-5 zeolite catalyst systems. The nature of acid site present on both parent, Ca and La modified ZSM-5 zeolite was then investigated by FTIR pyridine adsorption using a Nicolet 6700 FTIR spectrometer. In a typical adsorption procedure, 20–30 mg of zeolite sample was pressed into a self-supporting wafer and then loaded into a FTIR cell equipped with a ZnSe window. Thereafter, the cell was evacuated and its temperature was raised to 773 K. After 30 min residence time at 773 K, the cell was cooled to 323 K before pyridine probe molecules were introduced. The addition of pyridine molecule was sustained for 30 min. Thereafter, the cell was evacuated to remove physisorbed pyridine molecules. After this, FTIR spectrum of catalyst wafer was collected at 323 K and then at a 50 K interval temperature increase up onto 723 K. Spectra of adsorbed pyridine on zeolite samples were then obtained by subtracting FTIR spectra of samples treated with pyridine from untreated samples. The amount of Brønsted and Lewis acid were calculated according to peaks at approximately 1545 cm^{-1} and 1450 cm^{-1}, respectively. Extinction coefficients of 1.13 cm mol^{-1} and 1.28 cm mol^{-1} for Brønsted and Lewis acidities reported by Guisnet et al. [15] were used. The concentration of acid sites is calculated according to from Beer–Lambert's law:

$$C= A\varepsilon \times Sm$$

Where C is the concentration of acid sites [mmol g^{-1}], A is the area of band [cm^{-1}], S is the surface of the wafer [cm^2], ε is the molar extinction coefficient [cm mol^{-1}],

2.3. Catalytic evaluation of catalyst systems

The DTO for the parent and metal oxide modified zeolite was done in a Fixed-bed reactor made from quartz (i.d. 4 mm). The DTO was carried out at 673 K using 0.05 g of catalyst, and a DME flow rate of 1.3 mmol/h. Helium gas with a flow rate of 19 mmol/h was employed as carrier gas. A Shimadzu GC-14 B gas chromatography equipped an Al_2O_3 PLOT column and a flame ionization detector was used to analyze the products during the DTO experiments.

3. Results and discussion

3.1. Effect of Ca and La on structural and morphological properties of Al-rich ZSM-5 zeolite

Fig. 1 shows the XRD patterns of parent and metal oxide promoted H-ZSM-5. As clearly depicted in the XRD patterns, the addition of Ca, La or both La and Ca (co-impregnated) did not show any significant changes in the fingerprint of the parent H-ZSM-5 zeolite. Also, we did
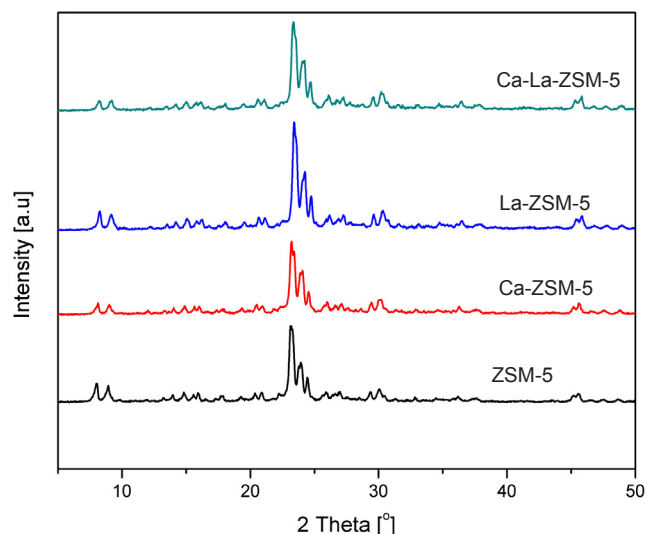

Fig. 1. XRD patterns of parent and metal modified ZSM-5 zeolites.