

Performance of Aluminophosphate Molecular Sieve Catalysts for the Production of Hydrocarbons from Wood-Derived and Vegetable Oils

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A wood-derived oil and canola oil (termed bio-oils) were converted catalytically over aluminophosphate catalysts, namely, SAPO-5, SAPO-11 and MgAPO-36. The catalysts were prepared and then characterized using BET surface area, pore size, X-ray powder diffraction, ammonia temperature-programmed adsorption and desorption, and NMR measurements. The test runs were performed in a fixed bed microreactor which was operated at 3.6 weight hourly space velocity (WHSV) and temperature ranges of 330–410 °C for wood-derived oil (WDO) and 375–550 °C for canola oil. The objective was to investigate the potential for the production of both liquid and gaseous hydrocarbon products from the conversion of bio-oils using aluminophosphate catalysts. With WDO, between 12 and 23 wt % of an organic liquid product (OLP) was obtained which contained an optimum of 61.5, 56.8, and 57.0 wt % (for SAPO-5, SAPO-11, and MgAPO-36, respectively) liquid hydrocarbons. All three catalysts were selective for both aromatic and aliphatic hydrocarbons in comparable proportions. With canola oil, between 12 and 48 wt % OLP was obtained. The optimum yields of hydrocarbons were 65.8, 51.1, and 45.3 wt % of OLP for SAPO-5, SAPO-11, and MgAPO-36, respectively. SAPO-5 and SAPO-11 were highly selective for aromatic hydrocarbons. On the other hand, MgAPO-36 produced high fractions of aliphatic hydrocarbons at temperatures below 450 °C and high aromatic hydrocarbons at temperatures above 450 °C. Furthermore, 8–17 and 5–63 wt % gas was produced with WDO and canola oil, respectively. The gas composition consisted mostly of C₁–C₄ hydrocarbons. The results showed that the conversion of bio-oils to hydrocarbons with aluminophosphate catalyst was low as compared to HZSM-5 catalyst. However, some potential exists for the production of hydrocarbons such as benzene (with WDO) and toluene and xylenes (with canola oil) as well as important gaseous hydrocarbons such as ethylene, propylene, and *n*-butane.

Introduction

Currently, bio-oils are obtained from two main sources, namely, from the fast pyrolysis of wood and from vegetable sources such as canola, soybean, linseed, palm, flax plants, etc. These two oil types are entirely different in nature. Pyrolysis oils are generally corrosive, acidic, polar, thermally unstable, and highly oxygenated (40–50 wt %).^{1,2} They contain a wide range of oxygenated compounds which may include phenols, acids, esters of organic acids, ketones, ethers, alcohols, furans, and aldehydes. Also, they contain about 20–50 wt % water. On the other hand, vegetable oils are almost pH-neutral, contain no water, and are relatively stable. They consist mainly of triglyceride molecules. The process to convert these oils to liquid and gaseous products which contain high hydrocarbon contents have been the focus of a number of research activities.^{1–5} Under certain processing conditions, these oils may have a strong potential for the production of liquid fuels such as high octane gasoline, or liquid products with high

cetane numbers. In addition, the gas fraction is rich in various hydrocarbons such as ethylene, propylene, and *n*-butane.³

In the literature, the conversion of bio-oils to hydrocarbons has been attempted with typical hydrotreating catalysts such as Co–Mo/Al₂O₃,^{1,4} zeolite catalysts such as HZSM-5,^{3,6} and activated alumina.⁵ The hydrotreatment of bio-oils takes place at high pressures and requires hydrogen, whereas conversion with ZSM-5 zeolite catalyst is at atmospheric pressure. Also, as a result of strong acid properties and medium size pore structure (which restrict the formation of large branched molecules), upgrading with HZSM-5 produces less coke compared to hydrotreating catalysts. Consequently, in recent work,^{7,8} we have investigated the conversion of bio-oils over a number of molecular sieve catalysts and amorphous silica–alumina catalyst. Our recent work,⁷ on the upgrading of a wood-derived oil (WDO) over

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various catalysts, namely, H-Y, H-mordenite, silicalite, and silica-alumina, has shown that by changing the catalyst type or its functionality (such as its acidity or pore size) the product distribution as well as the composition of the desired liquid and gaseous products could be changed. For instance, HZSM-5 gave a maximum organic liquid product (OLP) yield of 33.6 wt % of WDO. This OLP fraction contained 79.5 wt % aromatic hydrocarbons and 3.5 wt % aliphatic hydrocarbons. On the other hand, silica-alumina gave an optimum of 25.2 wt % OLP. This OLP fraction contained 47.6 wt % aliphatic hydrocarbons and only 4.8 wt % aromatic hydrocarbons.

Recently, a large family of novel aluminophosphate molecular sieve catalysts has been reported in the literature. Aluminophosphate molecular sieves were first reported by Union Carbide Corp.⁹ These catalysts not only exhibit properties of zeolites but also show unusual physicochemical properties ascribed to their unique chemical composition. The application of these molecular sieve catalysts in processes such as cracking of isooctane, crude oil upgrading, and isomerization of xylene and hexane as well as deoxygenation⁹⁻¹⁴ have shown their potential to be useful and scientifically challenging as their aluminosilicate zeolite counterparts.

Thus, in this work, the conversion of a wood-derived bio-oil (WDO) and canola oil were studied over SAPO-5, SAPO-11, and MgAPO-36 catalysts. These catalysts were selected on the basis of their pore size and acidity. The results were compared with the conversion of these oils over HZSM-5 and silica-alumina catalysts. In addition, the catalysts were thoroughly characterized and their performance evaluated.

Experimental Section

Feed Materials. The wood-derived bio-oil (obtained from maple wood) used in the present study was obtained from ENSYN Technologies Inc., Gloucester, Ontario, Canada, where it was produced by the rapid thermal pyrolysis process.¹⁵ The yield of the bio-oil was 74 wt % and it contained 21 wt % water (Karl Fischer titration). It consisted of 49.8 wt % carbon, 7.5 wt % hydrogen, and no nitrogen (CHN elemental analysis). The balance of 42.7 wt % was oxygen. In order to determine the composition of the WDO, it was distilled at 200 °C and under a vacuum of 172 Pa. About 42.4 wt % volatile fraction (organic liquid product (OLP)) and 36.6 wt % residue were obtained. The OLP consisted mainly of acid and esters, alcohols, aldehydes, ketones, phenols, and small quantities of ethers, furans, amines, aliphatic and aromatic hydrocarbons. The detailed chemical composition is given in Table 1.

The canola oil used in this work was obtained from CSP Foods, Saskatoon, Canada. It was of degummed and refined variety. The oil was composed of predominantly triglycerides¹⁶

Table 1. Composition of Wood-Derived Oil Determined by Distillation at 200 °C and 172 Pa-s

fraction	wood oil (wt %)
distillate	
organic liquid	42.4
water	21.0
nonvolatiles	36.7
Composition of Organic Liquid, (wt %)	
acids and esters	10.4
alcohols	5.3
aldehydes	10.9
aliphatic hydrocarbons	0.4
amines	0.5
aromatic hydrocarbons	5.6
ethers	2.2
furans	2.5
ketones	36.6
phenols	10.9
unidentified fraction ^a	14.7

^a Determined by difference.

(esters of 1,2,3-propanetriol) in which the carboxylic acid contributions were 60 wt % oleic acid, 20 wt % linoleic acid, 10 wt % linolenic acid, 2 wt % stearic acid, 4 wt % palmitic acid, and small amounts of eicosenic and erucic acids (approximately 4 wt %).

Catalyst Selection and Preparation. The three catalyst were selected in order to take advantage of the differences in pore size and acidity. The objective was to study the effect of these catalyst properties on the product yield and selectivities. In terms of pore size, SAPO-5 and MgAPO-36 contain large pores (0.8 and 0.75 nm, respectively) and SAPO-11 contains medium pores (0.56 nm). In addition, SAPO-5 and SAPO-11 had relatively high acidity compared to other aluminophosphate-based molecular sieves. SAPO-5 has performed favorably as an additive to FCC catalysts.¹⁷ Also, medium-pore SAPOs have proven to be active and selective for isomerization and C₈ aromatic reactions.¹⁴ On the contrary, pure aluminophosphate (ALPO's) catalysts are primarily nonacidic in nature. Hence their direct use as cracking catalysts is limited. However, incorporation of metals into ALPO's is known to increase their acidity as well as enhance their resistance to coke formation.¹⁷ The acidity in decreasing order is known to be as follows: Mg > Co > Zn > Si > Mn > Be > Fe.^{9,18} Thus, MgALPO was selected for the present work.

SAPO-5 and SAPO-11 catalysts were synthesized according to the method described by Lok et al.¹⁹

SAPO-5 catalyst was prepared as follows. About 23.06 g of 85 wt % orthophosphoric acid was added to 82.47 g of water to form solution A. To solution A, small amounts of 13.81 g of hydrated aluminum oxide (74.2 wt % Al₂O₃, 25.8 wt % H₂O) were added with stirring until the mixture (mixture A) was homogeneous. To mixture A was added a dispersion of 2.59 g of fumed silica (92.8 wt % SiO₂, 7.2 wt % H₂O) and 29.41 g of tri-*n*-propylamine and stirred to obtain a homogeneous mixture (mixture B). The reaction mixture was sealed in a stainless steel pressure vessel lined with Teflon and heated in an oven at 200 °C for 24 h. The solid reaction product was recovered by centrifuging, washed with water, and dried at room temperature. Later, it was calcined at 550 °C for 6 h.

SAPO-11 was prepared as follows. First, a solution A was prepared by combining 23.06 g of 85 wt % orthophosphoric acid and 23.06 g of water. Later, 13.81 g of hydrated aluminum oxide (a pseudo-boehmite phase, 74.2 wt % Al₂O₃, 25.8 wt % H₂O) was added to solution A in small amounts with continuous stirring until homogeneity was obtained (mixture

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A). To mixture A was added a mixture containing 3.9 g of fumed silica (92.8 wt % SiO_2 , 7.2 wt % H_2O) in 103.5 g of solution of 25 wt % tetra-*n*-butylammonium hydroxide in methanol. The resulting product was termed mixture B. Later, 20.41 g of di-*n*-propylamine was added to mixture B with stirring till a homogeneous mixture was obtained (mixture C). The final reaction mixture (mixture C) was placed in a stainless steel pressure vessel lined with Teflon and heated in an oven at 200 °C for 48 h. The solid reaction product was recovered by centrifuging, washed with water and dried in air at room temperature. Later, it was calcined at 550 °C for 6 h.

MgAPO-36 catalyst was synthesized according to the procedure outlined by Wilson et al.²⁰ In a typical method, first, a reaction mixture (mixture A) was prepared by combining 53.4 g of 85 wt % orthophosphoric acid and 66.3 g of a hydrated aluminum oxide (74.2 wt % Al_2O_3 , 25.8 wt % H_2O). To mixture A was added a solution prepared by dissolving 21.4 g of magnesium acetate tetrahydrate in 45.2 g of water (mixture B). To the resulting mixture (mixture B), 28.7 g of tripropylamine was added and stirred until homogeneous (mixture C). The reaction mixture (mixture C) was sealed in a stainless steel pressure vessel and heated at 200 °C for 48 h. The solid product was recovered by filtration, washed with water, and dried in air at room temperature. It was later calcined at 550 °C for 6 h.

Catalyst Characterization. The catalysts were characterized by the following techniques: X-ray powder diffraction (XRD), temperature-programmed adsorption and desorption (TPD) with ammonia, and measurement of their BET surface area and pore sizes. Elemental compositions as well as the solid state MAS NMR spectra were also determined.

The BET surface area and pore sizes were measured with Micromeritics ASAP 2000.

The XRD patterns were obtained using a Phillips X-ray diffractometer with a Fe K α radiation source and operated at 40 kV and 40 mA. The spectra was scanned from 6° to 70° at a rate of 2°/min.

Ammonia TPD was carried out as follows: First, anhydrous NH_3 (99.99% minimum purity, Matheson) was passed for 30 min over 400 mg of catalyst at 120 °C. After adsorption, the sample was purged with nitrogen for 1 h at 120 °C. TPD data were collected from 25 to 650 °C and at heating rate of 8 °C/min.

For NMR measurements, AM 360WB Bruker spectrometer equipped with a CP/MAS probe and magic angle spinning of 4 kHz was used. Phosphorus, aluminum, and silicon were scanned at 145.80, 93.84, and 71.55 MHz, respectively. The operating conditions were as follows: contact time of 1.5 ms, delay of 1 s, line broadening of 80 Hz, 90° pulse of 6.5 ms, temperature of 297 K, number of scans of 24 800 for silicon, 650 for aluminum, and 1200 for phosphorus.

Equipment Setup and Procedure. Catalytic runs were carried out in a fixed bed microreactor made of stainless steel (No. 316 SS) tubing, 380 mm long and 12.5 mm i.d. It was operated at atmospheric pressure, over a temperature range 330–550 °C and at 3.6 WHSV. Details of the reactor setup and run procedure are given elsewhere.²¹

A typical run was carried out as follows: The reactor was first loaded with 2 g catalyst (particle size range 500–1410 μm) and brought to the reaction temperature in a stream of argon flowing at 2 L/h. When the desired temperature was attained, the argon flow was stopped and the bio-oil was fed to the reactor by a micrometering pump (Eldex, Model A-60-S). The products at the end of each run included a liquid product, gas, coke (and char when WDO was used).

The reaction products leaving the reactor were separated into liquid (by trap cooling with a condenser setup) and gas products. The condenser setup consisted of two parts. The

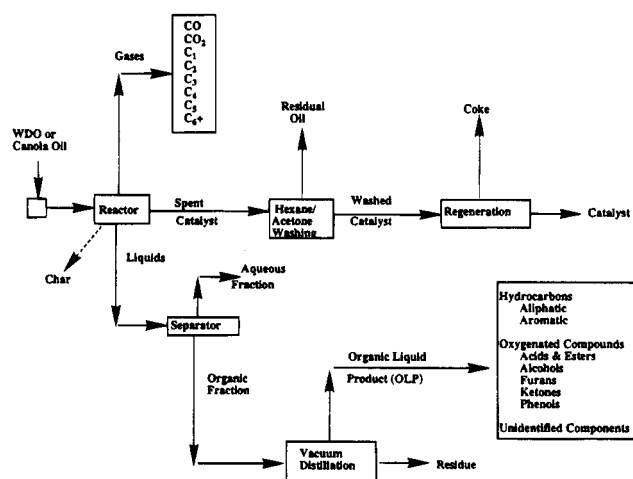


Figure 1. Scheme of upgrading, product collection, and analysis.

first condenser used cooling water (as coolant) flowing at about 4 °C and the second condenser used dry ice as coolant. The liquid product was distilled at 200 °C and a vacuum of 172 Pa using a Buchi GKR-56 distillation unit. These conditions were determined earlier²² and provided the optimum yield of organic distillate. Vacuum distillation of the liquid products yielded two fractions: a volatile and nonvolatile fraction which were identified as the “organic liquid product (OLP)” and “residue”, respectively.

The gas product was collected over brine solution. After each run (in the case of WDO feed), the char particles were removed from the reactor. Also, the spent catalyst was later removed from the reactor and washed with acetone (i.e., when WDO was used as feed). Similarly, the inside surface of the reactor was washed with acetone. The acetone-soluble portion was designated as “tar”. In the case of canola oil, the spent catalyst and the inside of the reactor were washed with hexane. The hexane-soluble portion was termed “residual oil” (or “unconverted oil”). The washed catalyst was then dried at 100 °C for 1 h followed by heating in an air flow for about 2 h at 550 °C to regenerate it. The difference in weight before and after regeneration of the washed catalyst was termed “coke”.

The entire upgrading, product collection, and analytical scheme is shown in Figure 1.

Analysis of Products. The gaseous product was analyzed by a GC (Carle CGC, Model 500) which was equipped with a combination of packed and capillary columns and flame ionization (FID) and thermal conductivity detectors (TCD). After normalization of the components, the molecular weight of the gas was determined from the average molecular weight and the total volume of the gas which evolved during the run. The OLP was analyzed by GC using a 30 m long capillary column and FID. The identity of the peaks was confirmed by GC/MS analysis and by the use of pure compounds. Details on the analysis of products are given elsewhere.²²

Results and Discussion

In this section, first the properties of the three catalysts are described based on the characterization studies. Second, the conversion characteristics of WDO and canola oil over these catalysts are presented. The results are compared with similar conversion studies over HZSM-5 and silica–alumina catalysts.^{8,22} Finally, based on the product distributions, reaction pathways are proposed for the conversion of these oils to liquid and gaseous hydrocarbons. In addition, an attempt is

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Table 2. Important Properties of Various Aluminophosphate Catalysts

catalyst	pore size, nm	BET surface area, m ² /g	acid area, ^a cm ² /g	acid density, ^b cm ² /m ²
SAPO-5	0.80	330	125.5	0.38
SAPO-11	0.56	205	76.0	0.31
MgAPO-36	0.75	196	15.5	0.07
HZSM-5	0.54	329	224.9	0.69

^a Total area under TPD curves. ^b Total acid area/BET surface area.

made to relate the catalyst characteristics with the yield and distribution of the products.

Catalyst Characterization. The surface area, pore sizes, acid density, acid area, and compositions of the final reaction mixture for the three catalysts are given in Table 2. SAPO-5 provided the largest catalyst surface area of 330 m²/g followed by SAPO-11 and MgAPO-36. The advantages of having a large surface area and high acid density for reaction are well established in the literature.^{18,23} SAPO-5 (pore size 0.8 nm) and MgAPO-36 (pore size 0.75 nm) fall within the large pore size category of molecular sieves, and SAPO-11 (0.56 nm) falls within the medium pore size range. Consequently, SAPO-5 would admit larger molecules than MgAPO-36 and SAPO-11.^{18,23}

The X-ray powder diffraction pattern of these catalysts in the range $2\theta = 6-50^\circ$ range are shown in Figure 2. The corresponding d values match very well with those reported in the literature^{20,24,25} thus confirming the identity of the catalysts as such. The spectra show sharp and distinct peaks on the baseline which indicate that the catalysts are all crystalline in nature.²¹

The TPD spectra of the three catalysts are shown in Figure 3. SAPO-5 and SAPO-11 exhibited three peaks and MgAPO-36, two peaks. SAPO-5 gave two distinctly different states of chemisorbed ammonia at temperature maxima (T_{\max}) of 159 and 369 °C and a third one at 584 °C. The T_{\max} for SAPO-11 was at 132, 240, and 455 °C and for MgAPO-36 at 111 and 365 °C. The acidic sites characterized by low-temperature peaks correspond to weak acid sites whereas those characterized by high-temperature peaks correspond to strong structural Bronsted and/or Lewis acid sites.¹¹ It is interesting to note that the area under T_{\max} decreased significantly from SAPO-5 to MgAPO-36 catalysts. The T_{\max} values for these catalysts occur at different temperatures. For instance, the first peak occurs at 159, 132, and 111 °C for SAPO-5, SAPO-11, and MgAPO-36 catalysts, respectively, indicating that SAPO-5 has higher acid site strength compared to other two catalysts. Among these catalysts, only SAPO-5 gave a desorbed ammonia peak at 584 °C. This peak corresponds to a strong acid. The amount of a gaseous base such as ammonia, pyridine, or quinoline adsorbed under a set of conditions is usually used as a measure of acid strength.²³ Most often, it is presented as the acid density. Thus, based on the acid density the acid strength for the three catalysts decreased in the order SAPO-5 > SAPO-11 > MgAPO-36.

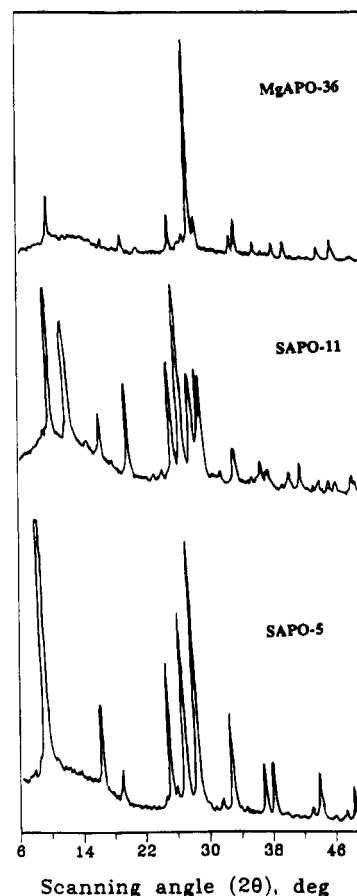
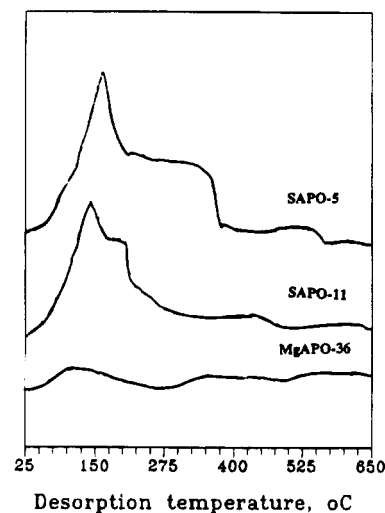
**Figure 2.** X-ray powder diffraction patterns of SAPO-5, SAPO-11, and MgAPO-36 catalysts.**Figure 3.** Temperature-programmed desorption diagrams for SAPO-5, SAPO-11, and MgAPO-36 catalysts.

Table 2 shows that as the catalyst BET surface area increases, the acid area (as well as acid density) also increases. Thus, it appears that a direct correlation may exist between acid area and surface area of the catalyst. A detailed discussion on the correlation between the acid areas and product yields will be discussed later.

The ²⁷Al and ³¹P NMR spectra of the three catalysts are shown in Figures 4 and 5, respectively. Solid state NMR is particularly important for providing information on the bonding of atoms as well as the position of acid sites in the aluminophosphate structure.²³ The spectra patterns for both ²⁷Al and ³¹P NMR in terms of peak

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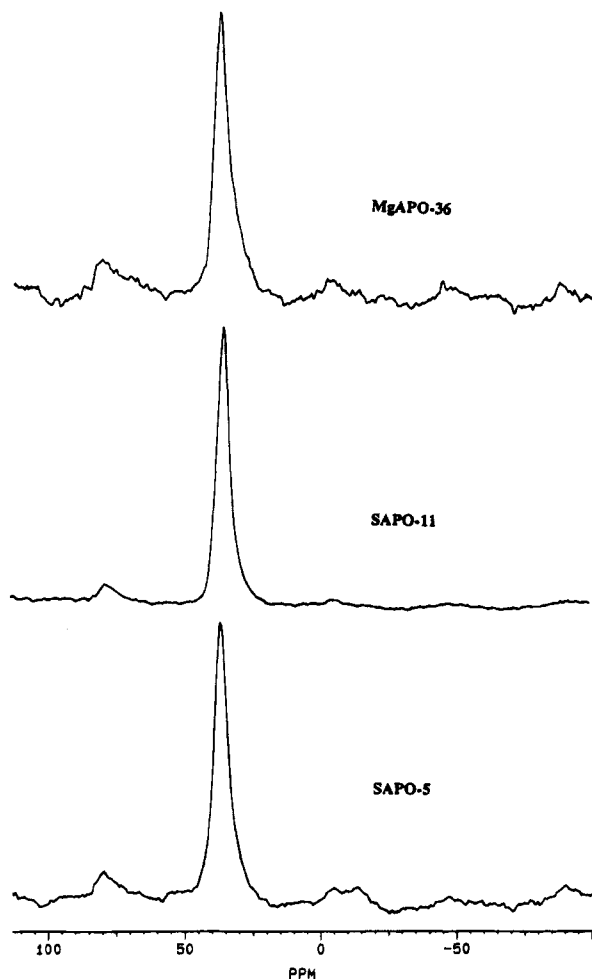


Figure 4. ^{27}Al NMR spectra of SAPO-5, SAPO-11, and MgAPO-36.

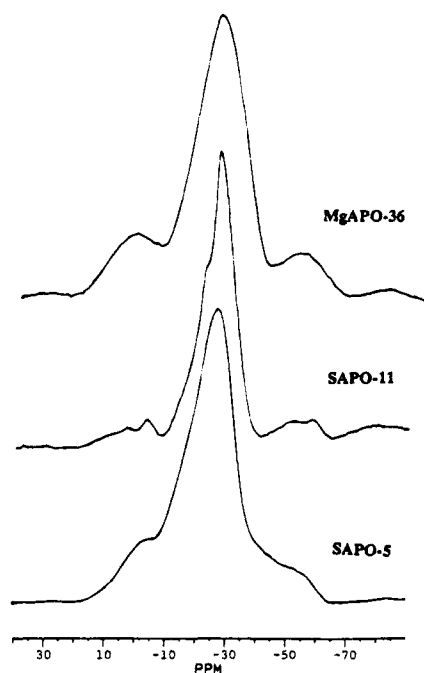


Figure 5. ^{31}P NMR spectra of SAPO-5, SAPO-11, and MgAPO-36.

shape and position are quite comparable with those reported in the literature.^{26,27} The major peaks obtained for ^{27}Al NMR (Figure 4) were at 36.69, 35.41, and 37.93 ppm for SAPO-5, SAPO-11, and MgAPO-36, respec-

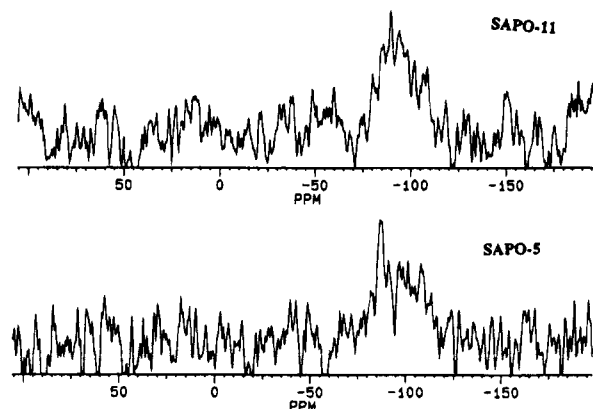


Figure 6. ^{29}Si NMR spectra of SAPO-5 and SAPO-11.

tively. These peaks are attributed to Al (4P) configuration.²⁶ The ^{27}Al spectra of our MgAPO-36 catalyst were similar to those reported in earlier works.^{24,28} For all the three catalysts, the Al atoms exist in tetrahedral environment. The shoulder peak at -25.64 and 33 ppm for SAPO-5 and SAPO-11 catalysts corresponds to the Al atom in framework positions. These Al atoms interact with adsorbed water. Consequently, they have coordination numbers higher than 4. A similar observation also was made in the case of VPI-5 catalyst.²⁹ Thus, it would appear that Al atoms in these different structures would behave differently compared to the situation where these atoms did not interact with water.

The ^{31}P NMR spectra of the three catalysts (Figure 5) show a major peak at -28.09 ppm which is attributed to P(4Al) configuration.²⁴ The shoulder peaks at lower ppm level is generally assigned to P atom associated with P-OH defective groups.^{24,28,30} The ^{27}Al and ^{31}P spectra compare well with similar ALPO_4 samples reported in the literature,²⁵ indicating tetrahedral coordination of Al and P in all the three samples. Additionally, it gives an indication that incorporating Si into the AlPO_4 structure does not affect the ^{27}Al and ^{31}P NMR spectra appreciably. Based on these results it appears that all the three catalysts do not contain any amorphous Al species.

The ^{29}Si NMR spectra for SAPO-5 and SAPO-11 catalysts are shown in Figure 6. They show the relative peak positions of various Si ($n\text{Al}$), (where n can be varied from 0 to 4 and is related to the number of Al atoms linked to a given Si atom). The spectra was more noisy compared to ^{27}Al and ^{31}P NMR spectra of Figures 4 and 5 which is typical of Si spectra.²⁷ The major peaks obtained for SAPO-5 and SAPO-11 were at -87.18 and -90.14 ppm, respectively, with broader peaks above -100 ppm and up to -120 ppm. Low peaks are observed at -90.14 and -108 ppm indicating that more than one type of silicon is present in SAPO-5 and SAPO-11 catalysts. Similar observations have been reported by earlier workers.^{26,30,31} Martens et al.¹¹ also studied

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the effect of Si substitution with ^{29}Si NMR spectroscopy for SAPO-5, -11, and -37 catalysts. They concluded from their study that silicon in SAPO-*n* materials appears from -89.4 to -106.7 ppm and involved seven peaks in this region. These peaks correspond to silicon in aluminosilicate framework in which different silicon atoms are associated with different types of Al and Si atoms. For instance, peaks at -86.4 , -93.4 , -98.2 , -102.3 , and -106.7 ppm correspond to the position of silicon in the aluminosilicate framework in which silicon atoms are in Si(4Al), Si(3Al.Si), Si(2Al₂Si), Si(Al₃Si), and Si(4Si) environment, respectively, as observed by Blackwell et al.²⁶ The peak at -112.8 ppm has been assigned to silicon in amorphous silica.¹¹ It is known that silicon atoms in amorphous silica or in 4Si environment do not contribute to the generation of Bronsted acid sites in the silicoaluminophosphate catalysts.²⁷ It thus appears that less than 100% of the silicon (only those present in crystalline framework environment) in the catalysts contributed to the generation of Bronsted and Lewis acid sites in these catalysts. Consequently, this leads to low acidity in comparison to HZSM-5.

The NMR characterization discussed above shows that the generation of acid sites in these catalysts are based on the interaction of Si and Al atoms and its framework. However, it would appear that not all the silicon atoms are involved in generating acid sites. In addition, the distribution of these sites varies with the catalyst. From TPD of ammonia studies also, it was shown that differences existed in the acid site distribution and strength of these catalysts. These differences in the catalyst characteristics imply that their effect on conversion as well as selectivity for various products during upgrading will also be different. Attempts are made in this work to correlate the acid site density of the catalysts with their product yields.

Catalytic Conversion of Wood-Derived Oil (WDO) and Canola Oil

The definitions of the terms conversion, yield, and selectivity as used in this work are given in the Appendix. In all the runs, the overall mass balances were better than 96%. In order to check for reproducibility, a number of runs were repeated. The experimental error was found to be less than $\pm 4\%$. These errors were calculated from deviations of the results from mean values of the repeated experiments. The largest error occurred in the measurement of the total liquid yields (about 3%). This error was mostly due to the process of transferring liquid products from the condenser to distillation vials and the distillation process itself.

Conversion of Wood-Derived Oil

The overall material balances for the conversion runs are given in Tables 3–5. The detailed liquid product compositions are also included in these tables. Among the three catalysts, SAPO-5 gave the highest yield of OLP followed by SAPO-11 and MgAPO-36 in that order. It can be seen by comparison that as the BET surface area and catalyst acidity decreased, the OLP yields also decreased. Thus, it would appear that both these catalyst characteristics (i.e., BET surface as well as the catalyst acidity) had a significant influence on the yield of the OLP.

Table 3. Overall Material Balances (wt % of WDO) and Composition of Organic Liquid Product from the Conversion of WDO over SAPO-5 Catalysts

product	SAPO-5		
	330 °C	370 °C	410 °C
coke	10.0	13.3	16.2
char	25.0	16.7	12.8
gas	8.0	10.3	14.0
organic liquid product (OLP)	20.8	22.2	19.5
tar	12.5	9.5	7.0
aqueous fraction	22.2	24.2	26.1
unaccounted fraction	1.5	3.8	4.4
Composition (wt % of OLP) of Organic Liquid Product			
aliphatic hydrocarbons	20.4	23.5	26.1
aromatic hydrocarbons			
benzene	28.3	27.5	34.7
toluene	0.3		
xylenes	2.7	1.6	0.7
C ₉ ⁺	6.3	2.9	
Σ aromatic hydrocarbons	37.7	32.0	35.4
oxygenated compounds			
acids and esters			1.2
alcohols	8.9	7.1	10.7
furans	4.1	5.3	5.1
ketones	2.2	7.3	6.2
phenols	2.7	3.5	1.0
Σ oxygenated compounds	17.9	23.2	24.2
unidentified compounds	24.0	21.3	14.3

Table 4. Overall Material Balances (wt % of WDO Fed) and Composition of Organic Liquid Product from the Conversion of WDO over SAPO-11 Catalysts

product	SAPO-11		
	330 °C	370 °C	410 °C
coke	4.1	7.5	13.0
char	23.6	18.0	15.0
gas	7.6	12.2	16.7
organic liquid product (OLP)	18.1	19.9	17.5
tar	18.2	11.9	5.2
aqueous fraction	24.1	26.3	29.5
unaccounted fraction	4.3	4.2	3.1
Composition (wt % of OLP) of Organic Liquid Product			
aliphatic hydrocarbons	18.9	24.4	21.3
aromatic hydrocarbons			
benzene	30.5	29.1	27.0
toluene			
xylenes		1.7	2.1
C ₉ ⁺	1.7	1.6	1.3
Σ aromatic hydrocarbons	32.2	32.4	30.4
oxygenated compounds			
acids and esters	2.3		
alcohols	15.0	12.8	15.0
furans	3.7	4.2	3.5
ketones	8.0	8.7	9.9
phenols	1.9	1.9	3.0
Σ oxygenated compounds	30.9	27.6	31.4
unidentified compounds	18.0	15.6	16.9

For all the catalysts, conversion of WDO to OLP increased with temperature reaching maximum values at 370 °C. These values were 22.2, 19.9, and 16.3 wt % for SAPO-5, SAPO-11, and MgAPO-36, respectively. Thereafter, the yields decreased with increase in temperature. The decrease in the yield of OLP at high temperatures was due to the conversion of WDO to gaseous products and coke. A similar observation was made during the upgrading of the same oil with HZSM-5 catalyst.²²

Composition of Organic Liquid Product (OLP). The OLP (Tables 3–5) consisted of aliphatic hydrocarbons, aromatic hydrocarbons, and oxygenated compounds. The oxygenated compounds mostly consisted of acids and esters, alcohols, furans, ketones, and phenols.

Table 5. Overall Material Balances (wt % of WDO Fed) and Composition of Organic Liquid Product from the Conversion of WDO over MgAPO-36 Catalysts

product	MgAPO-36		
	330 °C	370 °C	410 °C
coke	13.4	17.3	21.5
char	28.3	21.4	15.6
gas	5.5	10.1	15.2
organic liquid product (OLP)	14.9	16.3	12.5
tar	14.5	10.1	5.1
aqueous fraction	21.5	23.1	26.9
unaccounted fraction	1.9	1.7	3.2
Composition (wt % of OLP) of Organic Liquid Product			
aliphatic hydrocarbons	34.5	26.7	21.6
aromatic hydrocarbons			
benzene	21.2	23.4	27.8
toluene			
xylenes	0.5	0.7	0.9
C ₉ ⁺	0.8	0.8	0.9
Σ aromatic hydrocarbons	22.5	24.9	29.6
oxygenated compounds			
acids and esters	0.5		
alcohols	12.3	10.5	9.5
furans	5.2	5.0	4.4
ketones	9.9	8.7	7.3
phenols	2.0	2.2	2.2
Σ oxygenated compounds	29.9	26.4	23.4
unidentified compounds	13.1	22.0	25.4

The concentration of aromatic hydrocarbons varied with catalyst type and ranged between 22.5 and 37.7 wt % of OLP. SAPO-5 gave the highest yield of aromatic hydrocarbons with a maximum value of 37.7 wt % at 330 °C, and MgAPO-36 gave the lowest yield with a maximum value of 29.6 wt % at 410 °C. It is interesting to note that the effect of temperature on the three catalysts was significantly different. With SAPO-5, a minimum of 32.0 wt % aromatic hydrocarbons was obtained at 370 °C, whereas with SAPO-11 a slight decrease at high temperature (410 °C) was observed. With MgAPO-36, the yield of aromatic hydrocarbons increased progressively with temperature. These observations indicate that a complex combination of catalyst acidity, catalyst pore size, and temperature influence the formation of aromatic hydrocarbons.

It was interesting to observe that benzene was the single most abundant aromatic hydrocarbon produced (in most cases, over 90%) in the aromatic hydrocarbon fraction. Toluene and xylenes were obtained in relatively small amounts. This observation is in complete contrast to the results obtained from the conversion of the same oil over HZSM-5 catalyst.²² With HZSM-5, the selectivity for toluene and xylenes was high. The high yields of benzene with the aluminophosphate catalysts are probably due to a low rate of alkylation reaction which is the consequence of their lower acidity compared to the HZSM-5 catalyst.³² From Table 2, it is seen that the acid site density for HZSM-5 was high in comparison with all three aluminophosphate catalysts. The higher acid density may have resulted in higher rates of alkylation reactions leading to higher selectivities for C₇ and C₈ than C₆ aromatic hydrocarbons with HZSM-5 catalyst. Milne et al.³³ also state that the amount of benzene relative to that of xylene is an indication of the degree of methylation (or alkyla-

tion). The lower the ratio of benzene to xylene, the higher the extent of alkylation reactions.

The yield of aliphatic hydrocarbons in the OLP ranged between 20.4 and 34.5 wt % for the three catalysts. It was made up mostly of C₆–C₈ aliphatic hydrocarbons. Among the three catalysts, MgAPO-36 gave the highest aliphatic yield of 34.5 wt % at 330 °C. Among the aliphatics, the major compounds were *n*-hexane, heptane, and 2,2,4-trimethylpentane (isooctane, a fuel standard with an octane number of 100). Temperature had a significant effect on the production of aliphatic hydrocarbons. For instance, there was an increase in the concentration of aliphatic hydrocarbons for SAPO-5 and a decrease for MgAPO-36 catalyst. On the other hand, with SAPO-11 catalyst aliphatic hydrocarbon yield increased with temperature up to 450 °C and then decreased. These results are in contrast to those obtained with HZSM-5 catalyst in which low yields of aliphatic hydrocarbons were observed. Again, these higher yields of aliphatic hydrocarbons with aluminophosphate catalysts can be attributed to the lower acid strength possessed by these catalysts compared to HZSM-5 catalyst (Table 2).

In most cases, the results show that the aromatic hydrocarbon content of OLP increased with an increase in the acid density of catalyst. Consequently, SAPO-5 with its higher acid density gave high yields of aromatic hydrocarbons compared to MgAPO-36 which was low in acidity and strength. These observations are in agreement with the those reported in the literature.³⁴

These observations indicate that the reaction temperatures needed for optimum yields of aromatic hydrocarbons were 330 °C for SAPO-5, 370 °C for SAPO-11, and 410 °C for MgAPO-36 catalyst. The relative performance based on the optimum yields for aromatics hydrocarbons was of the order: SAPO-5 > SAPO-11 > MgAPO-36. Similarly, the optimum aliphatic hydrocarbon yields were obtained at the following reaction temperatures: 410 °C for SAPO-5, 370 °C for SAPO-11, and 330 °C for MgAPO-36 catalyst and the catalysts performance followed the order: MgAPO-36 > SAPO-5 > SAPO-11.

The amount of oxygenated compounds was also significant in the OLP fractions, thus indicating that further deoxygenation may be required in order to optimize the yield of both gaseous and liquid hydrocarbons. The maximum concentration of oxygenates for SAPO-5, SAPO-11, and MgAPO-36 were 24.2, 31.4, and 29.9 wt %, respectively. Among these oxygenated compounds, methanol and acetone were the main components. In comparison, the yields of oxygenated compounds with HZSM-5 catalyst were low. This result reemphasizes the role of catalyst acidity in the conversion of WDO. Since the rate of deoxygenation is a function of acid strength, it appears that the low extent of deoxygenation with aluminophosphate catalyst is a direct consequence of low acidity. For instance, in our earlier work³⁵ on the conversion of canola oil with a variety of catalysts, it was observed that catalysts with

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Table 6. Composition (wt % of Gas Product) of Gas Products Obtained with Aluminophosphate Catalysts and WDO

product	SAPO-5			SAPO-11			MgAPO-36		
	330 °C	370 °C	410 °C	330 °C	370 °C	410 °C	330 °C	370 °C	410 °C
methane	2.5	7.8	8.0	8.1	3.7	9.4	2.2	3.4	4.1
ethylene	18.5	24.2	30.6	5.9	4.8	10.1	2.1	3.6	4.1
ethane	0.7	2.0	2.0	2.0	0.9	3.0	3.2	2.5	1.5
propylene	12.0	14.7	19.4	15.5	21.5	39.9	4.2	5.4	7.7
propane	6.6	8.5	13.0	0.8	0.3	1.3	10.4	8.3	5.4
<i>n</i> -butane	20.1	8.8	9.9	7.8	7.8	10.2	6.9	5.8	3.1
isobutane	3.1	2.8	4.4		0.1	4.6	18.4	15.5	16.2
isobutylene	3.0	3.0	2.4	4.1	6.0	2.6	2.1	2.9	4.4
1-butene	1.0	0.7	0.5	0.6	2.9	4.2			
remainder of C ₄							15.5	18.6	25.1
C ₅	8.1	7.4	3.5	15.1	10.4	3.9	19.5	17.5	11.8
C ₆	6.8	2.1	1.1	8.3	6.9	1.3	10.5	9.4	4.9
CO ₂	13.6	12.5	10.5	10.0	13.2	6.5	2.6	4.7	7.5
CO	0.2	0.4	1.5	2.0	2.2	3.0	2.4	2.4	4.2
total	100	100	100	100	100	100	100	100	100
C ₂ –C ₄ olefin/ paraffin ratio	1.2	1.6	1.5	2.5	4.3	2.0	0.6	0.9	1.4

relatively low acidity such as aluminum-pillared clay and silica–alumina produced high amounts of oxygenated compounds in their OLP fractions compared with catalysts such as HZSM-5 and H-Y.

Gas Yield and Composition. As expected, the amount of gas product increased monotonically with temperature (Tables 3–5). For instance, the gas yield for SAPO-5 catalyst was 8 wt % at 330 °C and increased to 14 wt % at 410 °C. Similar increases in the gas yields with temperature were obtained for SAPO-11 and MgAPO-36 catalysts. These observations suggest that gas was one of the ultimate products of the cracking of WDO.

The composition of the gas products is given in Table 6 for all the three catalysts. It consisted of C₁–C₆ hydrocarbons, CO and CO₂. The high concentration of CO₂ indicates that a significant fraction of oxygen in WDO was rejected as CO₂. The method of oxygen removal was important for obtaining high hydrocarbon yields since the hydrogen content of the bio-oil was low. Thus, rejection of oxygen as CO₂ was favorable for hydrocarbon formation compared to oxygen rejection as H₂O.

The major hydrocarbons present in the gas fraction were ethylene, propylene, butane, and C₄ olefins. Of particular interest was the olefinic content of the gas phase. Plots (Figure 7) of olefin/paraffin ratio show a number of interesting observations. With SAPO-5 and SAPO-11, the hydrocarbon gas fraction was highly olefinic in nature. On the other hand, with MgAPO-36, the olefinic fraction was low especially at 330 and 370 °C. These observations imply that where high fractions of olefins (mostly ethylene and propylene) in the gas product are desired SAPO-5 or SAPO-11 should be used. Ethylene and propylene are well-known as the primary building blocks for the production of various plastics. Chang et al.³⁶ also observed that olefin formation was favored at low partial pressures of the feed, since they were the primary products of deoxygenation and cracking of O-containing compounds. Thus, the high olefin/paraffin ratios in this study may be due to the high water content (21 wt %) of the bio-oil which produces a low partial pressure of the organic components of the feed and as such high primary cracking and limited secondary cracking.

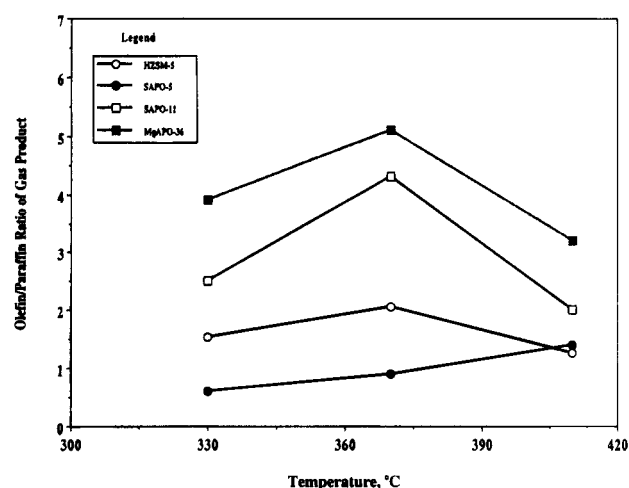


Figure 7. Comparison of the C₂–C₄ olefin to paraffin ratio of gas product for the conversion of WDO with aluminophosphate and HZSM-5 catalysts.

It is worth noting that various unsaturated C₅ and C₆ compounds were produced (Table 6). Of the three catalysts, MgAPO-36 gave high yields (maximum of 19.5 wt % of C₅ and 10.5 wt % of C₆) of these gases compared to SAPO-5 (8.1 and 6.8 wt %) and SAPO-11 (15.1 and 8.3). The higher yields of these high molecular weight gases with MgAPO-36 catalyst can be attributed to its low acidity. It is suspected that during cracking, the higher molecular weight gases are produced first. These are then cracked further (secondary cracking) to lighter molecular weight gases. The extent of the secondary cracking depends on the acidity of the catalyst. The higher the acidity, the higher the secondary cracking. Thus, the high fraction of C₅ and C₆ gases produced with MgAPO-36 is a consequence of its lower acidity compared to SAPO-5 and SAPO-11. Olefins in the range from C₅ upwards are chemical intermediates of considerable importance. For instance, straight-chain olefins in the C₆–C₁₀ range are used as feed to the oxo reaction, producing straight-chain plasticizer alcohols in the C₇–C₉ and C₉–C₁₁ categories.³⁷

Tar, Char, and Coke Formation. Tar, char, and coke formations are the main problems of WDO upgrading. As such it was worthwhile to investigate which of

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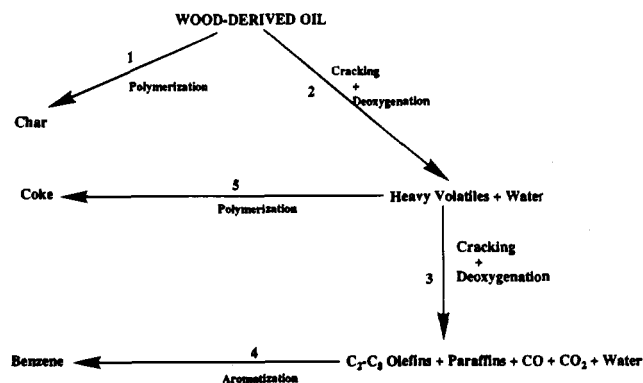


Figure 8. Proposed reaction pathway for the conversion of wood-derived bio-oil over aluminophosphate catalysts.

these catalysts minimized the formation of these products. With all the three catalysts, the amount of tar decreased with temperature. Thus, it appears that operating at higher temperatures was a means of limiting tar formation. On the other hand, the results show that SAPO-5 produces less tar especially at the lower temperatures where tar formation mostly occurs.

Between 12.8 and 28.3 wt % char was produced. The amount of char was over 20 wt % at 330 °C but decreased with temperature to between 12 and 15 wt % at 410 °C. The char was a solid carbonaceous material which was formed mainly above the catalyst bed. Char formation is a consequence of the thermal sensitivity of the fast pyrolysis oils.

Whereas the char and tar fractions decreased with temperature, the amount of coke increased with temperature and varied between 10 and 16.2 wt %, 4.1 and 13 wt %, and 13.4 and 21.5 wt % for SAPO-5, SAPO-11, and MgAPO-36 catalysts, respectively. These coke amounts are comparable to those reported by Chantal et al.⁶ and Adjaye and Bakhshi.²² It is interesting to note that coking was high with the larger pore aluminophosphates (i.e., MgAPO-36 and SAPO-5) compared to medium-pore SAPO-11. In our earlier work³⁴ also, we observed high coke formation with catalysts that contain large pore such as silica-alumina and aluminum-pillared clay compared to HZSM-5 catalyst. Guisnet et al.³⁸ also observed that on account of their limited sizes, medium-pore zeolites produced less coke compared to large-pore zeolites.

As mentioned earlier, coke and char formations were the major problems of WDO upgrading since it resulted in the deactivation of the catalyst. In most catalytic processes this coke problem could be minimized by a proper selection and tailoring of the catalysts. Based on these results, the overall performance in terms of minimizing coke and char formation was of the order: SAPO-11 > SAPO-5 > MgAPO-36.

Proposed Reaction Pathway. Based on the above results an attempt was made to suggest a reaction pathway that describes the conversion of WDO over aluminophosphate catalysts. This reaction pathway is shown in Figure 8.

The formation of the desired aromatic and aliphatic hydrocarbons in the liquid product as well as gaseous hydrocarbons from WDO involves a complex reaction

mechanism. The primary steps are the polymerization to form char (step 1) and cracking and partial deoxygenation²¹ to form an intermediate heavy volatile components and water (step 2). The char formation is the consequence of only thermal effects rather than catalytic effect. Further cracking and deoxygenation (step 3) of the heavy volatile components results in the formation of various olefins and paraffins as well as CO, CO₂, and water. Some of the olefins and paraffins thus produced compose the observed aliphatic hydrocarbon fraction. In addition, some of the olefins obtained in step 3 aromatize to produce benzene (step 4). The production of aromatic hydrocarbons from olefins has been well documented in the literature^{34,39} and may consist of reactions such as oligomerization, cyclization, and hydride transfer. Coke is formed through polymerization reactions of heavy volatile components (step 5).

The formation of aromatic and aliphatic hydrocarbons as well as the olefinic content of the gas products appears to be significantly affected by catalyst acidity and pore size. For instance, the more acidic catalysts (SAPO-5 and SAPO-11) produced more aromatic than aliphatic hydrocarbons. Thus, step 4 would be more significant for SAPO-5 and SAPO-11 than MgAPO-36. The olefinic content of the gas phase also appears to be affected by a combination of catalyst acidity and pore size. High olefin formation seem to be favored by high acidity and smaller pore size. For instance, SAPO-11 produces more olefins in the gas product than SAPO-5 and MgAPO-36 as a consequence of its medium-pore structure and comparatively higher acidity than MgAPO-36. Also, the extent of coke formation is controlled by the pore size of the catalyst. As mentioned earlier, the larger the pore size the greater the coke formation.

Comparison of Upgrading Performance with HZSM-5 and Silica-Alumina Catalysts. In the literature, HZSM-5 has been used^{1,3,4,6,7} to upgrade wood-derived oils. The OLP produced with HZSM-5 mostly consisted of aromatic hydrocarbons. Recently,⁷ we also carried out upgrading studies using silica-alumina as the catalyst. In this case, it was interesting to observe that the OLP consisted mostly of aliphatic type hydrocarbons. It was therefore of interest to compare the performance of the catalysts used in this study with the results obtained with HZSM-5 and silica-alumina catalysts.

The three aluminophosphate catalysts used in this study produced lower amounts of OLP compared to both HZSM-5 and silica-alumina catalysts. The low OLP yields are due to high tar, char, and coke formation with the three aluminophosphate catalysts. As can be seen from Table 7, the aluminophosphate catalysts produced more than 3-fold the amount of tar compared to HZSM-5 catalyst. Also, the combined coke and char yields were substantially higher with the aluminophosphate catalysts than with HZSM-5 catalysts.

The OLP fractions obtained with aluminophosphate catalysts consisted of a high hydrocarbon content than those obtained with silica-alumina catalyst. However, these values were lower than that of HZSM-5 catalyst. Also, whereas the aluminophosphate catalysts were

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Table 7. Comparison between Aluminophosphate and HZSM-5 Catalysts in Terms of Their Optimum Yields for Various Products from the Conversion of Wood-Derived Oil

product	catalysts				
	SAPO-5	SAPO-11	MgAPO-36	silica-alumina	HZSM-5
organic liquid product	22.2	19.9	16.3	25.2	33.6
coke + char	29.0–35.0	25.5–27.6	37.1–41.7	30.8–41.0	20.5–30.2
tar	7.0–12.5	5.2–18.2	5.1–14.5	0–10.4	0–4.1
total hydrocarbons ^a	61.5	56.8	57.0	54.7	86.7
aromatic hydrocarbons ^a	37.7	32.4	29.6	6.5	85.9
aliphatic hydrocarbons ^a	26.1	24.4	34.5	48.2	18.6

^a Weight percent of OLP.**Table 8. Comparison between Aluminophosphate, HZSM-5, and Silica-Alumina Catalysts in Terms of the Aromatic to Aliphatic Hydrocarbon Ratio of the OLP from the Conversion of WDO**

catalyst	temperature, °C		
	330	370	410
SAPO-5	2.0	1.5	1.5
SAPO-11	1.7	1.3	1.4
MgAPO-36	0.7	0.9	1.4
HZSM-5	1.5	22.7	107.4
silica-alumina	0.1	0.1	0.1

highly selective for benzene (about 90% of aromatic hydrocarbon fraction), HZSM-5 was mostly selective for toluene and xylene. As mentioned earlier, compared to HZSM-5, the low hydrocarbon yields with aluminophosphate catalysts are primarily due to the low catalyst acidity.³² It is well-known that high catalyst acidity is essential for enhanced hydrocarbon formation. For instance, hydrogen transfer reactions which are essential for hydrocarbon formation are known to increase with catalyst acidity. Thus, it appears that in addition to its shape selectivity, the high acid density (Table 2) of HZSM-5 catalysts contributed greatly to high amounts of hydrocarbons in the OLP.

It is interesting to note, however, that whereas the hydrocarbon content of OLP with HZSM-5 was predominantly aromatic in nature, those obtained with the aluminophosphate catalysts consisted of significant amounts of both aromatic and aliphatic hydrocarbons. On the other hand, silica-alumina catalyst produced significantly high fractions of aliphatic hydrocarbons. These observations have been expressed more meaningfully in Table 8 in terms of aromatic to aliphatic hydrocarbon ratios. As can be seen, the aromatic to aliphatic hydrocarbon ratio of HZSM-5 was significantly higher (especially at 370 and 410 °C) than those of the aluminophosphate catalysts. On the other hand, those of silica-alumina were much lower. Thus, it appears that HZSM-5 could be used as catalyst where a highly aromatic hydrocarbon liquid product is desired and silica-alumina where a highly aliphatic hydrocarbon content of OLP is desired. On the other hand, where a mixture of both aromatic and aliphatic hydrocarbons in the OLP is desired, the aluminophosphate catalysts appear to be the desired catalysts.

Conversion of Canola Oil

The overall material balances are given in Tables 9–11. The conversions for each catalyst increased with temperature and ranged between 80 and 97%. For instance, with SAPO-5 catalyst, the conversion at 375 °C was 84.4% compared to 97% at 550 °C. The results show that despite its lower acidity (compared to SAPO-

5), medium-pore SAPO-11 gave higher conversions than the large pore SAPO-5 and MgAPO-36. The results also indicate that the extent of canola oil conversion varied over the catalysts. Based on the optimum yields, the extent of conversion follows the order SAPO-11 > SAPO-5 > MgAPO-36. However, conversions were lower compared with HZSM-5 catalyst under identical process conditions. The high extents of conversions with HZSM-5 were due to its high rates of deoxygenation and cracking reactions³¹ culminating from its strong acid sites (Table 2).

Organic Liquid Product. The OLP yields (Tables 9–11) were highly dependent on reaction temperature and also on the catalyst pore size. With increase in temperature, the OLP yields increased to a maximum value and then decreased. It is interesting to note that these maximum values all occur at 450 °C for all three catalysts and were 36.3, 47.4, and 41.5 wt % for SAPO-5, SAPO-11, and MgAPO-36, respectively. Among the three catalysts, SAPO-11 gave the highest OLP yield followed by MgAPO-367 and SAPO-5 in that order. These results show that to optimize the OLP, the reactor has to be operated at 450 °C with SAPO-11. The higher OLP yields of OLP with SAPO-11 may be primarily due to its medium-pore structure. This observation is confirmed also by our earlier work³⁵ on the conversion of canola oil where it was observed that medium-pore HZSM-5 and silicalite catalysts produced higher yields of OLP fractions compared to large-pore H-mordenite and H-Y catalysts.

Composition of Organic Liquid Product (OLP). The OLP compositions for each catalyst also are given in Tables 9–11. The OLP consisted of mostly hydrocarbons and oxygenated compounds. Among the oxygenated compounds, methanol, acetone, furans, acids, and esters were the main products. The hydrocarbon fraction consisted mostly of aromatic hydrocarbons in the gasoline boiling range.

The OLP composition for SAPO-5 catalyst consisted of aromatic hydrocarbons, aliphatic hydrocarbons, and a significant fraction (10.7–33.5 wt % of OLP) of oxygenated compounds. Benzene, toluene, xylenes, and substituted benzenes were the major aromatic hydrocarbons and C₆–C₉ paraffins were the main aliphatic hydrocarbons. The yield of aromatic hydrocarbons increased with temperature from 24.1 to 62 wt % and reached its optimum at 550 °C. On the other hand, the concentration of aliphatic hydrocarbons decreased with temperature from 7.5 to 3.8 wt %. Thus, it would appear that in order to optimize the aromatic hydrocarbon content of the OLP with SAPO-5 catalyst, the reactor should be operated at high temperatures (550 °C). On the other hand, operation at lower temperature

Table 9. Overall Material Balances (wt % of Canola Oil Fed) and Composition of Organic Liquid Product from the Conversion of Canola Oil over SAPO-5

product	SAPO-5				
	375 °C	400 °C	450 °C	500 °C	550 °C
coke	38.0	33.0	20.0	15.0	13.4
gas	10.5	19.4	27.7	41.6	63.3
organic liquid product (OLP)	19.5	22.6	36.3	27.4	12.3
residue	15.0	12.0	9.0	5.0	3.0
water	13.0	11.0	10.0	8.0	7.0
unaccounted fraction	4.0	2.0	2.0	3.0	1.0
conversion	84.4	87.8	90.8	94.8	97.0
Composition (wt % of OLP) of Organic Liquid Product					
aliphatic hydrocarbons	7.5	6.1	7.2	6.0	3.8
aromatic hydrocarbons					
benzene	2.1	2.5	4.2	4.9	5.7
toluene	9.3	11.2	15.5	17.5	20.9
xylenes	5.4	6.2	8.4	9.0	12.2
C ₉ ⁺	7.3	9.6	10.3	17.1	23.2
Σ aromatic hydrocarbons	24.1	29.5	38.4	48.5	62.0
oxygenated compounds					
acids and esters	5.0	6.9	2.2	6.9	1.1
alcohols	13.1	10.0	6.3	5.0	4.3
furans	1.8	1.2	1.4	2.8	1.9
ketones	11.1	8.5	7.4	5.0	3.4
Σ oxygenated compounds	31.0	26.6	17.3	19.7	10.7
unidentified compounds	37.4	37.8	37.1	23.8	23.5

Table 10. Overall Material Balances (wt % of Canola Oil Fed) and Composition of Organic Liquid Product from the Conversion of Canola Oil over SAPO-11 Catalysts

product	SAPO-11			
	375 °C	400 °C	450 °C	500 °C
coke	40.5	30.4	13.8	10.0
gas	5.5	11.1	20.8	44.4
organic liquid product (OLP)	35.5	36.5	47.4	33.6
residue	14.0	12.0	8.0	4.0
water	9.0	8.0	8.0	5.0
unaccounted fraction	1.0	2.0	2.0	3.0
conversion	85.9	87.8	91.8	95.9
Composition (wt % of OLP) of Organic Liquid Product				
aliphatic hydrocarbons	9.4	10.9	8.6	11.7
aromatic hydrocarbons				
benzene	1.1	2.5	4.2	5.0
toluene	5.2	9.5	12.6	14.1
xylenes	5.9	7.6	8.9	10.2
C ₉ ⁺	12.2	10.9	7.3	10.1
Σ aromatic hydrocarbons	28.2	30.5	33.0	39.4
oxygenated compounds				
acids and esters	2.9	1.6	1.0	1.9
alcohols	8.8	6.5	7.9	4.3
furans	3.2	1.6	1.6	2.1
ketones	7.7	5.9	8.5	8.3
Σ oxygenated compounds	22.6	15.6	19.0	16.6
unidentified compounds	39.8	43.0	39.4	32.3

(375 °C) is needed to achieve high production of aliphatic hydrocarbons.

For SAPO-11, the maximum aromatic hydrocarbon yield was 39.4 wt % at 500 °C and the concentration of aliphatic hydrocarbons was also maximum (11.7 wt %) at the same temperature. With both catalysts (i.e., SAPO-5 and SAPO-11) it is seen that fairly high yields for aromatic hydrocarbons than aliphatic hydrocarbons were obtained.

When MgAPO-36 catalyst was used, the OLP consisted of high aliphatic hydrocarbon content below 450 °C. Above this temperature, the aromatic hydrocarbon content was more than the aliphatic hydrocarbons. With this catalyst, the concentration of the aliphatic hydrocarbons reached a maximum of 26.2 wt % of the OLP at 375 °C compared to SAPO-5 which gave 7.5 wt % of aliphatics at the same temperature. The aromatic

Table 11. Overall Material Balances (wt % of Canola Oil Fed) and Composition of Organic Liquid Product from the Conversion of Canola Oil over MgAPO-36 Catalysts

product	MgAPO-36			
	375 °C	400 °C	450 °C	500 °C
coke	36.5	28.4	16.5	9.5
gas	6.0	14.0	22.0	40.5
organic liquid product (OLP)	26.5	31.6	41.5	32.0
residue	19.0	15.0	10.0	7.0
water	10.0	8.0	8.0	9.0
unaccounted fraction	2.0	3.0	2.0	2.0
conversion	80.6	84.5	89.8	92.9
Composition (wt % of OLP) of Organic Liquid Product				
aliphatic hydrocarbons	26.2	21.5	19.5	15.8
aromatic hydrocarbons				
benzene	0.5	0.8	1.2	2.8
toluene	3.6	4.9	6.2	9.7
xylenes	3.2	3.7	4.4	6.2
C ₉ ⁺	2.9	3.1	7.7	10.8
Σ aromatic hydrocarbons	10.2	12.5	19.5	29.5
oxygenated compounds				
acids and esters	6.3	4.9	4.3	4.4
alcohols	10.5	7.9	6.5	5.5
furans	2.5	1.9	1.6	1.9
ketones	14.2	11.2	7.4	5.7
Σ oxygenated compounds	33.5	25.9	19.8	17.5
unidentified compounds	30.1	40.1	41.2	37.2

concentration varied between 10.2–29.5 wt % of OLP and mostly consisted of C₉⁺ hydrocarbons.

The above results show that SAPO-5 and SAPO-11 catalysts gave high yields of aromatic hydrocarbons than aliphatic hydrocarbons. On the other hand, MgAPO-36 catalyst gave high selectivity for aliphatic hydrocarbons. Since these catalysts possess molecular sieving properties, it would appear that differences in their acidity may have been the main reason behind the variations in the OLP compositions. For instance, the results show that in most cases, the yield of aromatic hydrocarbons followed the same trend as the acid strength of the catalyst; i.e., it increased with increase in catalyst acidity. Conversely, the yield of aliphatic hydrocarbons decreased with increase in acidity. Ammonia TPD observations (Figure 2) also indicate that SAPO-5 possessed higher acid site strength (based on T_{\max} values) compared to the other two catalysts,

Table 12. Composition (wt % of Gas Product) of Gas Products Obtained with Aluminophosphate Catalysts and Canola Oil

product	SAPO-5				SAPO-11				MgAPO-36			
	375 °C	400 °C	450 °C	500 °C	375 °C	400 °C	450 °C	500 °C	375 °C	400 °C	450 °C	500 °C
methane	0.3	0.3	1.4	4.0	6.5	9.9	15.6	14.5	2.3	1.0	2.3	2.9
ethylene	1.1	1.7	3.2	6.0	5.1	4.2	5.3	6.6	11.5	15.8	27.7	31.2
ethane	0.6	0.5	2.1	5.1	3.0	1.4	3.3	3.6	11.6	10.5	5.2	3.5
propylene	1.2	2.4	5.6	9.8	24.2	27.0	30.4	34.2	11.6	10.5	5.2	3.5
propane	28.8	22.5	23.3	22.9	2.9	3.8	6.2	3.2	17.3	14.3	7.5	4.2
<i>n</i> -butane	43.5	42.4	30.1	16.1	1.9	7.9	6.3	2.2	13.5	9.5	4.8	2.2
isobutane			3.4	6.2	13.8	16.7	15.4	15.9	3.9	4.4	1.3	1.5
isobutylene	9.1	8.7	9.3	10.4	7.2	7.4	7.9	7.4	3.9	5.1	3.2	1.5
1-butene		0.8	0.6		3.8	3.3	3.5	3.8				
remainder of C ₄	12.9	17.4	15.8	12.3	16.6	14.1	11.7	12.2	3.0	3.2	4.2	3.9
C ₅	1.1	2.4	3.2	3.5	8.0	7.6	3.4	3.8	8.5	7.5	6.4	2.5
C ₆	0.1		0.1	0.3	1.7	2.5	0.5	0.6	4.5	1.5	0.5	
CO ₂	1.3	0.9	1.8	3.0	8.7	2.4	2.4	2.3	2.1	1.8	2.2	3.2
CO			0.2	0.5	0.8	0.7	1.5	1.8	1.6	1.3	1.5	2.5
total	100	100	100	100	100	100	100	100	100	100	100	100
C ₂ –C ₄ olefin/ paraffin ratio	0.33	0.47	0.57	0.71	2.40	1.82	1.75	2.29	0.6	0.8	1.6	2.5

suggesting that the greater the number of acid sites with high strength, the higher the yield of aromatic hydrocarbons. This observation appears to be confirmed also by HZSM-5 which has high acidity and high acid site strength and consequently produced a high aromatic fraction in the OLP.

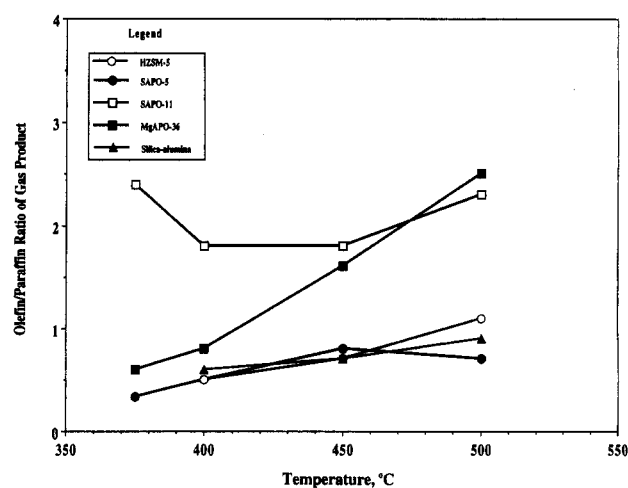
These catalysts also resulted in fairly high yields of oxygenated compounds formed in the OLP (Tables 9–11). The yield of these compounds decreased with temperature and ranged from 10.7 to 31 (SAPO-5), 15.6 to 22.6 (SAPO-11), and 17.5 to 33.5 wt % (MgAPO-36). Based on the optimum yields, it appears that medium-pore SAPO-11 gave lower amounts of oxygenated compounds compared to the larger pore catalysts. Overall, these results again suggest that the rates of deoxygenation over these catalysts were low compared to that of HZSM-5 catalyst.⁶

Gas Product Composition. The yield of gas product increased monotonically with temperature and ranged between 5.5 and 63 wt % of the canola oil feed, indicating that in some cases a high fraction of canola oil was converted to gas. The gas product consisted mostly of C₁–C₆ hydrocarbons, CO, and CO₂. The complete gas compositions are given in Table 12. The hydrocarbon gases were similar for each catalyst but their compositions were different.

SAPO-5 catalyst produced mostly C₃ and C₄ gases of which propane and *n*-butane were the most prominent compounds. The concentration of *n*-butane, in particular, decreased tremendously with temperature. These decreases were translated into increased yields in methane, ethylene, ethane, and propane probably from secondary cracking reactions. The total C₂–C₄ olefin fraction also increased with temperature. However, in general, the olefin/paraffin ratio was low and was always less than unity.

With SAPO-11, the gas product consisted of a high fraction of olefins. Propylene, *cis/trans*-butenes along with isobutane were the main components. Initially, the olefin/paraffin ratio was high (2.4) but then decreased to a minimum of 1.75 and then increased. Compared to SAPO-5 catalyst, SAPO-11 gave exceptionally high yields of olefins in the gas products.

The gas fraction obtained with MgAPO-36 consisted of C₁–C₆ gases without a clearcut selectivity for a particular gas product (especially below 450 °C). How-

**Figure 9.** Comparison of the C₂–C₄ olefin to paraffin ratio of gas product for the conversion of canola oil over aluminophosphate, HZSM-5, and silica–alumina catalysts.

ever, at higher temperatures (450–500 °C) the selectivity was mainly for ethylene (27.7–31.2 wt % of the gas fraction). The olefin/paraffin ratio also increased with temperature and reached a maximum of 2.5 at 500 °C.

Temperature had a significant effect on the gas product distribution. At lower temperatures, SAPO-5 and MgAPO-36 favored the formation of paraffins compared to olefins. However, as the temperature was increased, the olefin formation also increased. This variation has been shown in Figure 9 by the effect of temperature on C₁–C₄ olefin/paraffin ratio. This increase in low olefin content at high temperatures was due to the cracking of C₄ to C₆ hydrocarbon gases. SAPO-11, on the other hand, produced a high amount of olefins compared to paraffins at all temperatures. This ratio was always greater than 1.70. Of all the three catalysts, MgAPO-36 gave the highest olefin/paraffin ratio of 2.5 at 500 °C. The formation of olefins in the gas fractions appears to be controlled by a combination of temperature and catalyst acidity. High olefin formation is favored by high temperatures and low catalyst acidity. These observations suggest that during the process of producing various hydrocarbons the intermediates formed consisted of olefins. The effect of acidity of catalyst lies mainly in the conversion of these olefins to the final products. The catalysts with high acidity are probably able to hydrogenate the olefins

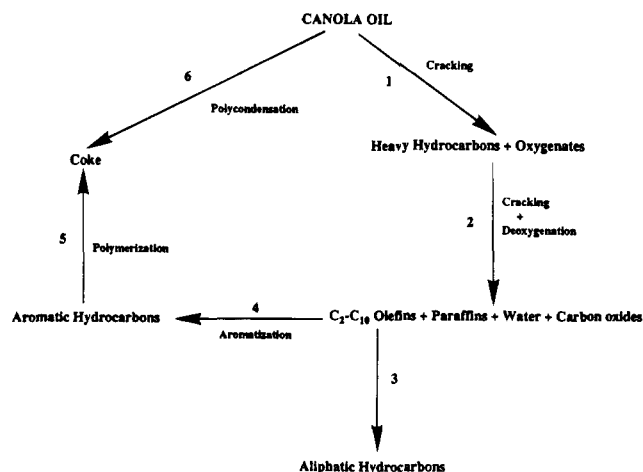


Figure 10. Proposed reaction pathway for the conversion of canola oil over aluminophosphate catalysts.

more effectively compared with the catalyst with low acidity. Consequently, SAPO-5 (with its high acidity) produces relatively more paraffins than SAPO-11 and MgAPO-36 catalysts.

These results show that SAPO-5 gives exceptionally high selectivities for propane (22–29 wt % of gas fraction) and *n*-butane (16–44 wt % of gas fraction), and SAPO-11 for propylene (between 24 and 34 wt % of gas product). MgAPO-36 gave high selectivity for mainly ethylene (11–31 wt % of gas) compared to the other hydrocarbon gases. It appears that these catalysts may have a potential for the production of olefins especially ethylene and propylene as well as other gases such as propane and *n*-butane from canola oil or similar feed materials.

Coke Formation. The amounts of coke formed for all aluminophosphate catalysts were high and ranged from 9.5 to 40.5 wt %. Interestingly, coke formation was high at low temperatures and decreased drastically with increase in temperature probably due to its gasification. Compared with HZSM-5 catalyst under similar conditions, the coke formation with these aluminophosphate catalysts was relatively high. The high amounts of coke with these catalysts were due to higher rates of polymerization and condensation reactions as well as their low acidity.

Proposed Reaction Pathway. Based on the above results, the reaction pathway shown in Figure 10 is proposed for the conversion of canola oil with aluminophosphate catalysts. With all the three catalysts, the conversion is initiated by a combination of thermal and catalytic cracking of the bulky canola oil molecules into intermediate fragments consisting of heavy straight or branched chain hydrocarbons and oxygenates (step 1). It is assumed that initial fragmentation takes place on the surface of the catalyst followed by diffusion into the catalyst pores. In the catalyst pores, the heavy hydrocarbons undergo secondary cracking to produce light aliphatic hydrocarbons (step 2). Additionally, the heavy oxygenates are cracked and some are deoxygenated to produce various aliphatic hydrocarbons, water, and carbon oxides^{5,21} (step 2).

The aliphatic hydrocarbons produced by step 2 consist of C₂–C₁₀ olefins and paraffins. The extent of their formation or the ratio of olefins to paraffins is controlled by the pore size and acidity of the catalysts. In addition, the extent of aromatization of these components through

further reaction (step 4) also depends on the type of catalyst. With SAPO-11 and SAPO-5 catalyst in particular (compared to MgAPO-36), a large fraction of C₂–C₁₀ fragments react through various aromatization reactions such as cyclization and hydride transfer^{36,38} followed by alkylation or isomerization to produce various aromatic hydrocarbons (step 4). On the other hand, with MgAPO-36, fairly even amounts of these fragments react to form aromatic hydrocarbons as well as aliphatic hydrocarbons (step 3).

Coke formation is assumed to take place through polycondensation reactions of the canola oil feed on the catalysts surface (step 6) and polymerization reactions within the catalyst pores (step 5). In the literature⁴⁰ also, it has been stated that cyclization and dehydrogenation of alkylaromatics to form polycyclic compounds are intermediate steps in coke formation.

Comparison of Conversion Performance with HZSM-5 and Silica–Alumina Catalysts

It was of interest to compare the performance of the catalysts used in this study with the results obtained earlier with HZSM-5 and silica–alumina catalysts. In Table 13, a comparison of the optimum yields with these catalysts is presented.

The OLP yields obtained with the aluminophosphate catalysts were lower than both silica–alumina and HZSM-5 catalysts. The low OLP yield for aluminophosphate catalysts is due primarily to the formation of coke. As can be seen in Table 13, the minimum amounts of coke formed with SAPO-5, SAPO-11, and MgAPO-36 were 13.4, 10.0, and 9.5 compared to 4.0 wt % with HZSM-5. In addition, the maximum coke yields with the aluminophosphate catalysts were more than 5 times higher than HZSM-5.

As can be seen in Table 14, the aluminophosphate catalysts produced lower amounts of hydrocarbons in the OLP compared to HZSM-5. On the other hand, for silica–alumina, the hydrocarbon content was comparable in value with those obtained with MgAPO-36 but lower compared to SAPO-5 and SAPO-11. It was stated earlier that the low hydrocarbon formation is due to the lower acidity of the aluminophosphate catalysts compared with HZSM-5 catalyst. With the exception of MgAPO-36, the other two aluminophosphate catalysts as well as HZSM-5 and silica–alumina produced significantly more aromatic hydrocarbons than aliphatic hydrocarbons in the OLP. This result implies that the aluminophosphate catalysts, SAPO-5 and SAPO-11, are excellent candidates for the production of aromatic hydrocarbons. However, MgAPO-36 produced more aliphatic hydrocarbons compared to the four catalysts (namely, SAPO-5, SAPO-11, HZSM-5, and silica–alumina).

In the case of the gas product, a comparison of the olefin to paraffin ratio (Figure 9) show that SAPO-11 in particular (and MgAPO-36) produced gases which were highly olefinic in nature than HZSM-5 and silica–alumina catalysts. Thus, it appears that there is a potential of producing olefins such as ethylene and propylene from canola oil using aluminophosphate catalysts.

(40) Pearce, R.; Patterson, W. R. *Catalysis and Chemical Processes*; Wiley: New York, 1981.

Table 13. Comparison between Aluminophosphate and HZSM-5 Catalysts in Terms of Their Optimum Yields for Various Products from the Conversion of Canola Oil

products	SAPO-5	SAPO-11	MgAPO-36	silica-alumina	HZSM-5
organic liquid product	36.3	47.4	41.5	53.0	56.0
coke (range)	13.4–38.0	10.0–40.5	9.5–36.5	10.0–27.0	4.0–7.0
total hydrocarbons ^a	65.8	51.1	45.3	48.7	88.9
aromatic hydrocarbons ^a	62.0	39.4	29.5	36.2	88.0
aliphatic hydrocarbons ^a	7.5	11.7	26.2	19.4	2.9

^a Weight percent of OLP.**Table 14. Comparison between Aluminophosphate and HZSM-5 Catalysts of the Aromatic to Aliphatic Hydrocarbon Ratio for Conversion of Canola Oil**

catalyst	temperature, °C			
	375	400	450	500
SAPO-5	3.2	4.8	5.3	8.1
SAPO-11	3.0	2.8	3.8	3.4
MgAPO-36	0.4	0.6	1.0	1.9
silica-alumina		1.3	2.4	2.9
HZSM-5	27.7	18.9	53.2	97.8

Summary and Conclusions

1. The three aluminophosphate catalysts, namely, SAPO-5, SAPO-11, and MgAPO-36, were thoroughly characterized using techniques such as X-ray powder diffraction, temperature-programmed desorption of ammonia, NMR analysis, BET surface areas, and pore sizes. The results showed that all three catalysts were crystalline in nature and of definite pore sizes (0.80, 0.56, and 0.75 nm for SAPO-5, SAPO-11, and MgAPO-36, respectively). The structures of all the aluminophosphate catalysts were evaluated using solid state NMR, which showed that aluminum, phosphorous, and silicon atoms were in the framework. The catalyst acidity was of the order: SAPO-5 > SAPO-11 > MgAPO-36.

2. WDO was converted over aluminophosphate catalysts to organic liquid products (12.5–22.2 wt % of WDO) containing 22.5–37.7 wt % aromatic hydrocarbons (such as benzene, toluene, and xylene) and 18.9–34.5 wt % aliphatic hydrocarbons (such as *n*-hexane, heptane, and isooctane). It was surprising to note that extremely high selectivity (accounting for almost 90% of aromatic hydrocarbon fraction) for benzene was obtained with these aluminophosphate catalysts when other catalysts such as HZSM-5, H-Y, and H-mordenite have shown relatively high selectivity for toluene, xylene, and other alkylated benzenes. Overall, the optimum yield of hydrocarbons (57–61.5 wt % of OLP) was comparable with that of silica-alumina (54.7 wt % of OLP) but lower than HZSM-5 catalyst (86.7 wt % of OLP).

3. The extent of gas production with WDO was between 5.5 and 16.7 wt %. SAPO-5 was highly selective for ethylene and propylene, SAPO-11 for propylene and MgAPO-36 for isobutane. The results show that aluminophosphate catalysts are highly selective olefins than to HZSM-5.

4. The conversion of canola oil over aluminophosphate catalysts produced between 19.5 and 47.4 wt %

OLP fractions which contained an optimum of 65.8, 51.1, and 45.3 wt % hydrocarbons (over SAPO-5, SAPO-11, and MgAPO-36, respectively). SAPO-5 and SAPO-11 were highly selective for aromatic hydrocarbons (such as toluene, xylene and C₉⁺ aromatic hydrocarbons) whereas MgAPO-36 was selective for both aliphatic hydrocarbons (such as heptane and isooctane) and aromatic hydrocarbons in comparable quantities.

In comparison, HZSM-5 produced higher yields of hydrocarbons in the OLP (optimum of 88.9 wt %) and silica-alumina produced an optimum of about 48.7 wt % which was lower than SAPO-5 and SAPO-11 but comparable with MgAPO-36.

5. The extent of gas production from canola oil was between 5 and 63.3 wt %. MgAPO-36 was highly selective for ethylene, SAPO-11 for propylene, and SAPO-5 for *n*-butane.

6. The organic liquid products obtained from both oils have the potential for use as transportation fuels on account of their hydrocarbon content. However, further upgrading may be required in order to further reduce the oxygen content, thus increasing its hydrocarbon content.

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Appendix

The terms "conversion", "yield" and "selectivity" as used in this paper are defined as follows:

conversion (%) =

$$(1 - (R(\text{wt } \%)/(100 - \text{UA}(\text{wt } \%))) \times 100 \quad (1)$$

$$\text{yield (wt \%)} = (P(\text{g})/\text{bio-oil fed (g)}) \times 100 \quad (2)$$

selectivity, *S* =

$$(P(\text{wt } \%)/(100 - P(\text{wt } \%)) - \text{UA}(\text{wt } \%))) \quad (3)$$

where *P* represents the products, i.e., coke, gas, organic liquid product, and aqueous fraction. UA represents the unaccounted fraction. *R* is residue.

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