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# Improved light olefin yield from methyl bromide coupling over modified SAPO-34 molecular sieves

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As an alternative to the partial oxidation of methane to synthesis gas followed by methanol synthesis and the subsequent generation of olefins, we have studied the production of light olefins (ethylene and propylene) from the reaction of methyl bromide over various modified microporous silico-aluminophosphate molecular-sieve catalysts with an emphasis on SAPO-34. Some comparisons of methyl halides and methanol as reaction intermediates in their conversion to olefins are presented. Increasing the ratio of Si/Al and incorporation of Co into the catalyst framework improved the methyl bromide yield of light olefins over that obtained using standard SAPO-34.

## Introduction

Methane is among the most important fossil resources today and, based on known available reserves, will continue to be so in the future. Methane is available not only as a fossil resource, a major component of natural gas, but also from a variety of renewable sources (e.g. biogas). The conversion of methane from renewable sources to higher hydrocarbons is potentially a large and important component of technologies for the production of sustainable fuels and chemicals.

The cost-effective and efficient conversion of methane to higher valued and more easily transportable liquid products remains a significant chemical and engineering challenge. The only significant commercial process to convert methane to liquid chemicals practiced today relies on the partial oxidation of methane to synthesis gas (CO and H2) followed by CO hydrogenation to liquid hydrocarbons using Fischer-Tropsch synthesis or methanol synthesis.<sup>1</sup> At present, the process economics require these plants to be very large with high capital investments.2

Looking for better solutions, researchers have investigated a variety of different approaches3-5 to selectively activate the C-H bonds of methane at low temperatures including transition metal complexes,<sup>4,6,7</sup> mercury complexes,<sup>8</sup> zeolites,<sup>5,9</sup> and novel high-performance polymeric solid state frameworks (CTF)10 as catalysts. The sulfuric acid based approaches of Periana *et al.*<sup>7,11</sup> and Schüth *et al.*<sup>10</sup> are promising with respect

to activity and selectivity, however to date, low yields<sup>12</sup> or other practical limitations of most of these potential pathways have prevented their translation into practical industrial processes.

One high-yield approach uses the low activation energy of methane halogenation to activate methane by reaction with halogens under relatively mild conditions to produce a reactive methyl halide intermediate.<sup>13,14</sup> Under controlled conditions, the major products are mono-halogenated methane  $(CH_3X)$  and di-halogenated methane  $(CH_2X_2)$ . From a molecular structure and bond strength standpoint, monohalogenated methane compounds are similar to methanol. Therefore, many of the pathways for converting methanol to higher hydrocarbons can be applied analogously to monohalomethane.<sup>15-18</sup> The primary focus has been on reactions with chlorine and bromine.<sup>13,19</sup> Looking at the bond strengths of different halogens, bromination of methane has significant advantages over chlorination primarily due to the weaker Br-C bond,<sup>20</sup> relative to Cl-C. This gives greater selectivity for monobromomethane and the resulting final hydrocarbon products. As it is a liquid at room temperature, bromine management has practical advantages over chlorine in terms of storage and delivery. As with any halogen based process, the need to use high-alloy (and high-cost) materials of construction to resist corrosion is an important engineering consideration.

Although there are structural and chemical similarities between methanol (C-OH) and mono-halogenated methane (C-X), the reaction thermodynamics, microkinetics, and practical process design details for methyl halide conversion are different than for methanol.  $^{15-17}$  There are several reports of CH<sub>3</sub>Cl conversion to hydrocarbons,<sup>21,22</sup> as well as reports of CH<sub>3</sub>Br conversion to both light olefins<sup>22,23</sup> and aromatic-rich fuel mixtures.<sup>23</sup> Very relevant to this work is a study<sup>22</sup>

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discussing the conversion of methyl halides to hydrocarbons over SAPO-34 which showed that SAPO-34 is an active, selective, and structurally stable catalyst for the conversion of methyl chloride and methyl bromide to olefins. However, in these studies the single-pass conversion was low due to limitations of the catalyst material.

In this report we describe improvements to SAPO-34 catalysts that give higher yield for methyl bromide coupling to light olefins. We also explore how the product distribution and yields depend upon the process parameters and catalyst structure.

## Experimental

## Synthesis of SAPO-34 and Co-SAPO-34

silicoaluminophosphate molecular-sieve SAPO-34 The samples were prepared following a procedure described by Keil<sup>17</sup> with minor modifications. A solution of 12.6 g of 85% phosphoric acid, 1.6 g of 37% HCl and 20.3 g of DI water was added to 27.2 g of aluminium isopropoxide in a polyethylene (PE) bottle. 4.0 g of Ludox SM-30 colloidal silica (Sigma Aldrich) was then added to the bottle followed by 1 min vigorous stirring. Subsequently, 56.2 g of 35% tetraethylammonium hydroxide (TEAOH, Aldrich) and 9.1 g DI water were added and the bottle was stirred again for 1 min. The mixture was then transferred to a Teflon-lined autoclave, and agitated for 48 h at room temperature. The approximate composition of the resulting gel is TEAOH :  $Al_2O_3$  :  $0.89P_2O_5$  :  $0.3SiO_2$  : 0.2HCl :  $64H_2O$ . The temperature was then increased to 215 °C, for 100 h without agitation. After washing the resulting white precipitate with DI water 10 times, the product was transferred to a porcelain cup, dried at 120 °C and then calcined at 600 °C for 6 h to yield a white powder. The presence of a pure SAPO-34 phase (CHA) was confirmed by XRD phase analysis (Fig. 1a). Samples with partial framework substitution of Co were prepared by mixing cobalt nitrate with the starting mixture solution with a mole ratio of Co/Al<sub>2</sub>O<sub>3</sub> approximately equal to 0.02 (Fig. 1b).



**Fig. 1** XRD patterns for the synthesized SAPO-34 (a) and CoSAPO-34 (b).

#### Experimental setup and procedure for coupling reactions

Coupling reactions were conducted in an atmospheric pressure fixed bed flow reactor system (Fig. 2). CH<sub>3</sub>Br was fed to a glass tube reactor (id 1 cm) through a micro liquid delivery pump (M6 Pump, VICI). The feed was diluted by nitrogen to achieve lower partial pressures and stable flow. The reaction temperature was varied in the range of 400 to 500 °C. The reaction residence time was varied over the range of 0.1 to 2.0 s. The effluent stream from the reactor was passed through a series of Teflon trap vessels each containing 4 ml of 4 M NaOH solution and 4 ml organic solution (8 wt% decane in dibutyl phthalate) where the HBr coproduct was neutralized and the organic products were captured. All remaining gas phase products were collected in a gas bag after passing through a final base trap (30 ml of 4 M NaOH solution) to prevent any residual HBr from entering the bag. For most of the experiments, reactions were run for one hour with all products trapped and analyzed. The coupling products were analyzed with three GCs, which measured (1) unconverted CH<sub>3</sub>Br, (2) gaseous hydrocarbon products  $C_1-C_6$ , and (3) liquid hydrocarbons including C4+, benzene, toluene, xylenes (BTX), and other products.

After one hour of reaction, the feed gas was switched to air and the reactor temperature raised to 500 °C in order to decoke the catalyst for at least 2 h. CO<sub>2</sub> released from decoking was captured in another trap prefilled with excess saturated Ba(OH)<sub>2</sub> solution. The amount of carbon deposited on the catalyst during coupling was determined by gravimetric analysis of the dried BaCO<sub>3</sub> precipitate.<sup>24</sup> Based on the quantitative analyses, CH<sub>3</sub>Br conversions, product selectivities (C mol base) and product yields (conversion multiplied by selectivity) were calculated. For all of the experiments, carbon balances were calculated based on the total carbon delivered to the reactor and the sum of all carbon measured in the traps and as coke. Experiments with carbon balances of  $100 \pm 5\%$  were considered to be acceptable and reportable; however, most of the results had a carbon balance of  $100 \pm 2\%$ .

Temperature dependency of coupling of CH<sub>3</sub>Br over SAPO-34 and Co-SAPO-34. Product samples were collected



Fig. 2 Experimental setup for CH<sub>3</sub>Br coupling reaction.



**Fig. 3** Conversion of  $CH_3Br$  and yields of light olefin and coke over SAPO-34 and CoSAPO-34 as a function of temperature.



**Fig. 4**  $C_2^{=}/C_3^{=}$  ratio (by weight) over SAPO-34 and CoSAPO-34.

in gas bags and liquid traps over 1 h at each temperature over the range of 400–500 °C in 25° increments. As shown in Fig. 3, the conversion of CH<sub>3</sub>Br over SAPO-34 increases significantly with temperature from 58 to 90% and the yield for LO (ethylene + propylene) increases from 34 to 60%. By plotting the ratio  $C_2^{-}/C_3^{-}$  (by weight) as shown in Fig. 4, it was found that the ratio increases almost linearly with temperature. Furthermore, as shown in Table 1, the

Table 1 Product distribution for SAPO-34 at different temperatures

	C mol selectivity, %							
	400 °C	425 °C	450 °C	475 °C	500 °C			
CH <sub>4</sub>	1.3	2.1	3.2	4.8	8.2			
$C_2H_4$	19.4	24.3	29.7	34.4	40.2			
$C_2H_6$	0.3	0.4	0.6	0.8	1.0			
$C_2H_4/C_2H_6$	64.7	60.8	49.5	43	40.3			
C <sub>3</sub> H <sub>6</sub>	39.3	35.9	32.5	27.1	24.1			
$C_3H_8$	7.0	5.2	4.8	3.6	2.4			
$C_3H_6/C_3H_8$	5.6	6.9	6.8	7.5	10.1			
C <sub>4-6</sub>	14.0	13.3	10.4	9.6	6.5			
BTXM+	2.8	4.4	3.7	3.1	3.7			
RBr	8.9	9.1	9.2	7.9	5.1			
Coke	7.0	5.3	5.9	8.6	8.9			

selectivity to propylene decreases and that to ethylene increases with increasing temperature. Fig. 3 shows the results of similar coupling experiments with Co-SAPO-34. The substitution of Co into the SAPO-34 framework results in a significantly higher CH<sub>3</sub>Br conversion at the same temperatures as the pure SAPO-34. However, the LO yields are unchanged and the coking is slightly increased.

As shown in Table 1, higher temperatures promote higher ethylene production, however, there is increased methane and decreased higher hydrocarbons production,  $C_{4-6}$ , which is consistent with increased hydrocarbon cracking. Brominated species, RBr, are decreased with increasing temperature as dehydrohalogenation takes place.

Co-SAPO-34 showed higher catalytic activity at lower temperature than regular SAPO-34; CH<sub>3</sub>Br conversion for Co-SAPO-34 was over 90% at 400 °C. Compared to regular SAPO-34, coke formation is higher, LO yields and  $C_2^{=}/C_3^{=}$  ratios are slightly higher at low temperature. Comparing product distributions, a major difference is that larger olefin/paraffin ratios were measured at low temperature from Co-SAPO-34 than observed from SAPO-34. All of these findings suggest that the incorporation of Co into the SAPO-34 framework likely changes the acidity as well as the surface and pore structures, resulting in a more favorable catalyst to perform the coupling reaction of CH<sub>3</sub>Br to LO and other products.

### Effect of residence time over SAPO-34

Coupling reactions of methyl bromide were run over SAPO-34 at 475 °C and 0.2 atm partial pressure. The residence time was varied from 0.5 to 4.0 s. The results are summarized in Fig. 5 and 6.

CH<sub>3</sub>Br conversion increases non-linearly with increasing residence time. Maximum LO yield near 60% was obtained at 2 s residence time as shown in Fig. 4. The  $C_2^{-}/C_3^{-}$  molar ratios did not change with residence time (Fig. 6). Coke amounts increase with the increased residence time. At very short residence time (<2 s), conversion increased faster than coking (exponential *vs.* linear dependency).

The dependence of product formation on residence time is not the same for all species.  $C_2^{-}$  and  $C_3^{-}$  selectivities decrease with residence time while CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and BTX selectivities increase with residence time (Fig. 6). Light olefins



Fig. 5 Dependence of  $CH_3Br$  coupling on residence time over SAPO-34 at 475 °C with 0.2 atm  $CH_3Br$ .



Fig. 6 Product selectivity of major compounds vs. retention time.



Fig. 7 Proposed mechanism converting CH<sub>3</sub>Br to light olefins.

are thought to be produced as an intermediate product at the initial reaction stage and they are subsequently converted to other products such as paraffin, BTX and finally coke as the reaction is allowed to proceed over the catalysts.

Oligomerization of light olefins to higher olefins, aromatization of olefins, alkylation of aromatics, further condensation to larger aromatics and ring condensation, and the eventual formation of coke are all considered part of the reaction pathway. On the other hand, as some amounts of highly active hydrogen species will be released in these reactions, these active hydrogen species will hydrogenate olefins to paraffins.

Fig. 7 illustrates a suggested CH<sub>3</sub>Br coupling mechanism which follows from analogous intermediates observed and predicted in MeOH coupling.<sup>15</sup>

### Influence of partial pressure on CH<sub>3</sub>Br coupling over SAPO-34 and Co-SAPO-34

Fig. 8 illustrates the influence of partial pressure on yield and conversion from the coupling reactions of methyl bromide over SAPO-34 and Co-SAPO-34. Table 2 contains a summary of the product distribution observed. The reactions were run for one hour at 500  $^{\circ}$ C with a residence time of 2.0 s.

As the partial pressure was increased from 0.2 atm to 0.5 atm, the CH<sub>3</sub>Br conversion decreased slightly, the  $C_2^{-}/C_3^{-}$  ratios remained constant, and the LO yields decreased. The yields of other products including CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, BTX and RBr are minimally increased (not shown). The same trends were observed with both SAPO-34 and Co-SAPO-34. In spite of the negative effect caused by increased CH<sub>3</sub>Br partial pressure, the light olefin yields still reached approximately 47% at 0.5 atm for both catalysts.



Fig. 8 Effect of partial pressure on CH<sub>3</sub>Br coupling.

 Table 2
 Effect of partial pressure on CH<sub>3</sub>Br coupling

PMeBr	Conv, %	LO yield	$C_2^{=}/C_3^{=}$ (wt)	Coke, %	C- balance, %				
SAPO-34, 500 °C, 2.0 s									
0.2	91.4	58.7	1.67	8.1	100.3				
0.3	91.7	52.6	1.64	9.6	112.7				
0.4	90.8	50.2	1.69	10.1	109.2				
0.5	88.1	46.9	1.90	7.3	105.6				
CoSAPO-34, 500 °C, 2.0 s									
0.2	97.9	60.2	1.67	11.7	100.4				
0.3	96.4	51.8	1.59	14.4	115.3				
0.4	96.3	48.7	1.62	15.1	100.2				
0.5	94.1	47.0	1.67	13.9	108.4				

#### Catalyst stability and reproducibility

To test the catalyst stability and reproducibility, 10 reactiondecoke cycles were run on SAPO-34 including 1 h of reaction and overnight decoking. Coupling reactions were run at 475 °C with 2 s residence time and 0.2 atm CH<sub>3</sub>Br while decoking was performed at 500 °C overnight with a flow of 5 cm<sup>3</sup> min<sup>-1</sup> air. As shown in Fig. 9, the catalysts show excellent stability and reproducibility in terms of CH<sub>3</sub>Br conversions, LO yields,  $C_2^{-}/C_3^{-}$  ratios, and coke amounts. No notable catalyst performance decay was observed under these conditions and no structure changes were measured from XRD analysis of the catalyst after the runs.



Fig. 9 Catalyst stability test over SAPO-34 at 475 °C, 2 s and 0.2 atm  $CH_3Br$ .



Fig. 10 Effect of  $SiO_2$  content on  $CH_3Br$  conversion, LO yield and coke formation.

### Effect of SiO<sub>2</sub> content in SAPO-34 on coupling reactions

As previously shown, changing the Si/Al ratio in the SAPO-34 structure changes the concentration of acid sites available for catalysis.<sup>25</sup> We synthesized five different Al/Si catalysts: S1, Si<sub>0.06</sub>AlP<sub>0.97</sub>O<sub>4</sub>; S2, Si<sub>0.10</sub>AlP<sub>0.94</sub>O<sub>4</sub>; S3, Si<sub>0.15</sub>AlP<sub>0.89</sub>O<sub>4</sub>; S4, Si<sub>0.30</sub>AlP<sub>0.72</sub>O<sub>4</sub> and S5, Si<sub>0.60</sub>AlP<sub>0.40</sub>O<sub>4</sub> and confirmed the structures with XRD measurements.

The activity tests were conducted at 475 °C with a residence time of 2 s and partial pressure of 0.2 atm (Fig. 10). The CH<sub>3</sub>Br conversion increases with the [Si] and reached 95% at [Si] of 0.60. Coke production stays constant, *ca.* 5%, at [Si] lower than 0.30 and then increased to 12% at an [Si] of 0.60. Higher light olefin yields were obtained for [Si] in the range from 0.2 to 0.3. This result suggests that the catalyst performance of SAPO-34 is directly related to the number of acid sites in the materials. However, as has been discussed above, the optimal conditions for the best LO yield and the best catalyst performance is not necessarily at the condition of high CH<sub>3</sub>Br conversion, at which point coking becomes significant.

## Discussion

Product analyses at different sets of reaction conditions, which include variation of temperature, partial pressure and residence time over both SAPO-34 and Co-SAPO-34 catalysts, show clear performance trends. The entire coupling reaction proceeds towards the formation of aromatics, alkanes and coke while light olefins are a group of intermediate products formed at an early reaction stage. According to the hydrocarbon pool mechanism suggested for MeOH coupling to LO,<sup>26</sup> the intermediate products are benzenes which are required for the further products are benzenes which are olefins could grow to bigger compounds which consequently clog the active pores and deactivate the catalyst until it is decoked.

The results indicate that smaller amounts of benzenes are produced using Co-SAPO-34 over SAPO-34 and therefore slow down the production of coke. The addition of hydrogen solution to reduce coke is another alternative, but hydrogen can be expected to react with the LO intermediates producing saturated alkanes.

## Conclusion

In general, it has been found that temperatures of approximately 475 °C and relatively short residence times (1-2 s) favor the formation of light olefins with a minimum amount of coke. Increasing the Si/Al ratio or incorporation of Co into the SAPO-34 framework promotes CH<sub>3</sub>Br conversion but also leads to higher rates of coke formation. Increasing CH<sub>3</sub>Br partial pressure does not significantly affect CH<sub>3</sub>Br conversion; however, the product distribution shifts towards heavier components. The C<sub>2</sub><sup>-</sup>/C<sub>3</sub><sup>-</sup> ratio almost exclusively depends on coupling temperature. Light olefins are recognized as the primary coupling products at the initial reaction stage, which if given longer product–catalyst residence times undergo a series of sequential reactions and are converted to byproducts such as BTX, light alkanes, and coke.

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