IV. CURRENT COMMERCIAL CATALYST MARKET

In this section, the current usage patterns of the major catalytic metals are considered. It should be noted that some catalyst metals, particularly cobalt, iridium, and paladium, are used extensively in metallurgical and other noncatalytic applications. The market factors affecting precious metal consumption are also considered.

A. Industrial Heterogeneous Catalysts and Metals[197-208]

The U.S. and the world catalyst markets have grown and will continue to grow because of: (1) increasing energy demand requirements; (2) the trend in petroleum refining towards the processing of heavier feedstocks, which drastically shorten catalyst life through coke formation and heavy metals contamination, which in turn cause deactivation of the catalyst; and (3) stiff environmental regulations which require a higher degree of removal of sulfur and nitrogen from feedstocks and stack gases.

Current catalyst consumption in the United States and the expected rate of growth over the next 5 years are summarized in Table 10 for the auto, chemical, and oil-refining industries. The demand for catalysts in the auto industry is relatively new, and this market is expected to be influenced by future directions in exhaust emission regulations, especially the demand for the precious metals used in catalytic converters. This has the potential of increasing consumption of the same catalyst metals used in petroleum refining.

TABLE 10

VALUE OF CATALYSTS USED IN THE UNITED STATES IN 1980 AND THE EXPECTED FUTURE INCREASE

Process	Consumption in 1980 (millions of dollars)	Expected Percent Average Annual Increase (1980-1986)
Auto Converter	348.0	6
Petroleum Refinery	1,004.0	3
Chemical Production	356.0	4
Coal Conversion	0.2	7
	1,708.2	

Source: U.S. Bureau of Mines statistics (1980-1982).

In oil refining, the most heavily used catalysts of all are those used in hydrotreating. The main function of these catalysts is to remove heteroatoms such as sulfur and nitrogen. Cobalt-molybdenum catalysts are the most popular, but some other metal combinations such as nickel-molybdenum, nickel-tungsten, and tungsten-molybdenum may have similar capability. The cobalt-molybdenum catalysts have been the most popular even though they are more expensive than the others. Figure 20 shows the current distribution of cobalt consumption in the United States, where it is a highly critical and strategic metal.[3]

B. Precious Metal Catalysts and Their Consumption

Demand for the platinum group, lanthanide, and actinide metals has increased in the catalyst market for two reasons: (1) precious metal catalysts have higher selectivity for specific products, and (2) they have a longer life because they are more resistant to catalyst poisoning. As shown in Figure 21, consumption of these metals in catalysts and in chemical production constitutes the major part of the market.

The current trend and the near term expected changes in the consumption of four platinum metals--platinum, palladium, rhodium, and iridium-are shown in Figure 22 for three major markets: petroleum refining, the chemical industry, and the auto industry. The instability of the platinum metal market can be attributed to several factors, such as world price fluctuations, improvement in ore recovery technology, consumption in new products, stockpiling, and speculation. The development of reclamation technology for waste catalysts would be expected to have a stabilizing effect on the precious metals market.

V. ALTERNATIVE CATALYSTS

From the material presented in earlier sections of this report, it can be seen that the most common catalytic metals expected to be used in the manufacture of substitute or synthetic fuels will be molybdenum, cobalt, nickel, tungsten, iron, and minor amounts of chromium and copper. Of these, cobalt, nickel, tungsten, and chromium are critical materials. The quest for alternative catalysts has moved in two directions: (1) replacement of critical materials with noncritical materials, and (2) development of efforts to improve reactivity and lengthen service life to reduce net catalyst consumption.

The Catalytica group[209,210] reviewed the reactivity and selectivity of catalytic materials and classified catalyst materials for coal conversion reactions; a summary of their work is shown in Table 11. In addition to metal type, catalyst reactivity and service life, choice of substrate, surface area, pore structure, and preparation procedure are important parameters.

A. Direct Coal Liquefaction Catalysts[211-213]

Boudart et al.,[209] reviewed and classified catalytic materials with respect to particular capabilities and attributes; the results of their work are summarized in Table 12. Among the materials shown, the oxides, sulfides, and solid acids of Co, Mo, Ni, W, Al, and SiO_2, as well as molten salts of Zn, Na, Fe, K, etc., have been studied extensively. The vast majority of direct coal liquefaction catalyst studies have focused on combinations of the oxides or sulfides of Co, Mo, Ni, and W, especially the well-known cobalt-molybdenum catalysts.

A number of studies have been reported in which cobalt-molybdenum, nickel-molybdenum, and molybdenum catalysts were compared for their effectiveness in direct coal liquefaction. Berry et al.[211] concluded that nickel-molybdenum was superior to other catalysts. In testing commercial catalysts for the H-coal process, Amoco found Amocat 1A (a cobalt-molybdenum catalyst) and SN 4475 (a nickel-molbydenum catalyst) were better than 1442 A (a cobalt-molybdenum catalyst), the designated catalyst for the process.[214] They also concluded cobalt may not be essential to the process.

This was confirmed by Thomas et al.,[213] who tested five catalysts in the H-coal bench-scale reactor with Illinois No. 6 coal in 10-day tests. The results of their work are summarized in Table 13. From the data it can been seen that a sample molybdenum catalyst (Amocat 18) functioned as well as molybdenum combined with nickel or cobalt. Clearly, direct liquefaction processes can be operated without critical or strategic metals with no significant change in the quality and type of products obtained. There are, however, some unresolved questions regarding catalyst stability and service life.

TABLE 11

EXAMPLES OF METAL-CATALYZED COAL CONVERSION REACTIONS

Reaction	Typical Catalyst Metals	High Activity Metals
Hydrogenation		
Aromatics	Group VIII, Mo, W, Re	Pt, Rh, Pd
CO	Group VIII, Cu	Ru, Fe, Ni, Co
CO_2	Co, Fe, Ni, Ru	Ru, Ni
Dehydrogenation	Group VIII	Pt, Pd
Dehydrogenation	Pt, Pd, Ir, Rh, Ru	Pt, Ir
Hydrogenolysis		
C-C bonds	Group VIII, Re, W, Mo	Ru, Ir, Ni
C-N bonds	Group VIII, Re, W, Mo, Cu	Ni, Pt, Pd
C-O bonds	Group VIII, Re, W, Mo, Cu, Ag	Pt, Pd
C-S bonds	Group VIII, Re, W, Mo, Cu, Ag	Pt, Pd, Rh
Isomerization		
Double Bond Shift	Group VIII	Pd, Pt
Skeletal	Pt, Ir, Pd, Au	Pt
Water-Gas Shift	Group VIII, Cu, Ag	Pt, Rh, Fe

Source: Boudart, M., J. A. Cusumano, and R. B. Levy, "New Catalytic Materials for the Liquefaction of Coal," EPRI 415, Final Rep., EPRI, 1975.

TABLE 12

CLASSIFIED CATALYTIC MATERIALS

Material	Example	Research Priority[a]	Advantage
Oxides	Simple: Al_2O_3, CoO, Cr_2O_3 Complex: $MgAl_2O_3$, $FeTiO_3$, $CuCrO_2$, $BaTiO_3$	High	Thermally and chemically stable; use as supports HDS ability with partial sulfidation Versatility with structures and stoichiometrics Oxidative regeneration possible
Solid Acids	TiO_2, SiO_2, ZrO_2, SiO_2, Zeolites, natural clays (montmorillonite), super acids (SbF_5/HF), supported halides ($AlCl_3/Al_2O_3$)	High	Extensive range of cracking activity Facilitates sulfur and nickel removal Thermally stable Controlled physical properties Oxidative regeneration possible
Solid Bases	CaO, MgO, $NaNH_2$, BaO, K_2O, Na_2O	Low	Not poisoned by H_2O, N, and S compounds Thermally stable Controlled physical properties Oxidative regeneration possible
Sulfides	Simple: VS, V_5S_8, MoS_2 Complex: CoV_2S_4, $SrZrS_3$, $Al_{0.5}Mo_2S_4$	High	Proven HDS and hydrogenation activity Versatility in complex sulfide formation Stable in H_2S Thermally stable
Carbides Nitrides	WC, Pt_3ZnC Fe_2N, Ni_3N_2, Ni_3AlN	Medium	Show some cracking, isomerization, and hydrogenation activity Thermally stable
Borides Silicides Phosphides	Ni_3B, FeB, ZrB_{12} TiSi, RhSi, $TaSi_2$ MnP, NiP, TaP_2	Medium	Thermal stability Possible chemical stability in H_2S (Group VIII) Show some hydrogenation-hydrogenolysis activity (borides)

(continued)

TABLE 12 (Concluded)

Material	Example	Research Priority[a]	Advantage
Metals and Multimetallics	NiCu, PtAu, NiW, RuCu, Cu_3Au, $ZrPt_3$	LOw	Preparable in high surface area Hydrogenation/hydrogenolysis activity
Molten Salts	$ZnCl_2$, Na_2CO_3	Medium	Cracking activity Effective contacting with coal Good heat transfer
Homogeneous Catalysts	$Co_2(CO)_8$, $RhCOCl_2$	Low	Catalyst/coal contacting very effective Possibly tolerant of sulfur and nickel compounds if catalyst doesn't degrade Controlled hydrogenation activity and selectivity (minimize H_2 consumption)
Anchored Catalysts	$SiO_2/OSi(C_2H_4)(Ph_2P)RhCl(CO)_2$	Low	Catalytic activity and selectivity of homogeneous catalysts retained

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[a] Priority H = High
M = Medium
L = Low

Source: Boudart, M., J. A. Cusumano, and R. B. Levy, "New Catalytic Materials for the Liquefaction of Coal," EPRI 415, Final Rep. EPRI (1975).

TABLE 13

PERFORMANCE OF FIVE COMMERCIAL COAL LIQUEFACTION CATALYSTS

	Weight Percent				
Catalyst	Metal Composition (% metal)	Conversion (MAF[a] Coal)	Sulfur in Resid Oil	C_4-975°F	Resid Oil
American Cyanamid 1442A CoMo	Co 2.8 Mo 15.6	93.7	0.46	40.1	24.6
American Cyanamid 4475 NiMo	Ni 2.5 Mo 15.4	94.2	0.41	42.9	22.1
Armak NiMo	Ni 1.6 Mo 15.0	93.9	0.42	42.4	22.0
Amocat 1A CoMo	Co 4.0 Mo 14.5	94.5	0.45	43.0	23.0
Amocat 1B Mo	Mo 10.6	94.0	0.35	41.9	22.0

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[a] MAF = Moisture and ash free basis.

The platinum and rare earth metals have been considered as promoters for direct liquefaction catalysts. Hinden[215] investigated the effects of these metals on the performance of cobalt-molybdenum catalysts. The results of his studies are summarized in Table 14, in which the coal conversion, distribution of liquid products between asphaltenes and oils, and the sulfur content of the asphaltene and oil fractions are compared. Hinden also explored the effect of catalyst support material using cobalt and molybdenum levels of 3 and 15% by weight, respectively. The results of this phase of his investigation are summarized in Table 15. From the data, it can be seen that choice of substrate can have a significant effect on the performance of a catalyst, with alumina being the best all around choice.

From Table 14, it can be seen that ruthenium, zinc, cerium and barium oxides, potassium chloride, and platinum and rhenium metal all had a positive effect on coal conversion that was attended by an increase in asphaltene yield and a decrease in oil yield. In the same study, tin, nickel, zirconium, copper, lead, phosphorus, iron, boron, cadmium, and germanium were found to have a negative effect. The maximum effect of support composition was an approximately 10% reduction in conversion level. From Table 16, the effect of rhenium metal as a promoter was greater than the effects of the oxides or sulfides of rhenium.

TABLE 14

METAL ADDITIVES EFFECT ON COBALT-MOLYBDENUM CATALYST[a]

Catalyst[a]	Additive[b]	Conv. (%)	Yield (%) Asph.	Yield (%) Oil	Sulfur (%) Asph.	Sulfur (%) Oil
HDS1442A	-	77.0	23.8	51.8	0.85	0.41
RuCoMo/	Ru (0.5)	79.8	27.5	45.6	0.84	0.44
ZnCoMo/	ZnO (5)	81.3	23.6	43.4	0.77	0.54
Ce/Al_2O_3 - CoMo/Al_2O_3	$CeO_2Al_2O_3$(5)	83.4	31.1	47.7	0.77	0.34
CoMo/Al_2O_3 Med. Pore	-	85.7	33.2	43.1	0.80	0.30
BaCoMo/Al_2O_3	BaO (1)	81.5	29.4	44.0	0.81	0.46
KClCoMo/Al_2O_3	KCl (5)	80.5	27.6	47.2	1.00	0.65
ReCoMo/Al_2O_3	Re (0.5)	82.5	29.0	54.5	0.80	0.34
PtCoMo/Al_2O_3	Pt (0.5)	82.6	29.2	46.9	0.77	0.37

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[a] 3% CoO-15% MoO_3.

[b] Other additives such as Sn, Ni, Zr, Cu, Pb, P, Fe, B, Cd, and Ge showed lower reactivity than HDS 1442A catalyst.

Source: Hinden, S. G., "Catalyst Development for Coal Liquefaction," Final Rep. FE-76-C-01-2335-32, NTIS, 1979.

TABLE 15

EFFECT OF SUPPORT COMPOSITION

Catalyst Support[a]	Conv. (%)
Al_2O_3	77.0
$LaSiAl_2O_3$	78.3
$LaZrAl_2O_3$	77.4
$BaZrAl_2O_3$	75.8
ZrO_2SiO_2	75.3
$CaOAl_2O_3$	69.3
$ZnOAl_2O_3$	71.9
$LaCrAl_2O_3$	72.5

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[a] All catalysts: 3% Co, 15% Mo O_3.

Source: Hinden, S. G., "Catalyst Development for Coal Liquefaction," Final Rep. FE-76-C-01-2335-32, NTIS, 1979.

TABLE 16

EVALUATION OF RHENIUM CATALYSTS[a]

Catalyst		Conversion (%)
$Co(ReO_4)_2/Al_2O_3$		76.6
$Co(ReO_4)_2/Al_2O_3$	med pore	78.0
Re_2S_7/Al_2O_3	med pore	78.5
$ReCoMo/Al_2O_3$	med pore	81.8

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[a] 5% Re on all catalysts.

Source: Hinden, S. G., "Catalyst Development for Coal Liquefaction," Final Rep. FE-76-C-01-2335-32, NTIS, 1979.

Alternate catalysts for direct coal liquefaction, then, can be a simple molybdenum catalyst or promoted metal systems. The use of molybdenum is attractive because no other metals are used. The more complex promoted catalysts may be more effective, but an economical reclamation technology would be needed to maintain the supply of catalyst metals. At a petroleum replacement level of 6 million barrels per day, the greatest leverage in cobalt and nickel savings would be obtained by the use of molybdenum alone in the H-Coal process. This leverage would decrease, for specific processes, approximately in the order Conoco>Mobil MTE>Fischer Tropsch> C E lummus two stage liquefaction.

B. Alternate Indirect Liquefaction Catalysts

Indirect liquefaction is a special case of well-known technology for manufacturing alcohols, aldehydes, methanol, and other chemicals from synthesis gas, the feedstock for indirect coal liquefaction. In addition, Sasol has been manufacturing transportation fuels from coal for more than 20 years; the Sasol catalysts are not strongly selective but produce a spectrum of products. The work-horse catalysts are iron oxide on alumina supports or fused iron and, as such, do not use critical metals. Various promotors such as potassium to favor olefin production have been reported.[216,217] Overall, a wide range of Fischer-Tropsch catalysts are commercially available which do not use critical materials; thus, there would be no constraints on future availability.

The MTG process developed by Mobil for producing gasoline from methanol is the most recent innovation in indirect liquefaction technology. The process is accomplished in two steps; in the first, the methanol is converted to dimethyl ether; and in the second, the dimethyl ether is converted to gasoline over Mobil's proprietary catalyst ZSM-5. Very little information has been published on the composition of this catalyst. Originally, the methanol synthesis was carried out at high pressure using a zinc oxide-chromia catalyst; in commercial operation, this has been replaced with a copper-zinc oxide catalyst which allows the synthesis to be carried out at lower pressure.

C. Methanation Catalysts

As with catalysts for direct liquefaction, development of alternate methanation catalysts has proceeded in two directions: (1) development of sulfur resistant catalysts which do not use nickel or other critical material, and (2) development of highly reactive promoted nickel catalysts. There is considerable interest in combining the water gas shift and methanation steps into a single step.

Vannice found the methanation reactivity per unit surface area for various metals to be in the order Ru>Fe>Ni>Co>Rh>Pd>Pt>Ir.[218] Iron is attractive as an alternative methanation catalyst because it is more reactive than nickel, and it is less expensive. It is, however, difficult to prepare stable forms of iron having high surface area, and such catalysts would be susceptible to sulfur poisoning.

There have been efforts to develop sulfur resistant catalysts capable of performing in a single reactor combining the water-gas shift and methanation reactions. A program sponsored by GRI employs a cerium molybdenum-aluminum system;[219,220] and in a program at Brookhaven National Laboratories, an iron-titanium catalyst is being investigated.[221]

Finally, an iridium promoted nickel on alumina catalyst is being tested at Stanford Research Institute.[222] All these investigations have been on a scale too small to permit estimation of consumption on a commercial scale. Thus, there are some prospective alternative catalysts but they have yet to be demonstrated on a large scale of operation.

D. Tar Sands and Heavy Oils

The chief loss of catalyst in upgrading tar sands and heavy oils is caused by deposition of the heavy metals in the feed on the catalyst. Zeolite catalysts are more tolerant of heavy metals than are other catalysts and might be used where primary upgrading by hydrotreating rather than coking is desired. Cobalt/molybdenum and nickel/molybdenum catalysts are used primarily to reduce sulfur and nitrogen levels while zeolite catalysts are used in hydrocracking heavy oils; hence the use of zeolites would be expected to produce lighter products with less change in nitrogen and sulfur levels. An antimony-based passivation system developed by Phillips Petroleum could also be used.[223] In this system an oil soluble antimony compound is mixed with the feed; the antimony compound passivates the heavy metals and prevents their deposition on the catalyst.

In the Demet III process developed by the Sinclair Refining Company, the heavy metals are removed from the catalyst in a water-based chemical treatment step.[224,225] The reactivity of the catalyst is restored by the treatment even after extended cycling through the process. Neither the Demet III process nor antimony passivation have been demonstrated on tar sands or shale oil, however.

VI. CONCLUSIONS AND RECOMMENDATIONS

The future availability of catalyst metals for the manufacture of synthetic fuels can be seen to be dependent upon the following factors: (1) the choice of processes used, (2) future developments in catalysts, and (3) future demand for catalytic metals in non-catalytic applications such as metallurgy and electronics. In their present state of development, some direct coal liquefaction processes would require substantial quantities of cobalt and molybdenum, while others have been shown to be capable of being operated without catalysts, in particular, SRC-II. Indirect liquefaction processes have been demonstrated on the commercial scale (SASOL) using catalysts which do not contain critical materials. The demonstrated processes for the manufacture of substitute natural gas do require nickel catalysts, but successful operation using new catalysts based on iron, titanium, and other materials has been demonstrated on the laboratory scale. Finally, by using a distillation with coking approach, shale oil, tar sands, and heavy crudes can be demetalized to minimize catalyst consumption in the subsequent refining and upgrading of these raw feedstocks. Thus, it is possible at least technically to operate a synthetic fuels industry without critical materials through choice of process and also through the use of alternative catalysts.

For synthetic fuels processing, catalyst development is being pursued in two directions: (1) the development of alternative catalysts which do not use critical or strategic metals, and (2) the development of sulfur resistant and highly reactive catalysts with long service lives. The latter would employ critical, strategic, and precious metals, but would offer attractive benefits such as milder processing conditions and process simplification. Widespread use of critical and strategic metals would make a reclamation industry desirable because this would extend metal supplies and have a stabilizing effect on metal prices. Without adequate economic incentives, however, it is doubtful that private industry would develop this capability in anticipation of need, particularly when a synthetic fuel industry may be capable of being operated without critical, strategic, or precious metal catalysts.

In general, the use of alternative catalysts are not perceived as leading to product slates significantly altered from those of demonstrated coal conversion processes. Molybdenum has been substituted for cobalt promoted molybdenum in direct coal liquefaction with no loss in depth of conversion or yield of C_4-975°F products. There are, however, unresolved questions regarding catalyst stability and service life.

The key issue of future availability of catalyst metals involves the very complex choices between catalytic processes and non-catalytic processes for manufacturing synthetic fuels. In a free economy, both types will undoubtedly be developed and perhaps used, with the ultimate choices being dependent upon proprietary, marketing, and other owner specific considerations.