Alcohols as Alternatives to Petroleum for Environmentally Clean Fuels and Petrochemicals

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In this review article, some of the challenging research areas related to the development of novel catalysts and catalytic processes for the chemical fixation of CO_2 by converting it to alcohols and ethers, and for the conversion of alcohols to olefins and other hydrocarbons are reviewed. Ethanol, methanol, and the ethers derived from them, such as DEE and DME, have good burning characteristics and may be considered attractive transportation fuel alternates. New processes for catalytic selective oxidation and dehydration of alcohols may open up new pathways for the production of olefins and other petrochemicals from non-petroleum feedstock. Developments in CO_2 capture and its chemical fixation processes will help reduce CO_2 emissions into the atmosphere and will produce alternative fuels to petroleum. All these new processes involve challenging catalysis research.
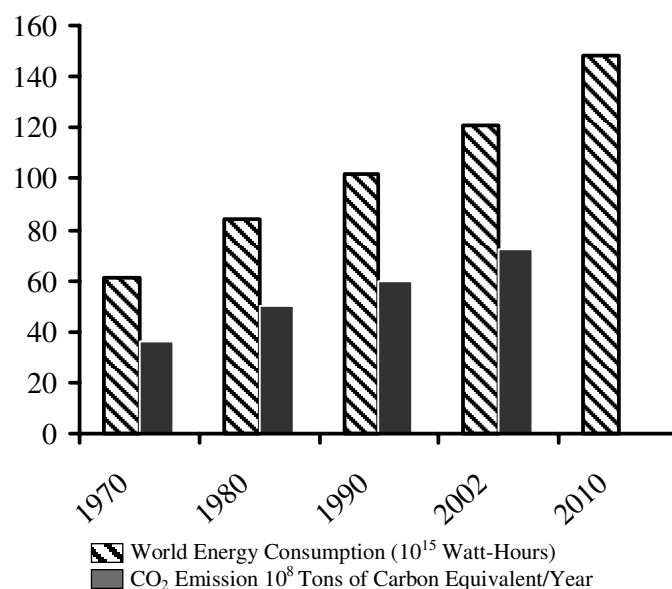
Key Words: Ethanol, methanol, bio-fuels, global warming, diethyl ether, dimethyl ether, selective oxidation, environmental catalysis, dehydration, CO_2 activation.

Introduction

Two of the most important problems of the next century are the rapid depletion of oil reserves, due to their excessive use for energy needs, and global warming. The most important cause of global warming is considered the increasing concentration of carbon dioxide in the atmosphere. Excessive use of fossil fuels as our major energy source is the main reason for both of these problems. Among the fossil fuels, petroleum is the most convenient fuel for use in transportation; at the currently high consumption rate the known oil reserves are expected to be depleted within about 40 years,[1] and at the current rate of consumption the known natural gas reserves are expected to be depleted within about 70 years. Although the discovery of new oil and natural gas reserves may postpone the complete depletion of these fossil fuels, significant fuel shortage problems are expected in the coming century. As shown in Table 1, the yearly consumption rates of petroleum and natural gas increased more than 200-fold during the last century.[2] Although petroleum and natural gas accounted for only about 2% and 1% of total energy consumption 100 years ago, today they account for about 38% and 23%, respectively. The increasing trends in world energy use and yearly CO_2 emission rates are shown in Figure 1. Increased CO_2 emission rates caused an increase in the atmospheric CO_2 concentration from about 295 ppm to 380 ppm during the last century. Additionally, the Earth's surface temperature was reported to increase by about 0.6 °C during the same period.[2−4]

Table 1. Changes in world energy consumption during the last century.[2]

Energy Source	1900 use (million tons of oil equivalent)	2001 use (million tons of oil equivalent)	Increase (fold)
Coal	501	2395	4.8
Petroleum	18	3913	217.3
Natural Gas	9	2328	258.6
Nuclear	0	662	-
Renewables	383	750	1.9
TOTAL	911	10,048	11.0
Energy Use per Person (tons of oil eq. /person)	0.517	1.633	3.2

World Energy Consumption (10^{15} Watt-Hours)
CO_2 Emission 10^8 Tons of Carbon Equivalent/Year

Figure 1. World energy use during the last 3 decades.[1,2,4]

The high rate of petroleum consumption is due to its excessive use in transportation. About 57% of oil was consumed for transportation purposes.[1] Its rapid rate of depletion will also cause a major problem for the synthesis of many of the petrochemical products we use in everyday life. Actually, petroleum and natural gas are raw materials that are too valuable to be burned wastefully for mobile and stationary energy needs. Recycling CO_2 by the synthesis of methanol and methanol economy was proposed in the recent publications by Olah et al.[1,5] A challenging solution to the problems of oil depletion and increased atmospheric CO_2 is the completion of the carbon cycle by the synthesis of hydrocarbons, starting from CO_2 (Figure 2). Synthesis of alcohols, ethers, and other hydrocarbons using CO_2 as the carbon source are major challenges in catalysis research. Moreover, advances in CO_2 capture and multifunctional reactor technologies are needed to complete the carbon cycle shown in Figure 2. The important role of catalysis research in this carbon cycle is emphasized in this review.
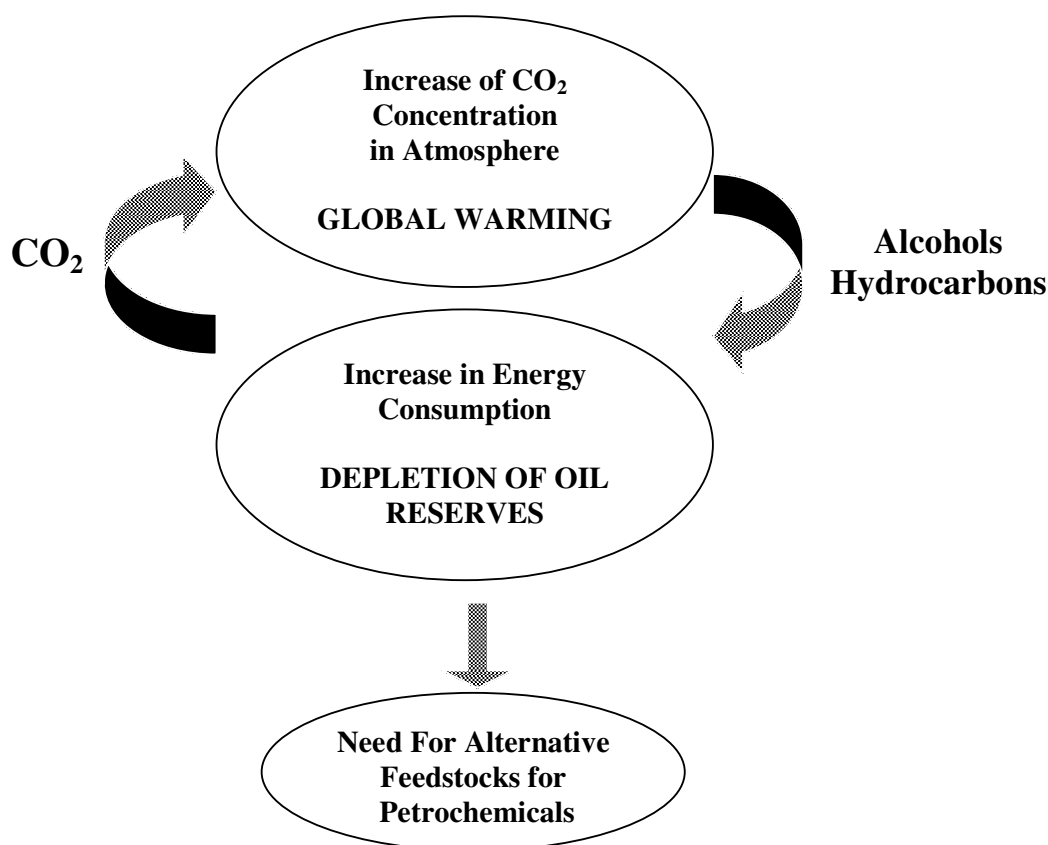
Figure 2. Two major challenging problems for environmental catalysis researchers.[1]

Alternates to transportation fuels

The volumetric heating values of the 2 major transportation fuels, namely gasoline and diesel fuel, are about 32 and 36 MJ/L, respectively.[1] In addition to the volumetric heating value, the octane number is another very important parameter for an alternative fuel for gasoline. Ethanol, methanol, and a number of ethers have very high octane numbers, over 100 (Table 2).[6−10] Ethanol, with an octane number of 113 and low Reid vapor pressure, is considered an excellent alternative to gasoline. The volumetric heating value of ethanol (about 21 MJ/L) is higher than that of methanol (which is about 15 MJ/L). Although the low vapor pressure of ethanol is an advantage from the point of view of its loss during the fueling of cars, it also causes some problems in cold-starting engines. Fuel regulations mandate that motor vehicle fuels should have sufficient vapor pressure to cold start, even at a temperature of –30 °C. Diethyl ether (DEE), which can be produced by the dehydration of ethanol over acidic catalysts, has a high vapor pressure and a very high octane number (Table 2). Consequently ethanol-DEE mixtures are considered excellent gasoline alternatives. The latent heat of ethanol is about 3.7 times higher than that of gasoline, which results in lower temperatures during combustion in the engine. Decreased engine temperature results in the formation of less NO_x. The engine compression ratio of ethanol-burning engines is also higher than the compression ratio of engines that burn conventional gasoline.

The combustion of alcohols and ethers produce much less unburned hydrocarbons and CO than does conventional gasoline. Tertiary ethers, such as MTBE (methyl tert-butyl ether), ETBE (ethyl tert-

butyl ether), TAME (tert-amyl methyl ether), and TAEE (tert-amyl ethyl ether), have excellent burning characteristics and are recommended as excellent octane-enhancing gasoline blending compounds. These ethers are produced by the etherification reactions of methanol and ethanol with isobutylene and isoamylene, respectively, over acidic resin catalysts.[6,11−14] Due to its relatively high water solubility and bad smell, MTBE created water pollution problems and its use as an octane-enhancing gasoline blending oxygenate was banned in some countries. However, the water solubility of ethanol-based ethers, such as TAEE and diethyl ether[15] (DEE), are about an order of magnitude less than MTBE (Table 2). Ethanol- and ethanol-based ethers are also considered more environmentally friendly gasoline-blending alternatives than methanol-based ethers.

Table 2. Some properties of gasoline, alcohols, and gasoline additives.[6−10]

	Gasoline Unleaded Gasoline	METOH	ETOH	MTBE	ETBE	TAME	TAEE	DEE
Octane Number	91 -95	116	113	110	111	> 105	> 105	> 110
Boiling Point (°C)	30 - 180	64.8	78	55	72	86	101	34.5
(RVP) Vapor Pressure, bar	0.6	0.31	0.16	0.55	0.28	0.10	0.015	1.07
Solubility (mg/L water)		Miscible	Miscible	43,000 54,000	26,000	20,000	4000	6900

Instead of the octane number, the cetane number is the key parameter for a diesel fuel. For a conventional diesel fuel, the cetane number is around 40-55. Fuels with high cetane numbers result in smoother engine operation and reduced emissions of NO_x, particulate matter, hydrocarbons, and CO. As shown in Table 3, cetane numbers of dimethyl-ether (DME) and especially DEE are much higher than premium diesel fuel,[15−18] while ethanol, methanol, methane, and propane have very low cetane numbers. In addition to the cetane number, flash point and pour point temperatures are also important parameters for a diesel fuel.[19] DME and DEE can be considered excellent alternatives for compression-ignition engine fuels. They can also be used as fuel-blending oxygenates. DEE was also reported to have similarly good cloud point depression properties as diesel fuel.[19] DME is reported to be a non-toxic and environmentally benign diesel fuel alternative, resulting in low NO_x emissions in premixed combustion.[20] Biodiesel, which is produced by the transesterification of oils with methanol, also has a cetane number comparable to conventional diesel fuel. However, the economics of using biodiesel as a diesel alternative is strongly dependent upon the utilization of large amounts of glycerol produced during the production of methyl esters of oils.

Methanol and ethanol may also be used in fuel cells to convert chemical energy into electrical energy. Alcohols have the major advantage of energy storage, as compared to hydrogen gas, to be used in fuel cells. The volumetric heating value of hydrogen gas (at 300 bars) is about an order of magnitude less than that of ethanol. Even for liquid hydrogen, the volumetric heating value is about one third that of alcohols (Figure 3). Requirements of very large storage tanks and safety issues are some of the problems associated with using hydrogen in fuel cells for transportation purposes. Moreover, the production of hydrogen by reforming fossil fuels creates significant amounts of CO and CO_2. Conversion of fossil fuels to hydrogen involves a large loss of energy. If hydrogen is produced by electrolysis of water, its overall efficiency is extremely low.[21] A hydrogen economy strongly depends upon the development of novel catalysts and new photocatalytic processes for water splitting.[22,23] Alcohols have high hydrogen storage capacity. One liter of

ethanol contains about 103 g of hydrogen, while one liter of liquid hydrogen contains only 70.8 g of hydrogen. Catalytic onboard autothermal reforming of bio-ethanol is another alternative for producing hydrogen[24] for fuel cell-powered motor vehicles, and for producing acetaldehyde for lean NO_x emission control.[25] A recent combinatorial study by Duan and Senkan[26] showed that Pd, Pt, Rh, Ni, and Cu are highly active catalysts for steam reforming of ethanol to produce hydrogen.

Table 3. Some properties of diesel fuel and alternatives.[15−18]

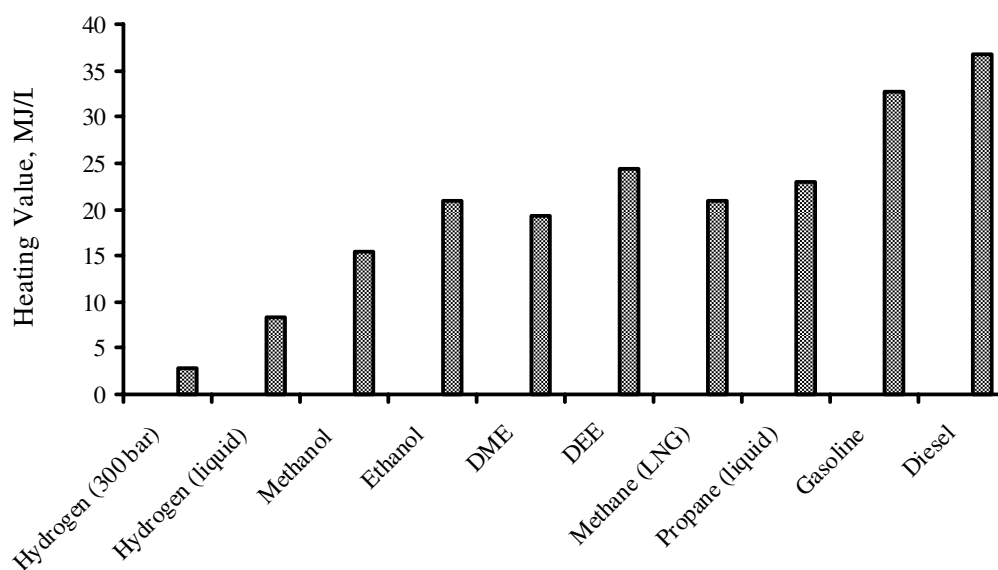|	Diesel Fuel	DME	DEE	ETOH	METOH	CH_4	C_3H_8
Cetane Number	40-55	55-60	85-96	8	5	3	5
Heating value (kJ/kg)	42,000	28,000	34,000	26,500	20,000	48,500	46,000
Flammability Limits (vol %)	0.6-6.5	3.4-17	1.9-36	4.3-19	5.5-36	5-15	2.1-19
Auto ignition Temperature (°C)	320	350	160	423	460	532	470
Boiling Point (°C)	180-350	-24.9	34.5	78	64.8	-161.5	-42

Figure 3. Volumetric heating values and boiling points of fuels.[1,9,18]

## Synthesis of alcohols, DME and organic carbonates from CO_2

Methanol and ethanol are considered alternative energy sources, as well as starting feedstock for the production of a number of petrochemicals. Methanol is conventionally produced from synthesis gas over Cu-ZnO-based catalysts.

$$CO + 2\ H_2 \leftrightarrow CH_3OH \quad \Delta H^o = -90.7\ \text{kJ/mol}$$

Thermodynamic limitations enforce the use of high pressures of over 50 bars in methanol synthesis. For this reaction, copper is considered the active metal, while ZnO enhances stability, prevents agglomeration

of copper, and neutralizes the acidity of the alumina support.

Synthesis of methanol directly from CO_2 has attracted the attention of researchers.

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H^o = -41 \text{ kJ/mol}$$
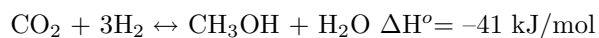
Recent studies have proven that the activity and stability of Cu-ZnO-based catalysts were significantly improved by doping the catalyst with ZrO_2.[27,28] ZrO_2 was reported to cause higher copper dispersion in the catalyst structure. ZrO_2-doped catalysts were found to have higher activity and selectivity in the synthesis of methanol from CO_2, rather than from CO.[27] Results reported by Sloczynski et al.[29,30] proved the significant effect of copper crystal size on methanol yield. These studies showed that the addition of Ga_2O_3 improved the stability of the catalyst and copper dispersion. Their results indicated that adding the oxides of Ga, B, etc. to $Cu/ZnO/ZrO_2$ catalysts caused alterations in both the activation energy and in the number of active centers.[29] These studies also showed that Cu-containing catalysts had much higher activity than Ag- and Au-containing catalysts.[30] However, in another recent study it was shown that Pd/ZnO catalysts showed much higher activity and selectivity in methanol synthesis from CO_2 than Cu/ZnO-type catalysts.[31] Different challenging catalytic routes for the synthesis of methanol starting from CO_2 and methane are discussed in the excellent book by Olah et al.[1] Novel electrochemical and photocatalytic processes were also proposed for the reduction of CO_2 to methanol, formaldehyde, and formic acid.

Bio-ethanol is produced by the fermentation of crop and sugar wastes. This process involves the capture and conversion steps of CO_2 by the green plants through a photosynthesis route. Direct synthesis of ethanol from CO_2 through a catalytic route has also attracted the attention of researchers.[32−36] Results obtained with Rh-Se-based catalysts supported on TiO_2, SiO_2, Al_2O_3, and MgO showed that ethanol synthesis from $CO_2 + H_2$ mixtures was observed only when TiO_2 was used as the support, through a path involving acetate species on the catalyst surface.[32] Fe/Cu/Zn/Al/K-based FT-type catalysts modified by Pd-Ga were shown to give high yields of ethanol due to the hydrogen spillover enhancement of the catalyst by Pd.[34] In this catalyst, the functions of Fe and Cu were reported to be C-C bond formation and OH group insertion.

As discussed in the previous section, DME has excellent potential to be used as an alternative fuel for compression ignition engines. Direct synthesis of DME by the hydrogenation of CO and CO_2 is a challenging process requiring the development of selective catalysts.[37−39] In the work by Erena et al.,[37] up to 78% DME yield values were reported using bifunctional CuO-ZnO/NaHZSM5-type catalysts. Studies carried out with sulfate-modified γ-alumina catalysts[38] indicated an increase in CO conversion from 0.85 to about 0.95 and an increase in DME selectivity from about 0.50 to 0.60, with an increase in sulfate content from 0% to 15%. The enhanced activity of the catalyst by the addition of sulfate was related to the increase in the acid strength of the catalyst.

Dimethyl carbonate (DMC) can also be used as an octane-enhancing fuel-blending compound[40] and is also recommended as a safe, non-corrosive green chemical, which can be used as an alternative to toxic chemicals such as phosgene and methylating agents.[41,42] Different catalytic processes were proposed in the recent literature for the synthesis of such organic carbonates directly by the reaction of CO_2, and methanol and ethanol.[41−44] Advantages of these processes include the chemical fixation of CO_2-using alcohols and producing highly valuable green chemicals.

$$2 \text{ CH}_3\text{OH} + CO_2 \rightarrow (CH_3O)_2CO + H_2O$$
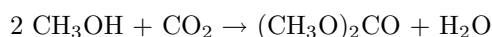
Some other novel processes involving supercritical CO_2 were also proposed for DMC synthesis[44,45] and for the chemical fixation of CO_2 during the cracking of heavy paraffins.[46]

CO_2 Capture by regenerable sorbents

For all the processes mentioned in the previous section, CO_2 capture from process and combustion gases is an important step. Pressure-swing adsorption, membrane applications, and wet scrubbing of process gases are some of the processes used for CO_2 removal. A number of new regenerable sorbents were proposed in the literature for high-temperature capture of CO_2 from process and fuel gases.[47−51] CO_2 captured at the source by chemisorption on such sorbents may then be recovered at much higher concentrations during the regeneration step of these sorbents. Among the sorbents proposed for the removal of CO_2, activated hydrotalcite-type clays have attracted the most attention in recent years.[48−51]

Hydrotalcite is a basic clay composed of positively charged brucite-like layers. Although there are different types of hydrotalcites, a typical composition of this clay is $Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$. It can be activated by calcining at a temperature over 550 °C by the removal of H_2O and CO_2. As reported in our recent work,[48] its surface area increased from 8.1 m^2/g to about 173 m^2/g, as a result of this calcination step. Breakthrough analysis of CO_2 capture by activated hydrotalcite showed that within the temperature range of 400-500 °C the CO_2 capture capacity of this sorbent was about 1.1 mmol/g. In the presence of water vapor, not much change was observed in the CO_2 sorption capacity of this sorbent.[48] Considering the presence of water vapor together with CO_2 in many of the process and fuel gases, this result is quite important. High activity of hydrotalcite for CO_2 removal in the presence of water vapor is also quite important for the sorption-enhanced reaction processes (SERP). Such a process is recommended to enhance hydrogen production by the reforming of natural gas coupled with the water gas shift reaction. In such a reactor, hydrogen production and carbon dioxide separation steps take place simultaneously in the same system, causing very high conversion levels as a result of the removal of CO_2 from the reaction medium and by shifting the reaction to the product side. In this manner, chemical equilibrium limitations can be overcome and higher conversions to hydrogen can be achieved. The hydrotalcite can then be regenerated to obtain concentrated CO_2 gas, which may then be used in the synthesis of alcohols and ethers.

Selective catalytic oxidation of ethanol and methanol

Recent studies on the selective catalytic oxidation of ethanol have focused on the production of acetaldehyde on vanadium-based oxide catalysts.[52−56] It is generally accepted that the reaction of oxidative dehydrogenation of ethanol over vanadium-based catalysts follows a redox mechanism.[52−54] The redox ability of vanadium to alternate between different valance states is the most important factor in such selective oxidation processes. The formation of ethoxy species was reported on the catalyst surface during this selective oxidation process.[53] The literature also shows that TiO_2-coated SiO_2 supports showed better performance than SiO_2-supported vanadium oxide catalysts.[55,56]

Our recent work[57] showed that very high yields of ethylene can be achieved by the selective oxidation of ethanol over vanadium-incorporated MCM-41-type mesoporous catalytic materials. Vanadium-incorporated silicate-structured mesoporous catalysts were prepared by a direct hydrothermal synthesis route as described in our recent publications.[57−59] The XRD patterns of these high surface area (over 1000 m^2/g) catalysts indicated the formation of the characteristic MCM-41 structure. As shown in Figure 4, a sharp increase in

ethanol conversion was reported over 300 °C. An increase in ethylene yield and a decrease in acetaldehyde yield were observed with an increase in temperature. An ethylene yield value of 0.66 reported at 400 °C with an O_2/ethanol feed ratio of 0.5 may open a new avenue for the production of ethylene from a non-petroleum feedstock, namely bio-ethanol. As was shown by Gucbilmez et al.,[57] the optimum catalyst activity was observed with a catalyst containing a V/Si ratio of 0.04 (Figure 5). Results showing that there was almost no ethylene formation in the absence of gas-phase oxygen proved the involvement of adsorbed oxygen in ethylene formation, while the formation of acetaldehyde was concluded to be due to the involvement of the lattice oxygen of the catalyst by a redox mechanism. Use of a copper-incorporated MCM-41-type mesoporous catalyst in the selective oxidation of ethanol was also illustrated by Velu et al.[60]

Partial oxidation of methanol over vanadian-based catalysts supported on mesoporous catalysts gave high yields of formaldehyde.[61,62] Results reported in the literature indicated that these catalysts were highly selective to produce formaldehyde and that the selectivity showed a decreasing trend with an increase in conversion.
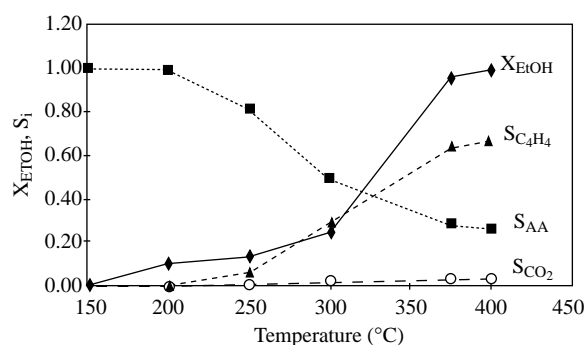

Figure 4. Ethanol conversion (X_{EtOH}) and product selectivity (S_i) values obtained using vanadium-incorporated MCM-41 with an O_2/EtOH feed ratio of 0.5.[57]
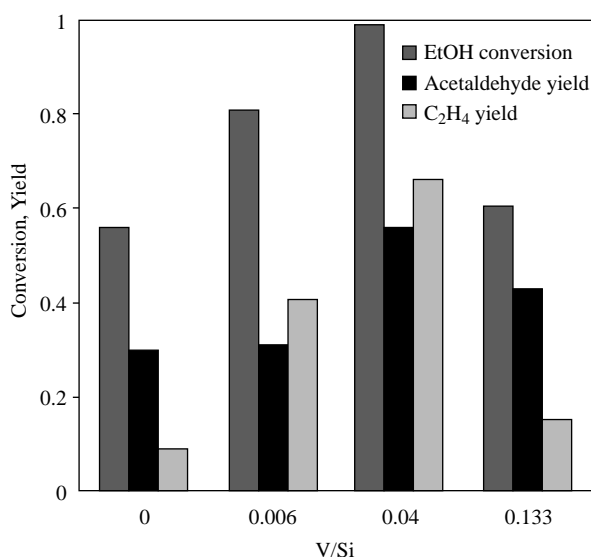

Figure 5. Ethanol fractional conversion, and acetaldehyde and ethylene yield values obtained with V-MCM-41-type catalysts containing different V/Si mole ratios (T = 400 °C; O_2/EtOH = 0.5 in the feed stream).[57]

Alcohols to hydrocarbons

Catalytic conversion of methanol to olefins and other hydrocarbons has attracted the attention of researchers, fuel producers, and the petrochemical industry during the last 2 decades. Details of the mechanism of methanol to hydrocarbon conversion reactions were reported in the review article by Stocker[63] and the process technology was reviewed by Keil.[64] It is generally thought that methanol was first dehydrated to dimethyl ether over solid acid catalysts and then DME was converted to light olefins and other hydrocarbons, including paraffins, higher olefins, aromatics, etc. As a result of the sorption of methanol on the catalyst surface, methoxy species are formed and these methoxy species react with methanol through a nucleophilic attack. ZSM5- and SAPO-type catalysts are generally used for the conversion of methanol to olefins.[65−69] The formation mechanism of a C-C bond on the catalyst surface is still debated in the literature[63,65] and a detailed review is given by Stocker.[63] The most popular catalyst used in methanol to hydrocarbon conversion is SAPO-34, which is a silicoaluminophosphate molecular sieve catalyst. Different researchers have tried to modify this type of catalyst by the incorporation of different metals into the catalyst structure. For instance, Ni-incorporated SAPO-34 was reported to yield 90% ethylene selectivity at 100% ethanol conversion[63] at 450 °C. Formation of a hydrocarbon pool of intermediate components in the porous structure of SAPO-type catalysts was proposed during the conversion of methanol to olefins.[70−71] In a recent article[72] up to 85%-90% ethylene plus propylene selectivity values were reported at near complete conversion of methanol in the UOP/Hydro MTO process.

Conversion of aqueous ethanol to hydrocarbons on H-ZSM5- and SAPO-34-type catalysts was also recently proposed.[73−75] Very high ethylene yields were also reported by the oxidative conversion of ethanol to ethylene over vanadium-incorporated silicate-structured catalysts in our recent work,[57] the details of which were discussed in the previous section.

Dehydration of alcohols to produce DME and DEE

The highly advantageous properties of DME, DEE, and DME/methanol and DEE/ethanol blends as alternative transportation fuels were discussed above. Onboard conversion of methanol to DME or ethanol to DEE using catalysts with an acidic character is a proposed technology for future motor vehicles.

$$2\ CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$

$$2\ C_2H_5OH \leftrightarrow C_2H_5OC_2H_5 + H_2O$$
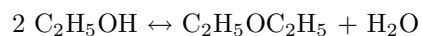
Acidic catalysts, such as nafion, Al_2O_3, and heteropolyacids, may be used for the dehydration of ethanol and methanol to DEE and DME, respectively. It was also reported that H-ZSM5 showed good activity for vapor phase dehydration of methanol to DME in the presence of water vapor.[76] The activities of Cs salt, and titania-supported molybdophosphoric and molybdovanadophosphoric acid catalysts in the dehydration of alcohols were also illustrated in the literature.[77,78] Generally speaking, acid catalysts show high activity in the dehydration of ethanol to DEE and ethylene, while basic catalysts act to dehydrogenate ethanol to produce acetaldehyde. In the dehydration reaction, alcohols are thought to adsorb on an acid site, forming ethoxy or methoxy species in DEE or DME synthesis, respectively. The work by Damyanova et al.[77] indicated that the incorporation of Ni into the heteropolyacid structure improved the dehydrogenation selectivity by decreasing the dehydration selectivity of methanol.

Our recent work[79] on the vapor phase dehydration of ethanol over different heteropolyacid catalysts showed that the activity trend of these catalysts followed silicotungstic acid (STA) > tungstophosphoric acid (TPA) > molybdophosphoric acid (MPA). The higher activity of STA was explained by the easier dehydration and higher stability of this catalyst than the other heteropolyacid catalysts, and by the higher number of protons of STA. A decrease in DEE selectivity and a corresponding increase in ethylene selectivity were observed with the heteropolyacid catalysts used in this work (Figure 6). Formation of ethylene was concluded to take place following parallel and consecutive routes with DEE. Although the presence of water vapor caused some decrease in catalyst activity, these catalysts were still highly active for the dehydration reaction of ethanol[79] in the presence of water. Dehydration of ethanol was also investigated using potassium and silver salts of tungstophosphoric acid catalysts,[80] and it was illustrated that catalytic activity is related to the acid protons and protons generated by dissociation of water molecules coordinated with silver cations.
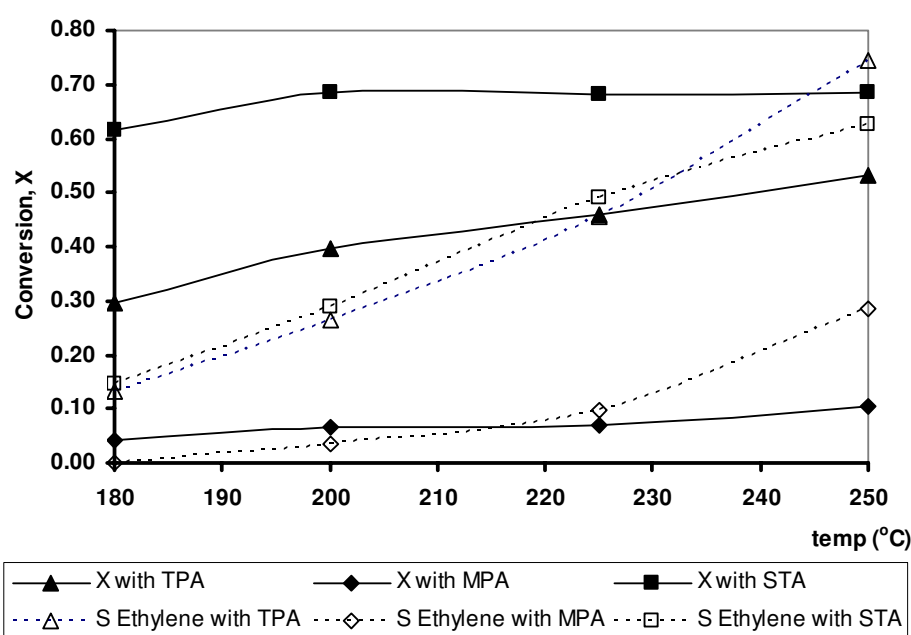

Figure 6. Ethanol conversion and DEE; ethylene selectivities over different heteropolyacid catalysts.[79]

Catalytic transformation of ethanol over vanadium/silicate molecular sieves indicated that the formation of acetaldehyde was mainly due to the involvement of vanadyl species (V=O), while DEE formation was due to the simultaneous involvement of vanadyl and V-O-Si species on the surface.[81] Similar conclusions were reached in our recent work on the selective oxidation of ethanol.[57] The mechanism of ethanol dehydration and dehydrogenation reactions was also discussed by Golay et al.[82] and Marin et al.[83]

Synthesis of tert-ethers (MTBE, ETBE, TAME, and TAEE)

As previously demonstrated at the beginning of this manuscript, tertiary ethers of methanol and ethanol have very high octane numbers, and they are recommended as octane-enhancing gasoline blending oxygenates (Table 2). Ethanol-based tert-ethers, such as ethyl tert-butyl ether (ETBE) and tert-amyl ethyl ether, have the advantages of higher octane numbers, lower vapor pressures, and lower water solubilities than MTBE and consequently they are considered more environmentally friendly octane-enhancing gasoline blending

compounds. These ethers are produced by the reaction of ethanol with isobutylene and isoamylenes (2-methyl-1-butene, 2M1B; and 2-methyl-2-butene, 2M2B) over acidic catalysts (Figure 7)
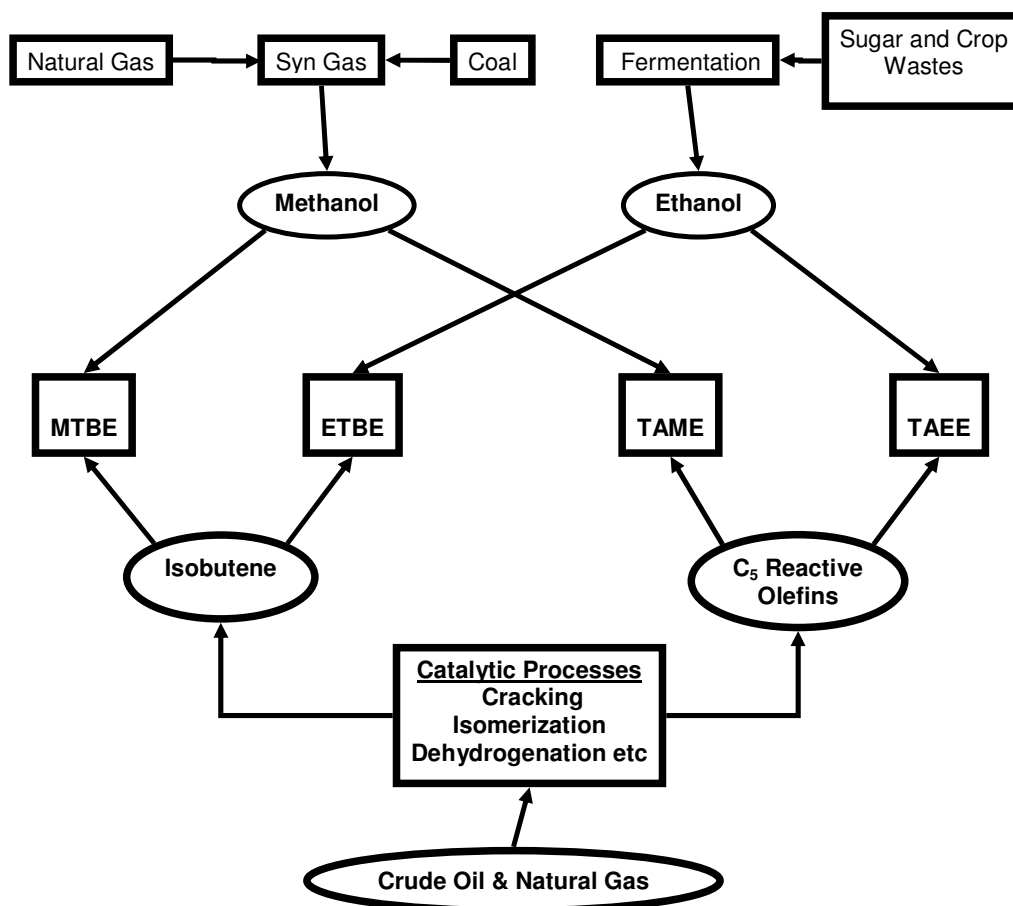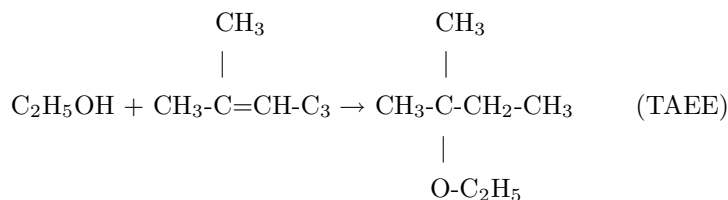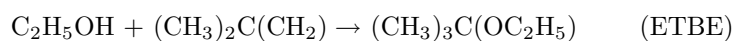
$$C_2H_5OH + (CH_3)_2C(CH_2) \rightarrow (CH_3)_3C(OC_2H_5) \qquad (ETBE)$$

$$C_2H_5OH + CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{C}\text{=}CH\text{-}C_3 \rightarrow CH_3\text{-}\underset{\underset{\displaystyle O\text{-}C_2H_5}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{-}CH_2\text{-}CH_3 \qquad (TAEE)$$

Figure 7. Tert-ethers of ethanol and methanol as octane-enhancing gasoline-blending molecules.

The presence of significant amounts of C_5 reactive olefins (isoamylenes) in FCC gasoline led to the idea of direct etherification of gasoline with ethanol to produce TAEE and consequently improve the burning and emission characteristics of the fuel.[11,84,85] Thermodynamic limitations in the synthesis of these ethers led to the idea of using multifunctional reactor systems, such as reactive distillation[13] and reflux-recycle-reactor,[14] for the production of TAEE, TAME, ETBE, etc.

Conventionally, acidic resin catalysts, such as Amberlyst-15, were used in the synthesis of these ethers. The hydrogen ion exchange capacities of these catalysts were shown to play a very significant role in their activity in the synthesis of such ethers.[86] As shown in Figure 8a, conversion of 2M2B to TAEE increases

linearly with an increase in the acid strength of the catalyst, while the conversion of more reactive C_5 iso-olefins, namely 2M1B, levels off at very high acid strengths (Figure 8b) due to the diffusion limitations in the resin catalyst at high reaction rates. The effects of diffusion limitations and the values of effective diffusion coefficients in such macroreticular resin catalysts were also investigated in our recent studies.[87,88]
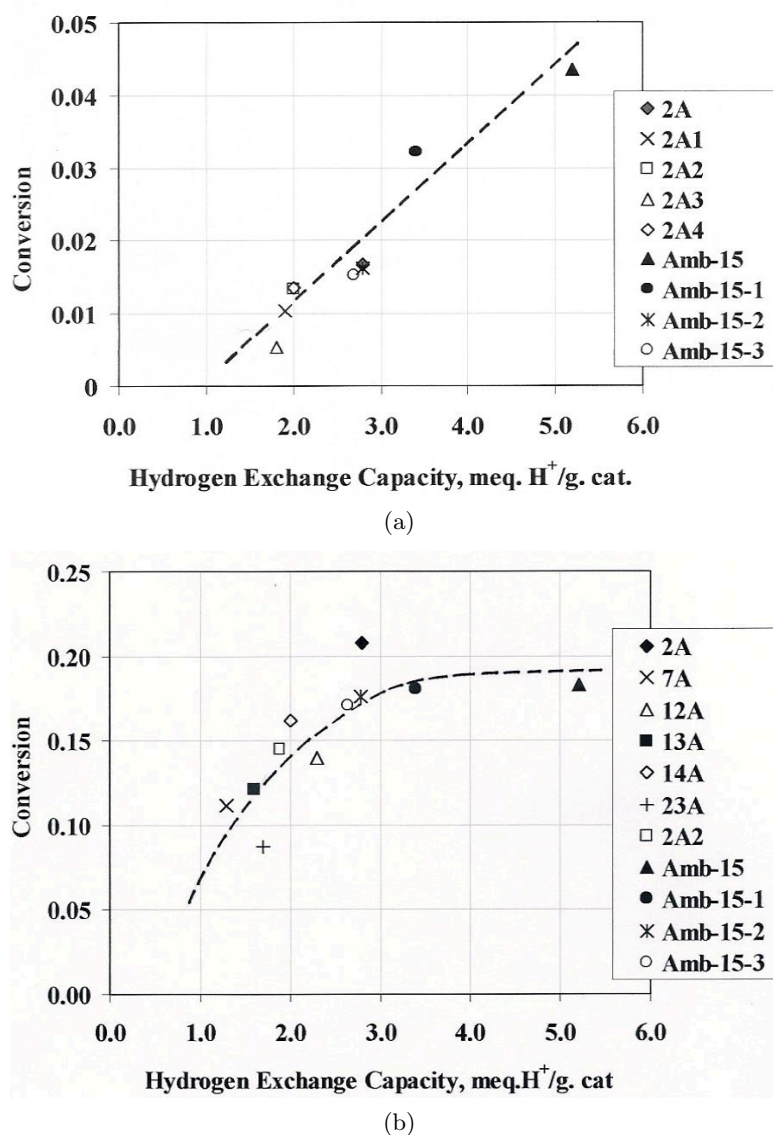

(a)

(b)

Figure 8. Conversion of 2M2B to TAEE (a) and 2M1B to TAEE (b) (T = 97 °C, 0.2 g Amberlyst-15, Q = 0.0158 cm^3/g liquid phase; inlet composition: 2.7% isoamylene in ethanol.[86]

Different reaction mechanisms are reported in the literature[89−92] for these etherification reactions. Recent diffuse reflectance FT-IR (DRIFTS) studies carried out during the reaction supported a Langmuir-Hinshelwood-type rate model involving adsorbed iso-olefin and alcohol molecules.[91,92] DRIFTS results showed that isoamylene molecules were adsorbed, forming a bridged structure between adsorbed alcohols and the –SO_3H sites of Amberlyst-15. Furthermore, the rate of TAEE formation was found to give a maximum at an ethanol activity of about 0.1.

Conclusions

Ethanol, methanol, DEE, DME, and their blends have highly attractive clean-burning characteristics, and are considered potential transportation fuel alternatives for both gasoline- and diesel fuel-powered motor vehicles. Development of new catalytic processes for the chemical fixation of CO_2 to produce alcohols, ethers, and other hydrocarbons may help reduce CO_2 emissions into the atmosphere and produce new feedstock for the synthesis of petrochemicals and fuels. Completion of the carbon cycle (Figure 9) by the synthesis of ethanol, methanol, and ethers may contribute to the solution of the 2 major problems of the next century, namely global warming and the depletion of oil reserves.

High yields of olefins obtained using novel catalytic processes by the selective oxidation and dehydration of alcohols have the potential to open new avenues for the production of petrochemicals from non-petroleum feedstock. Bio-ethanol, which can be produced by the fermentation of crop and sugar wastes, has the potential to be used widely in the coming decades, both for the synthesis of petrochemicals and for the formulation of new environmentally clean transportation fuels. Moreover, ethanol-based tertiary ethers, such as ETBE and TAEE, with their high octane numbers and low water solubilities, have very high potential to be used as gasoline-blending compounds.
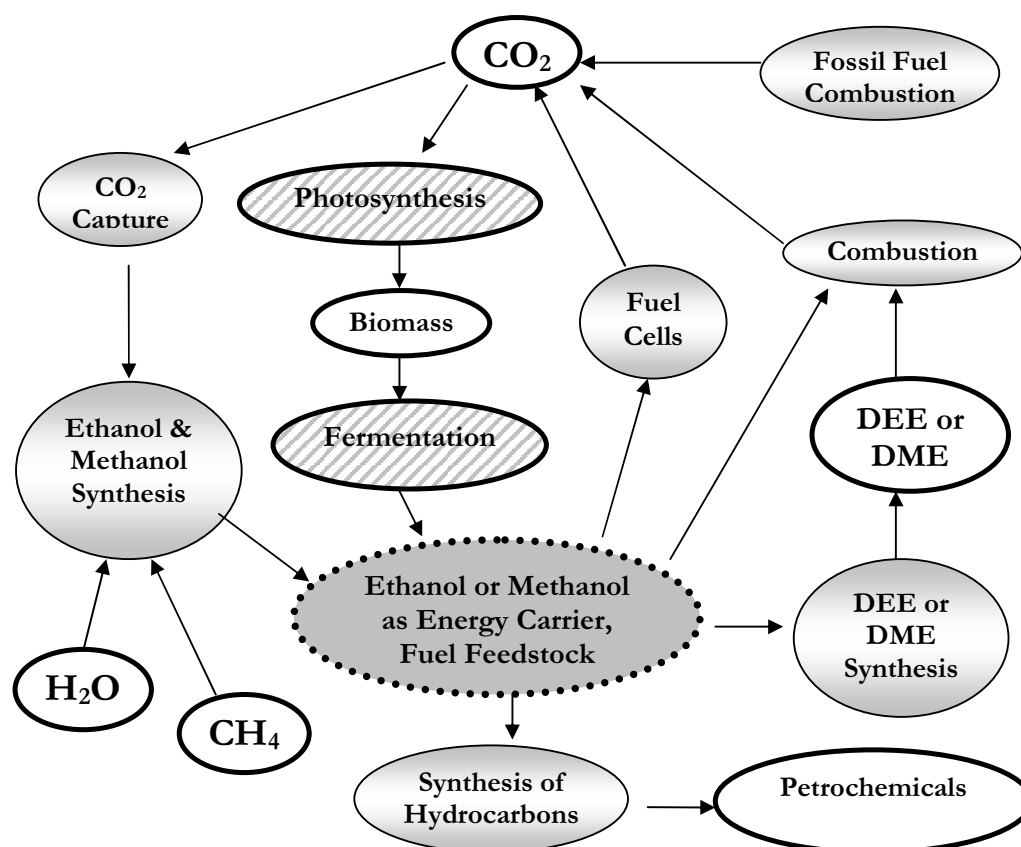

Figure 9. Carbon cycle based on ethanol and methanol.

All these potential alternatives for CO_2 fixation and conversion of alcohols to petrochemicals require the development of novel catalysts and catalytic processes.

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