Short communication

A ZSM-5/MCM-48 based catalyst for methanol to gasoline conversion

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ARTICLE INFO

ABSTRACT

A ZSM-5/MCM-48 aluminosilicate composite material as a catalyst for methanol to gasoline conversion was synthesised using a simple two step crystallisation process. The textural and structural properties of the composite were characterized using N_2-adsorption, XRD, SEM and HRTEM techniques. It was revealed that the ZSM-5 phase was inter-connected with the meso-structured MCM-48 phase. The ZSM-5/MCM-48 composite catalyst was shown to possess high activity and stability with low formation of aromatic hydrocarbons in methanol to gasoline (MTG) conversion. The high activity and stability of the novel ZSM-5/MCM-48 composite were attributed to the enhanced the mass transfer properties and reduced diffusion limitations due to the widened pore size distribution and lowered pore surface acidity of the composite material.

1. Introduction

There has been a continuing rise in the global demand for liquid transport fuels, and more than 95% of transport fuels are derived from petroleum [1]. Coal to liquid (CTL) and gas to liquid (GTL) are considered future sources of liquid fuels [2,3]. Among many CTL and GTL technologies being developed, the methanol-to-gasoline (MTG) route offers a desired solution, because the feed methanol for MTG can be readily manufactured from synthesis gas, which is easily produced by steam reforming of nature gas or gasification of coal or biomass [2,4].

ExxonMobil developed an MTG process in the 1970s. This process uses an HZSM-5 catalyst [5] due to its high surface area, acidic nature of its pores and well-defined porous structure. However, the HZSM-5 catalyst suffers from low selectivity towards C_5–C_{10} alkanes, high yields of aromatics, and carbon deposition thus requiring frequent regeneration. In the past 30 years, continuing R&D efforts have been focused on modification of HZSM-5 using various metals, such as $MoCl_5$ [6], CuO [7], ZnO/CuO [4] and Ga_2O_3 [8,9]. Those catalysts show even higher selectivity towards the undesired aromatics than the HZSM-5 catalyst. Literature reports indicate that the HZSM-5 catalyst with large pore volumes but narrow pore sizes and pore mouths, external surface areas and high populations of external active centres, possesses good stability but high selectivity to aromatics, owing to the high acidity of the pore surfaces [10].

High aromatic contents in gasoline are not desired [11] (although a complete lack of aromatics is not good either). However, there has been little literature on MTG catalysts with low selectivity towards aromatics in the public domain. Recent advances in the synthesis of composite micro/mesoporous materials are of interest in the development of new MTG catalysts due to their enhanced (compared to the zeolite itself) mass transfer properties and reduced diffusion limitations [12]. It was hypothesised that the micro/mesoporous composite materials that could simultaneously moderate the pore size distribution and lower the overall acidity of the pore surfaces thus improving the selectivity towards C_5–C_{10} alkanes and reducing the formation of aromatics and carbon deposition. In this short communication, we report our recent work on the synthesis of a ZSM-5/MCM-48 composite material and experimental and analytical evaluation of its use as an MTG catalyst.

2. Experimental

2.1. Preparation of materials and catalysts

The synthesis of the composite ZSM-5/MCM-48 (Si/Al = 80) utilised the advantages of several recent literature reports [12,13]. In a typical synthesis procedure, the precursor zeolite colloidal suspension was prepared by mixing 59.2 g H_2O (double distilled water), 11.3 g of 25 wt% tetrapropylammonium hydroxide (TPAOH), 21.2 g tetraethyl orthosilicate (TEOS) and 0.26 g aluminium

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isopropoxide while being continuously stirred for 4 h. The mixture was then transferred to an autoclave and heated to and maintained at 100 °C for 4 h. After cooling to room temperature, the resulting ZSM-5 suspension was added with a cetyltrimethyl ammonium bromide (CTAB) solution containing a stoichiometric amount of NaOH to obtain a final gel with molar compositions of 1 TEOS:0.12 CTAB:0.5 OH:0.0125 Al:118 H_2O. The gel was continuously stirred for 2 h at room temperature, then transferred to an autoclave and heated to and maintained at 150 °C for 8 h. The resulting solid, a ZSM-5/MCM-48 composite, was filtered, washed with double distilled water until there were no traces of OH ions, dried at 110 °C for 12 h and calcined at 550 °C for 6 h. A H-ZSM-5 zeolite (Si/Al = 80), obtained from Nankai University, China, was also employed in the experimentation as a reference.

To obtain the final MTG catalyst, the raw ZSM-5/MCM-48 composite was subjected to ion-exchange with a 0.05 mol/L NH_4NO_3 solution at 75 °C for 2 h in three consecutive cycles, followed by calcination at 500 °C for 4 h. The catalysts were obtained by physically mixing the ZSM-5/MCM-48 composite (95 wt%) and the H-ZSM-5 (95 wt%), respectively, with pseudo-boehmite (5 wt%) as a binder, under high humidity conditions.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were recorded using a DB ADVANCE powder diffractometer with Ni-filtered Cu-Kαradiation (40 kV, 40 mA). N_2 adsorption–desorption isotherms were measured using an ASAP2020M + C system after the sample was degassed under vacuum at 300 °C for 5 h. Pore size distribution was determined using the conventional Barrett–Joyner–Halenda (BJH) model. Scanning electron microscope (SEM) was performed with a Hitachi S-4800 field emission scanning electron microscope. High resolution transmission electron microscopy (HRTEM) images were recorded using a JEM 100CX microscope with an accelerating voltage of 200 kV.

2.3. Methanol to gasoline reaction test

The MTG reaction was conducted in a fixed bed reactor operating at 1.0 MPa and in the temperature range from 340 to 420 °C. The cylindrical fixed bed reactor was made of stainless steel with an internal diameter of 7 mm and was packed with 1.4 g of a catalyst. A plunger pump was used to feed liquid methanol (analytical grade) at 0.06 mL/min into an evaporator where it was mixed with N_2 as the carrier gas, heated and evaporated at 150 °C. The preheated reactant gas then entered the reactor at WHSV = 2.0 h^{-1}. The reactor exit stream was separated into gas, liquid hydrocarbons and reaction water fractions using an ice-cooled condenser. The gas fraction was analysed on-line using a GC (Agilent7890A) fitted with both TDX-01 and Propake-Q columns and both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The liquid hydrocarbons were analysed using a GC (Agilent7890A) fitted with a capillary column (OV-101) and an FID. An atomic carbon balance between the inlet (carbon in methanol) and the exit (the sum of carbon in all identified species, including unreacted methanol) streams under a steady state run was typically within 15%, with the difference being attributed to coke formation and carbon deposition.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of the calcined ZSM-5/MCM-48 composite. The basal peak (2 1 1) at $2\theta = 2.5°$ indicates the presence of MCM-48 [12,13] while the many sharp peaks in the ranges of 8–9° and 22–25° feature the ZSM-5 phases [12–14].
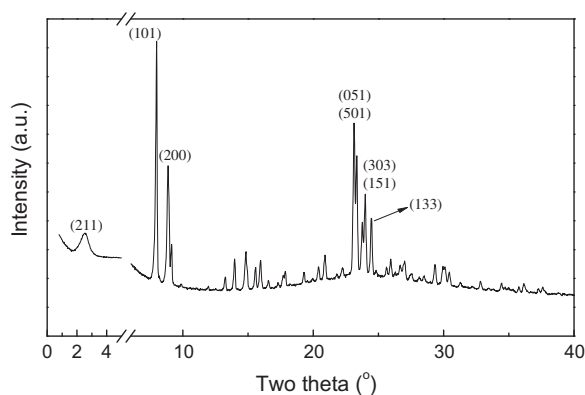

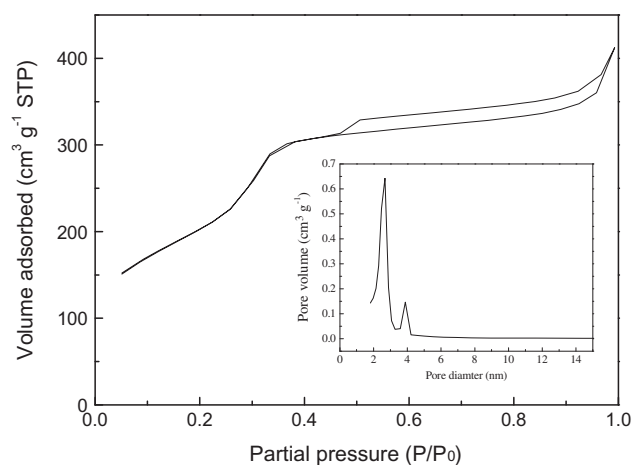**Fig. 1.** A typical XRD pattern of the ZSM-5/MCM-48 composite.

Fig. 2. Nitrogen sorption isotherm and pore diameter distribution of the ZSM-5/MCM-48 composite (insert).

Fig. 2 shows the N_2 sorption isotherm and pore diameter distribution of the ZSM-5/MCM-48 composite. It can be seen that the composite exhibits a typical irreversible type IV adsorption and desorption isotherm which is characteristic of mesoporous molecular sieves [15,16]. The pore size distribution reveals that there are two types of pores in the composite centred at 2.8 nm and 3.8 nm, respectively. Note that the average pore diameter of an H-ZSM-5 is
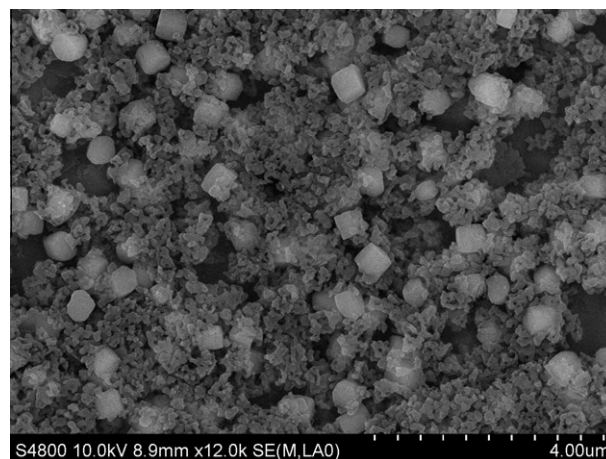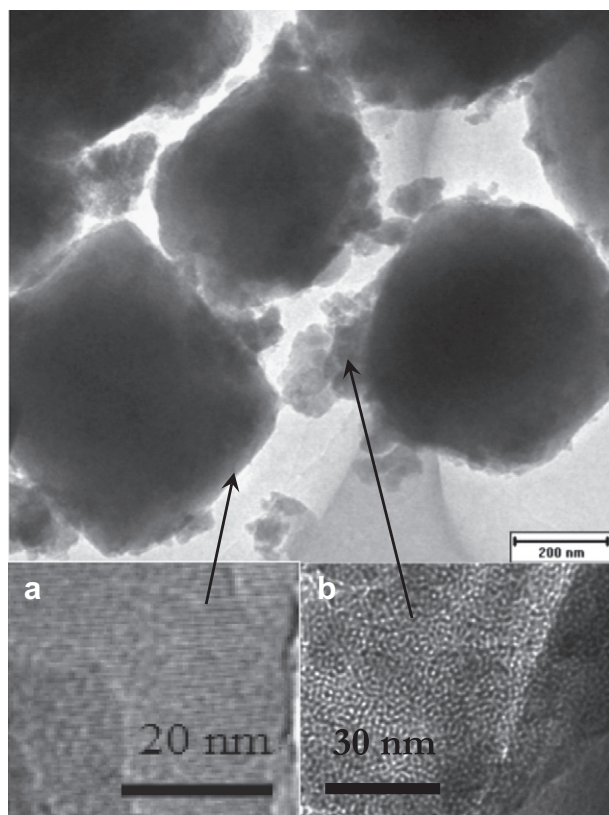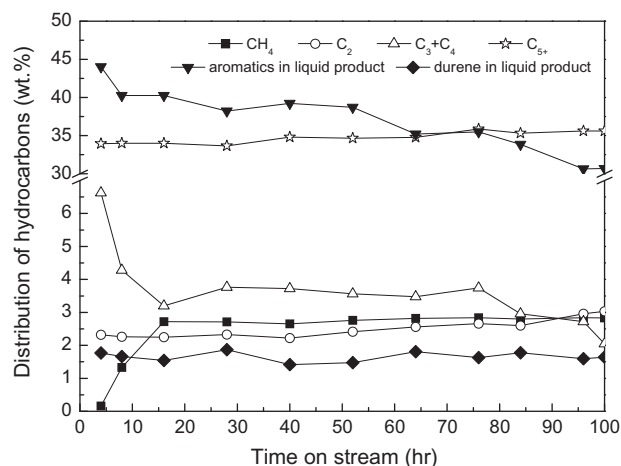

Fig. 3. An SEM image of the ZSM-5/MCM-48 composite.

Fig. 4. HRTEM images of the ZSM-5/MCM-48 composite where callout "*a*" shows a cubic particle and callout "*b*" shows irregular particle surface.

Fig. 5. Distribution of hydrocarbons in the liquid product versus reaction time over the ZSM-5/MCM-48 composite catalyst [T = 400 °C, P = 1.0 MPa, WHSV = 2.0 h^{-1}].

0.53 nm [17]. However, the so-called textural porosity of pure MCM-48 is not observed as the hysteresis at P/P_0 = 0.8–1.0 is absent [13]. Fig. 3 shows an SEM image of the ZSM-5/MCM-48 composite and Fig. 4 shows HRTEM images. The ZSM-5/MCM-48 composite synthesised appears to possess bi-modal particle size distribution with abundant small irregular particles at ca. 0.1 μm in sizes and large cubic particles at ca. 0.5 μm in sizes, believed to be the MCM-48 phase [12,18,19] and ZSM-5 phase [12], respectively. Some of the MCM-48 particles do not appear to be associated with the ZSM-5 phase while all ZSM-5 particles are covered with MCM-48 (also see the TEM images in Fig. 4). Fig. 4 illustrates that at the interface of ZSM-5 and MCM-48, the ZSM-5 phase is indeed inter-connected with the meso-structured MCM-48 phase, which confirms that the microporous and mesoporous channel systems are most probably interconnected [12]. The callout "*a*" in Fig. 4 clearly shows the pore structure of the large cubic crystals

in the composite, which is characteristic of the ZSM-5 phase. The cubic particles appear in the ZSM-5/MCM-48 composite synthesised is typically 0.3–0.5 μm, smaller than that of conventional H-ZSM-5 [12]. The MCM-48 phase has a wormhole-like pore structure as seen in callout "*b*" in Fig. 4. The loss of the cubic ordering normally seen in typical pure MCM-48 is a consequence of the aluminium incorporation into the MCM-48 structure [19].

The effect of reactor temperature on methanol conversion and hydrocarbon yields in different hydrocarbon fractions over the H-ZSM-5 and ZSM-5/MCM-48 composite catalysts are shown in Table 1. It is apparent that the ZSM-5/MCM-48 composite has a very high activity for MTG with the methanol conversion reaching 95% at 340 °C, increasing as the temperature rose, up to 99.8% at 420 °C. The yield of the C1—C4 hydrocarbons was generally low and, of great interest, the yield of the gasoline range hydrocarbons (C$_{5+}$) was around 29–34.5 wt%, over the temperatures examined. From Table 1, it appears that the optimum reaction temperature of this catalyst is in the vicinity of 380–400 °C. The content of aromatics in the liquid fraction increased with increasing temperature from 35 wt% at 340 °C to 46 wt% at 420 °C, which is significantly lower than that (ca. 64.6–84.3 wt%) observed with commercial HZSM-5 catalysts [20,21]. The major aromatics present were identified to be toluene, xylene, 3/4-ethyltoluene, 1,2,4-trimethyl benzene and durene. The content of durene in the liquid hydrocarbons was lower than 3.10 wt%, decreasing with increasing temperature. Though, the activity of the pure H-ZSM-5 was also high, poor selectivity to gasoline products was evident with high aromatics including durene. It is well known that the conversion of methanol to hydrocarbons on acidic zeolites is mechanistically complex. Several reaction mechanisms such as supra molecular origins of selectivity, reaction

Table 1
Performance of MTG reaction over the H-ZSM-5 (A) and ZSM-5/MCM-48 composite (B) catalysts at different temperatures [P = 1.0 MPa, WHSV = 2 h^{-1}].

Reaction temp. (°C)	Methanol conversion (%)		Hydrocarbon yield (wt%)[a]						Aromatics in liquid product (wt%)		Durene in liquid product (wt%)	
			CH$_4$ + C$_2$		C$_3$ + C$_4$		C$_{5+}$					
	A	B	A	B	A	B	A	B	A	B	A	B
340	93.1	95.0	2.8	3.1	19.4	10.8	18.5	28.9	70.8	34.8	30.8	3.1
360	96.1	97.0	3.0	3.2	13.9	5.0	23.7	33.6	64.7	40.2	32.7	3.0
380	98.3	97.1	0.7	3.0	12.3	4.8	27.6	34.4	72.3	41.5	11.0	2.8
400	99.2	99.3	0.9	2.4	13.0	6.2	27.3	34.5	82.3	44.3	12.9	1.7
420	99.5	99.8	1.9	1.8	13.7	7.3	26.7	31.7	84.3	46.4	7.8	1.1

[a] The yields of alkenes and alkanes in the fractions presented are combined.

centres and hydrocarbon pools have been proposed [22–24]. Though these are still debate topics, we do believe that the diffusion properties of the zeolites also play a major role in the formation and conversion of carbon-containing intermediates and coke deposition, a subject warranting further investigation in the near future.

Fig. 5 shows the distribution of the hydrocarbon products versus reaction time on the ZSM-5/MCM-48 composite catalyst for up to 100 h at 400 °C. The yield of the C_{5+} hydrocarbons maintained at around 35 wt%, and the durene content in the liquid hydrocarbons was less than 2 wt%. The content of aromatics in the liquid hydrocarbons decreased over time, from 44.0 wt% at 4 h to 25.7 wt% at 100 h. The reduction in the yield of aromatics may be attributed to the continuous coke formation and carbon deposition on the catalysts during the reaction [10]. A small amount of methane was detected at the beginning of the run for several hrs, and the methane yield rose to about 3.0 wt% after 15 h. This may be explained by the SEM observation of carbon deposition on the active sites. The C2 yield remained relatively constant over time and the C3 + C4 yield decreased from a high value of ca 6.6 wt% at beginning to a relatively stable value of ca 3.5 wt% after 15 h. Throughout the experiment, the methanol conversion remained at above 99%. There was trace amount of hydrogen in the gaseous product and no CO and CO_2 were detected.

4. Conclusions

Given the above observations, it is considered that the ZSM-5/MCM-48 composite catalyst synthesised in this work has high activity and stability for methanol to gasoline conversion. The interface of ZSM-5 and MCM-48, i.e. the interconnected microporous and mesoporous channel systems, has been shown to greatly influence the distribution of the hydrocarbon products comparing to these on pure ZSM-5 zeolite. These warrant further studies to ascertain the mechanism of its catalytic effect and the reaction pathways associated the methanol to gasoline process.

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