Hydrogenation Reactions of Model Titanium Compounds under Coal Liquefaction Conditions

Used catalyst and reactor deposits from a fixed-bed coal liquefaction unit show high concentrations of titanium and boron. The titanium was present as anatase, a titania polymorph. Hydrogenation reactions with and without catalyst were performed with model titanium and boron compounds under liquefaction conditions. The catalyst used was Harshaw 0402T 3% CoO − 15% MoO_3 on an alumina-silica support. Rutile remained unchanged by reactor conditions. In all other runs the titanium starting material, whether organic or inorganic in nature, converted to anatase. When the deposition of the reaction products was monitored, only that anatase derived from organic titanium compounds accumulated on and in the catalyst pellets to an appreciable extent.

M. TREBLOW
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260
and
C. A. SPITLER
and F. R. BROWN
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, Pittsburgh, PA 15236

SCOPE

Deactivation of catalysts used to aid in the liquefaction of coal is a significant problem. Typical catalysts consist of either promoted and unpromoted molybdenum or tungsten on high surface area aluminas. These type of catalysts are also used in hydrodesulfuring (HDS) of petroleum residua and generally contain 10–20 wt. % molybdenum (as MoO_3), with 0–5 wt. % cobalt (as CoO) as promoter, dispersed on a high surface area (~200 m^2/g) alumina support.

Two mechanisms implicated in catalyst deactivation are: (1) deposition of carbonaceous material; and (2) accumulation of metallic species at the surface and, to varying degrees, within the pores. Although the plugging of pore mouths by carbon occurs rapidly and causes severe loss of catalytic activity, the carbon can be removed by a controlled oxidation. This regeneration results in essentially complete carbon removal with the catalyst activity rising close to the initial level. On the other hand, the deposition of metal-containing species is a gradual process taking place in a much longer time frame. This problem is one of an irreversible deposition of materials. Once attached, the metals are affixed to the catalysts, causing an absolute loss of activity even after any controlled oxidation regeneration (Kovach et al., 1978; Ocampo et al., 1978).

Because of the irreversible nature of the metals deposition, it is necessary to determine their form in the coal. If the source can be located, it will lead to either the formulation of a better catalyst or a method of removing this material for a longer catalyst lifetime. Although titanium constitutes only about 0.1% of the weight of coal, in a fixed-bed reactor run at PETC (Pittsburgh Energy Technology Center) it accounted for between 13 and 24% of the reactor deposit (solid material lying between catalyst pellets) and 1.2–4.4% of the weight of the pellets. This titanium species was identified by X-ray diffraction as anatase (TiO_2) with a c axis that was 5.4×10^{-10} cm (0.054 Å) shorter than the literature value. The contracted c axis may be due to boron incorporation into the anatase lattice (either by replacing some of the titanium or by going into the interstices of the lattice), since boron was also found to disproportionately accumulate in the reactor deposit.

The source of the product titanium could be due to any combination of the following: (1) an amorphous, inorganic titanium compound in the coal that was converted to anatase during liquefaction; (2) small crystallites of anatase or rutile that existed in the coal and just accumulated on and around the catalyst during processing; or (3) titanium that was organically bound in the coal and that decomposed to form the inorganic mineral anatase during the run (Makovsky et al., 1980).

All three possibilities were investigated, with special emphasis on the possibility of organically bound titanium. If these organic compounds exist in coal, their unaltered removal from the coal would be a difficult, if not an impossible, undertaking. The approach was to react model organic titanium compounds under liquefaction conditions. These results are compared with those from runs using inorganic titanium compounds and with those from the fixed-bed reactor run previously mentioned. X-ray diffraction (XRD) was used to monitor the presence of crystalline titanium-containing materials. Scanning electron microscopy (SEM) was used to detect deposits on the surface of the catalyst pellets; an elemental mapping showed titanium concentration at various depths within the pellets.

CONCLUSIONS AND SIGNIFICANCE

This study indicated that some of the titanium initially present in coal may be organically bound. This organic titanium, possibly alone or in addition to the inorganic titanium in the coal, would be the source of the inordinately high concentrations of titanium deposited on and around direct coal liquefaction catalysts. Some effort has been made to demineralize coal before reacting to alleviate the formidable buildup of metals on catalysts and subsequent catalyst deactivation. The problem of metals accumulation due to organically-bound species in the coal will not be addressed by this activity. The possibility of this deposition on catalysts occurring appreciably from organically-bound species will have significant impact in the configuration or direct coal liquefaction processes and the catalysts chosen.

M. Treblow is presently with the Calgon Corp., Pittsburgh, PA 15230.

Only organically bound titanium would be the source for that Ti found within the catalyst pellets. The model compounds used were titanium (IV) cresylate, titanium (IV) nonylate, and titanyl tetraphenylporphyrin. In all the simulated liquefaction runs made, these organic titanium compounds converted to anatase. However, the *c* axis was not extracted from that for the naturally occurring mineral anatase, while the *c* axis for the anatase removed from the fixed-bed coal liquefaction reactor deposit was. This contraction may be due to incorporation of some other element from the coal other than boron.

Raman spectroscopy and XRD showed that anatase was present not only as reactor deposit but also on the surface of the pellets and, to varying degrees, within the pellets. When catalyst pellets were allowed to contact titanium (IV) cresylate (in tetralin) for 48 hours, SEM verified the presence of titanium throughout the entire pellet. As expected, although the trial using an amorphous TiO_2 as the starting material had anatase as the product, there was almost no penetration of titanium within the pellet. When these results were compared with those of an inlet pellet and outlet pellet from the fixed-bed reactor run, the same relationship occurred; the inlet pellet showed greater titanium penetration. Any organically bound titanium present in the coal might well be soluble in the coal liquids, thus providing a mechanism for the transport into the catalyst pellets. As these titanium-containing species are carried through the reactor, they could react, yielding an inorganic material that would adhere to the surface of the catalyst but not be deposited in the catalyst pores. The data on the pellets from the amorphous TiO_2 run and the outlet pellets showed the same low degree of titanium penetration.

INTRODUCTION

Metals deposition has been implicated in the deactivation of HDS catalysts. Their essentially permanent adherence to catalysts, with subsequent irreversible loss of activity, makes this a matter to be investigated. The deposition of carbonaceous material within the catalyst pores would block the passage of coal-liquid insoluble matter. Hence, of special importance are those metals that may originate as organically bound species in the coal. Their solubility in the coal liquids would give them easy access to the catalyst surface and a transport mechanism into the pores, where they would build up in high concentrations (Kovach et al., 1978).

Others have investigated the presence of organically bound metals in coal. Gluskoter (1975) studied the metallic elements that occur in trace quantities. These elements were grouped according to their affinities for organic combination, as determined by the specific gravity of the coal fractions in float-sink tests. Boron was in the lightest fraction in all four coals tested, along with the elements Ge and Be. Titanium was in the lighter fraction in three of the four coals, along with the elements V, Ga, P, and Sb. Given and coworkers (1975) examined the trace element composition of oils produced by liquefaction of three coals and found some enrichment of titanium in the oils; the presence of an organic combination of Ti in coal was suggested as the source of these species.

McGinnis (1978) studied the concentration of metal compounds in the slurries produced in noncatalytic liquefaction of four different types of coal. The high concentrations of certain metals, i.e., Ti, B, Mn and V, were observed. Titanium concentrated in the coal liquid filtrates to the greatest degree. The author proposed that this indicated the presence of organically-bound Ti.

Finkelman (1978) used a Scanning Electron Microscope (SEM) equipped with an energy-dispersive X-ray detector to locate and analyze the accessory minerals in Waynesburg coal. He considered that the best explanation for the observed differences between the amount of titanium in the accessory mineral (rutile) and the analytical total was that most of the element occurred as organically-bound titanium.

Kovach (1978) and his coworkers reported on the effects of metallic compounds on the loss of activity by hydrodesulfurization catalysts, e.g., $CoO\text{-}MoO_3/Al_2O_3$. The alkali and alkaline earth oxides caused the greatest degree of deactivation, while oxides of Ti, P and Si showed little deactivation, although they were easily absorbed by the catalyst. However, a high degree of catalyst poisoning occurred when the organometallic compound biscyclo-

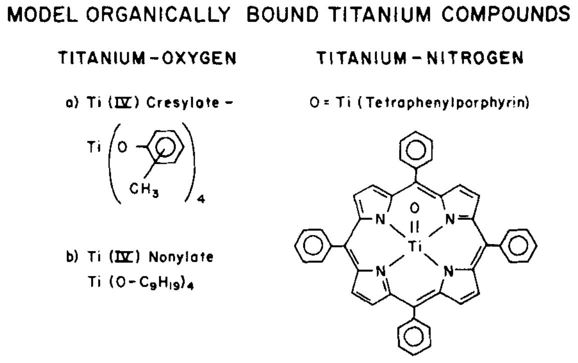

Figure 1. Organic titanium compounds used in Runs #1–10.

TABLE 1. HYDROGENATIONS OF TITANIUM AND BORON COMPOUNDS UNDER LIQUEFACTION CONDITIONS

		Conditions			Solid	*c*-Axis[b]
Run #	Reactants	Catalyst[a]	Autoclave[*]	% Recovery[d]	Products Identity[b]	(1 ± 0.01 $\times 10^{-8}$ cm)
1	Ti(IV) Cresylate	no	A	94	anatase	9.50
2	Ti(IV) Nonylate	no	A	76	anatase	9.52
3	Ti(IV) Cresylate	yes	A	88	anatase	9.50
4	O=Ti (Tetraphenyl-Porphyrin)	yes	A	70	anatase NH_4Cl	9.52
5	Rutile	yes	B	—	rutile	2.96
6	Anatase	yes	C	—	anatase	9.52
7	Amorphous TiO_2[c]	yes	A	74	anatase	9.51
8	Triphenylborate	no	A	74	B_2O_3, HBO_2	—
9	Triphenylborate + Ti(IV) Cresylate	no	A	96	B_2O_3 anatase	9.51
10	B(O-butyl)$_3$ + Ti(IV) Cresylate	no	A	95	B_2O_3 anatase	9.51
	Fixed-Bed Liquefaction Reactor	yes	—	—	anatase-like material	9.45

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[a] Harshaw 0402T $CoO\text{-}MoO_3/Al_2O_3\text{-}SiO_2$ catalyst (3% CoO, 15% MoO_3, 77% Al_2O_3, 5% SiO_2).

[b] By X-ray diffraction.

[c] Derived from LTA (low-temperature ashing) of titanium (di-*i*-propoxide) lactate.

[d] Refers to percent element recovered as product, e.g., Ti as TiO_2.

Autoclave conditions: 300 mL glass-lined rocking autoclave; 703–723 K, 2,200–2,400 psi H_2 ($1.516 \times 10^7 - 1.654 \times 10^7$ Pa).

10 mmole reactant in 50 mL of solvent with 1 g of catalyst.

[*] A = ½ h in tetralin; B = 1 h in panasol oil; and C = 4 h in panasol oil.

TABLE 2. CONCENTRATION OF Ti AND B IN FIXED-BED COAL LIQUEFACTION[a]

		Concentration (ppm wt.)				
			Reactor Deposits, Catalytic Run			
Atomic No.	Element	Feed Coal Kentucky hvBb	Avg. Inlet	Conc. Factor[c]	Avg. Outlet	Conc. Factor[c]
5	B	87	18,000	207	7,000	80
11	Na	250	4,000	16	2,100	8
12	Mg	750	4,700	6	4,200	6
15	P	130	1,500	12	1,200	9
19	K	2,300	5,000	2	6,800	3
20	Ca	4,200	82,000	20	17,400[b]	4
22	Ti	1,000	120,000	120	220,000	220
26	Fe	36,000[b]	111,000[b]	3	54,000	2

[a] Spark Source Mass Spectrometry data except where noted.
[b] AA = atomic absorption.
[c] Concentration factor = conc. metal deposited/conc. metal in feed coal.

pentadienyltitanium dichloride was used. The organometallic compound, which is soluble in tetralin and coal liquids, readily penetrated the catalyst pores. This compound resulted in a TiO_2 coating on the catalyst of 2.2% by weight.

At PETC, titanium was also of particular interest because of its inordinately high concentration in reactor deposits and on the used catalyst from a fixed-bed liquefaction run. The form of the titanium was identified as anatase, a TiO_2 polymorph. This report details the results of the study of the reaction of model organically-bound titanium and boron compounds that were hydrogenated in an autoclave under liquefaction conditions, both with and without a catalyst.

RESULTS AND DISCUSSION

Three groups of experiments were performed using the model titanium and boron compounds (Table 1). The titanium compounds were chosen to represent different organic classes; Ti in (1) an aromatic system; (2) a straight chain aliphatic system; and (3) as part of a chelation compound. In the first group (Runs 1 and 2), a tetraaryltitanate and tetraalkyltitanate, i.e., an alkoxide, were hydrogenated without a catalyst. Structures appear in Figure 1. In the second group (Runs 3–7), a hydrodesulfurization catalyst, Harshaw 0402T CoO-MoO_3 on an alumina-silica support, was present during hydrogenation of either various forms of titanium dioxide or an organically-bound titanium compound in the autoclave. Finally, in the third group (Runs 8–10), organoborates were hydrogenated without catalyst in the autoclave in the presence or absence of titanium (IV) cresylate. Conditions for the hydrogenation reactions are listed at the bottom of Table 1.

Titanium Concentration

Any solid material formed was analyzed using XRD. The data were collected on a Rigaku horizontal goniometer using a copper X-ray tube operated at 40kV and 35mA. All measurements were made with a one degree divergent slit, 0.3 mm receiving slit, receiving graphite monochromator, and scintillation counter with pulse height discrimination. All samples were ground finer than 20 micron and packed into a glass holder with an opening 16 × 8 × 0.5 mm. No binder or adhesive was needed.

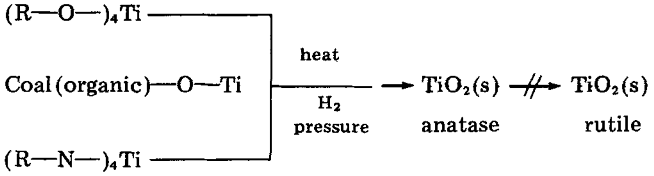
The inorganic product from all but one of the above experiments was identified by XRD to be the anatase form of TiO_2, with a *c* axis value within $\pm 1 \times 10^{-10}$ cm (±0.01 Å) of that of pure anatase 9.51 $\times 10^{-8}$ cm (9.51 Å). The only exception was in the reaction of rutile (Run 5). Rutile, which is the thermodynamically more stable polymorph, did not convert to anatase in the autoclave under the liquefaction reaction conditions. Yields of 70–94% of TiO_2 were obtained.

Included for comparison in Table 1 are the results of the material removed from a fixed-bed liquefaction. An anatase-like material was formed, having a *c* axis that differed from the literature value for anatase by 6×10^{-10} cm.

Rutile (Run 5) remained as rutile. When anatase (Run 6) was heated under the same conditions as rutile, the anatase remained as anatase. The thermodynamic properties of rutile and anatase do not differ sufficiently to cause conversion at 723 K. The equilibrium temperature for this conversion is reported at 1,188 K (Mason and Berry, 1968):

$$\text{anatase} \xrightleftharpoons{1,188\ K} \text{rutile}$$

Thus, the following mechanism is postulated for the conversion of an organically-bound titanium species in the model compounds studied, or possibly in coal itself, that leads to anatase. Such a scheme is postulated:



When amorphous TiO_2 (Run 7) derived from the low-temperature ashing of a titanium salt of an organic acid was reacted under the same hydrogenation conditions with the Co-Mo catalyst, the only product recovered was anatase. Again the pathway for conversion of titanium under liquefaction conditions leads to anatase.

Boron Concentration

Since boron concentrated in the reactor deposit by an 80:1 factor compared to the feed coal (Table 2), it was investigated as a potential impurity in the anatase lattice, causing the observed shortening of the *c* axis (Table 1) in the liquefaction reactor deposit. In Run 8, the triphenylborate was reacted alone in the autoclave to determine if any decomposition products formed. Both boric oxide and metaboric acid were recovered (74%) as the solid, insoluble products, and no unreacted starting material was recovered. Next, two reactions were run (9 and 10) in the autoclave under the same conditions as before but using as reagents, titanium (IV) cresylate along with triphenylborate in one case and tributylborate in the other case. Anatase and boric oxide were recovered nearly quantitatively as the solid, tetralin insoluble products (Table 1). The *c* axis of the anatase was found to be the normal 9.51×10^{-8} cm. Thus, it was concluded that boron was not the cause of the shortened *c* axis of the anatase from the liquefaction runs.

Penetration Studies

Because a coating had been observed to form on the catalyst pellets in fixed-bed coal liquefaction reactors, the coating formed on the catalyst pellets was studied in the three catalytic reactions (Runs 3, 4, and 7). As has been noted, anatase formed in nearly

TABLE 3. TITANIUM PENETRATION IN CATALYST PELLETS CoO-MoO_3/Al_2O_3-SiO_2

Run #	Reactants	TiKα/AlKα (At Edge)	Max. Deg. of Ti Penetration μm	Penetration Radius Ratio
4	O = Ti(Tetraphenyl-porphyrin)	3.0	700	0.44
3	Ti(IV) Cresylate	0.2	225	0.14
7	Amorphous TiO_2 from LTA	0.1	25	0.02
—	Fixed-Bed Liquefaction			
	Inlet Pellets	0.8	90	0.06
	Outlet Pellets	0.1	30	0.02

quantitative yields from the organically-bound titanium compounds, whether or not catalyst was present. In the catalytic runs, the pellets were observed to have darkened in color from a light tan to a dark green and to have become coated with a white powder in the course of the reaction. The pellets were examined for titanium content in the deposit and for penetration of a titanium species through the cross section of the pellets by SEM (scanning electron microscopy).

Examination by SEM of the catalyst pellets that were cleaved to obtain a cross section with a regular surface showed a varying relative concentration of a titanium species on the edge and penetration of titanium to varying depths (Table 3). Thus the pellets from the liquefaction run with titanyl tetraphenylporphyrin showed the most coating on the catalyst and the greatest degree of Ti penetration, while the reaction with amorphous titanium dioxide showed the least. (Graphs of the penetration effects are shown in Figure 2.) An SEM micrograph of a used catalyst pellet from the Ti (IV) cresylate run shows the rim of material on the outer surface of the pellet (Figure 3). In Figure 4 is the micrograph of another pellet from the same run. When the Ti concentration for that pellet was mapped, titanium was shown to constitute most of the rim. Examination of catalyst pellets from the fixed-bed liquefaction reactor by SEM showed a moderate coating of titanium, as evidenced by a micrograph and Ti mapping on an inlet pellet (Figure 5). The degree of penetration vs. the relative Ti concentration is presented for an inlet and an outlet pellet from the fixed-bed run in Figure 6.

It is expected that any organic titanium compounds present would be soluble in the titralin or, in an actual liquefaction run, would probably be soluble in the coal liquids and solvent used.

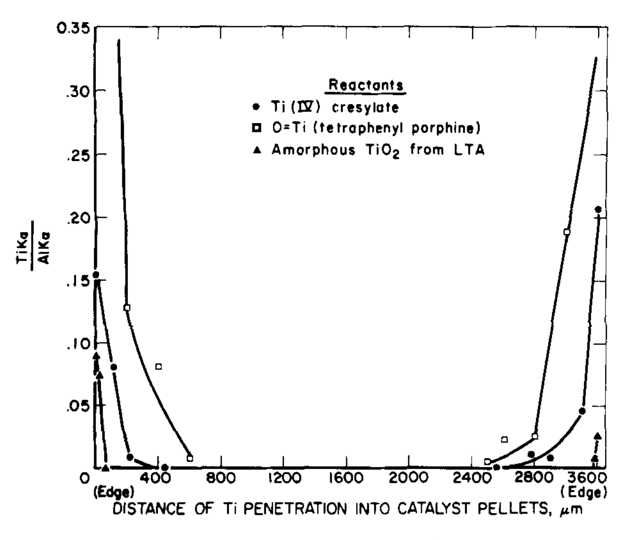


Figure 2. Plot of SEM intensity ratios of Ti Kα/Al Kα as a function of the Ti penetration distance for Runs #3, 4, and 7.

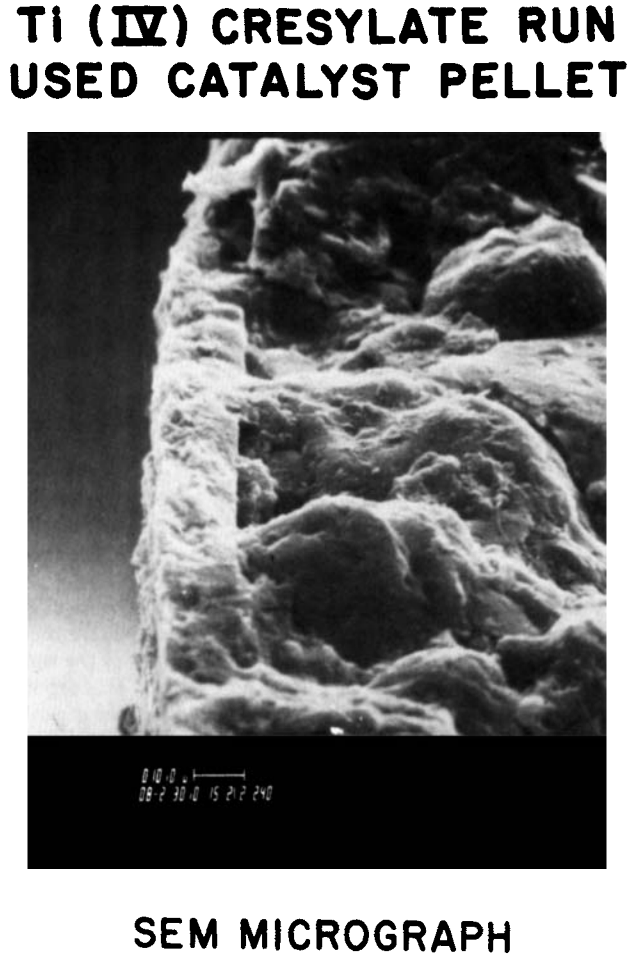
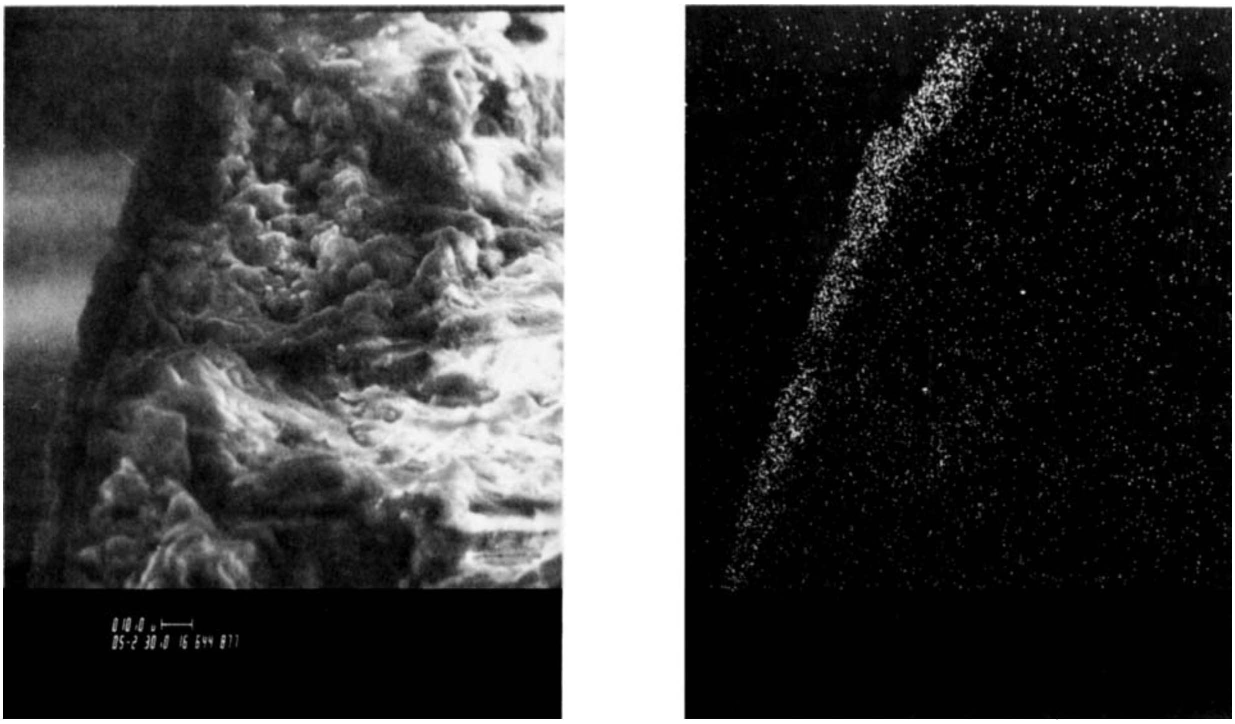


Figure 3. SEM micrograph of a used catalyst pellet from the Ti (IV) cresylate Run.

Because of their transport mechanism through the solvent, there would also be a great degree of penetration into the catalyst pores. The run with a starting material of an organic titanium compound should show the greatest degree of penetration, as is the case (Figure 2). At the beginning of an actual liquefaction run, the organic titanium would still exist; the inlet pellets should have the greatest titanium penetration. (This was the case in Figure 6.) The heating of the autoclave or reactor would cause these organics to decompose to an inorganic material after some time period. Some of the inorganic titanium—in this instance, anatase—may adhere to the catalyst surface but would demonstrate little or no penetration of the catalyst pores. This was the actual state of affairs for the outlet pellets from the liquefaction run. The same behavior is noted in the case of the run with amorphous titanium dioxide as starting material. This run demonstrates the same slight coating and slight penetration as what occurred for the outlet pellets. Thus both the amount of coating and the degree of titanium penetration appear to be greater for the organically-bound titanium species. Kovach et al. observed the same effect in their experiments on deactivation of coal liquefaction catalysts.

Other evidence that supports the solvent transport mechanism for titanium movement into the catalyst relates to the crystallite size of the product TiO_2 from three different runs. The average crystallite size is listed in order of decreasing degree of titanium penetration: Ti-porphyrin Run (1.55×10^{-5} *cm* TiO_2) > Ti (IV) cresylate Run (1.50×10^{-6} *cm* TiO_2) > Amorphous TiO_2 from LTA Run (9.70×10^{-6} *cm* TiO_2). The size of the crystallites of TiO_2 from the porphyrin run would block their passage into the catalyst pores. This would indicate that the Ti is getting into the pellets before it decomposes to an inorganic form.

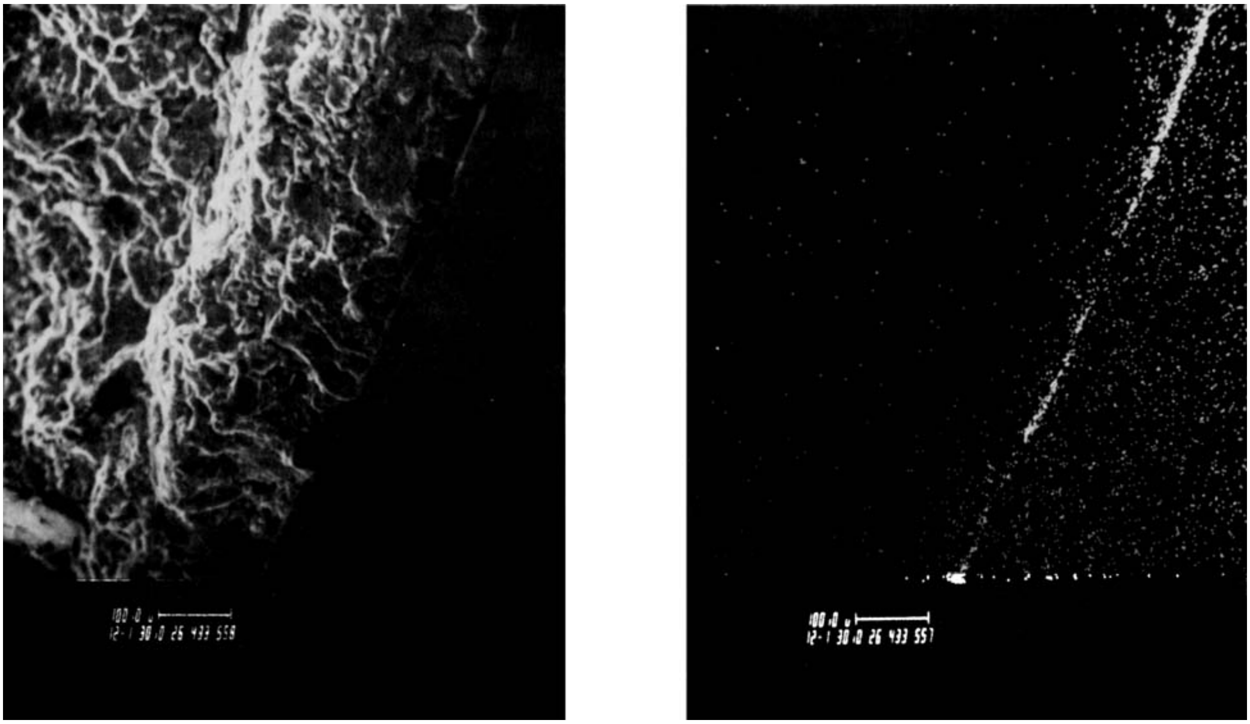
As mentioned previously, the depth of the titanium in the cat-


Ti (IV) CRESYLATE RUN
USED CATALYST PELLET

SEM MICROGRAPH

MAP OF TITANIUM CONCENTRATION

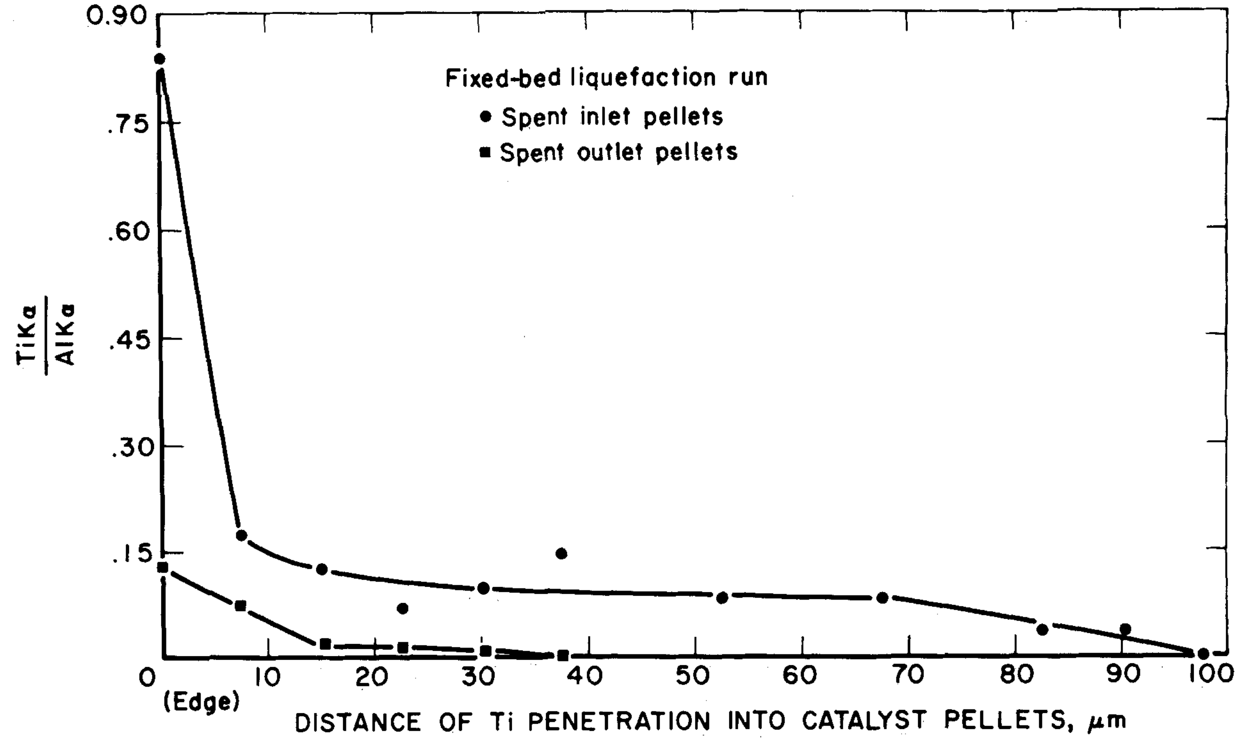
Figure 4. SEM micrograph and titanium concentration map of a used catalyst pellet from the Ti (IV) cresylate Run.


FIXED-BED LIQUEFACTION RUN
USED INLET CATALYST

SEM MICROGRAPH

MAP OF TITANIUM CONCENTRATION

Figure 5. SEM micrograph and titanium concentration map of a used inlet catalyst pellet from a fixed-bed liquefaction run.

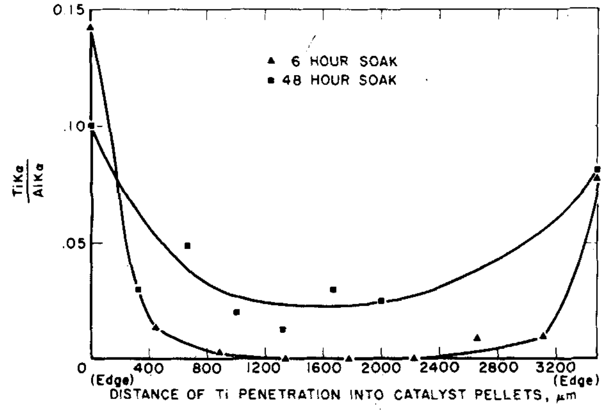


Ti Penetration in a $CoO-MoO_3/Al_2O_3-SiO_2$ catalyst

Figure 6. Plot of SEM intensity ratios of Ti Kα/Al Kα as a function of the Ti penetration distance in a fixed-bed inlet and outlet used catalyst pellet.

alyst pores results from a solvent transport mechanism. If allowed to remain in contact with the pellets for a long enough time, the organically-bound titanium should travel throughout the entire catalyst. Some catalyst pellets were soaked in a tetralin solution of titanium (IV) cresylate at ambient temperature and under a nitrogen atmosphere. Pellets were removed after 6 hours and after 48 hours and examined by SEM for penetration of titanium. Figure 7 shows Ti is ⅓ of the way through the catalyst in 6 hours and all the way through the pellet in 48 hours.

Thus, penetration of the catalyst pellet does occur for organically-bound titanium species, while for inorganic titanium species there appeard to be little surface accumulation and almost no penetration below the surface. The organic structure and the bonding of the titanium atom also appear to affect both the amount of the coating and the degree of penetration. The chelated bonding of the Ti atom in the hole of the planar porphine structure is certainly far stronger (and more stable) than in titanium tetracresylate. In the course of heating, the autoclave to above 673 K, under pressure over 2,000 psi H_2 (1.378×10^7 Pa), much of the organic material is decomposed. But the porphine structure probably endures much longer; hence, the opportunity for penetration is greater.



Soaking studies using Ti (IV) Cresylate-Tetralin solution and a $CoO-MoO_3/Al_2O_3-SiO_2$ catalyst

Figure 7. Plot of SEM intensity ratios of Ti Kα/Al Kα as a function of the Ti penetration distance in a $CoO-MoO_3/Al_2O_3-SiO_2$ catalyst soaked in a Ti (IV) cresylate-tetralin solution.

Having demonstrated that penetration of the catalyst pellets does occur with organically-bound titanium compounds under liquefaction conditions, it was necessary to determine the nature of the titanium species coating the pellets. Anatase is expected, since its two strongest lines appeared on the diffraction pattern of whole unground pellets from the fixed-bed reactor run. (The pellets were not ground in this case so that the surface species would not be diluted by the bulk alumina-silica catalyst.) To verify this, some used pellets from the titanium (IV) cresylate run (Trial #3) were examined. The coating was removed by first sonicating the pellets in water and then scraping them (under magnification) to remove any white material on the surface. The coating was identified as anatase by X-ray diffraction; the pattern is shown in Figure 8. X-ray fluorescence determined that the remaining portion of the pellet contained 0.6% Ti. When this portion was ground and examined by XRD, the two strongest lines of anatase were weak but observable superimposed on the strong alumina pattern. The presence of anatase was verified by Raman spectroscopy. Hence, not only the titanium on the surface but that within the pores is in the form of anatase. Since these experiments showed that inorganic titanium has no means of access to the catalyst pores, this anatase must be the decomposition product of the organic titanium species that the solvent carried into the catalyst pores.

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Reference in this paper to any specific commercial product,

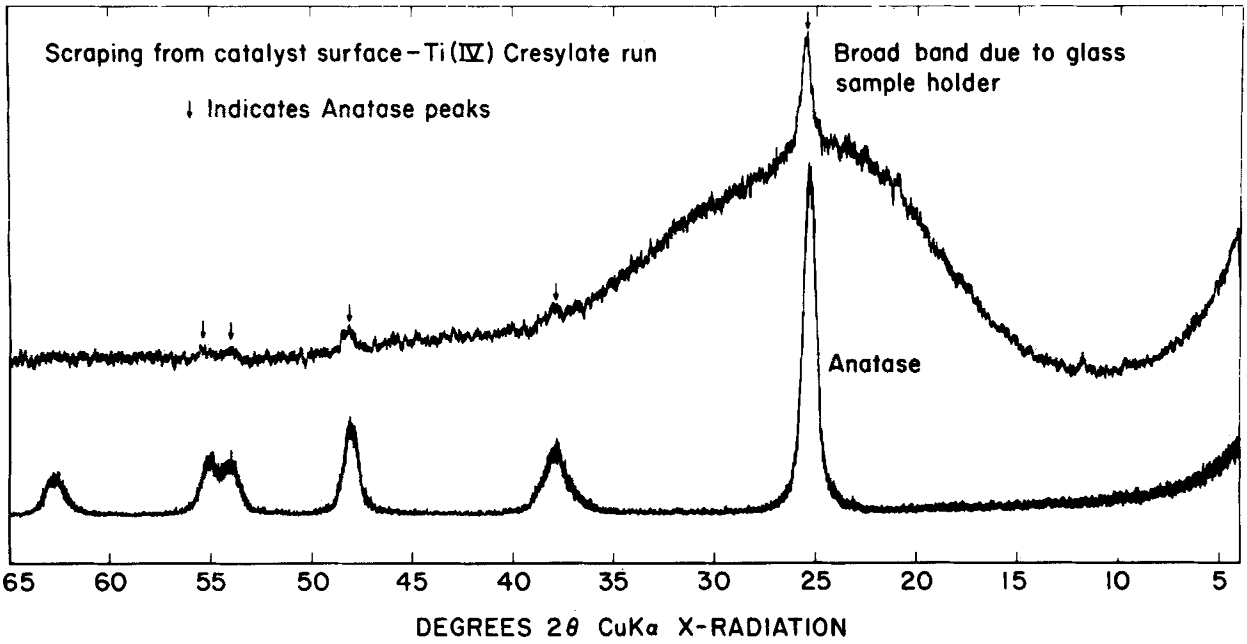

Figure 8. X-ray diffraction pattern of the white powder scraped from the surface of a used catalyst pellet from the Ti (IV) cresylate Run.

process or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

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Dynamic Simulation of Azeotropic Distillation Towers

Algorithms are presented for integration of the stiff ordinary differential equations using an adaptive semi-implicit Runge-Kutta (ASIRK) integrator; an A-stable, single-step, noniterative algorithm with step-size control. Unusual open loop responses are encountered for simulations of azeotropic distillation towers and the results suggest two control variables. The results support the contention that one steady-state regime of operation is unstable.

G. J. PROKOPAKIS and
W. D. SEIDER

Department of Chemical Engineering
University of Pennsylvania
Philadelphia, PA 19104

SCOPE

In 1978, we undertook to study the steady-state characteristics of azeotropic distillation towers (Prokopakis et al., 1981a). Our results demonstrated the extreme sensitivity of the steep concentration and temperature fronts to small changes in the boilup rate, product recovery and purity, and the reflux ratio, and led to an algorithm to locate feasible specifications for the configuration in Figure 6a (Prokopakis and Seider, 1983). Furthermore, they showed three regimes of operation, which were

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G. J. Prokopakis is presently at Columbia University.