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DEHYDROGENATION OF CYCLOALKANES CATALYZED BY
METALS IN SUPPORTED MOLTEN SALTS

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<p>This report presents the results of a set of studies, performed over the period, January 29 - December 12, 1987. The studies were designed to evaluate the potential advantages associated with the use of transition metal microcrystallites dispersed in molten salts in the dehydrogenation of cyclic hydrocarbons which are viewed as potential endothermic fuel candidates. Although both molten salt pools and Supported Molten Salt Catalysts (SMSC) were studied, only SMSC gave results which show any developmental promise for use in the endothermic fuels initiative presently underway at AFWAL.</p> <p>All of the SMSC studies were performed in packed tube reactors and were designed to permit comparison with data for conventional heterogeneous catalysts used under the same operational conditions (i.e., temperature, pressure, flow rate, catalyst loading, support, etc.). The majority of the studies involved the dehydrogenation of methylcyclohexane (MCH) to toluene.</p> <p style="text-align: right;">(continued on back)</p>					
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19. ABSTRACT (Continued)

This reaction system was selected because of the existing data base generated by the extensive studies at Shell Development using conventional heterogeneous platinum catalysts usually on alumina supports.

The observations considered of greatest significance in evaluating the catalyst preparations were mole percent conversion, mole percent cracking, rate of catalyst deactivation, and indications of the most probable mechanism of catalysts deactivation. The objectives did not encompass optimization of the SMSC technique in this application, but the preliminary results suggest that optimization studies are worthwhile.

Two modifications were made to the original statement of work. The first of ~~these~~ involved a one man-month study of platinum, in both conventional and SMSC mode, as an heterogeneous catalyst for the coupled dehydrogenation - Retro-Diels-Alder reaction of JP-10 (exo-octahydro-4,7-methano-1H-indene). The second modification, approximately a two man-month effort, involved as its primary endeavor the use of alkali metal hydroxide eutectics in SMSC for catalytic dehydrogenation of methylcyclohexane to toluene. (A. G.)

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I. INTRODUCTION

This report presents the results of a set of studies, performed over the seven month period, February 1 - September 30, 1987. The studies were designed to evaluate the potential advantages associated with the use of transition metal microcrystallites dispersed in molten salts in the dehydrogenation of cyclic hydrocarbons which are viewed as potential endothermic fuel candidates. Although both molten salt pools and Supported Molten Salt Catalysts (SMSC) were studied, only SMSC gave results which show any developmental promise for use in the endothermic fuels initiative presently underway at AFVAL.

All of the SMSC studies were performed in packed tube reactors and were designed to permit comparison with data for conventional heterogeneous catalysts used under the same operational conditions (i.e. temperature, pressure, flow rate, catalyst loading, support, etc.). The majority of the studies involved the dehydrogenation of methylcyclohexane (MCH) to toluene. This reaction system was selected because of the existing data base generated by the extensive studies at Shell Development using conventional heterogeneous platinum catalysts usually on alumina supports.¹

The observations considered of greatest significance in evaluating the catalyst preparations were mole percent conversion, mole percent cracking, rate of catalyst deactivation, and indications of the most probable mechanism of catalysts deactivation. The objectives did not encompass optimization of the SMSC technique in this application, but the preliminary results suggest that optimization studies are worthwhile.

Two modifications were made to the original statement of work. The first of these involved a one man-month study of platinum, in both conventional and SMSC mode, as an heterogeneous catalyst for the coupled dehydrogenation - Retro-Diels-Alder reaction of JP-10 (exo-octahydro-4,7-

methano-1H-indene). The second modification, approximately a two man-month effort, involved as its primary endeavor the use of alkali metal hydroxide eutectics in SMSC for catalytic dehydrogenation of methylcyclohexane to toluene.

II. MOLTEN SALT POOL STUDIES

The study of bulk molten salt pools, although determined to be of little value in the observation of catalytic dehydrogenation of cycloalkanes, has served as a useful source of information which has been helpful in designing SMSC systems. The information collected was of value in 1) evaluating various candidate eutectics for use in SMSC, 2) selection of catalyst precursors, 3) determining the rate and extent of hydrogen reduction of homogeneously dispersed catalyst precursors; and 4) permitting identification of the species produced by reduction of the catalyst precursor.

A. EUTECTICS

Studies of molten salt pools have been of value in characterizing the behavior of various molten salt eutectics under the operating conditions required for preparation of the catalyst or for observing dehydrogenation reactions at higher temperatures. The eutectic properties, observed during molten salt pool studies, included melting point, homogeneity of the catalyst precursor dispersion, vaporization tendencies, water retention, silica surface wetting, reaction with silica and/or alumina, and fluidity.

Molten salt pool studies were especially valuable in characterizing the eutectics which contained $ZnCl_2$. In our studies these eutectics were found to tenaciously retain water and to display relatively high vapor pressures as evidenced by deposition of $ZnCl_2$ at cold spots in the reaction apparatus. Since vaporization of molten $ZnCl_2$ changes the composition of

the eutectic and consequently raises its melting point, all eutectics containing $ZnCl_2$ were abandoned for use in SMSC.

The eutectics which have been evaluated in molten salt pool studies include the following:²

	<u>Eutectic</u>	<u>m.p. (°F)</u>
1.	$ZnCl_2/KCl$ (71/29 mole %)	504
2.	$ZnCl_2/KCl$ (68/32 mole %)	464
3.	$ZnCl_2/KCl$ (54/46 mole %)	442
4.	$ZnCl_2/KCl/NaCl$ (60/20/20 mole %)	397
5.	$KCl/LiCl$ (41.5/58.5 mole %)	682
6.	$KCl/NaCl/LiCl$ (26/36/38 mole %)	675
7.	$MgCl_2/NaCl/KCl$ (60/20/20 mole %)	729
8.	$CuCl/KCl$ (65/35 mole %)	282
9.	KOH	680
10.	$KOH/NaOH$ (53/47 mole %)	356

Molten pools of eutectics 2,4,5,9, and 10 were observed to wet the surface of a silica crucible. A molten pool of eutectic 8 did not wet silica. This property is significant if the molten salt is to be effective in forming relatively uniform thin films on the walls of the pores of silica supports.

B. CATALYST PRECURSOR REDUCTIONS

Metallic platinum dispersions in the halide molten salt pools #5 and #6 were successfully generated using hydrogen reduction. K_2PtCl_4 or K_2PtCl_6 were reduced to metallic platinum in these pools. In molten salts containing $ZnCl_2$, the long term retention of water always led to very rapid hydrolysis of $PtCl_4^{-2}$ to PtO upon melting of the eutectic. The reduction of PtO to metallic platinum, which occurred very rapidly in these eutectics

under a stream of hydrogen, may offer some advantages over reduction of platinum halides. Although platinum halides are more readily reduced, it has been reported that reduction of PtO produces smaller platinum particles.³ The use of PtCl_6^{-2} in eutectics containing ZnCl_2 also led to hydrolysis, producing PtO_2 , but the hydrolysis was not as rapid or as extensive as that of PtCl_4^{-2} . After reduction with hydrogen, significant quantities of PtO_2 remained. This system is complicated by the fact that K_2PtCl_6 was not very soluble in molten ZnCl_2/KCl eutectics which contained significant amounts of water. These observations established the incompatibility of ZnCl_2/KCl eutectics with K_2PtCl_6 as a catalyst precursor.

Dispersions of metallic nickel in ZnCl_2/KCl molten eutectic pools were generated by hydrogen reduction of homogeneously dispersed nickel(II) chloride, added as the hexahydrate. The identity of the metallic product was established by chemical means. Attempts to reduce cobalt(II) chloride in a ZnCl_2 (54 mole %)/ KCl (46 mole %) eutectic were unsuccessful, but in LiCl (58.5 mole %)/ KCl (41.5 mole %) hydrogen gas slowly gave complete reduction of CoCl_2 to metallic cobalt. Proof of the formation of metallic cobalt was established by chemical methods.

C. CATALYTIC ACTIVITY OF METAL DISPERSIONS

Dispersions of platinum generated in ZnCl_2/KCl molten eutectic pools were used unsuccessfully in attempts to dehydrogenate MCH. These dispersions also displayed no catalytic activity in the hydrogenation of cyclohexene or styrene. In these experiments, gaseous reactants were introduced to the system in several ways including bubbling through the eutectic, pressurizing the eutectic in an autoclave, and blowing a stream onto the surface of the eutectic. In no case was any catalytic activity observed. These results led to the decision to abandon molten salt pool

studies and to pursue only studies of supported catalysts. As we learned later, dispersions of metallic platinum in eutectics containing ZnCl_2 didn't show significant catalytic activity even when used in SMSC. Because of the successful observation of catalytic dehydrogenation activity by platinum used in SMSC, molten eutectic pool studies were abandoned as a preliminary test for catalytic activity.

III. SMSC STUDIES

All SMSC studies were done using the following general procedure;

- 1) loading the catalyst precursor and eutectic components on supports
- 2) loading the supports into the reactor tube
- 3) conversion of the catalyst precursor to catalyst
- 4) thermostating the reactor tube to the desired reaction temperature
- 5) thermostating the inlet and outlet tubes
- 6) heating the reactant reservoir to generate a vapor pressure
- 7) starting the flow of helium gas over or through the reservoir
- 8) GC sampling and bulk collection of product gases
- 9) mass spectral and ^1H NMR identification of collected product.

The results of the SMSC experiments were in every case compared to the results of an experiment using a conventional heterogeneous catalyst with the same support, and the same amount of catalyst under the same operating conditions. In these experiments the conventional catalyst was prepared in the same manner as the SMSC catalyst without inclusion of the components of the molten salt eutectic.

A. CATALYST PREPARATION TECHNIQUES

In Supported Liquid Phase Catalysis⁴, the liquid loading, q , is defined as;

$$q(\text{Loading}) = \frac{\text{Volume of catalyst solution occupying pores of carrier}}{\text{total pore volume}}$$

Thus, liquid loading can be varied from 0, which corresponds to conventional heterogeneous catalyst, to 1 where the internal pores are completely filled with the molten salt catalyst mixture.

The tabulations found in Table 1 gives the calculated values for molten salt liquid film thickness, and void space diameter as a function of liquid loading, q , for the two supports used in the reported studies.

Table 1. Molten Salt Film Thickness Variation With Liquid Loading

SiO₂, United Catalysts Inc., T-1571, average pore diameter = 180 (A)

q	Void Diameter (A)	Film Thickness (A)
0.10	170	5
0.20	160	10
0.30	150	15
0.40	140	20
0.50	128	26
0.60	114	33
0.70	100	40
0.80	80	50
0.90	56	62

Al₂O₃, United Catalysts Inc., T-2432, average pore diameter = 350 (A)

q	Void Diameter (A)	Film Thickness (A)
0.10	332	9
0.20	314	18
0.30	293	29
0.40	271	39
0.50	247	51
0.60	221	64
0.70	192	79
0.80	156	97
0.90	111	120

Consistent with theory, at very low levels of loading, the reaction rate or catalyst activity increases as q increases. As q increases further, diffusional resistances also increase, resulting in decreases rates of reaction or catalyst activity. Furthermore, theory predicts that there is an optimum loading level.⁴

Two different catalyst impregnation techniques were employed. These were the insipient wetness and the dipping impregnation methods. In both methods, the support pellets were held under vacuum for several hours before addition of the water or methanol solution carrying the components of the molten salt eutectic and the catalyst precursor. In the dipping method, whole support pellets were totally immersed into excess solution which was gently stirred with heating for 1 h. The pores of the pellets are assumed to be totally filled with solution by strong capillary action. Excess solution was decanted from the pellets.

In the insipient wetness method, a quantity of solution, exactly equal to the total pore volume of the pellets, was added to the pellets. It is reported that the insipient wetness impregnation method is advantageous because the actual amount of platinum in the pellets is accurately known, in contrast to the dipping impregnation method in which the concentration of the platinum remaining in solution changes as adsorption proceeds.⁵

In both methods the solvent water or methanol was removed by heating the pellets to 250°F under vacuum overnight after which the pellets are ready for charging the reactor.

The metal content of a prepared catalyst can be calculated using the following expression:

$$W_2 = V \times q \times W_1 \times C$$

where W_2 = weight percent of metal catalyst desired in pores

V = fraction of void in total volume of carrier

q - desired liquid loading of pore with eutectic

W_1 - weight percent of catalyst precursor

C - weight fraction of metal in catalyst precursor

The following calculation illustrates, for the saturation method, the use of this expression in calculating the relative amounts of components needed to prepare a catalyst having 20% liquid loading and 0.5% platinum with a eutectic composed of 55.5% KCl and 44.5% LiCl on United Catalysts T-374 alumina pellets which have 36% void volume.

$$\begin{aligned} \text{solving for } W_1: \quad W_1 &= W_2 / [V \times q \times C] \\ &= 0.5000 / [0.36 \times 0.20 \times 0.4016] \\ &= 17.3 \text{ weight } \% \text{ K}_2\text{PtCl}_6 \end{aligned}$$

$$\text{weight percent KCl needed} = [100.0 - 17.3] \times 0.555 = 45.9\%$$

(where 0.555 was the weight fraction needed for the eutectic)

$$\text{weight percent LiCl needed} = [100.0 - 17.3] \times 0.445 = 36.8 \%$$

To load 10 grams of the carrier, a volume of 20.0 ml is adequate for the total volume of solution. The rough assumption can be made that the mass of salts needed is simply the total volume multiplied by the desired loading factor. This involves assuming that the solid salts, the solvent, and the solution all have equal densities. In this illustration, 4.0g of salts are needed. Therefore, the following calculations can be made:

$$\text{weight of K}_2\text{PtCl}_6 \text{ needed} = 4.000\text{g} \times 0.173 = 0.692\text{g}$$

$$\text{weight of KCl needed} = 4.000\text{g} \times 0.459 = 1.836\text{g}$$

$$\text{weight of LiCl needed} = 4.000\text{g} \times 0.368 = 1.472\text{g}$$

After the support was loaded with the desired molten salt eutectic and catalyst precursor components, it was packed into the tube reactor and reduced by passing a stream of hydrogen. Several procedures were used in the catalyst precursor reduction step. These ranged from passing hydrogen gas at 700°F and 1 atm for 12 h with no period of calcining prior to

reduction to an opposite extreme of calcining at 840°F for 24 h followed by hydrogen reduction at 100 psi over a 24 h period during which the temperature was ramped from 250°F to 840°F. There is little doubt, as the data will show, that the dehydrogenation conversions of MCH to toluene displayed a sensitivity to the extent of catalyst precursor reduction. As will be seen (*vide infra*), the results do indicate that in almost all cases complete reduction of the catalyst precursor was not attained by passing hydrogen.

B. APPARATUS

Two separate apparatuses were used to characterize the activities of SMSC dehydrogenation catalysts. A general schematic diagram of these apparatuses is shown in Figure 1. The only significant difference in the two apparatuses is in the length of the tube reactor, the nature of the reservoir, and in the region used for preheating of the gaseous hydrocarbons prior to entering the catalyst bed.

In one apparatus, the reservoir is a 2.0 L autoclave which is thermostatically heated with a heating jacket and fitted with a sparge tube, immersed in the liquid hydrocarbon, for introduction of the helium sweep gas. This apparatus has a 1/2 in i.d. stainless steel tube, 24 in long, which is heated by a heating tape. The preheating region, of 6 in length, is packed with silica chips, and the supported catalyst is contained in a 12 in length.

In the second apparatus, the reservoir is a 800 mL gas storage tank which is thermostatically heated with heating tape. This tank is fitted with a tube which extends into the tank from the helium sweep tube at the top end of the tank. The 1/2 in i.d stainless steel tube reactor, 8 in long, is preceded in the flow stream by a 1/8 in stainless steel tube which

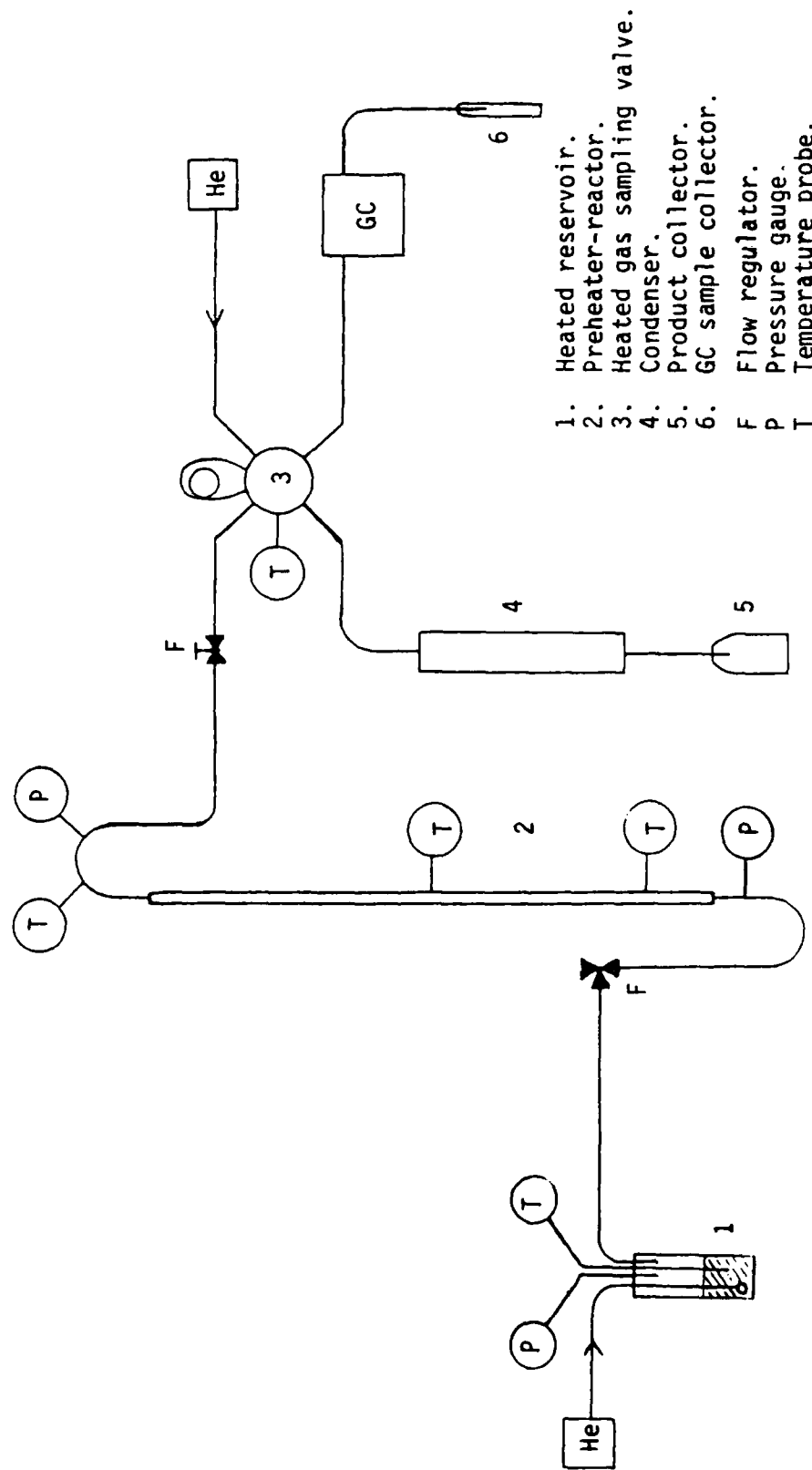


Figure 1. Schematic diagram of the apparatus.

is coiled around the body of the tube reactor. The tube reactor and the preheater region are both heated by the same heating tape.

In each apparatus the 1/8 in stainless steel tubes, exiting the reactor, pass through a heated gas sampling valve which is connected to the in-line gas chromatograph (Hewlett-Packard, Model 5750 with thermal conductivity detector). These lines are heated with heating tape to minimize condensation of reaction products prior to analysis. With higher boiling products these tubes are heated to greater than 350°F.

In a typical experiment, the reservoir temperature and the helium sweep gas pressure and flow rate are elevated only after the tube reactor is brought up to the desired temperature. In one of the apparatuses, the helium and hydrocarbon stream can be shunted around the reactor so that desired flow and pressure conditions can be reached before any reactant comes into contact with the catalyst. The total pressure of helium and hydrocarbon used were varied from 35 to 85 psi in order to adjust hydrocarbon flow rates. Product composition, determined by gas chromatography, is recorded with reference to the time of introduction of the first sample of hydrocarbon to the reactor.

C. METHYLCYCLOHEXANE DEHYDROGENATION

In the efforts reported here, the dehydrogenation of MCH has been studied more extensively than any other hydrocarbon because of the desire to evaluate SMC catalysts. The established data bank for catalytic dehydrogenation of MCH using heterogeneous catalysts, primarily platinum on alumina, has been used as a primary point of reference. In our studies two supports, silica and alumina, have been used to evaluate aspects of support composition on the catalyst efficiency and on potential side reactions. These studies have not involved a systematic variation in the pore size and surface area.

In the following pages the data from each dehydrogenation experiment giving significant results will be presented with all of the operational and systematic variables indicated. Any special experimental design or unusual observations will be presented with the results of the experiment.

1. PLATINUM CATALYSTS

Platinum catalysts were used on both silica and alumina supports.

a. SILICA SUPPORT

The silica support was United Catalysts Inc., # T-1571, used as 4-5 mm diameter spheres. The following characteristics are reported by the manufacturer in product bulletin CC-0381.

Major components: 93% SiO₂, 3% Al₂O₃, and 1% Fe₂O₃.

Surface area: 131 m²/g

Total pore volume: 0.71 cc/g

Average pore diameter: 180 A

Approximate bulk density: 30 lbs/CF

Crush strength: 8 lbs.

Experiment 1. MCH - Pt/SiO₂ ("conventional" heterogeneous catalyst)

Catalyst: Pt, 1%

Supported Molten Salt: n/a (q): 0.00

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 218 °F (103°C)

Reservoir Pressure (He + MCH): 105 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	883	95	3.1%	0%	96.9%
51	853	95	2.8	1.0	96.2
121	860	95	3.2	3.4	93.4
177	874	95	3.5	0	96.5
360	878	98	3.7	0	96.3
600	957	100	3.2	22.4	74.5
699	945	100	2.4	28.2	69.4
775	934	102	2.5	31.2	66.3
900	941	100	2.6	31.0	66.4

The results of this experiment, and subsequent repetitions, served as the basis for comparison of conventional Pt/SiO₂ catalysts with SMSC catalysts.

Experiment 2. MCH - Pt-KCl-LiCl/SiO₂

Catalyst: Pt, 1%

Supported Molten Salt: KCl(41.5 mole%)/LiCl(58.5 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 218 °F (103°C)

Reservoir Pressure (He + MCH): 95 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	815	85	93.6	6.4	-
766	828	85	1.5	93.0	5.5
803	1044	85	5.6	81.0	13.4
819	1108	85	0.3	72.3	17.4
833	1155	85	30.7	37.2	30.2
841	1164	85	31.9	33.7	32.7
886	1159	85	21.3	37.4	39.4
923	1162	85	26.4	28.9	41.0

The very low conversion of MCH to toluene observed at temperatures below 825°F, suggests that the melting point of the eutectic, when in the support pores, is above this temperature.

Experiment 3. MCH - Pt-KCl-LiCl/SiO₂

Catalyst: Pt, 1.7%

Supported Molten Salt: KCl(41.5 mole%)/LiCl(58.5 mole%) (q): 0.50

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 216°F (102°C)

Reservoir Pressure (He + MCH): 95 psi

Drying: 2 h, 302°F Reduction: H₂ gas, 1 atm, 14 h, 752°F

Elapsed Time(min)	Reactor Temp. (°F)	Reactor Press. (psi)	Cracked	MCH	TOLUENE
1	842	85	5.0	94.7	-
13	878	85	1.0	98.9	0.1
579	1044	85	2.0	97.4	0.5
756	1112	85	11.0	80.6	7.7
780	1184	85	36.0	25.5	37.7
829	1189	85	45.9	13.2	40.5

In this experiment as in Experiment 2 the period of reduction apparently was done at temperatures below the melting point of the eutectic components or at inadequate pressures. The initial low activity of the catalyst indicates that very little active catalyst is present. The gradual increase in activity is apparently due to increasing quantities of active platinum catalyst as the reaction proceeds.

Experiment 4. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.15

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 219 °F (104°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 14 h, 707°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	833	90	4.2	-	95.8
60	831	90	3.7	-	96.3
120	831	90	4.2	-	95.8
240	929	91	4.3	-	95.6
360	833	90	3.2	10.0	85.0
480	833	90	4.5	8.0	87.3
600	835	95	10.0	10.2	79.8
720	856	95	3.9	21.5	74.6
840	856	92	4.6	15.4	80.0
960	856	92	6.2	13.6	80.1

The initially observed conversion of MCH to toluene indicates that the catalyst precursor reduction has been effective. The increased effectiveness is probably attributable to the fact that the NaOH/KOH eutectic has a relatively low melting point, 356°F, which was exceeded by 350°F during the reduction step. This experiment demonstrates the decreased rate of deactivation of platinum when used in SMSC mode. Although the cracking is almost doubled that observed in the conventional catalyst, it is still only about 5%.

Experiment 5. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 218 °F (103°C)

Reservoir Pressure (He + MCH): 105 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	876	100	1.8	14.6	83.6
11	876	100	2.5	5.8	90.1
58	878	100	17.5	11.3	71.2
85	882	100	12.5	3.7	83.8
123	887	100	9.3	15.3	75.3
185	878	100	5.0	22.5	72.5
352	878	100	29.0	9.7	57.7
485	883	100	11.0	45.2	43.6
527	883	100	12.8	57.7	30.0

The results of this experiment suggest that a given quantity of catalyst, when dispersed in a larger volume of molten salt, displays a lower activity. This effect may have its origin in diffusional retardation since the molten salt liquid layer is thicker at higher liquid loading. This same effect could decrease the efficiency of hydrogen reduction of the catalyst at higher liquid loading. This would explain why the initial activity is lower at liquid loading of 0.30 than at 0.15. The calculated average thicknesses of molten salt films for the pore sizes used in this research are found in Table 1.

Experiment 6. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 3.3%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.50

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 218 °F (103°C)

Reservoir Pressure (He + MCH): 105 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 16 h, 770°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	860	94	67.3	-	32.0
27	860	90	41.4	-	57.0
63	860	90	20.8	-	78.0
97	860	93	16.3	1.0	76.3
134	860	93	21.9	1.5	69.7
191	867	91	8.6	2.4	92.1
281	865	90	9.1	4.5	91.3
358	865	92	2.6	3.3	94.0
540	865	92	13.7	2.6	83.6
600	869	95	3.0	14.9	82.1
650	865	90	2.6	15.5	80.7
695	865	90	2.5	12.9	82.5

The observations in this experiment are not inconsistent with the discussion found after Experiment 5. The relatively low activity observed in the initial conversion may be due to a less efficient or slower hydrogen reduction process accompanying the higher liquid loading. The higher platinum loading makes it possible for the catalyst to eventually attain an activity near that displayed in Experiment 4.

For Experiments 1 through 6 reported before, the total amount of catalyst preparation placed in the tube reactor was approximately 7 g. Experiments 7 through 11 were performed to study the effects of varying catalyst precursor reduction period, reactor temperature, and MCH feed composition on the catalyst performance. In these experiments the catalytic behavior of 1 g portions of a large catalyst preparation was examined while systematically altering these operational variables. The catalyst was used as a plug in the center 1 in of the reactor tube with approximately 3 in of SiO₂ support both before and after (i.e. upstream and downstream) the plug.

Experiment 7. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217.5 °F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 14 h, 698°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	799	85	12.5	22.0	65.5
11	802	85	2.0	18.6	79.4
22	804	85	1.9	27.5	70.6
95	806	85	0.5	94.6	4.9

Experiment 8. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217.5 °F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 28 h, 698°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	817	85	6.6	4.6	88.7
10	817	85	6.6	6.5	87.0
23	813	85	6.6	10.2	83.2
53	815	85	5.5	22.6	71.9
78	813	85	4.1	38.7	57.1
114	819	85	2.6	71.8	25.7
161	831	85	0.7	96.7	2.6

The results of Experiments 7 and 8 indicate clearly that the length of catalyst precursor reduction has a very significant impact, not only on the initial catalyst activity, but also on the observed rate of catalyst deactivation. In both cases the black color of the deactivated catalyst, which is light grey before MCH is passed, suggests that the mechanism of deactivation is by coking. The results of Experiments 7 and 8 further suggest that the rate of coking is retarded by increased extent of catalyst precursor reduction.

Experiment 9. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 127°F (53°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 14 h, 698°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	819	85	4.8	28.6	67.7
13	822	85	3.2	35.0	61.8
25	826	85	3.2	45.3	51.4
48	828	85	2.3	67.0	28.7
64	828	85	1.1	85.0	13.8
85	826	85	0.7	94.7	4.5

This experiment involves significantly lower MCH flow rates since the partial pressure of MCH is significantly lower in the feed gas. The results suggest that decreased flow rate does not significantly influence the MCH to toluene conversion nor the rate of catalyst deactivation. The spent catalyst was observed to be black as in Experiments 7 and 8.

Experiment 10. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217°F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 28 h, 698°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	705	85	3.0	7.7	89.4
8	705	85	2.3	10.7	86.9
31	705	85	1.8	14.0	84.1
53	705	85	1.7	17.0	81.4
66	707	85	1.6	19.3	79.1
106	705	85	1.4	21.3	77.3
167	707	85	1.4	25.7	72.9
285	707	85	1.5	30.6	67.9

These results, especially when compared to the results of Experiment 8, indicate that the MCH conversion to toluene is very high at this lower temperature for the adequately reduced catalyst. The significant decrease in the rate of deactivation and the very low occurrence of cracked products are both consistent with the anticipated decreased rate of coking at lower temperatures.

Experiment 11. MCH - Pt-NaOH-KOH/SiO₂

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217°F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 1 atm, 28 h, 698°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	457	85	16.0	78.6	5.4
11	455	85	0.5	93.8	5.7

The data are sparse simply because no significant conversion of MCH to toluene was detected in subsequent samplings. This is probably due to the fact that the molten salt components were either not molten at this low temperature or the high viscosity expected at temperatures just above the melting point led to very high diffusional retardation of catalytic dehydrogenation. Since the catalyst used in this experiment is the same as that used in Experiment 10 there is little doubt that the initial activity should be quite high if MCH reaches permeates the salt film.

b. ALUMINA SUPPORT

The alumina support used was United Catalysts Inc., # T-2432. The following characteristics are reported by the manufacturer in product bulletin CC-0381.

Major components: 99.0% Al_2O_3

Surface area: 85 m^2/g

Total pore volume: 0.70 cc/g

Average pore diameter: 350 A

Approximate bulk density: 40 lbs/CF

Crush strength: 17 lbs

Form: extrudate, 3/16 in D

Experiment 12. MCH - Pt/Al₂O₃ ("conventional" heterogeneous catalyst)

Catalyst: Pt, 1%

Supported Molten Salt: n/a (q): 0.00

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 131°F (55°C)

Reservoir Pressure (He + MCH): 60 psi

Drying: 2 h, 302°F. Reduction: H₂ gas, 100psi, 14.5 h, 779°F.

Elapsed Time(min)	Reactor Temp. (°F)	Reactor Press. (psi)	Cracked	MCH	TOLUENE
17	946	60	17.4	1.4	81.2
47	961	60	19.4	0.6	80.0
77	961	60	24.5	20.8	54.7
107	965	60	32.2	17.2	50.6
137	967	60	38.8	20.4	40.8
192	959	60	41.7	11.1	48.2
262	967	60	34.9	8.3	56.9
367	963	60	37.5	5.0	57.5
460	961	60	29.0	5.3	65.7
730	963	60	41.6	6.5	51.7
1550	959	60	36.2	0.0	63.8

The results of this experiment, and subsequent repetitions, served as the basis for comparison of conventional Pt/Al₂O₃ catalysts with SMSC catalysts.

Experiment 13. MCH - Pt-NaOH-KOH/Al₂O₃

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: variable

Reservoir Temperature: variable

Reservoir Pressure (He + MCH): variable

Drying: 2 h, 160°F. Reduction: H₂ gas, 100psi, 12 h, 788°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Reservoir Temp.(°F)	Flow cc/min	Cracked MCH	TOLUENE
10	952	60	115	47	69.8	10.1
20	914	60	117	70	33.4	13.7
40	892	60	115	70	17.2	14.1
50	874	80	118	23	22.6	9.5
70	860	73	118	30	22.9	20.8
120	862	73	118	26	25.8	22.5
180	862	73	115	26	26.2	26.2
240	860	73	109	26	27.4	30.1
300	853	65	126	26	26.4	32.1
360	862	61	127	26	31.7	37.4
470	864	57	136	30	27.3	36.4
600	860	57	122	30	25.5	45.5
1140	851	57	117	30	24.4	53.4
1200	905	57	118	30	27.0	67.6
1380	932	57	151	23	58.6	41.4
1440	928	57	153	46	44.7	42.4
2160	855	60	113	30	25.3	65.8
2640	849	62	118	30	29.0	71.0
3060	900	60	122	30	20.0	75.0

Although the experimental design in Experiment 13 seems to be characterized by randomness more so than order, the data are included to emphasize the general observation that catalyst activity can display significant increases during the experiment. Apparently the hydrogen reduction conditions used in the preparation of this catalyst did not permit sufficient reduction to give high initial activity. This is surprising in view of the fact that the conditions are more rigorous than those used in Experiments 7 and 9 in which initial MCH to toluene conversions exceeded 65%. These observations suggest that the support plays some role in determining the efficiency of the reduction process when a molten salt is present. It is possible that the alkali metal hydroxide eutectic dissolves enough Al_2O_3 to produce a eutectic which retards hydrogen reduction of the catalyst precursor at the temperature used in the reduction.

Experiment 14. MCH - Pt-NaOH-KOH/Al₂O₃

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 46 cc/min

Reservoir Temperature: 118°F (48°C)

Reservoir Pressure (He + MCH): 60psi

Drying: 40 h, 284°F. Reduction: H₂ gas, 85 psi, 12 h, ramped 248-842°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
30	846	60	29.2	0.0	70.8
60	844	60	9.6	0.4	90.0
90	842	60	10.0	1.0	89.0
120	844	60	10.0	3.0	87.8
210	838	60	8.6	10.1	81.3
240	852	60	8.1	4.9	87.0
300	887	60	14.0	2.0	84.0
330	844	60	6.0	17.4	76.6
360	860	60	8.7	14.3	77.0
420	854	60	9.0	19.0	72.0
480	905	60	15.0	5.0	80.0
540	836	60	4.6	31.8	63.6
750	867	60	8.2	28.5	63.3
1440	894	60	0.4	76.0	23.6

This catalyst displays a significantly greater activity than the "conventional" catalyst through 12.5 h but lower activity after 24 h. One of the possible contributions to the loss of activity, when alkali hydroxides are used as the eutectic, is the dissolution of Al₂O₃ or SiO₂ in

the eutectic. This would lead to an increasing melting point, which would eventually give diffusional retardation as the viscosity increased or no reaction if the molten layer solidified.

The used catalysts in Experiments 13 and 14 displayed less extensive coking than the "conventional" catalyst used in Experiment 12.

Experiment 15. MCH - Pt-KCl-NaCl-LiCl/Al₂O₃

Catalyst: Pt, 1.0%

Supported Molten Salt: KCl/NaCl/LiCl (26/36/38 mole%) (q): 0.30

MCH/He Flow Rate: 48 cc/min

Reservoir Temperature: 212°F (100°C)

Reservoir Pressure (He + MCH): 85 psi

Drying: 10 h, 302°F. Reduction: H₂ gas, 100 psi, 18 h, ramped

662-842°F.

Elapsed Time(min)	Reactor Temp. (°F)	Reactor Press. (psi)	Cracked	MCH	TOLUENE
40	846	85	79.1	0.7	20.2
60	846	85	69.9	2.1	28.8
90	844	85	62.6	2.0	35.4
120	844	85	58.6	1.5	39.9
150	847	85	51.5	0.5	48.0
180	847	85	41.4	0.0	58.6
240	847	85	32.0	0.0	68.0
300	847	85	34.8	0.0	66.0
360	849	85	34.9	0.0	65.1
420	849	85	32.2	0.0	67.8
480	853	85	32.1	0.0	67.9
540	844	85	33.3	0.0	66.7
600	847	85	19.8	0.0	80.2
1320	838	85	28.0	0.0	72.0

Experiment 16. MCH - Pt-KCl-NaCl-LiCl/Al₂O₃

Catalyst: Pt, 2.0%

Supported Molten Salt: KCl/NaCl/LiCl (26/36/38 mole%) (q): 0.30

MCH/He Flow Rate: 60 cc/min

Reservoir Temperature: 167°F (75°C)

Reservoir Pressure (He + MCH): 85 psi

Drying: 15.5 h, 302°F. Reduction: H₂ gas, 100 psi, 18 h, ramped

248-779°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
3	835	85	10.1	55.7	34.2
15	837	85	0.0	95.2	4.8
40	907	85	1.9	91.2	7.9
50	919	85	2.0	85.0	13.0
75	934	85	8.9	71.8	20.3
90	936	85	9.7	71.4	19.9
120	930	85	4.7	72.1	23.2
185	934	85	6.2	67.2	26.6
250	937	85	7.2	59.9	32.9
300	937	85	10.0	63.0	27.0
360	939	85	10.7	60.4	28.9
420	943	85	8.5	53.1	38.4
480	936	85	4.8	42.4	52.8
540	932	85	2.6	45.8	51.6
960	918	85	7.4	55.0	37.6
1080	930	85	6.0	53.5	40.5

The results of Experiments 15 and 16 seem to be inconsistent with one another in that the catalyst containing the highest percentage of platinum displays lower activity after extended periods but displays a higher initial activity.

In a separate experiment using the KCl/NaCl/LiCl eutectic, 2.0% Pt, and $q = 0.30$ it was observed that hydrogen reduction of the catalyst for two hours at 1022°F led to 70% initial conversion of MCH to toluene. This conversion remained nearly constant at 70%, with 30% cracking for 8160 min. When the reactor temperature was lowered to 896°F the conversion dropped to 20%. Upon raising the temperature to 932°F, the conversion returned to 65% in 45 min. These observations are apparently due to diffusional limitations or freezing at the lower temperature. Even if freezing occurred, some catalysis would be expected by microcrystallites which extended above the surface of the frozen eutectic. At 959° the conversion to toluene was 68%, with 32% cracking. At even higher temperatures the conversion to cracked product increased and toluene production decreased. Detailed data for this experiment are not reported because of a system leak discovered late in the experiment which made the flow measurements meaningless. The experiment is of value in that it indicates that the use of much higher temperatures in the reduction process can increase initial activities.

2. NICKEL CATALYSTS

Nickel catalysts were used, in each experiment, with the same silica support that was used with platinum catalysts.

Experiment 17. MCH - Ni/SiO₂ ("conventional" heterogeneous catalyst)

Catalyst: Ni, 1.0%

Supported Molten Salt: - (q): 0.0

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217°F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 302°F(vacuum). Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	824	85	30.3	24.9	44.8
11	824	85	45.3	40.7	12.1
22	824	85	49.5	43.2	6.4
80	824	85	52.7	47.3	-

The results reported are consistent with reports found in the literature for nickel used as a heterogeneous catalyst for the dehydrogenation of cycloalkanes. The initial activity observed here is somewhat higher than usually reported. The activity for conversion of MCH to toluene has decreased by a factor of seven in only 22 min under the conditions used.

Experiment 18. MCH - Ni-NaOH-KOH/SiO₂

Catalyst: Ni, 2.3%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217°F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 572°F(vacuum). Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	885	85	24.6	62.6	12.5
56	909	85	34.5	47.5	10.9
132	901	85	33.5	51.7	14.5
249	912	85	30.6	51.6	17.7
304	907	85	30.1	49.4	20.4
356	903	85	30.2	49.1	20.7
423	903	85	28.9	47.0	24.2
601	916	85	35.4	36.7	28.0
676	912	85	36.0	34.0	29.7
790	912	85	31.5	34.0	34.2

The last recorded product analysis represents the highest conversion observed in this experiment but this isn't necessarily the upper limit which can be reached since the experiment was arbitrarily terminated at 790 min. The gradual increase in activity suggests that the reduction procedure used is not converting all of the catalyst precursor to Ni. As hydrogen is released during the dehydrogenation of MCH in the molten salt, there is additional reduction of NiCl₂.

Experiment 19. MCH - Ni-NaOH-KOH/SiO₂

Catalyst: Ni, 3.8%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.50

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217°F (103°C)

Reservoir Pressure (He + MCH): 85 psi

Drying: 2 h, 572°F(vacuum). Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	846	85	15.9	78.4	4.3
43	848	80	21.0	71.5	6.7
90	842	80	12.7	78.6	7.3
150	842	80	12.7	79.3	7.5
220	842	80	12.1	79.9	7.7
280	842	80	13.4	78.0	8.4
327	842	80	11.5	80.4	8.0
690	842	80	13.0	77.5	9.4
768	842	80	11.9	78.3	9.7

As was observed with platinum SMSC, when the liquid loading is elevated to 0.50 the initial activity of the catalyst is lower. This catalyst displays a tendency to increase its activity for MCH to toluene conversion with time, but at a very slow rate. The catalyst pellets, removed from the reactor after the reaction, were all black on the outside but displayed the white color characteristic of the untreated pellets in the middle. This suggests that pore blockage has precluded thorough loading of the pellet and the catalytic activity observed was occurring at catalyst sites only near the outer surfaces.

Experiment 20. MCH - Ni-NaOH-KOH/SiO₂

Catalyst: Ni, 2.3%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

MCH/He Flow Rate: 30 cc/min

Reservoir Temperature: 217°F (103°C)

Reservoir Pressure (He + MCH): 100 psi

Drying: 2 h, 572°F(vacuum). Reduction: H₂ gas, 1 atm, 14 h, 752°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	Cracked	MCH	TOLUENE
1	921	85	11.8	80.5	2.8
66	1018	85	15.5	74.6	8.6
140	1071	85	22.6	59.2	16.9
230	1135	85	23.8	44.5	32.3
320	1139	85	19.7	32.1	44.6
360	1144	85	19.3	32.1	44.0
380	1245	85	41.9	6.9	47.9
680	1152	85	25.7	20.4	50.1
794	1162	85	29.1	13.5	54.3

The results of this experiment suggest, as did Experiment 18, that catalyst formation by hydrogen reduction in the eutectic is not very efficient. The catalyst pellets, removed from the reactor after the reaction, displayed evidence of coking but to a smaller extent than observed in Experiment 19. This may be associated with the lower liquid loading used in this experiment. This experiment, which was arbitrarily stopped at 794 minutes, suggests that nickel as a dehydrogenation catalyst in SMSC is much more effective than "conventional" nickel heterogeneous catalysts. With more extensive attempts to optimize the operational conditions for use of

nickel in SMSO, this catalyst certainly shows promise of competing with "conventional" platinum heterogeneous catalysts, not only in conversion, but in rate of deactivation.

D. DECAHYDRONAPHTHALENE DEHYDROGENATION

Decalin has been catalytically dehydrogenated using both a "conventional" platinum heterogeneous catalyst and a SMSC platinum catalyst using the same catalyst loading, the same support, and the same operating conditions.

Experiment 21. Decalin - Pt/Al₂O₃ ("conventional" heterogeneous catalyst)

Catalyst: Pt, 1%

Supported Molten Salt: n/a (q): 0.00

Decalin/He Flow Rate: 30 cc/min

Reservoir Temperature: 218 °F (103°C)

Reservoir Pressure (He + Decalin): 80 psi

Drying: 16 h, 302°F(vacuum). Reduction: H₂ gas, 100psi, 16 h, 842°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	DEC	NAPH	TET	OTHER
60	880	80	68	32	-	-
150	869	80	50	40	10	-
180	869	80	2	73	25	<1
330	880	80	7	93	-	<1
480	873	80	14	52	33	1
1080	877	80	11	38	50	1
1170	880	80	28	28	38	62

In contrast to every experiment in which MCH was dehydrogenated, the catalyst did not display significant greying or blackening after the dehydrogenation of decalin. Apparently the cracking products of decalin and its dehydrogenation products do not lead to the formation of coke.

Experiment 22. Decalin - Pt-KCl-NaCl-LiCl/Al₂O₃

Catalyst: Pt, 1.0%

Supported Molten Salt: KCl/NaCl/LiCl (26/36/38 mole%) (q): 0.30

Decalin/He Flow Rate: 70 cc/min

Reservoir Temperature: 212°F (100°C)

Reservoir Pressure (He + Decalin): 80 psi

Drying: 12 h, 302°F. Reduction: H₂ gas, 100 psi, 16 h, 1022°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	DEC	NAPH	TET	OTHER
30	986	80	-	62	-	38
60	973	80	-	39	-	61
180	928	80	-	92	4	4
240	928	80	-	92	4	4
300	914	80	-	79	19	2
360	901	80	-	80	16	4

After vacuum drying at elevated temperature, the impregnated support pellets were placed into the tube reactor. As was observed in Experiment 21, no catalyst coking occurred for the platinum SMSC catalyst. The SMSC catalyst appears to be more active than the conventional Pt catalyst in that decalin is not detected at any time with the SMSC catalyst. The SMSC catalyst does not produce tetralin, in 360 min, at the level produced by the "conventional" platinum catalyst in 180 min. These results suggest that the advantages offered for catalytic dehydrogenation by the SMSC method are greater for decalin than for MCH although advantages are obvious for both.

E. *exo*-OCTAHYDRO-4,7-METHANO-1H-INDENE (JP-10) DEHYDROGENATION

JP-10 is of interest because of the possible occurrence of a coupled Retro-Diels-Alder reaction which would take place spontaneously after catalytic dehydrogenation occurs. JP-10 has been catalytically dehydrogenated using both a "conventional" platinum heterogeneous catalyst and a SMSC platinum catalyst using the same catalyst loading, the same support, and the same operating conditions.

Experiment 23. JP-10 - Pt/Al₂O₃ ("conventional" heterogeneous catalyst)

Catalyst: Pt, 1%

Supported Molten Salt: n/a (q): 0.00

Decalin/He Flow Rate: 60 cc/min

Reservoir Temperature: 203°F (95°C)

Reservoir Pressure (He + JP-10) 80 psi

Drying: 16 h, 302°F(vacuum). Reduction: H₂ gas, 100psi, 16 h, 842°F.

Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	JP-10	DCP ^a	C ₈ H ₁₀	OTHER
90	937	80	6	-	-	94
210	941	80	7	-	-	93
300	896	80	14	8	-	78
870	918	80	45	21	12	22
975*	928	80	8	22	8	62
1110	928	80	24	18	5	53
1200	972	80	45	26	24	5

The data collected in this experiment display an unexplainable cyclic behavior rather than a monotonic variation anticipated as catalyst activity falls off. The materials listed as OTHER seem to be minimum and the C₈H₁₀ seems to be maximum when the lowest conversion of JP-10 occurs. Examination of the catalyst after the reaction revealed extensive coking. The formulas of some of the species included in OTHER were determined using mass spectroscopy. A proposed relationship between a number of these and C₈H₁₀ will be discussed after the presentation of the SMSC catalysis results in Experiment 24.

^a dicyclopentadiene

* The reactor was restarted after a line was unplugged.

Experiment 24. JP-10 - Pt-NaOH-KOH/Al₂O₃

Catalyst: Pt, 1.0%

Supported Molten Salt: NaOH/KOH (47/53 mole%) (q): 0.30

JP-10/He Flow Rate: 60 cc/min

Reservoir Temperature: 203°F (95°C)

Reservoir Pressure (He + JP-10): 80 psi

Drying: 16 h, 572°F(vacuum). Reduction: H₂ gas, 100psi, 15.5 h, 752°F.

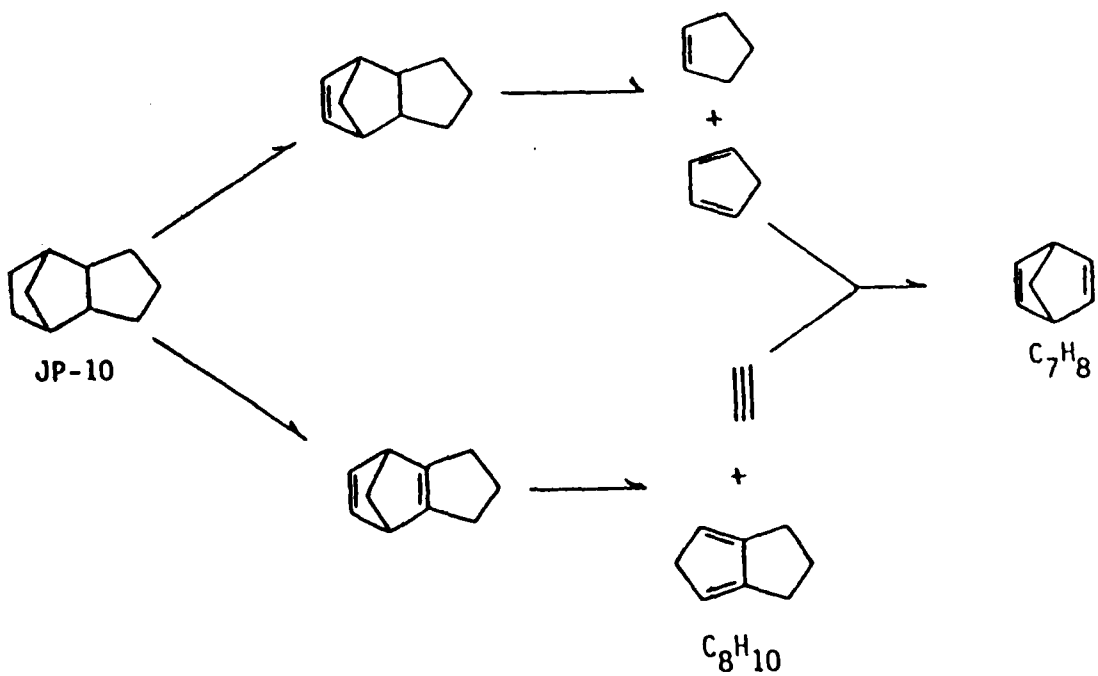
Elapsed Time(min)	Reactor Temp.(°F)	Reactor Press.(psi)	JP-10	DCP ^a	C ₈ H ₁₀	OTHER
90	905	80	22	-	22	56
180	891	80	57	-	14	29
315	900	80	9	66	6	19
1050	889	80	17	12	57	14
1080	907	80	19	60	12	9
1125	909	80	25	10	25	40
1245	903	80	8	12	58	22
1335	896	80	13	13	47	27
1410	905	80	11	13	37	39
1890	909	80	5	13	72	10

^a dicyclopentadiene

The data from this experiment also display the cyclic behavior mentioned in the discussion of Experiment 23. A significant portion of the species marked OTHER contains low molecular weight volatile species which apparently arise by way of some cracking mechanism. These products reach maximum productivity when JP-10 conversion is lowest and vice versa.

The most striking thing about the data from this experiment is the production of C₈H₁₀ (as determined by gas chromatography - mass spectral

analysis) which increases as the reaction proceeds. The production of this species represents a major pathway in the observed reaction. Another interesting species found in the OTHER grouping is C_7H_8 . One possible reaction sequence which ties all of these products together is shown in Scheme 1. This scheme is consistent with the experimental design currently used which involves sampling the product gas stream by gas chromatography after it has passed through a length of 1/8 in stainless steel tubing and has cooled several hundred degrees. Diels-Alder reactions, which would be spontaneous at the lower temperatures downstream from the reactor, could give rise to many of the observed products. The observation of C_7H_8 is especially of importance since this species is known to form very rapidly and spontaneously at $400^\circ F$ and lower by the Diels-Alder reaction of acetylene and cyclopentadiene. The method of analysis used in this experiment would not permit direct detection of acetylene but its production can be inferred by detection of its Diels-Alder addition products and by the detection of C_8H_{10} , the second product formed in the Retro-Diels-Alder reaction which produces acetylene.



SCHEME 1.

CONCLUSIONS

The use of metal microcrystallites heterogeneously dispersed in supported molten salts for catalytic processes represents a new technology. The results reported herein represent the first data available and should be considered very preliminary.

The method of SMSC applied to catalytic dehydrogenation of cycloalkanes appears to offer some potential for overcoming problems previously encountered in this process.¹ The experiments reported here were done at very low flow rates and without high extremes in temperature or pressure. The true potential of this technology will not be known until studies are done at much higher flow rates.

In dehydrogenation of methylcyclohexane under the same operating conditions, platinum SMSC catalysts display comparable activity but much better stability to deactivation than "conventional" platinum heterogeneous catalysts. Nickel SMSC catalysts display both higher activity and increased catalyst lifetime when compared to "conventional" nickel heterogeneous catalysts. In dehydrogenation of decalin, a platinum SMSC catalyst displayed higher activity than a "conventional" platinum heterogeneous catalyst. In dehydrogenating JP-10, a platinum SMSC catalyst displayed higher activity and decreased rate of deactivation relative to a "conventional" heterogeneous platinum catalyst. In addition, this catalyst displayed an apparent selectivity for sites of dehydrogenation which made it possible to produce acetylene in a subsequent Retro-Diels-Alder reaction.

The optimization of SMSC catalysis of cycloalkane dehydrogenation, which should generate a catalyst superior to a "conventional" heterogeneous catalyst will require in-depth studies of the systematic and operational variables.

REFERENCES

1. Nixon, A.C., *A Study on Endothermic and High Energy Fuels for Airbreathing Engines*, 1986.
2. Janz, G.J., *The Molten Salt Handbook*, Academic Press, 1967.
3. (a) Fogar, K., *Catalysis*, 1984, 6, 227.
(b) Romanowski, W., *Highly Dispersed Metals*, John Wiley & Sons, 1987.
4. (a) Datta, R.; Rinker, R.G., *J.Catal.*, 1985, 95, 181.
(b) Datta, R.; Savage, W.; Rinker, R.G., *J.Catal.*, 1985, 95, 193.
(c) Datta, R.; Rydant, J.; Rinker, R.G., *J.Catal.*, 1985, 95, 202.
5. a. Lee, S.; Aris, R., *Catal.Rev.-Sci.Eng.*, 1985, 27, 207.
b. Heise, M.S.; Schwarz, J.A., *J.Coll.Interface Sci.*, 1985, 107, 237.