HIGH PERFORMANCE OXYFUELS

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ABSTRACT

Alcohols and ethers are being used increasingly in gasoline blends because they provide economic octane enhancement (important because of phase-out of lead) and because they decrease CO levels in auto emissions. Gasoline containing oxygenates at the 2% O level is mandated in six metropolitan areas. Methyl-tertiary-butyl ether, (MTBE) and ethanol each constitutes 1% of overall U. S. gasoline usage. The criteria for synfuels are not cents per MM Btus but are based on their performance values.

Opportunities for improvements for conversion of syngas to oxygenates are catalysts which 1) have higher selectivity to molecular species useful as high performance fuels and which eliminate methane formation, 2) operate at lower temperatures and pressures, thus lowering plant costs, 3) integrate coal gasification and oxygenate synthesis, 4) improve fuel use.

Promising research includes catalytic concepts of dual functionality; controlled metal particle size; bimetallics, zeolites; organometallic precursors; enzymes; melt and slurry systems; catalysts design by expert systems (AI). Likewise, research on surface structure and reaction mechanisms is providing critical guidance in development of these concepts.

MOTIVATION FOR OXYFUELS

In the past, the principal tool for energy policy has been the market place. Recently however, social and political issues have become important in determining policy, particularly those which concern environmental protection and balance of trade/national security. Gasoline and diesel fuels manufactured from petroleum resources have been our traditional transportation fuels. However, importation of foreign oil has been rising rapidly and now

accounts for about 50% of our petroleum usage, contributing greatly to our 12 digit balance of trade deficit. Further, due in large part to automobile exhaust emissions, many parts of the US have major ozone problems and as many as 65 metropolitan areas have not attained federal CO standards (1).

Oxyfuels, particularly alcohols and ethers, can help alleviate these problems (2). Oxyfuels can be made from natural gas and from abundant coal resources. There are two immediate benefits from the use of oxyfuels. First, concern for the environment has let to the phase-out of lead in gasoline which has created a need for octane enhancement of the gasoline pool. Blending in oxyfuels can provide needed octane enhancement. Secondly, blending of oxygenates can lower CO emissions and reduce active hydrocarbon emissions which lead to ozone formation. Six metropolitan areas, Denver, Albuquerque, Los Angeles, Los Vegas, Phoenix, Reno and Tucson, require that gasoline contain oxygenates corresponding to 2% oxygen. This can be met by use of about 11% MTBE or 6% ethanol. Consideration is being given to increase requirements to about 3% O.

A further motivation for oxyfuels is provided by the Alternative Motor Fuels Act (PL 100- 494, 1988). This act gives American automobile companies a real incentive to start building cars powered by alternative fuels by adjusting the Federally mandated average fuel economy rating to reflect gasoline saved by those vehicles.

Because of their favorable performance in automobile use, oxyfuels are now valued, not on the basis of their heats of combustion, that is, cents per MM BTU, but on their values in contributing to environmental protection and octane enhancement. It is on the basis of their favorable performance that oxyfuels have a potentially large future. This future can be enhanced by improved technology for fuel manufacture an use. Improved technology has been the subject of intensive research, the main topic of this paper.

STATUS

Oxygenates of interest as fuels are shown in table 1 (2). Most are manufactured by a two step process. First, synthesis gas, a mixture of hydrogen and carbon oxides, is

made from methane, coal or petroleum fractions including residua. Then the synthesis gas is reacted over a catalyst which directs the hydrogenation of the carbon oxides to the desired products. These may be hydrocarbons as in SASOL, South Africa, or oxygenates, particularly methanol or mixed alcohols.

Fuel ethanol is produced by fermentation of corn or sugar cane. Isopropanol and sec-butyl alcohol are made by hydration of propylene and butylenes, respectively. Tert-butanol is a byproduct in the manufacture of propylene oxide. Fuel ethers are manufactured by reacting the appropriate alcohol with either isobutene or isopentene.

Oxygenates have penetrated the 300 million gallon per day motor fuel market in the U.S. to an increasing extent. At present, ethanol and MTBE each are being used to the extent of 3 million gallons per day. The growth in the use of MTBE has been phenomenal. The first MTBE plant was built in Italy in 1973. The growing U.S. manufacture and use is shown in table 2. Note that MTBE represents an indirect but straightforward method of using methanol in gasoline. MTBE is regarded as a more satisfactory method of using methanol in gasoline blends because of its better compatibility with gasoline compared with methanol.

Another recognition of the value of MTBE is seen in the action by ARCO to manufacture and distribute 'emission control gasoline', EC-1. This reformulated gasoline contains MTBE and is designated for use in autos which are not equipped with catalytic converters. EC-1 contains a minimum of 1% oxygen by weight.

IMPROVED TECHNOLOGY FOR OYXFUELS

There are significant opportunities for improvements in the manufacture of fuel oxygenates from syngas (3). Promising catalytic research results have been reviewed in a report (4) prepared for the International Energy Agency, sponsored in part by D.O.E. A variety of new concepts have been investigated with the aim of improved synthesis of fuel oxygenates. Included are: catalysts derived from alloys, catalyst designed by artificial intelligence, base catalysts systems, dual function catalysts, enzymes, hybrid catalysts, melt systems, multimetal components, organometallic precursors, partial poisoning, particle size

control, Raney metals, ship-in-a-bottle fabrication, and slurry systems.

The application of these catalytic concepts can provide four types of improvements:

I) Higher selectivity to molecular species useful as high performance fuels; elimination of methane formation.
II) Lower plant investment and operating costs.
III) Savings by integration of gasification and synthesis.
IV) Improved fuels use.

I IMPROVED SELECTIVITY

Mixed alcohols are desired as fuels because, when blended in gasoline, they raise octane ratings and also decrease CO emissions from autos. The distributions of alcohols for mixed-alcohol processes which have been developed are shown in table 3. It would be desirable for the synthesis reaction to provide a larger proportion of ethanol and less methane formation.

Particle size control of selectivity.

An interesting approach to selectivity control is through the use of control of the catalyst metal particle size. As shown in figure 1 (5), using Rh/SiO_2 catalysts, methanol is produced selectively at high Rh dispersion, while C_2 oxygenates are favored by larger particle size, for example 0.35 nm. Methane formation increases with decreased dispersion. The rationale for this catalysts structure/performance relationship can be understood on the basis of the concept that for formation of methane and higher alcohols, the catalysts must possess a multiplicity of sites, presumably neighboring, so as to accommodate simultaneous dissociative chemisorption of CO and of H_2. Larger ensembles of metal atoms are more likely to be able to provide these multisites than smaller crystallites and hence larger crystallites favor formation of methane and higher alcohols.

Multimetallic catalysts for selectivity control.

The impetus for research utilizing supported Rh catalysts can be traced to the discovery at Union Carbide that selectivity to ethanol can be improved by adding small amounts of modifying metals such as Fe (6). Recently, Arakawa and co-workers (7) have extended this research area

in a systematic way and have classified promoters of Rh-based catalysts according to those which increase or decrease metal dispersion, and those which accelerate CO dissociation. The suggested effects therefore on selectivity to oxygenate synthesis are depicted schematically in figure 2 (7).

Dual functionality for selectivity control.

The concept of dual function catalysts capable of balanced acceleration of two different types of chemical reactions has been used successfully, for example in naphtha reforming (8). Recently, dual functionality has been shown to operate in an important way in CO hydrogenation in which CO and H_2 are activated on separate but related catalytic sites. An important feature of the recognition of dual functionality is that it permits an understanding an consequent fabrication of catalysts of superior capabilities. Dual functionality is illustrated by recent research results obtained with molybdenum-containing catalysts containing added a) group VIII metal or b) alkali metal.

$Rh/Mo/Al_2O_3$. Supported Rh catalysts have been known to hydrogenate CO to oxygenates and, as mentioned above, selectivity can be increased by addition of small amounts of modifying metals. However, recently it has been discovered that the addition of large amounts of molybdena increases greatly activity for CO hydrogenation (9, 10, 11, 12, 13). Selectivity to oxygenates is also increased. Pertinent research results obtained at the University of Delaware are now discussed. A 3% Rh/Al_2O_3 catalysts was tested at 250° (all temperatures are °C) using a $H_2/CO=2$ mixture at 30 MPa. 28% of the CO was hydrogenated. However with the addition of 7.5% Mo (in oxide form), activity was increased 12-fold (same conversion at 36,000 GHSV). Selectivity to oxygenates increased to 66%.

The number of Rh sites active for CO activation were identified by CO chemisorption. It was found that CO chemisorption decreased from 112 micromoles per gram of the Rh/Al_2O_3 catalyst to 28 micromoles for a Rh/15% Mo/Al_2O_3 catalyst whilst activity for CO hydrogenation increased 38-fold. Thus activity per Rh site (identified by CO chemisorption) the turn-over frequency was increased 150-fold by the addition of the molybdena!

In other experiments (ethylene hydrogenation) it was established that CO inhibits the hydrogenation capability of Rh/Al_2O_3 catalyst but this inhibition does not occur with $Rh/Mo/Al_2O_3$ catalysts. Additional insight was gained from kinetic measurements. It was also found that CO inhibits CO hydrogenation capability of Rh/Al_2O_3 but not of $Rh/Mo/Al_2O_3$.

These and other characterization measurements have led to the concept that a dual site mechanism operates in which CO is activated by Rh metal and H_2 by Mo in a +5 or +4 oxidation state (12). a spill-over effect occurs (10) with activated H migrating to react with activated CO Fig. 3 (12). Increased activity is believed to be due to increased hydrogenation capability, previously limiting. An important feature is that H_2 activation occurs on Mo sites which are not inhibited by CO. CO inhibits H_2 chemisorption on Rh sites. The increased oxygenates and decreased methane formation are due to the increased hydrogenation of activated, undissociated CO.

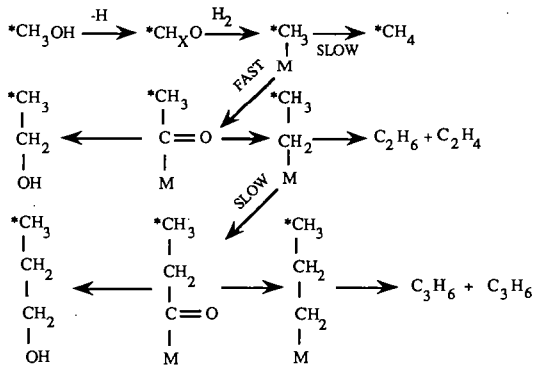
It was determined that the apparent Eactivation for methanol formation (18Kcal/mole) is much lower than that for methane formation (34 Kcal/mole). This also attests to the difference in mechanism for formation of these two C_1 chemicals. Differences in Eact for methane and methanol also provides for control of selectivity by operation at lower temperatures for higher selectivity to oxygenates (14).

The importance of these results is that they provide a guide for the design of better catalysts through an understanding of catalyst structure/performance. Of particular promise is the guidance provided in the search for the best Rh-Mo inter relationship, an opportunity highlighted by the 150-fold increase in activity per site. How to make more of these super-active sites!

<u>Alkali-MoS_2-Support.</u> Bifunctionality has also been identified for Mo-containing catalysts comprised of alkali-MoS_2-support that catalyze CO hydrogenation to oxygenates. It has been proposed (15) that CO is activated by the alkali and H_2 is dissociatively activated by MoS_2. Large

amounts of alkali are required. Cesium was found to be particularly effective.

Considerable understanding of the mechanism of CO hydrogenation was obtained by injecting ^{13}C enriched CH_3OH into the CO/H_2 reactant gas (15). It was shown that the CH_4 which is formed contained appreciable amounts of ^{13}C, indicating that methane synthesis could occur via intermediates derived from methanol. In the C_2-C_4 alcohols, there was preferential ^{13}C enrichment of the terminal carbons. This observation and related experiments led to the conclusion that the formation of ethanol occurred through CO insertion into a methyl intermediate bound to the surface to form an acyl precursor which can be hydrogenated to produce ethanol as shown below.



That the methyl intermediate is derived from an oxygenated species is clear since only the terminal carbon of ethanol is enriched. The mechanism of carbon chain growth to form C_3 and C_4 alcohols is reported to be similar to that of ethanol synthesis, that is, via CO insertion into a surface-bound alkyl.

It was also shown that the addition of cobalt to the alkali-MoS_2-support catalyst provided for C_1 to C_2 homologation step which leads to ethanol as the dominant product. The synthesis pattern over alkali/Co/MoS_2 catalysts that maximize ethanol are opposite to those

observed with Cs/Cu/ZnO catalysts which minimizes the formation of ethanol due to chain growth by rapid beta addition rather than CO insertion.

Mixed alcohols synthesis over MoS_2 catalysts, including those doubly promoted with alkali and group VIII metal, has been the subject of a substantial development effort. High yields of ethanol were demonstrated over $K/CoS/MoS_2$, table 3 (16). Of particular importance is the observation that homologation of alcohols occurs to a significant extent. This was taken as an explanation for the great deviation from the Anderson-Shulz-Flory distribution pattern (16). As pointed out, the commercial significance is that methanol, the lowest value alcohol in the mixed alcohol product, can be adjusted via recycle to any desired level and/or that inexpensive purchased methanol could be fed along with syngas dramatically increasing reactor productivity.

Isoalcohols/MTBE

It should be pointed out that higher alcohols synthesized over $Cu/ZnO/A_2O_3$ catalysts have a branched chain structure. Of the butanols synthesized in the Lurgi process, 70% are isobutanol (2-methyl-propanol) (no tertiary butanol). This has a number of implications. One is that the isobutanol can be dehydrated to form isobutylene which can then be reacted with the methanol to form MTBE. Thus, valuable MTBE can be synthesized entirely from syngas. Reactions for MTBE are given in Fig. 4. This suggests the possibility that through research a way could be devised to manufacture MTBE from syngas either in a single step or at least in fewer steps.

II LOWER PLANT COSTS

Although the conversion of syngas to methanol is highly selective, 99%, its manufacture can be improved by improving thermal efficiency and/or by reducing recycle and purification costs. This has led to engineering ideas for process improvements which could lower plant investment and operating costs.

Slurry catalysts. For instance, a major effort is underway to develop a liquid-phase methanol synthesis process in which catalyst particles are suspended in an inert liquid

medium. This system prevents excessive temperature increases and so permits higher syngas conversion per pass, reducing expensive recycle. The catalyst is also able to provide shift reaction in which CO reacts with water to produce H_2 and CO_2. This permits the use of less expensive syngas having lower H_2/CO ratios. The so-called LPMEOH process has been operated at 8 tons per day production rate and construction and operation of a commercial plant has been proposed (17).

Integrated Synthesis/Separation. A novel approach to circumvent thermodynamic equilibrium limitations to CO hydrogenation is to remove methanol from the reactor as it is formed (18). A trickle flow principle has been demonstrated in which synthesis catalyst pellets form a stationary bed and solid adsorbent trickles downward over (through) the packed bed. This Gas-Solid-Solid-Trickle-Flow-Reactor has been demonstrated; synthesis conversion proceeds to complete conversion.

Ultra high-activity catalysts.

Alloys. A still different approach is to search for catalysts so active that CO hydrogenation can be carried out at much lower temperatures, say 175°, than is used conventionally, about 250°. Perhaps the research on dual function catalysts can lead to such a catalysts. Catalysts derived from an intermetallic copper/Thx alloy precursor have been discovered by researchers at the BuMines at Reno (19) to exhibit extraordinary high activity for methanol synthesis by CO hydrogenation. Workers at ICI (20) extended this discovery and demonstrated that a catalyst derived from CuCe0.5 precursor is active for synthesis as low as 100°. Moreover, a stable activity of 25 moles of methanol per Kg catalyst per hour was obtained. However, this catalyst is irreversibly deactivated by small amounts of CO_2 in the syngas. This presents a challenge to understand the reaction mechanism and to utilize this discovery in practical process technology.

Base catalysts. An entirely different liquid phase catalytic system for methanol manufacture involves the reaction of CO with a strong base such as sodium methoxide. As shown in the following equations, methyl formate can be prepared, followed by catalytic hydrogenation of the methyl formate to methanol.

$$CH_3OH + CO \xrightarrow{NaOCH_3} HCOOCH_3, + 2H_2 \xrightarrow{\text{Cu catalysts}} 2CH_3OH,$$

$$CO + 2H_2 \longrightarrow CH_3OH$$

The synthesis reaction is carried out at 80° and 3 MPa, whilst the hydrogenation is operated at 110-180°. To be economic, it is deemed essential that the synthesis and hydrogenolysis be combined. Thus, a hydrogenation catalyst which is active at a lower temperature is needed. Some success has been obtained using highly active Raney copper (21).

A 1984 report (22) by scientists at Brookhaven describes a novel approach to methanol synthesis. Two catalyst components are in the liquid phase, a metal (molybdenum) carbonyl that activates CO and a hydride that hydrogenates the carbonyl to methanol and is regenerated by reaction with hydrogen. A further improvement was reported in which synthesis temperature of 100° were used indicating extraordinary activities for methanol synthesis. Technical information has not been made public.

III INTEGRATED GASIFICATION-OXYFUEL SYNTHESIS: IG-OS

The objective of IG-OS is the conversion of the crude hydrocarbon feed stocks to oxygenates in one step or at least, without separation, in one reactor. This may or may not involve the intermediate production of CO and H_2. Intensive research efforts are underway to convert methane by direct oxidation to alcohols or to ethylene which can be hydrated to ethanol. It is proposed that the direct conversion of coal to oxygenates may also be possible. Related to this concept is the observation that methane formation occurred in the Synthane process of coal gasification. This led to the suggestion of IGHS, integrated gasification/hydrocarbon synthesis (23). Actually it has been demonstrated that by the addition of a nickel catalyst during coal gasification, a considerable amount of methane can be synthesized. However, the nickel catalyst became deactivated by sulfur. Coal gasification

usually occurs at temperatures above 800°. However, the gasification temperature can be lowered by the use of alkali catalysts. The synthesis of methanol occurs usually at 250° and for higher alcohols temperatures of 350° + can be used. For integrated coal gasification/oxygenate synthesis it will be necessary to develop combination catalytic systems which perform gasification and oxysynthesis at the same temperature. The combination catalyst system may include capability for oxidation, steam/carbon reaction and synthesis. The synthesis catalyst must be sulfur stable, not believed to be impossible considering the success of MoS_2 catalysts in alcohol synthesis.

IV CATALYSTS FOR IMPROVED FUEL USE

The value of a fuel should be judged in terms of effectiveness in the system: fuel manufacture/fuel use. Catalysis can contribute to more efficient use of oxyfuels. Syngas can be made available as a fuel by the catalytic decomposition of methanol or by catalytic reaction of methanol with steam. There is a gain in fuel efficiency if waste heat is used to carry out the endothermic conversion of methanol to syngas fuel. When waste exhaust heat is used (available on-board an auto or power plant) a gain in efficiency of 15-20% is predicted to be possible (24) although in actual tests fuel consumption benefits have been lower.

Catalysts for improved diesel fuel use is also possible. Diesel engines are more efficient because of the high compression ratio at which they operate. However, use of hydrocarbon diesel fuels is recognized as causing pollution, a situation which could be improved by the use of methanol. However, the combustion characteristics of heat methanol are not favorable for diesel (non-spark plug) use. The use of an additive such as AVOCET - termed a "chemical spark plug" - is being developed (25). An additional opportunity would be to develop in-cylinder catalysts which would provide for favorable methanol combustion under diesel conditions.

Finally, it should be said that many believe that methanol will become a major fuel not only as an alternative for diesel, but also for gasoline as well. This is being recognized in two recent events. The first is the

marketing in California by Arco and Chevron of M-85 which contains 85% methanol. The second is the extensive testing being carried out with flexible fuel vehicles, FFV, which can operate on gasoline, methanol or any combination of these (2).

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Table 1. FUEL OXYGENATES PROPERTIES

	METHANOL	ETHANOL	ISOPROPYL ALCOHOL	SECONDARY BUTYL ALCOHOL	TERTIARY BUTYL ALCOHOL	MIXED ALCOHOLS	MTBE METHYLTERTIARYBUTYL ETHER	ETBE ETHYLTERTIARYBUTYL ETHER	TAME TERTIARYAMYLMETHYL ETHER	GASOLINE
	MeOH	EtOH	IPA	SBA	TBA	MAS*	MTBE	ETBE	TAME	GASO
Blending Octane $\frac{RON + MON}{2}$	101	101	106	99	100	106	108	111	102	87
Heat of Combustion Thousands BTU's Per Gallon	64.5	76.5	94.6	101.4	101.1		108.5	116.5	111.9	124.8
Density	0.79	0.79	0.79	0.80	0.80	0.80	0.75	0.74	0.77	0.74
Pounds Per Gallon	6.6	6.6	6.6	6.8	6.8	6.7	6.3	6.2	6.4	6.2
Boiling Point Degrees C	64.6	78.5	82.4	99.5	82.6	range	55.4	72.8	86.3	range
Production In USA, 1987 Millions of Gallons/Day	3.0	2.9	0.6				2.8			300

Fuels of 0.79 density weigh 6.6 pounds per gallon, 277 pounds per barrel of 42 US gallons; 1 ton contains 7.2 barrels or 303 gallons.

Table 2. U.S. production of MTBE and methanol consumption for MTBE millions of gallons per year

Year	MTBE	Methanol
1982	190	65
1983	250	85
1984	370	130
1985	430	150
1986	830	290
1987	1030	360
* 1989	1530	534
** 1989	2010	700

* Capacity
** Capacity + planned

Table 3. Composition of fuel alcohols from syngas

Alcohol, %	C_1	C_2	C_3	C_4	C_{5+}	Other oxygenates	Catalyst
MAS (SEHT)	69	3	4	13	9	2	K/Zn/Cr
Substifuel (IFP)	64	25	6	2	2.5	0.5	K/Cu/Co/Al
Octamix (Lurgi)	62	7	4	8	19	--	alkali/ Cu/Zn/Cr
AS (Dow)	26[a]	48	14	3.5	0.5	8	CoS/MoS_2/ K

[a] Methanol can be recycled to extinction, increasing ethanol %.

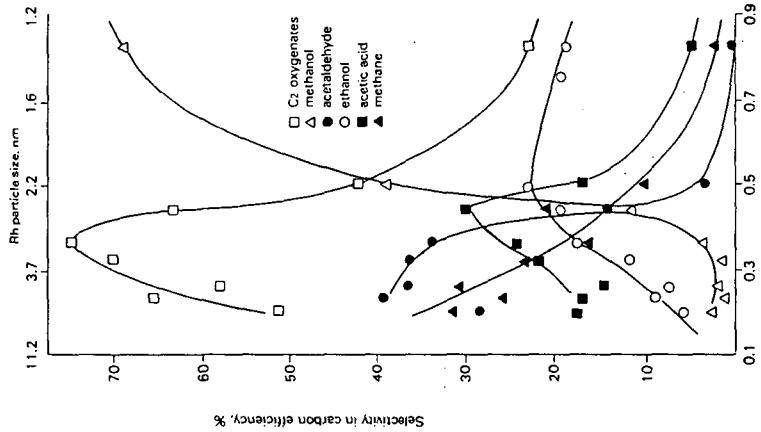

Figure 1. Relationship between dispersion and selectivity

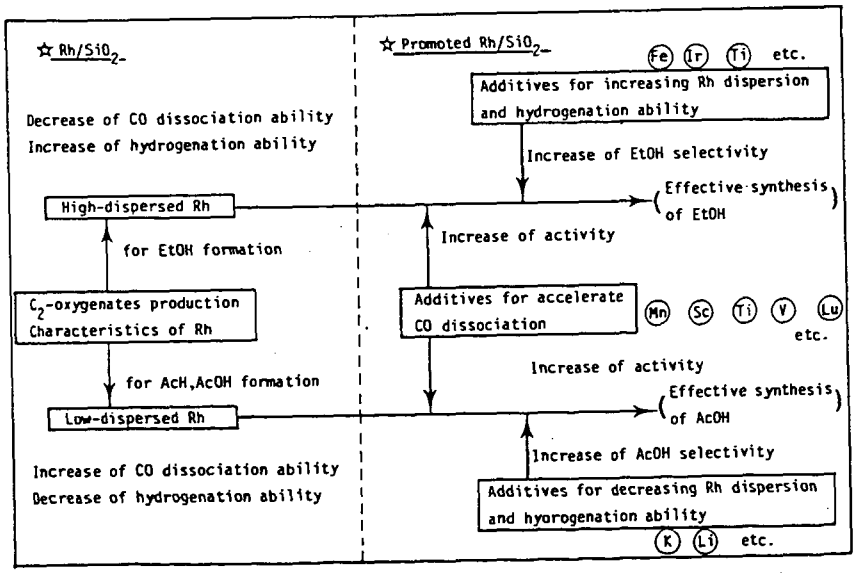

Figure 2. The roles of additives for effective synthesis of EtOH and AcOH.

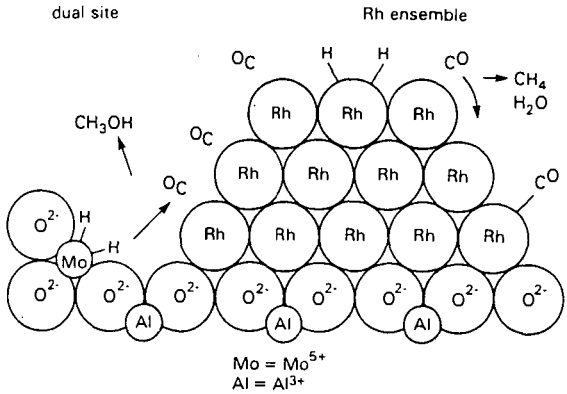

Figure 3. Proposed structure/reactivity scheme, rhodium-molybdena-alumina catalyst

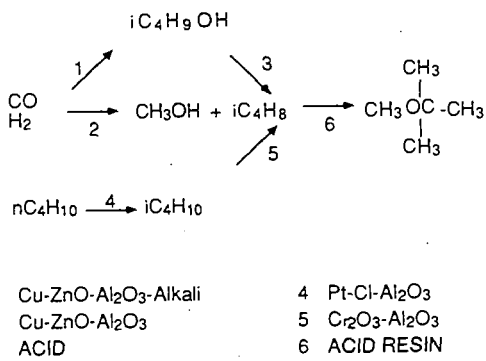

Figure 4. Synthesis of Methyl-tertiary-butyl ether, MTBE