



Dynamic modification of pore opening of SAPO-34 by adsorbed surface methoxy species during induction of catalytic methanol-to-olefins reactions

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ABSTRACT

Here, we report that the 8-membered ring pore opening of SAPO-34 zeolite can be significantly modified by an adsorbed surface methoxy species (SMS) during the induction period of the catalytic methanol-to-olefins process, which offers molecular sieving properties. It is due to the physical obstruction caused by the surface methoxy species, which also modifies the adsorption properties of other hydrocarbons. Synchrotron X-ray powder diffraction and Rietveld refinement reveal that the SMS is dynamically created from methanol dehydration on a Brønsted acid site near the narrow pore windows. Thus, industrially desirable lower olefins such as ethylene and propylene can be favourably made at the expense of higher olefins. The crystal structures and fundamental understanding in altering the olefin selectivity during induction may allow rational optimisation in catalytic performance under complex fluidised conditions. This work offers additional but alternative insights to the ‘dual cycle’ mechanistic study of the catalytic methanol-to-olefins process.

1. Introduction

In the formulation of the strategic national energy policies of many countries, the uneven geographical distribution of fossil fuels and associated CO₂ emissions are significant issues. As a result, identifying alternative fuels and platform chemicals are critical. Typically, methanol from coal or biomass processing from oil-starved countries is regarded as a potential alternative to mitigate these problems [1]. It can be used as a direct fuel or key chemical for the synthesis of commodity chemicals through various methanol-to-hydrocarbons (MTH) processes, such as to olefins (MTO), aromatics (MTA) and gasoline (MTG), etc. [2,3]. It is anticipated that the reliance over methanol will continue in the foreseeable future, due to the rapidly growing demand for consumer goods. Most of the industrial MTH processes employ the use of zeolite catalysts. It is however not yet clear how the specific hydrocarbon products are produced from the methanol feed and the influence of zeolite structure on their pathways. It is generally accepted that, particularly by the extensive work by Kolboe and co-workers, the MTO reaction mechanism involves a dual cycle mechanism which involves both aromatic and alkene cycles [4–9]. Methanol molecules first adsorb onto an interior Brønsted acid sites (BAS) in zeolites, then they rapidly dehydrate and form C–C bonds and polymerise at high temperature

forming a ‘hydrocarbon pool’ (HCP) intermediate in the induction period. Methyl (CH₃) species from methanol decomposition or dehydration are believed to be constantly fed into the HCP while alkenes are split off. Attempts have been carried out to analyse the transient products to form or decompose from the HCP at different time-on-stream (TOS) in hope to get clues on the mechanisms [10]. However, this proves to be difficult due to some intrinsically fast reactions complicated by secondary reactions with aromatics and carbonaceous depositions that can also modify zeolite catalysis in a dynamic manner. Nevertheless, it has been independently demonstrated that the HCP contains polymethylbenzene as the primary intermediate at steady state, where the degree of methylation depends on the topology of the zeolite porous structure and spatial arrangement of the BAS [11].

Previous reports on the pore size effect of zeolites on product selectivity have been summarised by Olsbye et al. [12] The choice of zeolite catalysts depends on the product selectivity, e.g. SAPO-34 primarily gives lower olefins, but H-ZSM-5 mostly gives aromatics [13]. The framework structures of zeolites with respect to the substrates and products have been studied extensively by various characterisation techniques, including X-ray diffraction [14], BET/BJH methods [15] and isotopic switch experiments [16], etc. The product size/shape selectivity is commonly attributed to the mass transfer and transition

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state effects [17]. The former circumvents merely the formation or diffusion of ‘over-sized’ products by its zeolite framework, by acting as a molecular sieve. Whereas, the latter is caused by the confined space within the zeolite framework, which influences the formation of certain transition state species. However, such assumption is based on the rigid models of zeolite frameworks or carbonaceous species filled zeolites with respect to product molecules, where the dynamic modifications or interactions of the pore openings in proximity to the active BAS by reaction species are commonly ignored.

The industrial MTO process requires the capture of product gases of an appropriate composition under a fixed contact time before the air-regeneration of the carbonaceous-fouled zeolite catalyst in a fluidised-bed reactor. Typically, a minimum induction period of about 20 min, dependent on the reaction conditions, is applied to the industrial MTO process over the SAPO-34 catalyst [6]. During the induction, the product gas is empirically shown to contain large quantity of *i*-butene, pentene and other C₅⁺. However, at steady state, more desirable lower olefins, such as ethylene and propylene, are the major products, which match the downstream needs for the synthesis of polyethylene (PE) and polypropylene (PP) [18]. Thus, a rational reduction of undesirable induction phase for higher olefins and the end of the phase for carbonaceous deposition would be of both academic and practical importance.

By using synchrotron X-ray powder diffraction (SXRD) and Rietveld refinement, our group have recently revealed the structures of organic adsorbates (such as pyridine, ammonia and methanol) even at low surface coverage inside various zeolite frameworks [19–23]. Based on diffraction evidence, the bond distances and angles of these organic species about the surface BAS can be measured within experimental errors, which could offer addition information to the traditional spectroscopic techniques. In light of these works, we have designed a low-dead-volume capillary reactor gas-cell to study the catalytic activity-structure relationship, using the optimised high-brightness synchrotron X-ray beam at Beamline I11 in Diamond, UK. Hereby, we report a dynamic modification of the molecular 8-membered ring (MR) opening to the super-cage of the pore opening in SAPO-34 during the early stage of MTO induction process. It is found that a low degree of carbonaceous deposition in confined space does not offer much blockage to the gaseous products. Using SXRD-mass spectroscopy (MS) with Rietveld refinement, selective gas uptake and density functional theory (DFT) calculations, it is demonstrated for the first time that the molecular entry window of the 8-MR pore opening of SAPO-34 is modified dynamically by a surface methoxy species (SMS) at a steady state on the zeolite framework. This offers a molecular sieving effect and modifies the adsorption properties of the zeolite. Both facilitate the desirable C₂⁼/C₃⁼ production, and deny higher olefins from passage after the induction period. Simply, the SMS renders a ‘door-keeping’ effect to deny the less desirable n-C₄⁼ products.

2. Experimental

2.1. Synchrotron x-ray powder diffraction (SXRD) and Rietveld refinements

SXRD data were collected at Beamline I11, Diamond Light Source, Harwell, UK [24]. The energy of the incident X-ray flux was set at 15 KeV. The wavelength and 2θ-zero point were refined using a diffraction pattern obtained from a high-quality silicon powder (SRM640c). High-resolution SXRD data were obtained from the zeolite samples using the multi-analyser crystals (MAC) detectors. The patterns were collected in the 2θ range 0–150° with 0.003° data binning. Each MAC pattern was collected for an hour for good statistics. A capillary reactor cell was specifically designed for this reaction in the SAPO-34 sample under SXRD in a controllable manner, see Fig. S1 in the Supplementary Materials (SM) (see SM/methods for more information).

For the Rietveld refinement analyses, similar procedures as our

Table 1

Product distribution of SAPO-34 of the MTO process at industrial reaction conditions at 460 °C with 100% conversion of methanol (data provided by SRIPT-SINOPEC). The powder catalyst was pressed into a pallet and loaded in a fixed-bed reactor.

TOS (min)	Product distribution (wt%)									
	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	(CH ₃) ₂ O	MeOH	C ₄ ⁼	C ₅ ⁺	C ₂ ⁼ + C ₃ ⁼
5	1.7	29.0	0.9	35.2	8.2	0.1	0.0	18.0	6.9	64.1
10	1.9	31.1	1.1	35.8	6.7	0.0	0.0	17.2	6.1	66.9
20	2.5	37.4	1.1	35.4	3.6	0.0	0.0	14.8	5.2	72.8
30	2.4	42.6	1.0	35.2	2.1	0.0	0.0	12.4	4.3	77.8
35	2.5	44.5	0.9	34.7	1.6	0.0	0.0	11.5	4.2	79.2
40	2.4	46.1	0.8	34.6	1.3	0.1	0.0	10.6	4.0	80.7
45	2.5	47.5	0.8	34.2	1.0	0.1	0.0	9.9	3.9	81.7
50	2.5	48.6	0.7	33.9	0.9	0.2	0.0	9.3	3.8	82.5
55	2.6	48.9	0.7	33.3	0.7	0.7	0.0	8.8	4.3	82.2
60	2.6	49.3	0.6	32.6	0.6	2.2	0.0	8.3	3.7	81.9

previous works have been carried out (the details can also be found in SM) [19–23].

3. Results

The commercial powder SAPO-34 sample (space group of R-3) has a surface area of 510 m² g⁻¹. It has an average cubic particle size of 5 μm that is ideal for Rietveld refinement. From the structural formula of Al_{0.81}Si_{0.19}PO₂ (silicon-doped aluminium phosphate), it contains 3.4 BAS per unit cell and a total BAS concentration of 1.1 mmol g⁻¹. We first studied the MTO induction process over SAPO-34 under the typical industrial conditions, using a fixed-bed packed reactor at 460 °C at SRIPT-SINOPEC where 100% conversion of methanol was achieved. Table 1 displays the product distribution. Despite the total conversion of methanol at the early stage of induction, the C₂⁼ + C₃⁼ selectivity increases progressively over longer TOS, from 64.1% to 82.5% after 50 min TOS. Interestingly, the corresponding C₄⁼ selectivity decreases over longer TOS from 18.0% to 9.3%. The propane (C₃H₈) concentration also decreases over longer TOS, which is in favour of the desired olefinic products, as previously discussed. This is extremely useful from the industrial perspective if we can finely tune the productivity towards the desired olefin products with shorter TOS. However, the reasons behind the change in product selectivity in the time course have not yet been well-studied in the literature.

4. Discussion

To rationalise time-dependent product selectivities in catalysis, we recently designed a high-pressure, low-dead-volume catalytic capillary gas-cell for SXRD measurements in Beamline I11, Diamond Light Source, UK (see SM/Methods and Figure S1). A powder SAPO-34 sample was first kept in the gas-cell (diameter of 0.7 mm) under a He flow rate of 2.5 mL min⁻¹ at 1 atmosphere via a methanol saturator (kept at RT). While analysing the out-let gas using a mass spectrometer (MS), the SAPO-34 sample was scanned with parallel but high-brightness synchrotron X-ray beam at an energy of 15 keV, to study the structure-activity relationship. The sample was first heated to 460 °C and injected with a stream of methanol vapour under a He flow rate of 2.5 mL min⁻¹ via a methanol saturator (kept at RT at 1 atmosphere) for 2-min TOS. After 2 min of methanol injection, the sample was kept 5 min to remove any adsorbed methanol at 460 °C. Then the sample was brought down to RT, where SXRD was collected. This is followed by repeated 2-min TOS of methanol injection at 460 °C, 5 min of residue removal at 460 °C, and SXRD scanning at RT. The on-line MS of methanol substrate and C₂⁼-C₄⁼ were simultaneously monitored (traces

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