Catalytic Conversion of Methanol to Olefins on SAPO-*n* (*n* = 11, 34, and 35), CrAPSO-*n*, and Cr−SAPO-*n* Molecular Sieves

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The catalytic conversion from methanol to olefins has been studied for SAPO-11, SAPO-34, and SAPO-35 silicoaluminophosphate molecular sieves with and without chromium incorporation. The selectivity for methanol conversion to ethene and propene has been investigated as a function of structure type, silica content, chromium location, and chromium concentration. Among protonated H−SAPO-*n* materials, SAPO-34 shows the highest selectivity for ethene and propene, whereas SAPO-11 shows the longest lifetime for catalytic activity. The variation of silicon content indicates that there is an optimum silicon content in SAPO-34 for the best catalytic activity. Incorporation of Cr into the framework of SAPO-*n* increases the lifetime and the selectivity toward ethene compared with those from Cr incorporation by ion exchange. This is interpreted as an acidity difference between synthesized CrAPSO-*n* and ion-exchanged Cr−SAPO-*n*. CrAPSO-11 also increases the lifetime, the distribution of ethene and propene, and the selectivity toward ethene compared with SAPO-11. However, SAPO-34 and CrAPSO-34 with higher Si content compared to that of SAPO-11 show similar selectivity toward ethene and propene, but CrAPSO-34 has a longer lifetime. The chromium influence is smaller in CrAPSO-34 compared to CrAPSO-11. With an increase in Cr amount, CrAPSO-11 shows higher selectivity toward ethene and propene and has a longer lifetime.

Introduction

Light olefins are important components for the petrochemical industry. Conventionally, they are produced by thermal cracking of naphtha. The importance of the research efforts to viable routes in the production of basic chemicals, independent of oil, cannot be overlooked. Methanol, which can readily be produced from coal or natural gas via synthesis gas ($CO + H_2$) by existing and proven technologies, offers an interesting alternative. Mobil's announcement of a zeolite-based process for the conversion of methanol into gasoline provided a new route for the conversion of coal to gasoline.[1,2] The importance of light olefins as intermediates in the conversion of methanol to gasoline was soon recognized. As a result, several attempts were made to selectively produce light olefins from methanol on zeolite catalysts.[3,4,5]

The development of microporous silicoaluminophosphate (SAPO) molecular sieves offered interesting perspectives for methanol to olefins (MTO) conversion.[6] The use of SAPOs for MTO conversion relies on different structures and a variation in acidity. Isomorphous substitution of silicon into a microporous aluminophosphate usually confers a negative charge on the framework with charge-balancing protons that act as Brönsted acid sites. Therefore, it is possible for SAPOs to be used as solid acid catalysts. However, the strength of the acid sites in SAPOs depends on its framework structure. The acidity, along with the size and the shape of the micropores, in a SAPO material determines its activity, selectivity, and lifetime for an acid-catalyzed reaction.

Among the more than 20 SAPOs, SAPO-11 is one of the most extensively studied. The structure of SAPO-11 has one-dimensional 10-ring channels linked to one another via four- and six-rings and has no zeolite structured analogue. SAPO-34 is an analogue of the zeolite, chabazite. It has nearly spherical cages linked by eight-ring windows. SAPO-35 is analogous to the zeolite, levynite, and is made up of cages connected via single six rings and double six rings.

The incorporation of transition-metal ions into framework sites of silicoaluminophosphate molecular sieves is also of interest for the design of novel catalysts. SAPOs can be modified to improve catalytic performance by isomorphous substitution of elements having

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different electronegativities, concentrations, and distributions in the framework. Transition-metal ions can be incorporated by ion-exchange in addition to isomorphous substitution.[6] Transition-metal-substituted SAPOs such as MeAPSO-34 and MeAPSO-18 have been tested by several groups.[7,8] Inui et al. and Thomas et al. reported independently that nickel-containing SAPO-34 is an effective catalyst for MTO conversion, yielding close to 90% ethene at almost 100% conversion at a reaction temperature of 450 °C.[7,9]

In this study, the catalytic conversion from methanol to olefins is studied for SAPO-11, SAPO-34, and SAPO-35 with and without chromium incorporation. The selectivity from methanol to ethene and propene has been investigated as a function of SAPO structure type, silicon content, and chromium location and concentration.

Experimental Section

Synthesis. The preparations of SAPO-11 and CrAPSO-11 have been described.[10] SAPO-34 was prepared as previously described.[11] CrAPSO-34 was prepared hydrothermally using morpholine as the organic template. Synthesis was carried out in a 100 cm^3 stainless steel reactor lined with Teflon at autogenous pressure without agitation. Taking into account the similar sizes and charges of Cr^{III} and Al^{III}, the molar composition of the reaction mixture for the synthesis of CrAPSO-34 was initially chosen as $0.01\ Cr_2O_3/0.99\ Al_2O_3/1.0\ P_2O_5/0.4\ SiO_2/2R/60\ H_2O$, where R stands for morpholine. In a typical synthesis, 5.74 g of pseudoboehmite was slurried in 15 mL of H_2O and stirred for 2 h. Then, 0.27 g of chromium chloride hexahydrate dissolved in 5 mL of H_2O was mixed with 9.22 g of phosphoric acid, and the solution was added dropwise to the alumina slurry. After the mixture was stirred for about 2.5 h, 1.44 g of fumed silica mixed with 10 mL of H_2O was added dropwise. The mixture was stirred for 1 h. To this mixture, 6.97 g of morpholine was added dropwise, and the final mixture was stirred for 24 h for aging before heating to 473 K for 2 days in the autoclave. After crystallization, the product was separated from the mother liquor, washed with water, and dried at 353 K overnight. The as-synthesized sample was calcined in O_2 by slowly raising the temperature to 823 K and holding at this temperature for 12 h to remove the organic template. SAPO-35 was made as reported earlier.[12] The gel compositions of the reaction mixtures for the SAPO-*n* materials are summarized in Table 1. Liquid-phase ion-exchanged (L)Cr−SAPO-*n* and solid-state ion-exchanged (S)-Cr−SAPO-*n* were prepared as previously described and retained the SAPO-*n* structure.[13]

Measurements. Powder X-ray diffraction (XRD) patterns of the calcined products were obtained on a Philips 1840 diffractometer with Cu Ka radiation (40 kV, 25 mA) at a 0.01 step size and 1 s step time over the range $5° < 2\theta < 50°$. The samples were prepared as thin layers on aluminum slides.

Chemical analysis of the samples was carried out by electron microprobe analysis with a JEOL JXA-8600 electron beam superprobe operated at a beam voltage of 15 kV and a current of 30 nA. Si and O were calibrated with diopside, $CaMgSi_2O_6$, Cr with metallic Cr, Al with anorthite, $CaAl_2Si_2O_8$, and P with monazite. Prior to measurement, the samples were prepared as pressed pellets to make a dense material with a reasonably smooth surface. The electron beam was defocused to 10 mm diameter to minimize the damage caused to the specimen by heating. Data were collected from 3 to 5 randomly chosen regions and averaged to represent the bulk composition. The precision was usually <1% for all elements, and the accuracy is estimated at 2−3% for cations and 5% for oxygen.

Table 1. Gel Compositions for SAPO-*n* (*n* = 11, 34, and 35) and CrAPSO-*n* Materials

catalyst	gel composition[a]
SAPO-11	$0.1\ SiO_2/Al_2O_3/P_2O_5/R_1/40\ H_2O$
CrAPSO-11(1)	$0.1\ SiO_2/0.005\ Cr_2O_3/0.995\ Al_2O_3/P_2O_5/R_1/40\ H_2O$
CrAPSO-11(2)	$0.1\ SiO_2/0.01\ Cr_2O_3/0.99\ Al_2O_3/P_2O_5/R_1/40\ H_2O$
SAPO-34(1)	$0.3\ SiO_2/Al_2O_3/P_2O_5/2.0\ R_2/60\ H_2O$
SAPO-34(2)	$0.6\ SiO_2/Al_2O_3/P_2O_5/2.0\ R_2/60\ H_2O$
SAPO-34(3)	$1.0\ SiO_2/Al_2O_3/P_2O_5/2.0\ R_2/60\ H_2O$
CrAPSO-34	$0.3\ SiO_2/0.005\ Cr_2O_3/0.995\ Al_2O_3/P_2O_5/2.0\ R_2/60\ H_2O$
SAPO-35	$0.6\ SiO_2/Al_2O_3/P_2O_5/1.5\ R_3/55\ H_2O$

[a] R_1 stands for diisopropylamine. R_2 stands for morpholine. R_3 stands for hexamethyleneimine.

Catalytic Testing. The catalytic performance for methanol conversion was tested in a tubular quartz reactor 10 mm in internal diameter. The calcined samples were pelletized, and then crushed to particles prior to being sieved. Then, 0.2 g of sieved samples with a particle size between 150 and 180 μm was loaded into the reactor. The catalysts were activated at 450 °C under a 10 mL/min nitrogen flow for overnight. The total reaction pressure was approximately 1 atm, of which the fractional pressure for methanol was 0.19 and that for nitrogen 0.81. The catalysts were tested at 400 °C. The weight hourly space velocity (WHSV) was 1.25 h^{-1}. The injection was done in 10 s. The products were analyzed by on-line gas chromatography with a Varian 3300 gas chromatograph equipped with a flame ionization detector and a 9 m × 0.32 mm i.d. capillary column packed with Chrom P AW 60/80. Selectivities are expressed as molar percentages. Retention times and response factors were calibrated by using a standard gas mixture.

Results

Powder X-ray Diffraction. Figure 1 shows the powder XRD patterns of calcined SAPO-11, SAPO-34, and SAPO-35. These patterns match the intensities and line positions reported.[10−12] Synthesized CrAPSO-11, CrAPSO-34, and CrAPSO-35 exhibit patterns similar to those of the corresponding SAPOs.

Electron Microprobe Analysis. The chemical composition of these samples was measured by electron microprobe analysis as given in Table 2. The observed framework chemical compositions for SAPO-34 and SAPO-35 suggest Si substitution for P. In SAPO-11, Si substitutes for both Al and P with the amount of substituted P being larger than that of substituted Al.[10−12]

Catalytic Testing. *1. Shape Selectivity.* Figure 2 shows the percent of ethene and propene in the product as a function of time on stream (TOS) for calcined SAPO-11, SAPO-34 with a gel molar ratio of Si/Al = 0.3, and SAPO-35 at 400 °C. All of the SAPOs convert methanol to ethene and propene at 400 °C, but the selectivity and catalytic lifetimes vary significantly. At TOS = 10 min, SAPO-34 and SAPO-35 exhibit similar selectivity toward ethene and propene (about 75%), followed by SAPO-11 (~ 45%). At TOS = 70 min, SAPO-34 shows a slight increase in the selectivity to ethene and propene, SAPO-11 decreases to 25%, and SAPO-35

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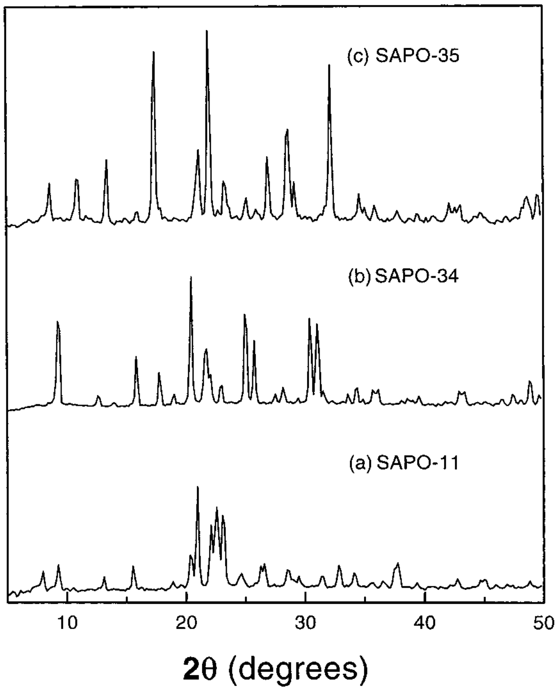

Figure 1. X-ray powder diffraction patterns of calcined (a) SAPO-11, (b) SAPO-34, and SAPO-35.

Table 2. Elemental Analyses for SAPO-*n* (*n* = 11, 34, and 35), CrAPSO-*n*, (S)Cr−SAPO-*n*, and (L)Cr−SAPO-*n* Materials

catalyst	elemental analysis
SAPO-11	$(Si_{0.028}Al_{0.493}P_{0.479})O_2$
CrAPSO-11(1)	$(Cr_{0.002}Si_{0.028}Al_{0.493}P_{0.477})O_2$
CrAPSO-11(2)	$(Cr_{0.006}Si_{0.023}Al_{0.491}P_{0.480})O_2$
(L)Cr−SAPO-11	$(Cr_{0.003}Si_{0.025}Al_{0.490}P_{0.482})O_2$
(S)Cr−SAPO-11	$(Cr_{0.002}Si_{0.027}Al_{0.490}P_{0.481})O_2$
SAPO-34(1)	$(Si_{0.105}Al_{0.473}P_{0.423})O_2$
SAPO-34(2)	$(Si_{0.142}Al_{0.481}P_{0.376})O_2$
CrAPSO-34	$(Cr_{0.002}Si_{0.114}Al_{0.492}P_{0.392})O_2$
(L)Cr−SAPO-34	$(Cr_{0.002}Si_{0.122}Al_{0.489}P_{0.387})O_2$
(S)Cr−SAPO-34	$(Cr_{0.003}Si_{0.125}Al_{0.483}P_{0.389})O_2$
SAPO-35	$(Si_{0.131}Al_{0.475}P_{0.394})O_2$

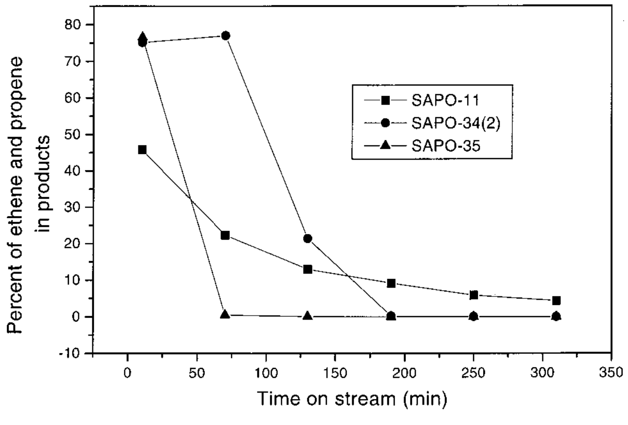

Figure 2. Percent of ethene and propene in the total products from methanol as a function of time on stream for SAPO-11, SAPO-34, and SAPO-35.

is deactivated very rapidly. At TOS = 130 min, SAPO-11 and SAPO-34 exhibit 15% and 20% selectivity to ethene and propene, respectively. The deactivation rate decreases in the order SAPO-35 ≫ SAPO-34 > SAPO-11. Figure 3 shows the percent of C_2−C_4 olefins in the product at TOS = 70 min for SAPO-11, SAPO-34, and SAPO-35. The selectivity decreases over SAPO-34 as ethene > propene > butene. While the selectivity over SAPO-11 is propene ~ butene > ethene, the selectivity toward C_2−C_4 olefins decreases in the order SAPO-34 > SAPO-11 ≫ SAPO-35.

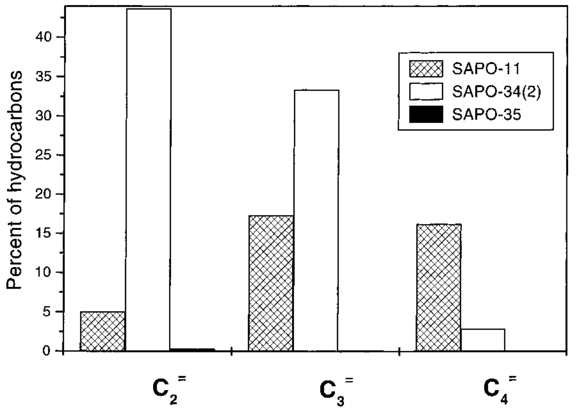

Figure 3. Percent of C_2−C_4 olefins in the products at TOS = 70 min for SAPO-11, SAPO-34, and SAPO-35.

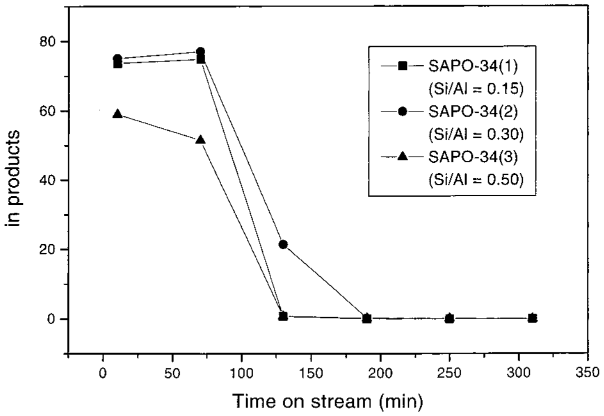

Figure 4. Percent of ethene and propene in the total products from methanol as a function of time on stream for SAPO-34 with different Si contents.

2. *Si Content.* In addition to shape selectivity, other catalyst characteristics which influence the catalytic performance of SAPO-*n* materials have also been identified. Variations in the SAPO-34 gel composition were used to prepare samples with different Si contents. Figure 4 shows the percent of ethene and propene in the product as a function of Si content for calcined SAPO-34. Figure 4 indicates that for SAPO-34 with an increase of Si/Al from 0.15 to 0.3 (gel molar composition), there is an increase in the selectivity to ethene and propene. When Si/Al reaches 0.5, the selectivity decreases. The optimum Si/Al ratio is 0.3. A comparison of SAPO-34 with different Si/Al ratios shows that the lifetime of SAPO-34 (Si/Al = 0.3) is longer than the other two.

3. *Comparison of Catalytic Performance between CrAPSO-n, H−SAPO-n, (L)Cr−SAPO-n, and (S)Cr−SAPO-n.* Figure 5 shows a comparative plot of the percent of ethene and propene in the products as a function of TOS for synthesized CrAPSO-34, H−SAPO-34, liquid-state ion-exchanged (L)Cr−SAPO-34, and solid-state ion-exchanged (S)Cr−SAPO-34. The selectivity of CrAPSO-34 is slightly higher than that of H−SAPO-34 at TOS < 120 min. However, at TOS = 130 min, SAPO-34 loses its activity and CrAPSO-34 remains 68% active. Although (S)Cr−SAPO-34 shows a similar activ-

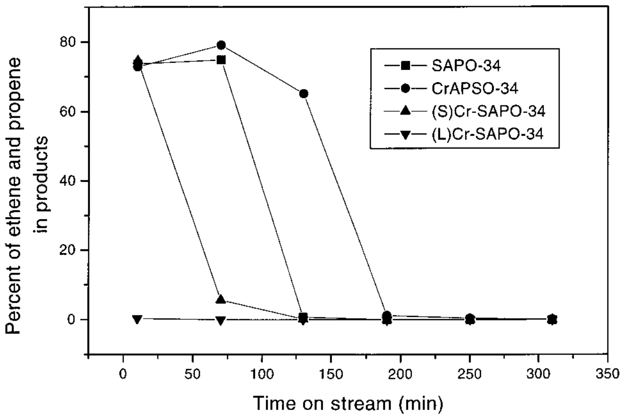

Figure 5. Percent of ethene and propene in the total products from methanol as a function of time on stream for SAPO-34, CrAPSO-34, (S)Cr–SAPO-34, and (L)Cr–SAPO-34.

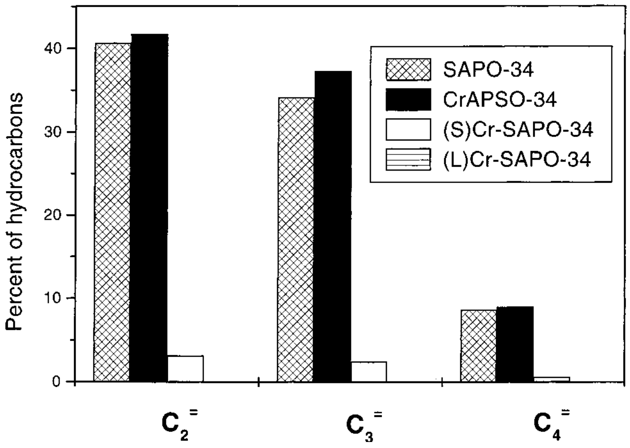

Figure 6. Percent of C_2–C_4 olefins in the products at TOS = 70 min for SAPO-34, CrAPSO-34, (S)Cr–SAPO-34, and (L)-Cr–SAPO-34.

ity at TOS = 10 min, it decays rapidly. (L)Cr–SAPO-34 is not active for methanol conversion. In summary, the lifetime order of SAPO-34 samples is CrAPSO-34 > SAPO-34 > (S)Cr–SAPO-34 > (L)Cr–SAPO-34. Figure 6 shows the percent of C_2–C_4 olefins in the products at TOS = 70 min for CrAPSO-34, H–SAPO-34, (L)Cr–SAPO-34, and (S)Cr–SAPO-34. The selectivity decreases as ethene > propene ≫ butene over SAPO-34. The activity of these samples is CrAPSO-34 ~ SAPO-34 ≫ (S)Cr–SAPO-34 > (L)Cr–SAPO-34.

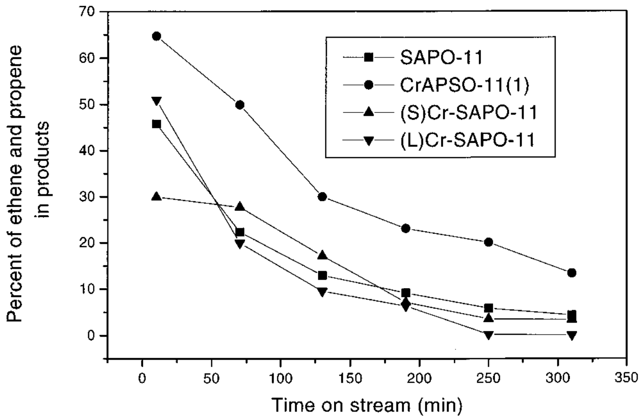

Figure 7. Percent of ethene and propene in the total products from methanol as a function of time on stream for SAPO-11, CrAPSO-11, (S)Cr–SAPO-11, and (L)Cr–SAPO-11.

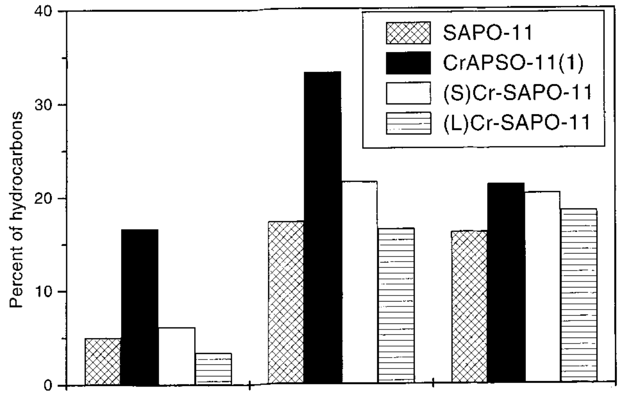

Figure 8. Percent of C_2–C_4 olefins in the products at TOS = 70 min for SAPO-11, CrAPSO-11, (S)Cr–SAPO-11, and (L)-Cr–SAPO-11.

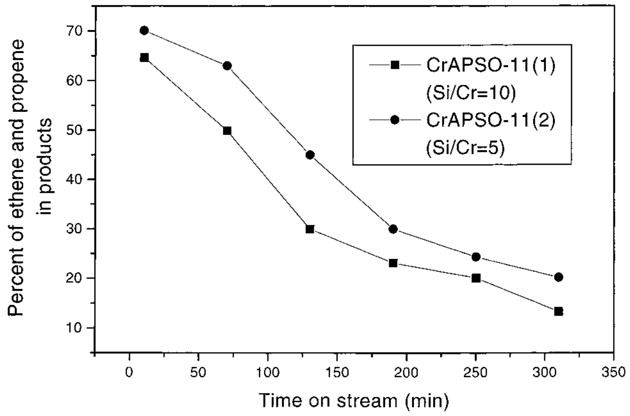

Figure 9. Percent of ethene and propene in the total products from methanol as a function of time on stream for CrAPSO-11 with different Cr contents.

Similar studies were extended to SAPO-11 structures. A comparative plot of the selectivity to ethene and propene as a function of TOS for SAPO-11, CrAPSO-11, (L)Cr–SAPO-11, and (S)Cr–SAPO-11 is given in Figure 7. All of the samples show a similar trend. CrAPSO-11 shows a selectivity ~20% higher than those of (L)Cr–SAPO-11 and SAPO-11. The initial selectivity of (S)Cr–SAPO-11 is the lowest among the four SAPO-11 materials. Compared with SAPO-34 materials, the decay is faster at TOS < 130 min but slower after that. Figure 8 shows the distribution of C_2–C_4 olefins in the products at TOS = 70 min for these four SAPO-11 materials. For CrAPSO-11, the selectivity to propene is higher than that to ethene and butene. For the other three SAPO-11 materials, it seems that propene and butene have similar selectivities which are higher than that for ethene. Comparison between Figures 6 and 8 shows that CrAPSO-11 generates the highest percent of C_2–C_4 olefin products (~75%), which is ~ 15% lower than that for CrAPSO-34.

4. Effect of Cr Concentration in Synthesized Materials. The effect of Cr concentration on methanol conversion is shown in Figure 9. CrAPSO-11 with Si/Cr = 5 shows ~10% higher selectivity to ethene and propene than does CrAPSO-11 with Si/Cr = 10. Figure 10 shows the distribution of C_2–C_4 olefins in the products at TOS = 70 min for CrAPSO-11 with Si/Cr = 5 and 10.

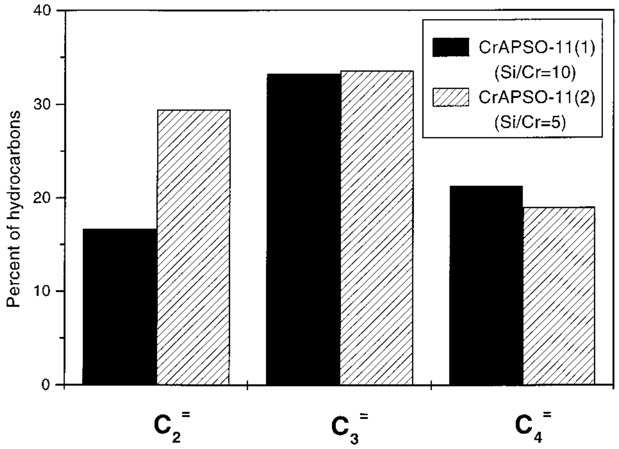

Figure 10. Percent of C_2–C_4 olefins in the products at TOS = 70 min for CrAPSO-11 with different Cr contents.

Discussion

The main reaction steps of the methanol conversion to hydrocarbons can be summarized as follows.[14,15] Methanol is first dehydrated to dimethyl ether. The equilibrium mixture formed, consisting of methanol, dimethyl ether, and water, is then converted to light olefins. In the last step of this scheme, the light olefins react to form paraffins, aromatics, naphthenes, and higher olefins by hydrogen transfer, alkylation, and polycondensation. A major goal of methanol conversion is to obtain higher selectivity of C_2–C_4 olefins. Olefin production is improved by higher reaction temperature, shorter contact times, and lower pressures.[16] Structure and acidity are two important factors which affect the catalytic conversion of methanol to olefins over SAPO materials.

Structural Effects. SAPO-34 has rhombohedral symmetry. Its framework consists of double six-rings arranged in layers in the sequence ABCABC. The hexagonal prisms formed in this way are linked by tilted four-membered rings. The resulting framework possesses large, ellipsoidal cages (7.5 Å × 8.2 Å) composed of double six-rings at the top and bottom, six eight-rings (4.5 Å × 4.1 Å) in rhombohedral positions, and six pairs of adjacent four-rings. The cavities are interconnected to six others by puckered elliptical eight-rings.

SAPO-35 is a small pore molecular sieve with eight-ring openings. The polyhedral cages observed in SAPO-35 are hexagonal prisms and levyne cages. The levyne cages are connected through six-rings and double six-rings. These cages are accessible through eight-ring windows of dimension (3.6 Å × 4.8 Å). Although SAPO-35 has a structure similar to that of SAPO-34, the levyne cage is about half the size of the SAPO-34 chabazite cage.[5,17]

Four vertexes of each tetrahedron are linked to form 4-, 6-, and 10-rings in SAPO-11. These rings are interconnected by six-ring windows. The three-dimensional framework is produced by linking the remaining vertexes that project alternately up and down normal to these sheets. Columns of 4-, 6-, and 10-rings are formed parallel to the *c*-axis. The 10-rings have an elliptical cross section of 6.3 Å × 3.9 Å.

Acidity Effects. The theoretically possible isomorphous substitution mechanisms (SM) are Si for Al (SM1), Si for P (SM2), two Si atoms for one Al and one P, simultaneously, (SM3) in SAPOs.[18] The compositions of the SAPO-11, SAPO-34, and SAPO-35 are given in Table 2. For SAPO-11, the Al/P ratio is larger than 1.0, suggesting the occurrence of SM2. Furthermore, the Al fraction of tetrahedral atoms is lower than 0.5, pointing to SM3.[18] These results are consistent with the literature for similar synthesis conditions and aluminum source.[18] The composition of SAPO-34 in Table 2 indicates that Si undergoes dual substitution mechanisms (SM2 + SM3) although the majority of the silicon probably enters the framework via SM2 which is consistent with MAS NMR spectroscopy.[11] The Si-substitution mechanism in SAPO-35 is quite similar to that in SAPO-34 in the sense that Si mainly replaces P as shown by the chemical composition in Table 2. The Si/(Si + Al + P) ratio of 0.028 for SAPO-11 is smaller than that (0.13–0.14) for SAPO-34 and SAPO-35. On the basis of the analysis above, it is reasonable to assume that the concentration of acid sites is SAPO-11 < SAPO-34 ~ SAPO-35. This conclusion is consistent with Fourier transform infrared (FTIR) and temperature-programmed desorption (TPD) of NH_3 studies on these materials.[19,20] SAPO-11 and SAPO-34 contain at least three different types of OH groups by FTIR: silanol groups at 3745 cm^{-1}, P–OH vibrations at 3675 cm^{-1}, and bridging Si–OH–Al at 3620 cm^{-1}. The acidity of the first two groups is much lower than that of Si–OH–Al. Compared to SAPO-34, SAPO-11 has more Si–OH and P–OH groups.[20] TPD of NH_3 shows that the strength of the Brönsted acid sites in SAPO-11 is less than that of SAPO-34.[19] We found no direct comparisons of the number of acid sites between SAPO-34 and SAPO-35 in the literature. However, the number of acid sites in SAPO-34 is presumably slightly higher than that in SAPO-35 for the same Si concentration.[5,17]

The strength and concentration of acid sites along with the size and shape of the micropores in a SAPO catalyst determines its activity, selectivity, and lifetime for the methanol conversion reaction. Since SAPO-35 and SAPO-34 have similar pore openings and comparable acidity, the initial selectivity to ethene and propene is almost the same (75%). Klinowski et al. have monitored the shape-selective catalytic conversion of methanol to low-molecular-weight olefins over SAPO-34 using ^{13}C and ^{1}H MAS NMR.[21] The size of the eight-ring windows in SAPO-34 limits the gas-phase products to linear C_2 and C_3 species. However, the species predominately present in the intracrystalline space are branched C_4 and C_5 saturated hydrocarbons such as isobutane and isopentane. They are too large to leave the intracrystalline pore system and become trapped,

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thus imposing an additional steric constraint on the diffusion of linear hydrocarbons. This favors the diffusion of C_2 and C_3 species out of the crystallites and is responsible for the high selectivity of SAPO-34 for ethene and propene. Among SAPO-11, SAPO-34, and SAPO-35, SAPO-11 has the lowest concentration of accessible acid sites, and the strength of these acid sites is relatively weak. The 10-ring channels in SAPO-11 allow large hydrocarbon molecules to form and diffuse, so the selectivity toward ethene and propene is lower (45%).

Deactivation. The main factors that determine the deactivation rate of a microporous material for a catalytic reaction are typically pore geometry and concentration of acid sites.[22] The deactivation rate decreases in the order SAPO-35 > SAPO-34 > SAPO-11. Since the levyne cage size of SAPO-35 is much smaller than the chabazite cage in SAPO-34, it can more easily be blocked by coke, so this may explain why SAPO-35 deactivates more rapidly than SAPO-34. The deactivation rate for SAPO-11 is much smaller than the rates for SAPO-34 and SAPO-35, although SAPO-11 has the lowest initial selectivity. The acid site concentration in SAPO-11 is much smaller than those in SAPO-34 and SAPO-35; hence, coke formation is slower in SAPO-11. Thus, SAPO-11 deactivates more slowly than SAPO-34 and SAPO-35. Furthermore, the larger 10-ring channels of SAPO-11 have a higher coke capacity before blocking occurs.

Silicon Concentration. We studied the catalytic performance over SAPO-34 with different amounts of silicon. Only a few studies address this point, although it is well-known that the number and strength of acid sites have a major effect on the methanol conversion reaction. Figure 4 indicates that increasing Si/Al from 0.15 to 0.30 (gel molar composition) increases the selectivity to ethene and propene. When Si/Al is increased further to 0.5, the selectivity to ethene and propene decreases. The optimum Si/Al ratio is 0.3. A comparison of SAPO-34 with different Si/Al ratios shows that the lifetime of SAPO-34 with Si/Al = 0.3 is greatest. This trend is different from that observed in SAPO-18 with different Si contents.[23] In SAPO-18 with Si/(Si + Al + P) increasing from 0.028 to 0.095, the activity at lower temperature increases and deactivation decreases. SAPO-18 with the highest Si/(Si + Al + P) ratio is the best catalyst on the basis of activity and deactivation rate. This difference may be explained as follows. In SAPO-34, most of the silicon substitutes for phosphorus and the number of Brönsted acid sites is higher than that in SAPO-18. The higher the number of the acid sites, the higher the rate of coke formation, with consequent deactivation due to coke blocking the pores. The result that the selectivity to small olefins for SAPO-34 with Si/Al = 0.5 is lower than that for SAPO-34 with Si/Al = 0.15 and 0.3 confirms that proper acidity control inhibits the formation of coke and allows highly selective conversion of methanol to light olefins.

Effect of Cr Incorporation. Transition-metal-substituted aluminophosphates and silicoaluminophosphates have been tested for methanol catalytic conversion by several groups.[7-9] Nickel-containing SAPO-34 is one of the best catalysts for methanol-to-olefin conversion.[7,9] NiAPO-18, which has a similar framework structure, is one of the poorest catalysts for the MTO reaction.[8] ZnAPO-18, CoAPO-18, and MgAPO-18 are all very reactive at temperatures above 350 °C.[8] So, the role of the particular transition-metal ion is important in this reaction.

Earlier literature suggested that chromium is not incorporated into SAPO frameworks.[24] Through ESR and ESEM studies, we suggest that Cr is incorporated into SAPO frameworks and probably replaces phosphorus rather than aluminum.[10,13] Thermogravimetric analysis (TGA) data also support Cr(III) substitution for P(V) rather than for Al(III) in as-synthesized CrAPSO-11 because new, strong acid sites are indicated in CrAPSO-11 versus SAPO-11. Cr(III) substitution for Al(III) should not generate new acid sites because there is no charge change, whereas Cr(III) substitution for P(V) does generate new acid sites.[10] FTIR and acidity measurements indicate that CrAPSO-11 shows an increase in the number of the acid sites compared to those in SAPO-11 and ion-exchanged Cr−SAPO-11.[25]

Our results show that chromium substitution into the SAPO-11 framework greatly increases its selectivity toward ethene and propene as well as its lifetime. CrAPSO-11 shows ~20% higher selectivity than do (L)-Cr−SAPO-11 and SAPO-11. The difference in the selectivity toward ethene and propene between SAPO-11, CrAPSO-11 and ion-exchanged Cr−SAPO-11 cannot be attributed to structural modification due to the incorporation of chromium because the XRD patterns of these materials are almost identical. The acidity difference caused by chromium incorporation is a more likely cause.

Several authors investigated a correlation between Brönsted acidity and methanol conversion activity.[26,27] The catalytic activity and selectivity of SAPO-34 and Me-SAPO-34 (Me = Co, Ni) for the conversion of methanol to olefins has been investigated.[26] The catalytic performance for the conversion of methanol to olefins was found to be closely related to the number of strong acid sites present. Treatments such as steaming, silanization, and poisoning of strong sites by ammonia all reduced the number of strong acid sites and reduced catalytic performance. A recent study of MeAPO-5 (Me = Mn, Co, Ni, Mg, Zn, and Zr) for methanol conversion also supported a relationship between the number of Brönsted sites and catalytic activity.[27]

CrAPSO-11 has higher selectivity than SAPO-11 probably due to an increase of acid sites by the incorporation of Cr as shown by TGA data.[10] Similarly, CrAPSO-11 shows a higher skeletal isomerization efficiency than SAPO-11 and ion-exchanged Cr−SAPO-

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11.[25] The similarity of selectivity toward ethene and propene between SAPO-11 and (L)Cr−SAPO-11 may be explained by the Si-substitution mechanism in SAPO-11. In SAPO-11, two Si substitute for one Al and one P more than Si substitutes for P. The number of acid sites is small, and there is no large acidity difference between (L)Cr−SAPO-11 and SAPO-11.

CrAPSO-11 with Si/Cr = 5 shows ~10% higher selectivity to ethene and propene than that of CrAPSO-11 with Si/Cr = 10, especially the selectivity to ethene. This result is similar to that for NiAPSO-34.[28] With an increase of Ni incorporation, the selectivity toward ethene increases from 60% to 90%.

Liquid-phase ion-exchanged Cr−SAPO-34 catalyzes methanol only to dimethyl ether since the amount of hydrocarbons in the reaction products is negligible. This is similar to AlPO-18, which is not active since it has low acidity.[22] In liquid-phase ion-exchanged Cr−SAPO-34, protons have been replaced by Cr (III). Incorporating Cr into SAPO-34 via solid-state ion exchange has little effect on the overall selectivity toward ethene and propene.

It appears that incorporation of Cr into framework sites makes the catalyst more resistant to deactivation. An increase in the lifetime for CrAPSO-34 containing chromium in framework sites versus (S)Cr−SAPO-34 containing chromium in ion-exchange sites is most probably due to a different location of the active chromium(V) center. Cr(V) in solid-state ion-exchanged Cr−SAPO-34 is in a cation position and is easily reduced by methanol or olefin products to Cr(II). Cr(II) is very active for the polymerization of olefins. The olefin intermediate products form aromatics and coke to block pore openings, so Cr−SAPO-34 deactivates rapidly. However, framework Cr(V) in CrAPSO-34 is more resistant to reduction by methanol and olefins compared with (S)Cr−SAPO-34. Framework Cr(V) prevents polymerization of olefins in the product. So less coke is formed in CrAPSO-34 which also has a longer lifetime than solid-state ion-exchanged (S)Cr−SAPO-34.

Elemental analysis clearly shows that the Cr/(Cr + Si + Al + P) ratio is much smaller than the Si/(Cr + Si + Al + P) ratio in CrAPSO-34. In another words, the Cr effect on the catalytic performance is smaller compared to that of silicon. In CrAPSO-11, the amount of Cr incorporated into the framework is larger than in CrAPSO-34 and Cr has a larger effect on the catalytic performance. This probably explains why SAPO-34 and CrAPSO-34 have similar selectivity toward ethene and propene, whereas CrAPSO-11 shows higher selectivity toward ethene and propene.

Conclusions

The catalytic conversion from methanol to olefins has been studied for SAPO-11, SAPO-34, and SAPO-35 silicoaluminophosphate molecular sieves with and without chromium incorporation. The selectivity for methanol conversion to ethene and propene has been investigated as a function of structure type, silicon content, chromium location, and chromium concentration. Among protonated H−SAPO-*n* materials, SAPO-34 shows the highest selectivity for ethene and propene, whereas SAPO-11 shows the longest lifetime for catalytic activity. The variation of silicon content indicates that there is an optimum silicon content in SAPO-34 for the best catalytic activity. Incorporation of Cr into the framework of SAPO-*n* increases the lifetime and the selectivity toward ethene compared with Cr incorporation by ion exchange. This is interpreted as an acidity difference between synthesized CrAPSO-*n* and ion-exchanged Cr−SAPO-*n*. CrAPSO-11 also increases the lifetime, the distribution of ethene and propene and the selectivity toward ethene compared with SAPO-11. SAPO-34 and CrAPSO-34 with higher Si content than that of SAPO-11 show similar selectivity toward ethene and propene, but CrAPSO-34 has a longer lifetime. The chromium influence is smaller in CrAPSO-34 compared to CrAPSO-11. With an increase in Cr amount, CrAPSO-11 shows higher selectivity toward ethene and propene and has a longer lifetime.

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