

Final Technical Report
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Project Title: Autothermal Styrene Manufacturing Process with Net Export of Energy

Project Period: 9/1/2010-8/29/2011

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1. Executive Summary

The overall objectives of the project were to: a) develop an economically competitive processing technology for styrene monomer (SM) that would reduce process energy requirements by a minimum 25% relative to those of conventional technology while achieving a minimum 10% ROI; and b) advance the technology towards commercial readiness. This technology will be referred to as OMT (Oxymethylation of Toluene).

The unique energy savings feature of the OMT technology would be replacement of the conventional benzene and ethylene feedstocks with toluene, methane in natural gas and air or oxygen, the latter of which have much lower specific energy of production values. As an oxidative technology, OMT is a net energy exporter rather than a net energy consumer like the conventional ethylbenzene/styrene (EB/SM) process.

OMT plants would ultimately reduce the cost of styrene monomer which in turn will decrease the costs of polystyrene making it perhaps more cost competitive with competing polymers such as polypropylene, the latter of which is made from propylene monomer-the third most energy

intensive chemical consuming some 700 trillion Btu/yr or more than 200% of that of styrene monomer. If the estimated energy reduction per SM plant is achieved and implemented in 50% of the current US plants, this would translate to a savings of about 40 trillion Btu/yr which is equivalent to about 6.4 Million Bbl F.O.E. per year that need not be imported from the OPEC countries.

Based on the DOE's annual emissions report, petrochemical feeds are the largest source of CO₂ emissions from nonfuel use of fossil fuels. The proposed OMT technology would decrease life cycle emissions of CO₂ relative to those of the conventional EB/SM process by about 58%. This decrease in life cycle CO₂ emissions results from using less energy intensive feedstocks; lower power consumption; and minimal fuel consumption.

A preliminary process design flowsheet and material and energy balances were formulated based on literature data and our styrenics flowsheet engineering expertise; and minimum targets for economic competitiveness developed. The following table lists the key performance parameters and values from the literature; minimum performance for competitiveness; and targeted performance for superior economics relative to those of the conventional EB/SM route. The primary minimum performance requirement is at least a 49% yield of toluene /pass to styrene monomer.

<u>Performance Parameter</u>	<u>Lit. Result</u>	<u>Target Performance</u>	<u>Min. Required Performance</u>
Methane/Toluene Molar Feed Ratio	10	4	≤5
Toluene Conversion per Pass	76.3%	80%	≥70%
Selectivities of Converted Toluene			
to SM	69.3%	74%	≥72%
Total to C6-C8 ring compounds	86.3%	93%	≥90%
to other by-products	13.7%	7%	≤10%
Catalyst Life, Years	--	>1	≥0.5

The critical project objective was to discover at least one catalyst for conversion of toluene and methane feedstocks to SM under oxidative conditions that achieved the minimum economical performance targets (Milestone 2). The best per pass yields of toluene to styrene monomer + ethylbenzene achieved were only in the range of 15-20%. Since we were unable to discover a catalyst that performed at a level close to our minimum economic requirements, none of the other objectives of the program could be met.

The key assumption in the program was that the literature references represented viable and accurate catalyst performances for toluene oxymethylation. It was assumed that these catalysts as baseline performance can be improved to meet the minimum targeted performance by applying some of the Lummus proprietary catalyst and catalyst support technology. Research was carried out between 1990 and 2000 by primarily three research organizations, namely, Korea Research Institute of Chemical Technology; SUNY-Buffalo and Beijing University. While none of the reported data reached the targeted SM (+EB) yields, there was a definite progression in improved performance by almost 600% and we believed that there was a reasonable potential for enhancing those performances. However, it is possible that what was reported as the step change increase in catalyst activity and selectivity also carried with it the issue of rapid deactivation and that what was reported was initial data. To be viable commercially the minimum required performance would need to be maintained at least several weeks.

2. Comparison of Actual Accomplishments with Project Goals and Objectives

As per the SOPO program had been split into six Tasks and fourteen subtasks.

Task 1.0 Project Management and Reporting.

The following deliverables were associated with Task 1.0

- 1) Program Plan Document containing all Milestones, Schedules, Materials Requirements
- 2) Latest Catalyst Screening data
- 3) Preliminary Conceptual Design Document
- 4) Database of Catalyst Formulations meeting minimum targeted performance specifications
- 5) Proposed Stage 3 Plan
- 6) Final Report

Task 1 Comparison of Goals and Accomplishments

Program Plan Document – due 10/31/10, submitted 10/19/10

Catalyst Screening Data –provided.

Potential Benefits Assessment assuming successful development /commercialization of the improved styrene technology using target values – Included as Appendix C and submitted in the Quarterly Report for the period ending December 31, 2010.

Preliminary Conceptual Design Document – Unable to deliver due to failure to attain Milestone #2-

Database of Catalyst Formulations meeting minimum targeted performance specifications- Unable to discover catalyst which meets minimum targeted performance.

Proposed Stage 3 Plan – Unable to deliver due to failure to attain Milestone 2.

Commercialization Plan – Unable to deliver due to failure to attain Milestone 2

Task 2.0 Oxymethylation Catalyst Formulation Program

Task 2 was the preparation of catalyst candidates. There were three subtasks:

Subtask 2.1- Formulate catalyst candidate compositions and catalyst synthesis methods.

Subtask 2.2 – Prepare gram size samples of up to approximately 150 powdered catalyst formulations in lab equipment.

Subtask 2.3- Analyze/characterize selected fresh and spent catalyst samples

Task 2 Comparison of Goals and Accomplishments

Status- Our intent was to eventually synthesize samples that, upon testing would meet our performance targets. As noted we were unable to achieve this goal.

Catalyst Formulations, –85 samples prepared

Catalyst Analysis - provided

Task 3.0 Continuous Lab-Scale Oxymethylation Catalyst Screening Studies

Task 3 was the testing of selected catalyst candidates from Task 2 in lab-scale reaction systems. There were three subtasks:

Subtask 3.1- Establish baseline performance with catalyst compositions reported in the literature

Subtask 3.2 – Perform continuous bench-scale test scans for catalyst candidates

Subtask 3.3- Develop correlations of effect of catalyst type and condition severity on conversion/selectivity

Task 3 Comparison of Goals and Accomplishments

Status -Unable to achieve Milestone #2 (Establish baseline performance with catalyst compositions reported in the literature)

Task 4.0 Engineering Scaleup /Process Economics Evaluation Studies

Task 4 was the engineering evaluation task of the economic potential of the oxymethylation technology. Six key subtasks were identified:

Subtask 4.1 – Establish preliminary design basis / targets for a conceptual commercial-scale OMT facility

Subtask 4.2- Perform preliminary heat and material balances

Subtask 4.3- Generate preliminary major equipment specs

Subtask 4.4 – Perform baseline economic analyses to determine minimum conversion/selectivity performance requirements for economic competitiveness

Subtask 4.5 – Compare the minimum requirements with economics that reflect data collected in Task 3.

Task 4 Comparison of Goals and Accomplishments

Task 4 was not performed since were unable to achieve Milestone #2

Task 5.0 Plan for Stage 3 Bench- Scale Process Development Unit (PDU)

Task 5 was to identify scaleup requirements for a Stage 3 PDU. There would be three subtasks:

Subtask 5.1 – Determine the reactor design and associated equipment scaleup requirements for a commercial size plant

Subtask 5.2 - Develop a technical and cost plan for demonstrating OMT technology in a bench-scale process development unit

Subtask 5.3 – Identifying the costs and potential partners for a Semi-Works demonstration unit

Task 5 Comparison of Goals and Accomplishments

Task 5 was not performed since were unable to achieve Milestone #2

Task 6.0 Potential Benefits Assessment

Task 6 was to I assess the potential benefits to the US styrene industry of implementing the proposed oxymethylation technology

Task 6 Comparison of Goals and Accomplishments

Status— Initial Benefits Assessment provided based on assumed performance. Updated Benefits Analysis not performed since we were unable to meet Milestone 2.

3. Summary of Project Activities

- a. Introduction
- b. Chemistry
- c. Catalyst Background and Literature Survey
- d. Catalyst Selection,
- e. Preparation and Analysis
- f. Experimental Unit and Operating Conditions
- g. Catalyst Test Results and Conclusions
- h. Recommendations and Proposed Future Studies
- i. References

3a.Introduction

Oxidative methylation of toluene (OMT) was proposed as an alternative or an implemented process to the current ethylbenzene/styrene monomer (EBSM) process.

The focus of this project was on the search for suitable OMT catalysts. Main challenges were:

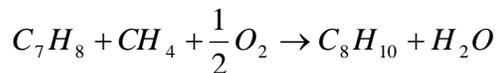
- 1) Activating the methane molecule, requiring high temperature
- 2) Achieving high selectivity at high temperature (700-800°C),
- 3) Finding a stable material at reaction condition which can also provide stable catalytic performance,
- 4) Minimizing selectivities of both light and heavy byproducts at with the same catalyst. (Directionally, increasing conversion to EB and styrene can lead to higher selectivity losses to aromatic dimmers and PAHs, high oxidative activity to prevent formation of undesired heavy byproducts can result in high CO_x formation)

3b.Chemistry

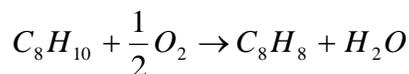
While the objective was to maximize styrene yield, EB and styrene were both considered desired products. Reactants of OMT are oxygen, methane and toluene. Reaction temperature needs to be higher than 700°C to effectively activate methane. A highly complex reaction network emerges at such high temperature. Reaction between methane and toluene can form many alkylated compounds with EB, styrene, and xylenes being the main products. Methane and toluene can each be coupled oxidatively or non-oxidatively to form their respective dimers. Methane can go on to be oligomerized to form higher hydrocarbons and/or combined into aromatics even leading to PAH. Products of these reactions go on the form other byproducts. Other than a variety of hydrocarbons, the presence of oxygen caused formation of many oxygenates besides CO_x. These reactions can be sorted into desired reactions, undesired reactions and possible byproduct reactions that can be advantageous.

Desired reactions:

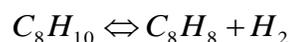
- 1) Oxidative methylation of toluene (OMT) to ethylbenzene (EB):



2) Oxidative dehydrogenation of EB to styrene:



Besides the main reactions, non-oxidative dehydrogenation reaction of EB is also desired:

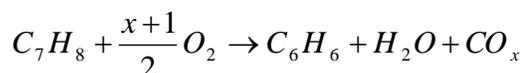


This non-oxidative dehydrogenation reaction can also happen in OMT with limited oxygen composition and/or low oxidative activity.

The most important step is the methylation of toluene on its methyl group. This can be achieved by using basic catalysts. Acidic catalysts will instead cause the alkylation on the aromatic ring (either direct alkylation or transalkylation).

Undesired reactions:

1) Dealkylation of toluene to benzene:



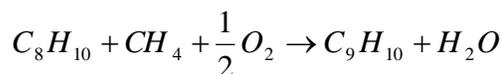
While benzene is mainly formed by thermal oxidative dealkylation, it can also be formed in two other reactions: aromatization of methane and disproportionation of toluene.

2) Toluene to xylene:

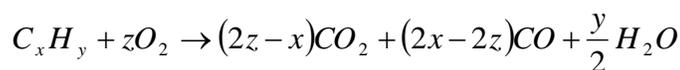


The higher the acidity the more xylenes can be formed via methylation. There is no clear evidence of any favorable conditions of disproportionation other than in the absence of oxygen and methane.

3) Cumene formation:



4) Oxidation of hydrocarbons to CO and CO₂:



5) Oxidation oligomerization of methane:

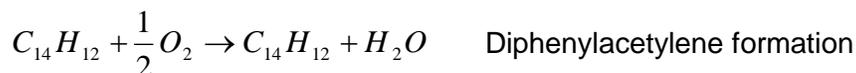
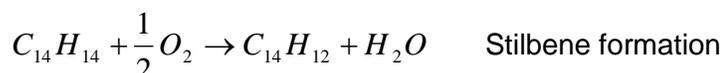
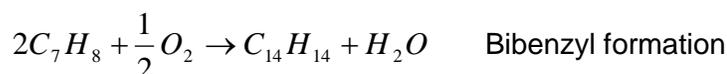




Other than ethane, ethylene, acetylene, propylene and butadiene, relatively smaller amounts of other oligomers such as propadiene, butenes and pentenes can be also present depending on the catalyst used. Ethylene can be a desired intermediate since it can react with benzene to potentially form EB.

The reactions above are the widely investigated oxidative methane coupling (OCM) reactions. The majority of the catalysts used are basic mixed metal oxides. Similar operating condition and ability to activate methane make mixed metal oxides good candidates as potential OMT catalysts.

6) Dimerization of toluene:



7) Coking / formation of PAH (polycyclic aromatic hydrocarbon):

Aromatization and thermal decomposition can lead to formation of PAH. The main products are naphthalene, phenanthrene and carbon. The exact mechanisms are uncertain. One possible route is aromatization of methane with benzene.

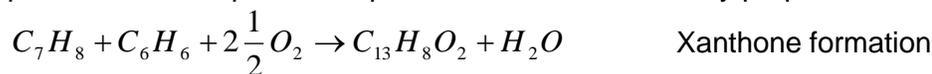
8) Formations of main oxygenate products:



Since benzaldehyde is an intermediate product of oxidative dealkylation it is generally present in higher amounts in products formed using non selective catalysts.

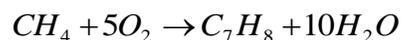
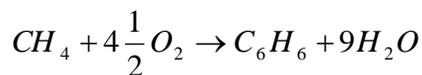


Phenol is only present in small but detectable traces when there is a substantial amount of benzene also present in the product. Although benzene is an intermediate step to phenol, their composition in products are not necessarily proportional.



Xanthone is present in higher amount when reaction is carried out using a non-selective catalyst with relatively low oxidative activity and sometimes relatively higher PAH yields.

9) Aromatization of methane to single ring compounds:



Further aromatization leads to undesired PAH formation (coke formation). However, aromatization is usually carried out in acidic catalysts and since deactivation due to heavy coking is the certain fate of such catalysts, they are not suitable for OMT.

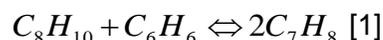
Desired side reactions:

10) Formation of EB from byproducts:



This is a reaction from the existing EB/styrene production processes and can minimize the benzene formation if occur in the OMT process. However, acidic catalysts, not basic ones, are effective for such reaction.

11) Transalkylation of benzene and xylene to form toluene:



A catalyst enabling this reaction can potentially minimize formation of both benzene and xylene.

Although there is a highly complex reaction network, examining the main reactions and major side reactions can provide clear indication of catalytic performance and clues to some reaction pathways.

3c.Catalyst Background and Literature Survey

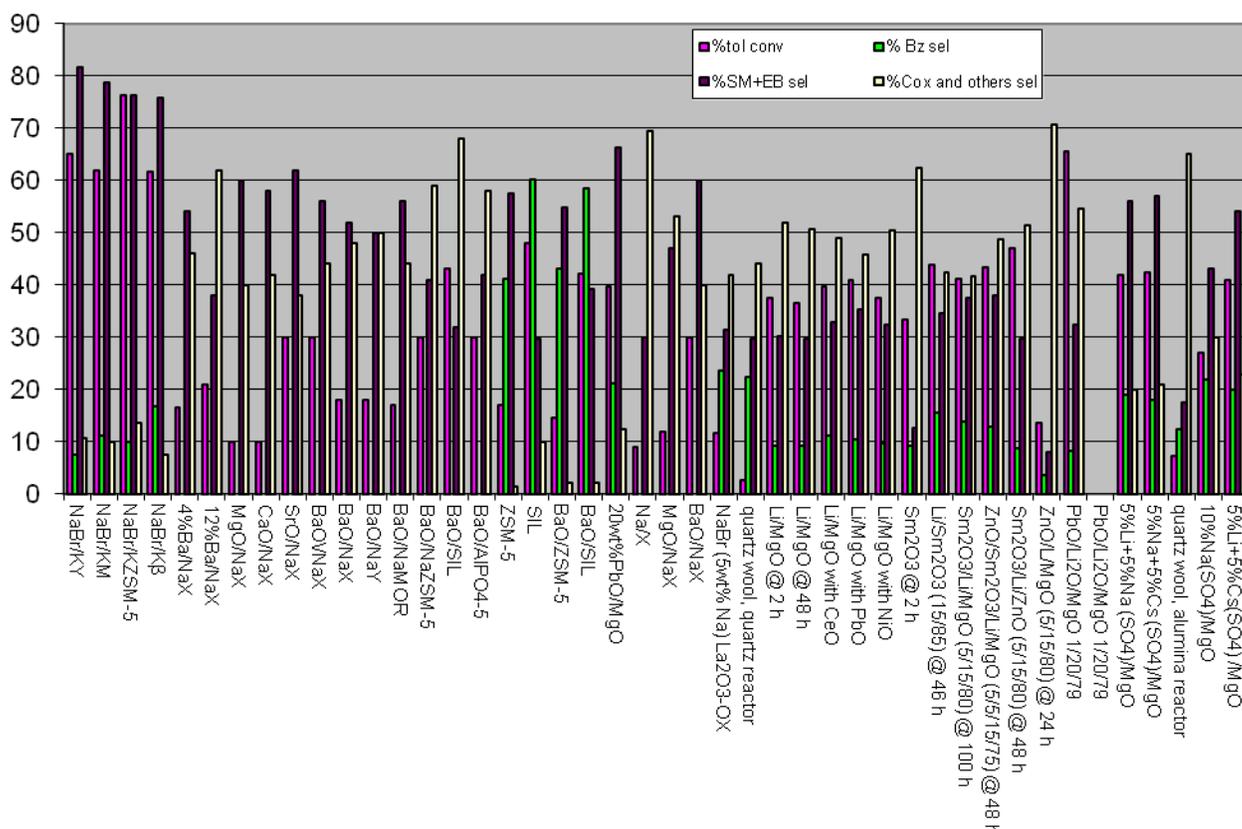
Oxidative methylation of toluene by methane is not an easily achieved reaction due to the extreme differences in their activation energies between methane and toluene. While toluene can be activated in the lower 100 °C temperature range, methane needs at least 6 fold higher temperatures for activation.

The oxidative methylation of toluene was discovered by Khcheyan et al. in the 1970's who reported that the presence of various transition metal oxides can lead to the reaction. The process proceeds with an appreciable yield in the presence of various catalysts, such as the oxides of Fe, Co, Ni, Ti, V, Bi, Mo or Zn. However, details regarding catalysts compositions, method of preparation and promoter effect have not been disclosed. Later some researchers employed some of the oxidative methane coupling catalysts for the process and also found that the reaction is also catalyzed by basic oxides, such as mono-alkali promoted alkaline earth oxides, transition metal oxides or rare earth oxides. On the basis of catalysts used for the oxidative coupling of methane (OCM) to form C2 hydrocarbons, several groups employed methane coupling catalysts for the oxidative methylation of toluene with methane.

Several research groups such as Khcheyan et al, Osada et al, Khan et al and Kim et al have employed metal oxides for the oxidative methylation of toluene with methane. Generally alkali metal oxides, alkaline earth metal oxides and mixed oxides of elements from the two groups, which typically possess high basicities, have been tested further while rare earth and transition metal oxides have only been through preliminary screening in among these studies.

Two groups, Kovacheva et al. (aka Arishtirova et al.) and Zhou et al. have published results in the late 1990s to early 2000s. Both groups use alkali metal ion-exchanged zeolites as support. Kovacheva and Arishtirova et al focus on increasing basicity of the zeolite supports with alkaline earth metal oxides (MgO and BaO). Zhou et al focus on alkali bromide promoted zeolites.

The following histogram is the performance summary of best performance data selected from available OMT literature. Although data collected are within a range of conditions, temperature from 700 to 800°C and feed ratios vary, the summary provides clear comparison among general types of catalyst: zeolites and metal oxides.



Best Catalytic Performance Data from OMT Literature

Zhou et al presented the best results to-date. While some groups account for both vapor and liquid products (all for studies of MMO) with Khan et al presenting the most detailed material balance in their results, the two groups studying zeolites only analyzed liquid products. However, Zhou et al have shown exceptionally good results, up to 60% yield of EB and styrene, while others are all lower than 30% with similar test conditions. The following table shows the catalyst screening results by Zhou et al in Chinese Chemical Letters, v 11, n 9, p 827-830, 2000.

OMT over Modified Zeolite Catalysts (Zhou et al.)

Catalyst	Conversion (mol%) C ₇ H ₈ ^b	Selectivity(%)					Yield(%)			
		C ₈ H ₈ ^c (BZ)	C ₈ H ₁₀ ^d (EB)	C ₈ H ₈ ^e (ST)	Total C ₈ ^f (ST+EB)	ST/EB ^g	C ₈ H ₆ (BZ)	C ₈ H ₁₀ (EB)	C ₈ H ₈ (ST)	Total C ₈ (ST+EB)
Li ₂ O/KY	25.5	28.1	32.3	25.8	58.1	0.80	7.2	8.2	6.6	14.8
Na ₂ O/KY	37.5	31.5	28	21.6	49.6	0.77	11.8	10.5	8.1	18.6
K ₂ O/KY	38.4	40.1	26.1	16.9	43	0.65	15.4	10	6.5	16.5
Ca ₂ O/KY	57.1	40.0	15.9	36.4	52.3	2.29	9.1	9.1	20.8	29.9
NaCl/KY	29.6	14.2	40.6	22.4	63	0.55	4.2	12	6.60	18.6
NaBr/KX	65.0	11.8	11.3	64.4	75.7	5.70	7.7	7.4	41.9	49.3
NaBr/KY	65.0	7.5	8.3	73.4	81.7	8.84	4.9	5.4	47.7	53.1
NaBr/KM	62.0	11.2	10.8	68.0	78.8	6.30	6.9	6.7	42.2	48.9
NaBr/ KZSM5	76.3	9.9	7.1	69.3	76.4	9.76	7.6	5.4	52.9	58.3
NaBr/Kp	61.7	16.7	7.1	68.7	75.8	9.68	10.3	4.4	42.4	46.8
KBr/KX	52.2	21.5	18.1	46.8	64.9	2.59	11.2	9.5	24.4	33.9
KBr/KY	58.9	14.8	17.9	51.0	68.9	2.85	8.7	10.5	30.0	40.5
KBr/KM	57.4	16.3	16.1	56.4	72.5	3.5	9.4	9.2	32.4	41.6
KBr/ KZSM5	58.2	15.6	13.6	58.6	72.2	4.31	9.1	7.9	34.1	42.0
KBr/Kp	60.1	14.0	13.3	58.0	71.3	4.36	8.4	8.0	34.9	42.9

Note: a. T_r = 973K, W = 0.3g, CH₄/O₂/C₆H₅CH₃/N₂ = 24:6:2.33:20 (mL/min). The results presented were obtained after 2h of reaction. The yield is on the basis of moles of toluene converted
b. toluene c. benzene d. ethylbenzene e. styrene f. ethylbenzene + styrene
g. ST/EB = selectivity ratio of styrene to ethylbenzene.

Properties that led to catalyst selection and the hurdles associated in the making Desired characteristics of catalysts:

The main catalytic property that contribute to the oxymethylation of toluene is the basic nature of the catalysts for generation of the methyl (CH₃•) radicals from methane and the benzyl (C₆H₅CH₂•) radicals from toluene as reported by Arishtirova *et al.* Kim *et al* proposed that any C₈ hydrocarbons are formed by cross coupling of benzyl and methyl radicals generated by the detachment of hydrogen from methyl group of toluene and methane respectively. Very high temperature (600-900°C) is required to activate methane. To achieve high selectivity, the catalyst must be active enough to activate significant amount of methane without oxidizing toluene.

Zeolites: In the late 1990's researchers began investigating basic zeolites for the oxidative methylation of toluene. Study has shown that aromatic – ring alkylation of toluene takes place over acid zeolites, while the side –chain alkylation occurs preferentially over basic zeolites.

Since strong Bronsted acids are conjugated to weak Bronsted bases, the existence of protons in zeolites has to be associated with basic sites (ref. Stud. Surf.Sci.Catal. 65, 157,1991). From this analogy it follows that complete ions exchange with alkali metal ions neutralizes not only the Bronsted acid centers but also creates weak basic center, so that alkali ion exchanged zeolites can be used as basic catalysts.

It is possible to prepare alkali metal oxides within the pore of the zeolite. These so called "ion added" zeolites have been used as basic catalysts in a number of reactions (ref. J. Catal. 119, 497, 1989; Catal Today 19, 151, 1994). An additional method where zeolites are used as support is the impregnation of the pores with clusters of alkali atoms which can act as base themselves.

Alkali-exchanged zeolites have demonstrated the highest activities and selectivities for side-chain alkylation of toluene with methanol (ref. J.Catal.173, 1998,490).It has been demonstrated that the alkylation of toluene with methanol requires basic sites to activate the "C" atom in the methyl group of toluene (ref. J. Catal. 64, 1980, 284).

A significant obstacle for the preparation of such solid bases is the strong inherent acidity of zeolites. The presence of traces of acidity which will catalyze undesired side-reactions makes it difficult to carry out base-catalyzed reactions on an industrial scale and no

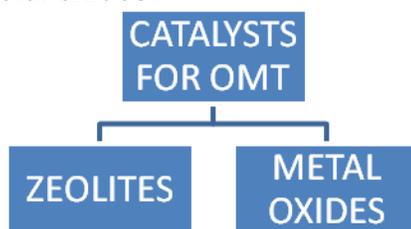
commercial applications (ref. Angew. Chem. Int. Ed. Engl. 27, 226, 1998) have been reported (ref. Stud. Surf.Sci.Catal. 84, 1375, 1994).

Metal oxides : Researchers have reported that oxidative methylation of toluene is catalyzed by alkali-promoted metal oxides, such as alkali/alkaline earth metal oxides, alkali/transition metal oxides, and alkali/rare earth metal oxides, which are active in the oxidative coupling of methane as well. However most of these catalysts reported suffer from low selectivity toward desired products and also poor stability with time-on-stream. Research is ongoing on these basic oxides.

Khan et al (1993) claimed that substantial synergistic effect is obtained in the oxidative coupling of methane by using various alkali-metal compounds promoted magnesia instead of mono-alkali promoted magnesia. The higher enrichment of the surface layer with alkali ions and alkaline ions is seen to be responsible for the superbasic nature of the catalysts.

3d. Catalyst Selection, Preparation and Analyses

Based on the available literature, two categories of catalysts were selected for catalyst synthesis and screening for oxidative methylation of toluene by methane. They are (i) **zeolites** and (ii) **metal oxides**.



Catalyst Synthesis of zeolite catalysts

List of **zeolites** synthesized

Catalyst ID	Zeolites
361-26,361-25,370-37B, 380-1 & 380-3	K-ZSM-5 (SAR= 23)
361-18A	10 wt % NaBr on K-ZSM-5 (SAT=23), air calcined @ 550C
361-18C	10 wt % NaBr on K-ZSM-5 (SAR=23), air calcined @ 500C
361-21B	10 wt % NaBr on K-ZSM-5 (SAR=23), N ₂ calcined @ 500C
361-30	Na-ZSM-5 (SAR= 23), air calcined @ 500C
361-30A	10 wt % NaBr on Na-ZSM-5 (SAR=23), N ₂ calcined @ 500C

361-(32A+32B+48A+48B)	Calcined Superbeta (using programmed calcination)
361-33	K-Superbeta, air cal. 500°C (from original TEA-Superbeta)
361-34	Na-Superbeta, air calcn. 500°C
361-33A	10 wt % NaBr on K-Superbeta, N2 calcined @ 500C
361-34A	10 wt % NaBr on Na-Superbeta, N2 calcined @ 500C (dried in a shallow dish)
361-37	Rb-Superbeta, air calcn. 500C
361-38	Cs-Superbeta, air calcn.500C
361-37A	10 wt% NaBr on Rb-Superbeta, rotovap, N2 calcn.500C
361-38A	10 wt% NaBr on Cs-Superbeta, rotovap, N2 calcn.500C
Catalyst ID	Zeolites
361-38B	10 wt% NaBr on K-Superbeta, rotovap, N2 calcn.500C
361-34B	12 wt% Ba on Na-Superbeta
361-51	K-Y (made from CBV901)SAR = 80, H form
370-3	MgO/Na-Superbeta
361-51A	10 wt % NaBr on K-Y, rotovap, N2 calcn.500C
370-4	CaO on Na-Superbeta, air calcined. 500C
370-6	Li-Superbeta, air calcn.500 C
370-6A	10 wt% NaBr on Li-Superbeta, rotovap, N2 calcn.500 C
370-38	6 wt % NaBr on K-ZSM-5 (SAR=23), rotovap, N2 calcined @ 500C
370-37-1	10 wt % NaBr on K-ZSM-5 (SAR=23), rotovap, N2 calcined @ 500C
370-47	K-ZSM-5 (SAR= 280)
370-47A	6 wt % NaBr on K-ZSM-5 (SAR=280), rotovap, N2 calcined @ 500C
370-40-1	K-Y (made from CBV100)SAR = 5, Na form

370-40-2	6 wt % NaBr on K-Y(SAR=5), rotovap, N2 calcn.500C
380-5	6 wt % NaBr on K-ZSM-5 (SAR=23), rotovap, N2 calcn.550C

Synthesis of K, Na, Rb and Cs ion exchanged zeolites (361-25,361-26, 361-30,361,33,361-34,361-37, 361-38,361-51, 370-40-1,370-47)

The synthesis of the ion exchanged zeolites was done based on literature published by Zhou et.al. Approximately 30 g of the corresponding commercial zeolites from Zeolyst International (ZSM-5: CBV2314, CBV 28014; zeolite Y: CBV901 & CBV100 and zeolite super beta: CP806E) were charged into a 1000 ml three necked round bottomed flask. Approximately 1.5 l of 0.5 M of each of the corresponding metal nitrate solutions was prepared in volumetric flasks. 300 ml of 0.5 M metal nitrate solutions were added to the 30 g of the corresponding zeolites for ion exchange at 90 °C, four times for 2 hours each. After ion exchange the solid was filtered and dried at 125 °C for 6 hrs followed by calcining the solid at 500 °C for 5 hrs followed by natural cooling. The alkali ions will be loaded as oxide form after the calcinations stage.

In order to ensure the validity of the alkali metal cations exchange, selected ion exchanged zeolites were subjected to characterization by XRF (x-ray fluorescence) for determination of their chemical composition.

Loadings of alkali metal oxides on various zeolites

Components (mol %) / Zeolite type	silica	Alumina	K ₂ O	Na ₂ O	Rb ₂ O	Cs ₂ O	Silica/ alumina
CBV2314(NH ₄ -ZSM-5)	95.8	4.2	none	none	none	none	22.8
370-37B (K-ZSM-5)	90.9	4.1	4.9	none	none	none	22.2
CP806E(TEA-superβ)	94.9	4.6	none	0.45	none	none	20.7
361-33 (K-superβ)	89.2	3.4	7.4	none	none	none	26.2
361-34 (Na-superβ)	89.3	3.6	none	7.01	none	none	24.5
361-37 (Rb- superβ)	91.6	3.7	none	none	4.6	none	24.4
361-38(Cs- superβ)	85.1	3.5	none	none	none	11.4	24.1
CBV901(H-Y)				none	none	none	80
361-51 (K-Y)	97.2	1.2	1.5	none	none	none	79.8

The XRF results represent the variation of the chemical composition with the respective ion exchanges. Based on the results, it is clear that after the alkali ion exchange all of the zeolites are loaded with a certain amount of the alkali metal oxide while maintaining the chemical integrity of each of the zeolites which is represented by the silica/alumina ratios. The silica /alumina ratios of each of the zeolites essentially help in holding the respective zeolite structures.

Synthesis of NaBr promoted ion exchanged zeolites (361-18A,361-18C,361-21B, 361-30A,361-33A,361-34A,361-37A,361-38A,361-38B,361-51A,370-6A,370-38,370-37-1,370-47A,370-40-2 and 380-5)

For preparing 6 wt% or 10 wt % NaBr promoted zeolites approximately 15 g of the corresponding ion exchanged zeolite was impregnated with NaBr solution by stirring the mixture for approximately 2 hrs, evaporated to dryness in a rotovap, air dried at 125 °C overnight and finally calcined in N₂ at 500-550 °C for 5 hrs. For catalysts 361-18A, 361-18C the final calcinations was done in air instead of nitrogen as mentioned by Zhou *et.al* and the final product did not show any NaBr (refer to Table 3). In order to understand the effect of NaBr on the performance of toluene alkylation and its relation to C8's selectivity (EB+ Styrene), the loading of the promoter NaBr was varied between 6-10 wt%.

The loading of the NaBr on the alkali ion exchanged zeolites was verified by XRF on some selected catalysts (Table 3).

Loadings of NaBr on selected zeolites

Components (mol%)/ Zeolite type	silica	Alumina	K2O	Na2O	Rb2O	Cs2O	NaBr	Silica/ alumina	NaBr/ Alumina
361-18A 10 wt% NaBr/K-ZSM-5 (air calcn)	91.6	4.1	3.2	1.1	none	none	none	22.5	na
361-18C 10 wt% NaBr/K-ZSM-5(air calcn)	91.5	4.1	3.4	1	none	none	none	22.4	Na
361-21B 10 wt% NaBr/K-ZSM-5(N2 calcn)	91.5	3.24	4.8	0.3	none	none	0.05	28.2	0.0013
361-33A 10 wt% NaBr/ K-superβ 5(N2 calcn)	88.1	3.6	4.9	1.11	none	none	2.3	24.5	0.6
361-34A 10 wt% NaBr/ Na-superβ (N2 calcn)	87	2.9	none	4.3	none	none	5.7	29.7	1.96

361-37A 10 wt% NaBr/ Rb-super β (N ₂ calcn)	85.4	3	none	none	3.7	none	7.8	28.2	2.6
361-38A 10 wt% NaBr/ Cs-super β (N ₂ calcn)	77.3	2.9	none	none	none	10.4	9.4	27	3.3
361-51A 10 wt% NaBr/ K-Y(N ₂ calcn)	90.4	0.89	1.7	none	none	none	7	107.2	8.3
370-38 6 wt% NaBr/ K-ZSM-5 (N ₂ calcn)	88	3.6	4.2	none	none	none	4.3	24.4	1.2

Besides the calcinations of the NaBr loaded catalysts in nitrogen, evaporating the solids in a rotovap also had an impact on the NaBr loadings. Catalysts that were dried in an oven after impregnation did not show sufficient NaBr loading as compared to samples that were evaporated to dryness in the rotovap. The final calcination has an impact on the NaBr loading.

With modifications in catalyst preps, higher NaBr loadings were possible. The NaBr loadings also change the NaBr/Alumina ratio which indirectly has an effect on the basicity since a higher NaBr/Alumina ratio increases the basicity of the zeolite.

Synthesis of zeolites modified with alkali earth oxides (361-34B, 370-3 and 370-4)

361-34B which is 12 wt% Ba on Na-Superbeta was synthesized based on the method described in Applied Catalysis A: 213(2001) 197-202(Arishtirova et.al). To approximately 15 g of the Na-Superbeta (361-34) was added the required amount of 0.1M Barium nitrate solution and stirred for mixing at 80C for 1 hr. The mixture is then evaporated to dryness at 70C in a rotovap followed by oven drying at 120C overnight. The dried solid is then air calcined at 550C for 7 h.

370-3 (MgO on Na-Superbeta) and 370-4 (CaO on Na-Superbeta) were prepared based on the synthesis method described in Applied Catalysis A: 223(2002)121-128(Arishtirova et.al). To approximately 12 g of the Na-Superbeta was added the required quantity of 0.1M Magnesium nitrate or 0.1 M Calcium nitrate solution corresponding to the alkaline earth oxides that was being used for modifying the zeolite, stirred for 1 h at room temperature. Then the mixture was evaporated to dryness, followed by drying overnight at 120C. The dried solid was the calcined at a programmed temperature increase up to 550C for 2 h and the catalyst was held at 550 °C for 5 h. At this stage the alkali earth nitrates were converted to the corresponding oxides in the process of calcinations.

Analyses of zeolite based catalyst

X-ray diffraction

An X ray diffraction pattern was obtained on as modified K-ZSM-5 (large batch which is a mixture of 380-1 + 380-3) which was synthesized in the exact same procedure as the Zhou *et.al* literature. Based on the XRD pattern, we determined that the K-ZSM-5 maintained the structural integrity of the original ZSM-5. No extra peaks or loss of peaks

could be determined. The 6 wt% NaBr loaded K-ZSM-5 (380-5) which was synthesized from the large batch (a mixture of 380-1 + 380-3) was also subjected to an XRD analysis. The basic structure of the K-ZSM-5 was still maintained with no loss in intensity of the peaks (based on superimposing the pattern of both). In case of 380-5, small extra peaks of NaBr could be seen further confirming the presence of NaBr promoter on K-ZSM-5.

Results on change in catalyst acidity with alkali ion exchange and promoter treatment

CO₂ chemisorption followed by temperature programmed desorption would be the preferred method to determine the strength of the basicity of the as-synthesized zeolites. However, an indirect method would be to measure the decrease in acidity of zeolites after alkali metal exchange and NaBr promotion and the change in total acidity could be then directly related to the basicity of the catalyst. Here we have undertaken the latter indirect method for determining the total acidity of the modified zeolites.

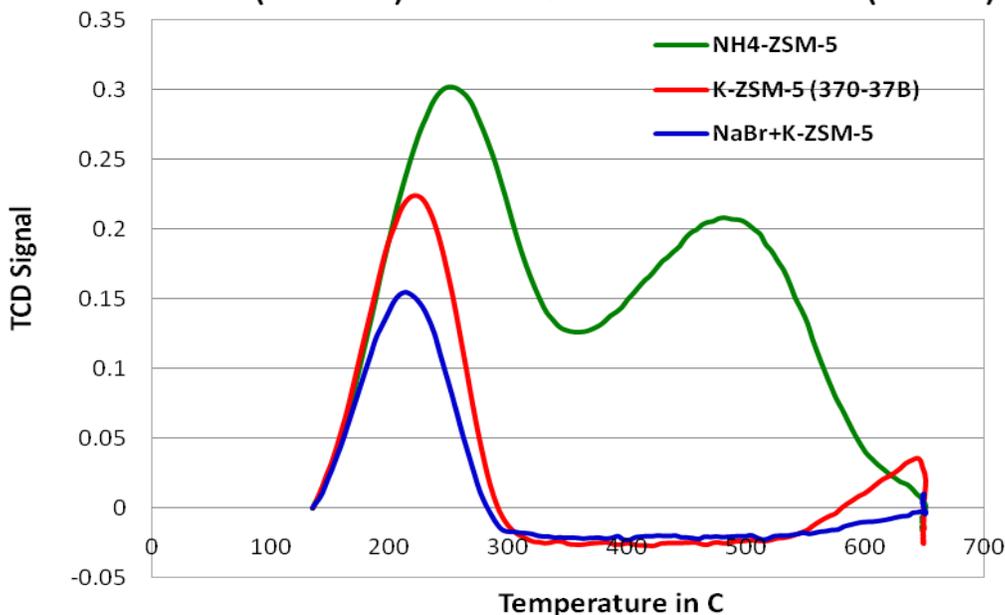
For comparison purposes, ammonia TPD measurements were carried on an as received zeolite CBV2314 (NH₄-ZSM-5), K + ion exchanged CBV2314 (370-37B) and on NaBr promoted 370-37B (370-38). For NH₄-ZSM-5, there is a peak at 240 °C which is due to the desorption of adsorbed NH₃ on the weak acid sites and the peak at 478 °C is due to the desorption of the adsorbed NH₃ to the strong acid sites. The peak area corresponding to the low temperature for 370-37B decreased due to the “K” loadings and the high temperature peak disappeared (possibility of being associated with Bronsted acid sites which were exchanged by “K” during ion exchange process). The disappearance of the peak at high temperature indicates that “K” oxide species migrates into the channels of the ZSM-5 zeolite and preferentially interact with the bridging hydroxyl groups which are generally considered strong acid sites. Also, the “K” species inside the channels of ZSM-5 replaced / consumed the strong Bronsted acid sites, hence the strong Bronsted acid sites decreased. The total acidity of the 370-37B has been reduced by 70 % by the ‘K’ exchange on NH₄-ZSM-5 and the overall acidity of NaBr promoted K-ZSM-5 got reduced by 81 % (Table 3.4.2).

In conclusion we can say that acidity of NH₄-ZSM-5 is substantially decreased with “K” exchange and with NaBr as a promoter.

Acidity measurements by NH₃ TPD on catalyst samples and catalyst precursors

Measured Acidity	NH ₄ -ZSM-5 (CBV2314)	370-37B (K-ZSM-5)	370-38 (6 wt% NaBr + K-ZSM-5)
mL/g @ STP	34.74	9.48	6.54
mmol/g @ STP	1.55	0.42	0.29

NH₃-TPD acidity comparison between NH₄-ZSM-5 (CBV2314), K-ZSM-5 (370-37B) and 6 wt% NaBr on K-ZSM-5 (370-38)



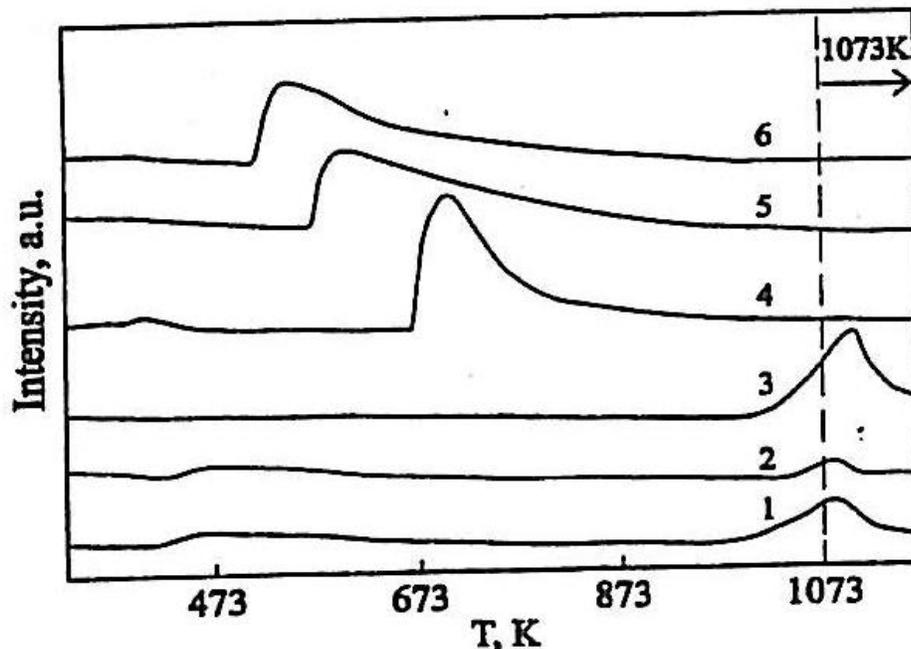
Strength of Acidity measurements by NH₃ TPD on catalyst samples and catalyst precursors

Acidity and basicity of KY zeolites promoted with alkali metal halides was studied by NH₃TPD and formic acid -TPD by Zhou et.al. They found that NH₃-TPD patterns of KY zeolites promoted with alkali metal halides had one desorption peak in the temperature range 178-185 °C, which indicates that the alkali metal halide promoted KY zeolite had weak Lewis acidic centers. TPD plots of formic acid desorbed from alkali metal halide promoted KY zeolite were low and wide curves, and these wider desorption peaks appear in the temperature range 210- 340 °C. The results indicated that the alkali metal halide promoted KY zeolite had moderately strong Lewis basic centers. In conclusion the alkali metal halide promoted KY zeolites had weak Lewis acidic centers and moderately strong Lewis basic centers. It seemed likely that the weak Lewis acidic centers and strong Lewis basic centers are active centers for oxidative methylation of toluene with methane.

Change in zeolite basicity with alkali earth oxide modification

This is in reference to the alkali earth oxide modified zeolites (12 wt% Ba on Na-Super β , MgO on Na-Super β and CaO on Na-Super β) and their relation to basicity based on the literature published by Arishtirova et.al in Applied Catalysis A: 213(2001) 197-202 and in Applied Catalysis A: 223(2002)121-128. Basicity may be evaluated using TPD (temperature programmed desorption) of CO₂. According to Arishtirova the amount of desorbed CO₂ and the temperature of maximum desorption of CO₂ are the criteria for the amount and strength of basic sites, respectively. They studied the basicity on BaO modified X and Y zeolites and came to the conclusion that the basicity is determined by the chemical composition and especially the aluminum content. According to their study, higher aluminum content in X zeolites provided higher basicity (due to the higher

electronegative charge of the framework oxygen) and selectivity for C₈ hydrocarbons as compared to Y zeolites. Strong basic sites with T_{max} above 700 °C were registered after BaO modification of X zeolite (Figure 2).



TPD profiles of CO₂ adsorbed on alkali earth oxide modified zeolites (1) BaO/NaX (2) BaO/NaY (3) BaO/NaMor (4) BaO/NaZSM-5 (5) BaO/Sil (6) BaO/AlPO₄⁻⁵ (adapted from Applied Catalysis A: 243,2003,191-196)

Arishtirova also commented that the appropriate location of BaO in the zeolite structure determines the basicity. They also related basicity of BaO/NaZSM-5 mainly to the basicity of BaO itself, to its appropriate location in the ZSM-5 structure, leading to higher accessibility for the reagents as compared to X, Y and mordenite structures. Further decrease in basicity of BaO/SIL which is a structure analogue of ZSM-5 was related to the absence of carrier of basicity in the structure of silicalite (lack of aluminum oxygens).

Metal Oxides

List of **metal oxides** synthesized

Catalyst ID	Metal oxides
361-42	33.5 wt% PbO on MgO (rotovap after impreg.)
361-44	20 wt% PbO on MgO(rotovap after impreg.)
361-45	5.6 wt% PbO on MgO(rotovap after impreg.)
361-46	1 wt% PbO on MgO(rotovap after impreg.)

361-49	15 mol% Li on MgO
361-50A	5 mol% Pb +15 mol% Li + 80 mol% MgO
361-50B	1mol% Pb +15 mol% Li + 84 mol% MgO
370-1	5 wt % NaBr on Cerium oxide, rotovap, N2 calcn.
370-2	5 mol% Ni +15 mol% Li + 80 mol% MgO
370-31	5 mol% Ni + 2 mol% Pb + 13 mol% Li + 80 mol% MgO
370-34	3 mol% Ni + 1 mol% Pb + 1 mol% La+ 15 mol% Li + 80 mol% MgO
370-36	25 mol% Li + 75 mol% MgO
370-41	1.9 wt% La ₂ O ₃ on MgO
370-43	5 mol% Na + 5 mol% K + 90 mol% CaO
370-44	22.5 wt% La ₂ O ₃ on CaO
370-45	28.7 wt% La ₂ O ₃ on MgO
370-46	3 mol% Ni + 1 mol% La + 1 mol% La+ 16 mol% Li + 80 mol% MgO
370-46A	25 mol% Na on MgO
370-48	25 mol% K on MgO
370-51	4 mol% Ni + 1 mol% La + 25 mol% Li + 70 mol% MgO
370-52	MgO (COMMERCIAL)
380-4A	CaO (COMMERCIAL)
380-4	25 mol% Li + 75 mol% CaO
380-6	25 mol% Li + 75 mol% MgO (repeat of 370-36)
380-9	5 wt% Sodium tungstate on silica gel
380-10	Lithium oxide from Lithium acetate

Synthesis of 361-42, 361-44, 361-45, 361-46, 361-49, 361-50A, 370-50B, 370-31, 370-34, 370-2, 370-46, 370-46A, 370-48, 370-51, 380-4 (Li/MgO and metal oxides + Li/MgO, Li/CaO)

The above catalysts were synthesized based on the methods described in Applied Catalysis A: General, 87, 1992, 115-129 by Kim et.al. The catalysts (Li/MgO, Metal oxide + Li + MgO) were prepared by conventional wet impregnation method. MgO was mixed with an aqueous solution of Lithium nitrate and a given metal nitrate. The slurry formed was then dried at 120 °C in air. After drying the catalysts were calcined at 650 °C for 15 h.

Synthesis of 370-1 (5 wt % NaBr on Cerium oxide)

This catalyst was synthesized based on the method described in Applied Catalysis, 53, 1989 L19-L21. Loaded catalysts were prepared by impregnating aqueous solutions of alkali metal halides on to Cerium oxide. After impregnation, the solid was dried in air at 120 °C overnight followed by calcination at 800 °C for 6 h.

Synthesis of 370-36, 370-41, 370-44, 370-45 and 380-6 (metal oxides on MgO and CaO)

370-36 and 380-6 which is 25 mol% Li on MgO was synthesized based on the process described in J. Chemical Technology and Biotechnology, 1998, 72, 99-104. This literature refers to low temperature catalysts (500-700 °C) for oxidative methane coupling. 25 mol% Li on MgO was prepared by impregnating Fisher grade MgO with Lithium nitrate under stirred mixing for 2 hrs at room temperature, followed by evaporation to dryness at 70 °C and overnight drying at 120 °C. The final product was calcined in air at 750 °C for 6 h.

370-41 (1.9 wt% La₂O₃ on MgO) was made by impregnating calculated amount of Lanthanum nitrate solution for loading 1.9 wt % La₂O₃ on commercial Fisher made MgO. The impregnation was done in a sonicator at room temperature for 4 hrs, evaporated to dryness at 70C, followed by overnight drying at 120C. The solid was then calcined at 850 °C for 4 hrs. The synthesis process was adopted from J. of natural gas chemistry no 19, no. 2, 2010, 173-178 which mentioned the catalyst for oxidative methane coupling.

Catalyst 370-44 (22.5 wt% La₂O₃ on CaO) and 370-45 was prepared based on J. of natural gas chemistry no 19, no. 1, 2010, 25-30. Similar to 370-41, this catalyst was prepared by impregnation method. However, the final solid was calcined at 950 C for 10 hrs.

Synthesis of 370-43 (Na + K on CaO)

370-43 is 5 mol% Na + 5 mol% K on CaO which was prepared based on the synthesis process described in Applied Catalysis A 102, 1993, 233. This literature refers to catalysts for the oxidative methylation of toluene with methane to ethylbenzene and styrene. Appropriate aqueous solutions of NaOH and KOH with equimolar alkali content were prepared separately by dissolving the salts in distilled water. Both the solutions were introduced simultaneously into an aqueous slurry of CaO under vigorous stirring at 80 °C and heated until a thick paste is formed. This was followed by evaporation to dryness, drying overnight at 120 C followed by calcinations in air at 750 °C for 15 h.

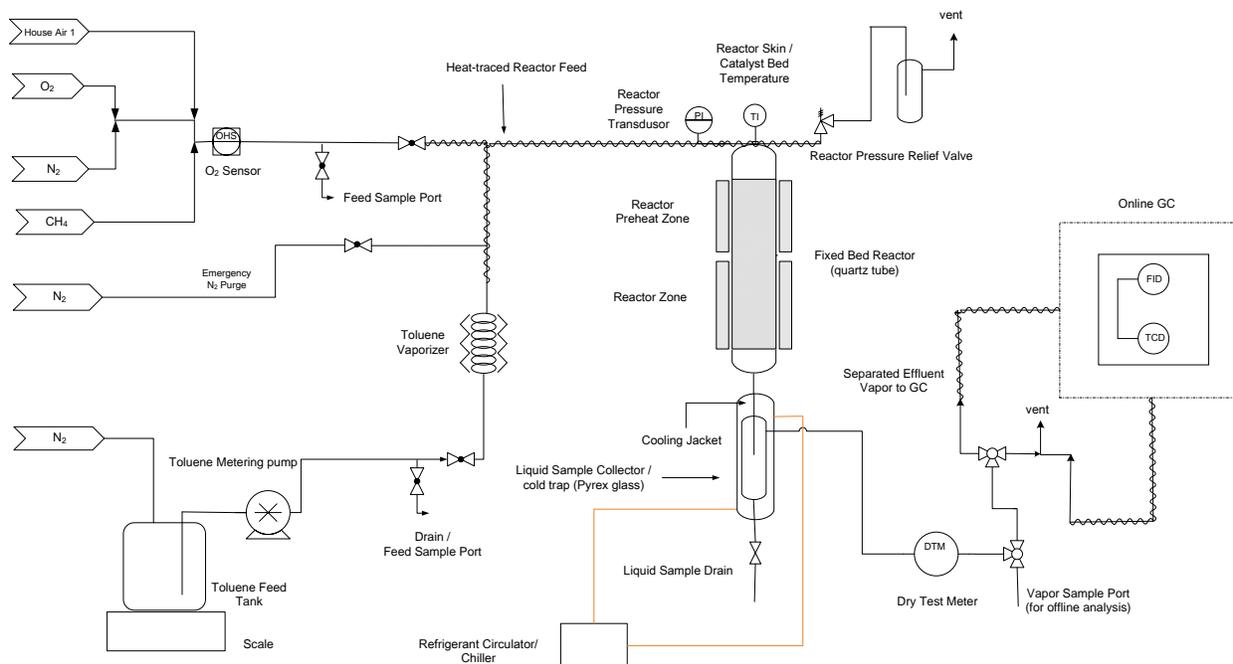
Synthesis of 380-9 (sodium tungstate on silica gel)

380-9 is 5 wt% sodium tungstate on silica gel and was prepared based on J. of Physical Chemistry, 99, 1995, 4566. The starting material was Sylopol silica gel obtained from Grace Davison. The silica gel was impregnated with aqueous solution of sodium tungstate dihydrate, followed by evaporating to dryness, overnight drying at 120 °C and calcining at 800 °C for 3 h.

Synthesis of 380-10 (Lithium oxide)

The synthesis of Lithium oxide from Lithium acetate was prepared based on literature published for oxidative methane coupling in Journal of Natural Gas Chemistry 17, 2008, 313. Approximately 10 g of lithium acetate dihydrate was mixed in flat porcelain plate with sufficient distilled water to form a thick paste and left in oven at 120 °C overnight. The dried solid was then decomposed at 600 °C for 6 hrs under flowing air, and further calcined at 750-850 °C in static air for 6 h.

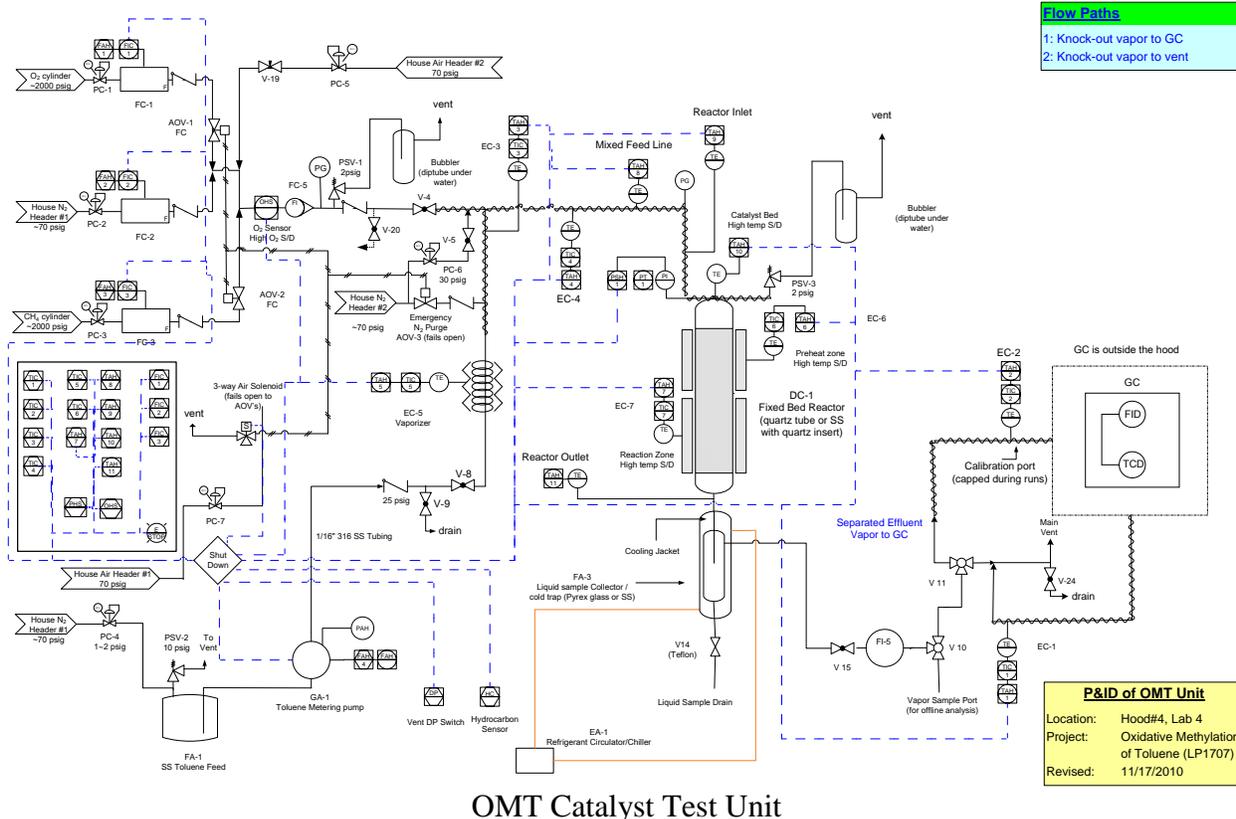
3e. Experimental Unit and Operating Conditions



Simplified Process Flow Diagram of OMT Catalyst Test Unit

A schematic representation of the OMT unit is as shown above. For all more details of the unit, see the figure below. The house nitrogen supply provided nitrogen feed, emergency shutdown purge and toluene feed tank blanket. Oxygen feed can come from house air or UHP oxygen (99.9%) cylinder. Each vapor feed nitrogen, oxygen/air and methane is fed through respective mass flow controller (MFC) prior to mixing with other feeds. Nitrogen feed is mixed with oxygen/air prior to mixed methane. The vapor feed is then monitored by an in-line oxygen sensor prior to entering heat-traced feed line. Toluene is kept in feed tank pressurized with nitrogen blanket at no more than 10 psig (usually less than 5 psig with pressure relief valve set at 10psig). Toluene is fed as a liquid by pump out of the feed tank via diptube through a metering pump (downstream of which there is a 25psig check valve to maintain positive head through the pump). The toluene is then vaporized at atmospheric pressure. Heated toluene vapor meets the other heated vapor feeds in the heat-traced feed line then going into the reactor. The reactor heater consists of two heating zones, the preheat zone and the reactor zone. Reactor is a $\frac{1}{2}$ " OD quartz tube packed with catalyst in the reaction zone and quartz chips above and below the catalyst bed separated by quartz wool. The reactor effluent enters a cold trap directly below the reactor. The cold trap is a vapor liquid separator with cooling jacket of circulated refrigerant near 0°C. Liquid products are condensed in the trap and cooled vapor exits the trap to sampling line to GC then vented up the hood. Sample ports are available for vapor feed, liquid feed, liquid products and vapor products to be collected and analyzed offline. Online analysis is only for vapor products limited by capabilities of the online GC.

A more detailed representation is shown below. An emergency shutdown occurs when any of the temperature and pressure is over alarm limit, there is a leakage of flammable gas (detected by the gas monitor) or oxygen in vapor feed stream is over the composition alarm limit.



Operating Condition

The best results to-date presented by Zhou et al are from screening of NaBr promoted alkali ion exchanged zeolites such as 6-10wt% NaBr on KZSM5 or KY. Conditions in their works are used in this study for all catalyst tests.

Table 4.2.1 OMT test conditions

Source	Temperature (°C)	Reactor	Pressure	Molar feed ratio (CH ₄ :O ₂ :tol:N ₂)	GHSV (h ⁻¹)
Zhou et al.	700 (up to 710)	OD quartz tube	Atmospheric	24 : 6.2 : 2.33 : 20	4757
This study	700-720*	1/2" OD x 3mm wall quartz tube	1-1.6 psig	23.5 : 5.3 : 1.7 : 19.5	5010

*Reaction temperature in catalyst bed may change over time ranging from 700 to 720. Difference in feed ratio and space velocity are due to limitations of flow control. A 2psi pressure alarm limit is set to protect oxygen sensor. Although the size of catalyst in literature is 40-60 mesh, 20-40 mesh is used in this study instead to keep operating pressure within 2 psig.

Product is separated by condenser kept at 0°C with coolant consists of a 50/50 wt% water-ethylene glycol mix chilled and circulated through chiller providing a cooling jacket maintaining condenser temperature. If condenser temperature goes lower, ice forms in condenser diptube plugging entrance to the condenser.

In this study, although product liquid condenser is at 0°C, significant amount of aromatics can still be present in vapor (0.8-1.5vol% in vapor, 30-60wt% of total aromatics in overall product stream). Solid products can also form. Light vapor components, major aromatic components in both liquid and vapor; and oxygenates in both liquid and vapor were quantified. Solid products are dissolved in known amount of toluene to form liquid sample for analysis. Heavy components such as polycyclic aromatic hydrocarbons and oxygenated derivatives can only be identified but not accurately quantified. Such heavy products can be accounted for with estimate of their total weight which takes up no more than 1% of liquid sample even in worst cases in this study. Individual heavy component selectivity is therefore deemed negligible.

Reactor

Reaction temperature range recommended in all OMT literatures is from 700-800°C. Reactor material narrows down to stainless steel, ceramic furnace tube or quartz tube. For oxidative reactions, iron exhibits catalytic activity for combustion. Tests were performed with conditions in table 4.2.1 to compare quartz and stainless steel reactor for this application. All attempts using a metal reactor failed due to the difficulties of coating and sealing the metal with two types of ceramic/quartz based sealant at reaction temperature. Although both are capable of adhesion on both metals and glass, type 1 is typically for insulation and type 2 is as cracked pipe sealant. Both have temperature rating of 900°C. Detail tests with metal reactor tube are shown in the following table:

Table 4.2.2-1 Reactor configurations proven unsuitable for OMT conditions

Reactor	Reactor insert	Coating/Sealant	Catalyst	Result based on O ₂	Note
SS, Autoclave	no	Type 1	no	Inconsistent partial O ₂ conversion	coating cracked
SS, Autoclave	no	Type 2	no	complete O ₂ conversion	coating cracked
SS, Autoclave	no	no	no	complete O ₂ conversion	
SS, Autoclave	Quartz	Type 1	no	Inconsistent partial O ₂ conversion	sealant cracked
SS, Autoclave	Quartz	Type 2	no	Inconsistent partial O ₂ conversion	sealant cracked
SS, Swagelok	Quartz	Type 1	no	Inconsistent partial O ₂ conversion	sealant cracked
SS, Swagelok	Quartz	Type 2	no	complete O ₂ conversion	sealant cracked

The metal reactor with quartz insert was later replaced with a quartz reactor. Liquid product collection was also changed from metal to Pyrex glass condenser with a cooling jacket. These changes served to minimize metal catalyzed reactions. The initial run in the quartz reactor without catalyst showed no significant consumption of O₂ and proved the viability of the material.

Due to the low pressure ratings of quartz and Pyrex glass, no high pressure tests could be performed.

Khan et al (1993) used an alumina tube in their OMT experiments and found higher activity in their blank test than the test with quartz tube carried out here in this study. In the following table comparing results of the three reactor material, stainless steel caused near complete consumption of oxygen (limited reactant); alumina shows some activity while quartz is the most inert showing lowest toluene conversion (2%) but best selectivity (to EB and styrene). The extent of reactions occurring in the quartz tube can be characterized as base line activity.

Table 4.2.2-2 Impact of Reactor Material

Source	This study	This study	Khan et al.	Suzuki et al.	This study
Heating zone	Two zones	One zone			Two zones
Reactor	Quartz	Quartz	Alumina	Quartz	316 SS
Packing	Quartz	Quartz	Quartz	Quartz	Quartz
Conv%					
O ₂	9.9	2.5	54		~100
Toluene	4.9	2	7.4	2.7	~100
CH ₄	1.8	3.9	1.7		
Sel%					
CO _x	75.9	24	65	44	
Benzene	4.0	24	12.5	22.5	
C8 (EB+styrene)	10.2	31.6	17.4	29.8	
Xylenes	0.6				
Benzaldehyde	9.8	17.1			
Heavies in liq	0.06	1.5			
Solid (coke, polymer etc.)	0	0			

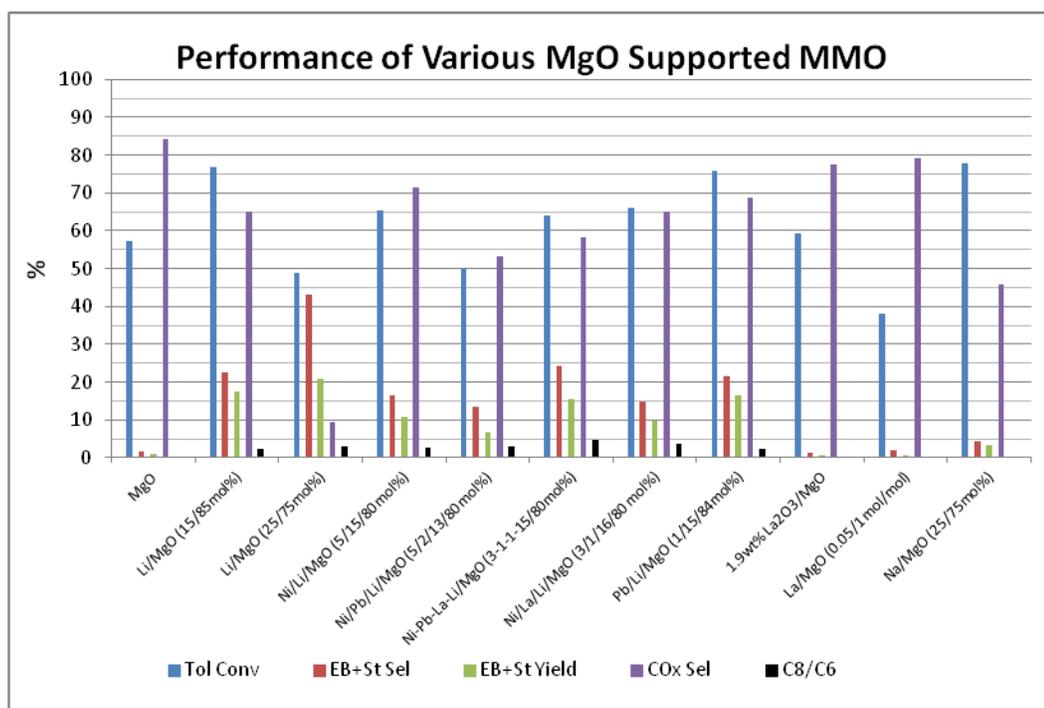
The most inert material for this application is quartz. As reactor heating zone is reduced (only one heating zone on instead of both), reactivity is lowered and C8 selectivity is significantly improved, indicating reaction occur in quartz reactor are thermal reactions and not catalytic reactions occurred on quartz and the more the thermal effect favors side reactions the longer the reactants stay at reaction temperature. Most reliable data should

be obtained with minimum length of reaction zone (just enough to heat the entire bed to reaction temperature) and in quartz reactor with quartz packing around catalyst bed.

3f. Catalyst Test Results and Conclusions

MMO:

MgO has been studied as catalyst support by several research groups such as Kim et al on OMT and Khan et al on both OMT and OCM. Kim et al have shown improvement of yield to EB and styrene by addition of Pb on MgO while addition of Ni does not have significant impact. Khan et al have presented result of alkali metal oxide promoted MgO and CaO. Other works presented in review by Oliver et al on OCM have shown use of rare earth promoter, mainly La. MgO have shown desired basic properties with relatively low oxidative activity (compared to other alkaline earth oxides) in terms of selectivity to ethane, ethylene, EB and styrene. In this study, MgO supported MMO have been synthesis with various promoters Ni, La, Pb and alkali metals one at a time and also some combinations of them to test their effects on catalytic performances for OMT. Start up of all MMO tests is heating in 170cc/min N₂ and 10cc/min O₂ to reaction temperature then change to conditions shown in table 4.2.1 and remain so for the duration of the run. Results at 3 hours on stream are summarized in the following histogram.



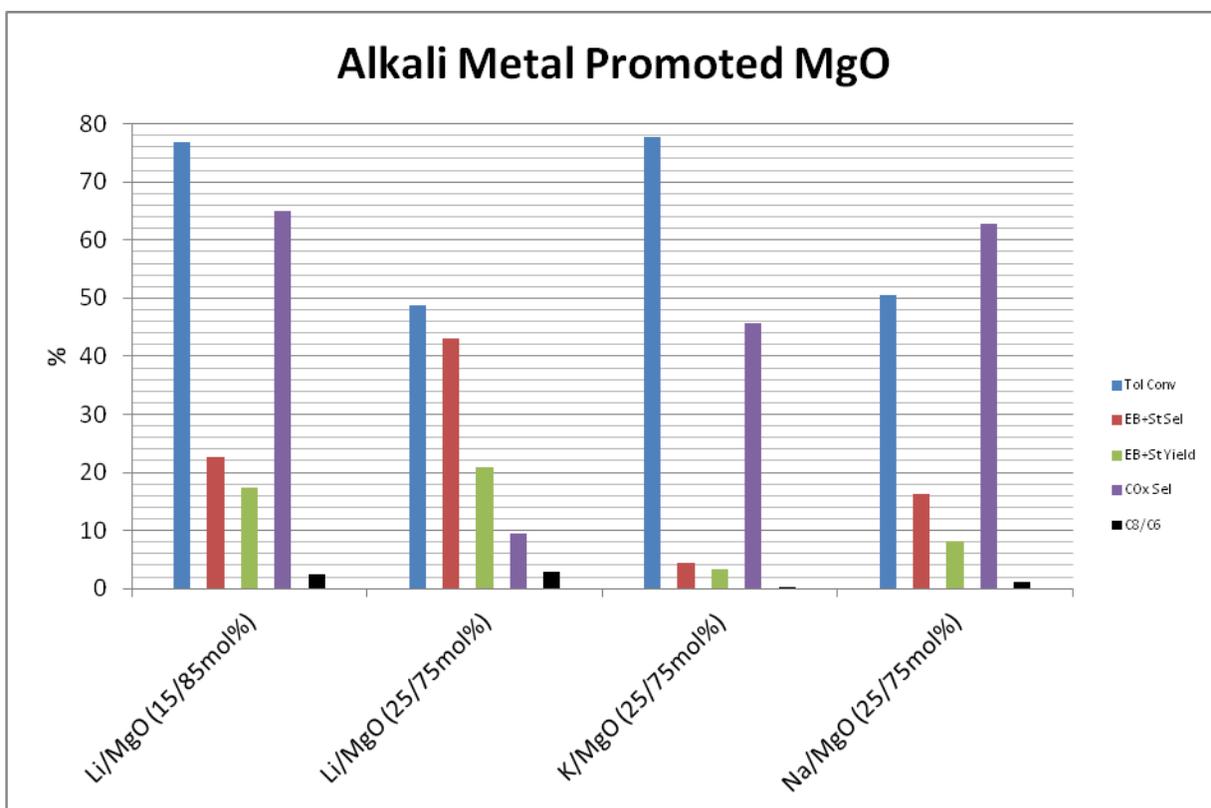
Catalytic performances of MgO supported MMO

MgO alone shows very low C8 (EB and styrene) yield of 1%. Addition of La does not improve the OMT performance of MgO. Among alkali metal promoters Li of which 15mol% on MgO can improve yield to 17.4 and 25mol% can improve yield to 21%. No higher Li compositions tested due to concern of signs of melting observed (white spots fused onto wall of quartz reactor tube). Addition of alkali metals significantly improves catalytic performance for OMT confirming advantage of basicity. Addition of Pb on

Li/MgO (15mol%Li) does not have an impact of yield while addition of Ni leads to higher CO_x selectivity and lower yield at 10.8%. Ni/Pb/Li/MgO further reduces the yield to 6.7%. However, addition of La to Ni/Pb/Li/MgO improves the yield to 15.8%. The reason for this synergistic effect is unknown.

The addition of Pb also leads to formation of solid crystals (predominantly toluene dimers stilbene and bibenzyl). Other tests with higher Pb content (15mol, 20mol and 27.5mol %) on MgO with conditions from Kim et al all lead to plugging of the reactor outlet by toluene dimer crystals. Due to such operational problem because of presence of Pb, MMO involving Pb has not been investigated any further.

The effect of alkali metal is so far the most promising promoter on MgO or other alkaline earth metal oxide supports. To compare the effects of different alkali metal promoters on MgO, Na and K counterparts of 25mol% Li/MgO have been tested and the results are as shown in the following histogram.



Performance data of alkali metal on MgO

The order of promoters from most selective towards EB and styrene is Li>Na>K while oxidative activity is the opposite Li<Na<K. Higher coverage of Li on MgO can lead to higher yield as shown. Higher alkaline promoter content has yet to be tested. Although basicity increases in the order of increasing atomic weight of alkali promoter, selectivity decreases in this order due to increasing oxidative activity observed by increasing conversion, decreasing C₈/C₆ ratio and increasing CO_x selectivity. Benzene formed in these cases is mainly from oxidative dealkylation.

MgO versus CaO

Catalyst	Toluene conversion (%)	EB+styrene Selectivity (%)	EB+styrene yield (%)	EB / Styrene	Benzene Selectivity (%)	C8 / C6	COx Selectivity (%)	Comments
MgO	57.2	1.7	1.0	1.13	14.0	0.12	84.1	3h
CaO	70.1	12.7	8.9	0.78	10.4	1.22	70.4	3h
	74.3	4	3.0	0.82	13.6	0.29	80.2	3rd-6th h

The table above shows CaO results in much better yield than MgO. CaO is known to have higher basicity than MgO. Better conversion with CaO is due to higher oxidative activity, hence also lead to better EB/Styrene ratio. Unless the promoters have significantly better synergistic effect with MgO, CaO can be considered the better choice of support.

The best alkali promoted catalyst from previous results is 25mol% Li/MgO. Results have shown that it deactivates very quickly is therefore not stable. 25mol% Li/CaO however shows far better stability while yield remains close while its MgO counter-part shows rapid decline over time

Table 5.1-2 25mol% Li/MgO versus 25mol% Li/CaO

Catalyst	Catalyst ID#	Toluene Conversion (%)	EB+styrene Selectivity (%)	EB+styrene Yield (%)	EB to Styrene	Benzene Selectivity (%)	C8 to C6	COx Selectivity (%)	Comments
Li/CaO (25/75 mol%)	380-4	42.3	35.5	15.0	3.93	14.0	2.54	37.1	3h
		34	41	13.9	3.88	12.6	3.25	29.8	3-6h
		47.8	35.6	17.0	3.62	9.7	3.67	42.0	3h, <u>rerun</u>
Li/MgO (25/75mol%)	370-36	48.8	43	21.0	4.24	15.0	2.87	9.4	3h
		52.1	27.8	14.5	3.15	11.0	2.53	52.3	4th-9th hr
		49	21.4	10.5	3.17	11.0	1.95	60.9	next day

It has to be noted that both catalysts with such high Li content were found to be partially melted and fused to the quartz reactor tube wall after the run. Although achieving relatively high yield than other catalysts tested, high Li content is proven to be less tolerant to the high reaction temperature and subjected to irreversible damage such as melting observed in this study and separation from support observed in the studies by Khan et al. These catalysts are therefore not feasible for long term operations for OMT.

Zeolite Screening:

Zhou et al provided catalytic performance data for OMT with modified zeolite catalysts as shown in table 3.2.2. Due to lack of vapor product analysis COx selectivity is unknown. Aromatics in the vapor are also not account accounted for. True selectivity may be significantly lower.

OMT over Modified Zeolite Catalysts (Zhou et al.)

Catalyst	Conversion	Selectivity(%)					Yield(%)			
	(mol%) C ₇ H ₈ ^b	C ₆ H ₆ ^c (BZ)	C ₈ H ₁₀ ^d (EB)	C ₈ H ₈ ^e (ST)	Total C ₈ ^f (ST+EB)	ST/EB ^g	C ₆ H ₆ (BZ)	C ₈ H ₁₀ (EB)	C ₈ H ₈ (ST)	Total C ₈ (ST+EB)
Li ₂ O/KY	25.5	28.1	32.3	25.8	58.1	0.80	7.2	8.2	6.6	14.8
Na ₂ O/KY	37.5	31.5	28	21.6	49.6	0.77	11.8	10.5	8.1	18.6
K ₂ O/KY	38.4	40.1	26.1	16.9	43	0.65	15.4	10	6.5	16.5
C ₅₂ O/KY	57.1	40.0	15.9	36.4	52.3	2.29	9.1	9.1	20.8	29.9
NaCl/KY	29.6	14.2	40.6	22.4	63	0.55	4.2	12	6.60	18.6
NaBr/KX	65.0	11.8	11.3	64.4	75.7	5.70	7.7	7.4	41.9	49.3
NaBr/KY	65.0	7.5	8.3	73.4	81.7	8.84	4.9	5.4	47.7	53.1
NaBr/KM	62.0	11.2	10.8	68.0	78.8	6.30	6.9	6.7	42.2	48.9
NaBr/ KZSM5	76.3	9.9	7.1	69.3	76.4	9.76	7.6	5.4	52.9	58.3
NaBr/K β	61.7	16.7	7.1	68.7	75.8	9.68	10.3	4.4	42.4	46.8
KBr/KX	52.2	21.5	18.1	46.8	64.9	2.59	11.2	9.5	24.4	33.9
KBr/KY	58.9	14.8	17.9	51.0	68.9	2.85	8.7	10.5	30.0	40.5
KBr/KM	57.4	16.3	16.1	56.4	72.5	3.5	9.4	9.2	32.4	41.6
KBr/ KZSM5	58.2	15.6	13.6	58.6	72.2	4.31	9.1	7.9	34.1	42.0
KBr/K β	60.1	14.0	13.3	58.0	71.3	4.36	8.4	8.0	34.9	42.9

Note: a. T_r= 973K, W=0.3g, CH₄/O₂/C₆H₅CH₃/N₂ =24:6:2.33:20(mL/min). The results presented were obtained after 2h of reaction. The yield is on the basis of moles of toluene converted
b. toluene c. benzene d. ethylbenzene e. styrene f. ethylbenzene + styrene
g. ST/EB = selectivity ratio of styrene to ethylbenzene.

Heating prior to start of the run can be in nitrogen only (170cc/min N₂) or in mix of nitrogen and oxygen (170cc/min N₂ and 10cc/min O₂). As shown below, heating up in nitrogen only keeps the catalyst relatively stable over the first 8h on stream. This is because oxygen can react with NaBr. The earlier oxygen is introduced the earlier detrimental removal of NaBr occur.

Impact of feed for start up heating

Catalyst	Catalyst ID#	SiO ₂ /Al ₂ O ₃	Run time (h)	T(°C)	Start up feed for heating	Toluene conversion (%)	EB+styrene selectivity (%)	EB+styrene yield (%)
6wt% NaBr/KZSM5	370-38	23	3	710-720°C	N ₂	52.4	13.5	7.1
		23	8	710-720°C		51.4	16.2	8.3
6wt% NaBr/KZSM5	370-38	23	3	710-720°C	N ₂ +O ₂	56.9	15.6	8.9
		23	8	710-720°C		53.6	7.2	3.9

To maximize C₈ selectivity, initial stability of catalyst and for fair comparison of all zeolite catalysts, all zeolites catalysts tested used the same start up heating procedure, being heated to reaction temperature in 170cc/min N₂.

In this study, samples were taken at earliest 3 hours on stream to have enough product samples for analysis instead of 2 hours as done by Zhou et al. Results finding KZSM5 is the best among unpromoted zeolites with 2% yield of C₈ (EB+styrene) while others are virtually non-selective. Alkali oxide promoted KZSM5 and super beta are also non-selective. NaBr was selected as the only alkali bromide promoter used in this study. NaBr promoted NaY only showed no more than 1.8% yield. The best zeolite catalyst tested was 6wt% NaBr promoted KZSM5 with 8-9% yield. The low measured yield may be due to rapid deactivation of catalyst in two ways: 1. Deactivation of KZSM5 and 2. elimination of NaBr at reaction temperature with presence of O₂.

ZSM5:

NaBr promoted KZSM5 results in much better selectivity and yield than unpromoted KZSM5. HZSM5 (NH₄ZSM5 pretreated at 550°C in N₂ flow for 4 hours) results in much higher selectivities to benzene and xylenes with significantly lower selectivities to EB and styrene than KZSM5. These results have confirmed:

1. Ion exchange with alkaline metal is necessary to reduce acidity to improve selectivity;
2. NaBr being an effective radical initiator contributes to better selectivity.

Comparison of various versions of ZSM5

Catalyst	6wt% NaBr/KZSM5 (380-5)		HZSM5	KZSM5	Target
Skin T(°C)	682	682	685	685	
	710-720*	710-720*	710-720*	710-720*	
P(psig)	1	1	1	1	
CH ₄ :Tol	14	14	14	14	<5
Feed volume ratio (CH ₄ :O ₂ :tol:N ₂)	23.5:5.3:1.7:19.5	23.5:5.3:1.7:52	23.5:5.3:1.7:19.5	23.5:5.3:1.7:19.5	
GHSV (h ⁻¹)	5010	8300	5010	5010	
Contact time (sec)	0.72	0.43	0.72	0.72	
Run time	3h	3h	3h	3h	
Tol conv%	42.4	34.5	68.6	50	>70
CH ₄ conv%	2.8	near 0	8.8	6	
O ₂ conv%	19.1	19.3	98.7	77.4	
Sel%					
Bz	21.7	22	31.3	14.5	
EB	11.4	7.6	0.9	2.8	
Styrene	4.4	3.2	0.4	1.4	>72
Xylenes	0.2	0.09	1.3	0.2	
Cumene	0	0	0	0	
EB+St	15.8	10.8	1.3	4.2	>90 (EB+St+Bz)
CO _x	28.2	49.8	64.8	77.4	
Benzaldehyde	16.5	11	0.1	2.9	
Napthalene	0.72	0.3	0.6	0.1	
DimethylNapthalene	10.1	3.6	0.5	0.3	
C ₁₄	3.1	1.1	0.02	0.1	
EB+St Yield%	6.7	3.7	0.9	2.1	
	2.59	2.38	2.25	2.00	
Other Heavies and solids	3 (l, dark heavy oil)	1.1 (l)	0.05(l)	0.2(l)	
	New Optimal bed location. Heavy oil formed	Diluted feed at higher GHSV			

Dark heavy oil formation can be observed when using NaBr/KZSM5. Dark oil indicates high selectivity of heavy products, predominantly PAHs and their oxygenated derivatives with main components such as xanthone and phenanthrene according to GCMS analysis. While diluted feed with higher nitrogen flow limits formation of heavy PAH and heavy oxygenate components, it also results in lower conversion and selectivity.

NaBr promoted KZSM5 achieves significantly higher yield than KZSM5. This verifies the advantage of NaBr as an effective radical initiator. KZSM5 achieves significant higher yield than the acidic form HZSM5. HZSM5 leads to significantly higher selectivity to benzene and xylenes.

The following table shows the comparison between ZSM5 support with silica/alumina ratio of 23 and 80. Higher silica/alumina ratio results in lower conversion and but higher yield. Although the exchanged ZSM5 with lower silica alumina ratio is believed to be more basic (Kovacheva et al.), the more alumina present the higher oxidative activity is.

Table 5.2.2-2 Impact of silica/alumina ratio of ZSM5

Catalyst	Catalyst ID#	SiO ₂ /Al ₂ O ₃	Run time (h)	T(°C)	Startup feed for heating	Toluene conversion (%)	EB+styrene selectivity (%)	EB+styrene yield (%)
10wt% NaBr/KZSM5	361-26A	23	3	710-720°C	N2	62.2	0.6	0.4
		23	8	710-720°C		54.2	0.4	0.2
10wt% NaBr/KZSM5	361-29	80	3	710-720°C	N2	45.7	3.1	1.4
		80	8	710-720°C		48.3	4.1	2.0

Catalyst Test Conclusions:

- The best catalysts found in this study were 25mol% Li supported by CaO or MgO with 14 to 17% yield in 6h on stream, Li/CaO being relatively stable.
- The only suitable reactor material found was quartz.
- Thermal reactions favor formation of CO_x, benzene and benzaldehyde.
- Limiting the reactor hot zone to just enough to heat entire catalyst bed to reaction temperature and quick cooling on the outlet can maximize C8 (EB and styrene).
- Very few xylenes can be formed on basic catalysts.
- Reliable catalytic performance data should be obtained by taking into account of products in all phases and not just liquid due to significant amount of carbon can be in the vapor such as CO_x and solid such as coke and oligomer crystals.
- The basicity of the catalyst is not the only deciding factor of performance for OMT. Effective catalyst should have relatively low oxidative activity to limit CO_x and other oxidation byproducts.
- Among various unpromoted basic zeolites tested, KZSM5 have shown the best yield while other zeolites X, superbeta, TUD1-Alumina and and Y are virtually non selective for OMT.
- Among promoted zeolites, 6wt% NaBr promoted K exchanged ZSM5 is the best with 8-9% initial yield (3 hours on stream). Low selectivity of zeolite catalysts for OMT, compared to MMO with MgO and CaO support, is thought to be caused by Lewis acid property of the alumina content.
- Silica, such as TUD1-silica same as reactor material is inert.
- Halide salts have very low melting points in the presence of steam and can react with oxygen. A halide salt such as NaBr as promoter although effectively initiate radicals, its rapid elimination by oxidation, melting and decomposition leads to irreversible change of the catalyst. This is not feasible for prolonged operation.

3g.Recommendations and Proposed Future Studies:

Catalyst

More stable catalyst promoters than NaBr are needed. More combinations of basic mixed metal oxides containing two or more alkali, alkaline earth and untested high temperature tolerant transition metal oxides should be explored.

Zeolites typically go through rapid decline in selectivity (within several hours on stream); though tolerant to high temperature, zeolites were not suitable catalysts or catalyst supports for OMT. Silica due to its tolerance to high temperature and virtually inert property may be the most suitable type of support or catalyst bed diluent.

Further studies should search for:

- Highly basic catalysts with low oxidative activity,
- High tolerance to OMT reaction temperature (high melting point),
- Catalyst with limited oxygen mobility (relatively stable in oxidative or reductive environment).

In addition:

- Highly selective (not necessarily with high conversion) catalysts (such as Li/MgO) for oxidative coupling of methane (OCM) are good candidates.
- Among the OCM catalysts, silica supported tungstate salts and high temperature tolerant carbonates such as BaCO₃ are worth exploring. BaCO₃ has been shown effective for low temperature OCM both as support or promoter though ethane and ethylene selectivity is lower than the typical OCM at 800°C or higher with other catalysts. (Wang et al.)
- W has been used for OCM catalysts in the form of sodium tungstate supported by silica promoted by Mn.
- Mn/NaWO_x/SiO₂ has been proven to be the best OCM catalyst to-date. However, NaWO_x has a melting point below 700°C and lower in hydrate form. Tests done in this study have shown melting of sodium tungstate and thus no stable and selective results obtained for OMT. Other forms of tungstate have yet been tested.

Silica as an inert material is ideal for catalyst bed dilution. To achieve dilution active catalyst can be synthesized on silica support or simply use physical mix of silica with the active catalyst.

Dilution of a catalyst with high oxidative activity may improve selectivity towards EB and styrene. For a catalyst achieving higher selectivity than silica, dilution will lead to more favorable conditions for undesired thermal reactions.

Test Unit

In this study, although the product liquid condenser was set at 0°C, a significant amount of aromatics can still be present in vapor (0.8-1.5vol% in vapor, 30-60wt% of total aromatics in overall product stream). Solid products can also be formed.

Only thorough analysis for all product phases can achieve accurate results for catalytic performance data and yield. Better analytical methods to quantify solid product components should be developed for further studies if selectivities to coke components and toluene dimmers are deemed significant.

3h.References:

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Appendix A Catalyst Sample Listing

Serial no:	Catalyst ID	Catalyst description
1	340-1	8%NaBr/K-ZSM-5
2	340-2	8%NaBr/K-ZSM-5
3	340-4	8%NaBr/K-ZSM-5
4	340-5	8%NaBr/K-ZSM-5
5	340-6	8%NaBr/K-ZSM-5
6	340-11	8%NaBr/K-Y
7	361-26,361-25	K-ZSM-5 (originally NH4-ZSM-5)
8	361-18A	10 wt % NaBr/K-ZSM-5 - air cal.550C
9	361-18C	10 wt % NaBr/K-ZSM-5 - air cal.500C
10	361-21B	10 wt % NaBr/K-ZSM-5 - N2 cal.500C
11	361-30	Na-ZSM-5-air,500 cal.
12	361-30A	10 wt %NaBr/Na-ZSM-5 - N2,500 cal.
13	361-29	10 wt % NaBr/K-ZSM-5 - N2,500 cal.
14	361-32A/ 361-32B/361-48A/361-48B	Calcined super beta(using the programmed calcination)
15	361-33	K-Super beta, air cal. 500C (from originally H-Super beta)
16	361-34	Na-Superbeta, air cal.500C
17	361-33A	10 wt % NaBr/K-Super beta,N2 cal.500 C
Serial no:	Catalyst ID	Catalyst description
18	361-34A	10 wt% NaBr/Na-Super beta,N2 cal.500 C(dried in shallow porcelain dish)
19	361-37	Rb-Super beta, air cal. 500C
20	361-38	Cs-Super beta, air cal. 500C
21	361-37A	10 wt % NaBr/Rb-Super beta, N2 cal. 500C(rotavap)
22	361-38A	10 wt % NaBr/Cs-Super beta, N2 cal. 500C (rotavap)
23	361-33B	10 wt % NaBr/K-Super beta,N2 cal.500 C (rotavap)
24	361-42	33.5 wt % PbO on MgO (rotavap after impreg.)
25	361-44	20 wt % PbO on MgO (rotavap after impreg.)
26	361-45	5.6 wt % PbO on MgO (rotavap after impreg.)
27	361-46	1 wt% PbO on MgO (rotavap after impreg.)

28	361-26A	10 wt % NaBr/K-ZSM-5 - N2 cal.500C (rotavap)
29	361-34B	12 wt % Ba/ Na-Superbeta
30	361-47	Na-Superbeta, air cal.500C
31	361-48A/ 361-48B	Calcined super beta(using the programmed calcination)
32	361-49	15 mol% Li/MgO
33	361-50A	5mol% Pb+15 mol% Li + 80mol% MgO
34	361-50B	1mol% Pb+15 mol% Li + 84mol% MgO
35	361-51	K-Y (made from CBV901)

Serial no:	Catalyst ID	Catalyst description
36	370-1	5 wt % Na on Cerium oxide (NaBr/CeO ₂)
37	370-2	5mol% Ni+15 mol% Li + 80mol% MgO
38	370-3	MgO/ Na -Superbeta (on 361-47)
39	361-51A	10 wt % NaBr/K-Y (made from CBV901)
40	370-4	CaO/ Na -Superbeta (on 361-47)
41	370-5	Na-Superbeta, air cal.500C
42	370-6	Li-Superbeta, air cal.500C
43	370-7	Calcined super beta(using the programmed calcination)
44	370-6A	10 wt % NaBr/Li-Superbeta (N ₂ calcined @ 500 C)
45	370-10A	Na -Y Dry Syn (@ 85 C for 36 hrs)
46	370-10B	Na -Y Dry Syn (@ 85 C for 24hrs)
47	370-12A	Na Beta Dry Syn(@ 155 C for44 hrs - lab 12 oven)
48	370-12B	Na Beta Dry Syn (@ 155 C for24 hrs - lab 9 oven)
49	370-15	Na-ZSM-5 Dry Syn (@ 158 C for 25 hrs)(to be repeated)
50	370-16	10 wt % NaBr/Na-Y DrySyn,N ₂ cal.500 C (rotavap)
51	370-17	Na -Y Dry Syn (@ 85 C for 36 hrs) (large batch)
52	370-18A	Na-ZSM-5 Dry Syn (@ 170 C for 25 hrs)repeat of 370-15
53	370-18B	Na-ZSM-5 Dry Syn (@ 158 C for 40 hrs)repeat of 370-15
54	370-20	NaBr on 270-12A (flask broke)
55	370-21A	Na-ZSM-5 Dry Syn (@ 170 C for 25 hrs)repeat of 370-18A
56	370-21B1	Na-ZSM-5 Dry Syn from 370-21A (170 C / 40 hr)-slightly gritty and liquid separation (the TPAOH was increased)
57	370-21B2	Na-ZSM-5 Dry Syn from 370-21A (180 C / 40 hr)(the TPAOH was increased)
58	370-31	5 mol% Ni + 2 mol% Pb+ 13 mol% Li + 80 mol% MgO
59	370-34	3 mol% Ni + 1 mol% Pb+ 1 mol% La+ 15 mol% Li + 80 mol% MgO
60	370-36	25 mol% Li/MgO
61	370-37 A / 370-37B	K-ZSM-5 from NH ₄ -ZSM-5

62	370-38	6 wt % NaBr on K-ZSM-5 , on sample 361-26
63	370-40-1	K-Y (made from Na-Y with silica/alumina= 5)
64	370-40-2	6 wt % NaBr on K-ZSM-5 , on sample 370- 37A
65	370-41	1.9 wt % La ₂ O ₃ / MgO
66	370-42-2	6 wt % NaBr on K-Y , NaBr impregnated on sample 370-40-1
67	370-42-1	K-ZSM-5 from NH ₄ -ZSM-5 (calcined at high temp 720 C under air)
68	370-43	5 mol% Na + 5 mol% K / CaO
69	370-44	22.5 wt % La ₂ O ₃ / CaO
70	370-37-1	10 wt % NaBr on K-ZSM-5 , on sample 370- 37B (for comparison with 6 wt % NaBr on new batch of K-ZSM-5)
71	370-45	28.7 wt % La ₂ O ₃ /MgO
72	370-46	3 mol% Ni + 1 mol% La+ 16 mol% Li + 80 mol% MgO
73	370-46A	25 mol% Na/MgO
74	370-48	25 mol% K/MgO
75	370-47	K-ZSM-5 (silica/alumina= 280)
76	370-47A	6 wt% NaBr on K-ZSM-5 , on sample 370-47
77	370-49	6 wt % NaBr on Si-TUD-1
78	370-50	6 wt % NaBr on Al-TUD-1
79	370-51	4 mol% Ni + 1 mol% La + 25 mol% Li + 70 mol% MgO
80	370-52	MgO
81	380-1	Making of a large batch of K-ZSM-5 from NH ₄ -ZSM-5
82	380-3	Making of a large batch of K-ZSM-5 from NH ₄ -ZSM-5
83	380-4	25 mol% Li + 75 mol% CaO
84	380-4A	CaO
85	380-5	6 wt % NaBr on 30 g of (380-1 + 380-3), N ₂ CALCN. 550C / 5 hrs

Appendix B Catalyst Test Data

	Catalyst	Catalyst ID#	Heating Method	Toluene Conversion (%)	EB+styrene Selectivity (%)	EB+styrene yield (%)	
12/3/2010	None (20-40mesh quartz packing)		Two zone heating	4.9	9.5	0.5	3h
12/16/2010	5.6wt%PbO/MgO	361-45	Two zone heating				Reactor plugged by C14 crystals
12/20-12/21/2010	27.5wt%PbO/MgO	361-44	Two zone heating	39	1.7	0.7	3h, more Pb leads to more solid formation and plugs reactor
12/14/2010	10wt% NaBr/KY	340-11	Two zone heating	13.4	3.2	0.4	3h
12/15/2010			Two zone heating	40.7	4.5	1.8	3-6h
12/13-12/14/2010	10wt% NaBr/KZSM5	361-21A	Two zone heating	20.5	10.8	2.2	Conversion too low and unstable
12/21/2010	Na2O/KZSM5	340-1 to 340-6	Two zone heating				NaBr not deposited properly,, non-selective
12/22/2010	Pb/Li/MgO (5/15/80mol%)	361-50A	Two zone heating	39.6	0.8	0.3	3h
1/4/2011	None (20-40mesh quartz packing)		Lower zone heating	2	31.6	0.6	3h (most inert)
1/5/2011	NaBr/CeO2	370-1	Lower zone heating	37.6	5.8	2.2	3h
1/14/2011	KZSM5	361-25	Lower zone heating	56.5	17.1	9.7	3h
1/14-1/15/2011			Lower zone heating	53.6	1.2	0.6	significant selectivity lose, 6h
1/20-1/21/2011	KZSM5	361-25	Lower zone heating	43.2	2.4	1.0	1/2 the oxygen feed
2/15/2011	KZSM5 (N2 Startup)	370-37	Lower zone heating	57.8	1.2	0.7	3h (strated with N2 Heating)
2/15/2011		370-37	Lower zone heating	48.4	1.7	0.8	3rh-8th hr
2/16/2011	KZSM5 (720°C Cal, N2 startup)	370-42-1	Lower zone heating	44.6	0.8	0.4	3h (strated with N2 Heating)

2/16/2011		370-42-1	Lower zone heating	57.7	1.1	0.6	3rh-8th hr
2/17/2011	KZSM5 (N2+O2 startup)	370-37	Lower zone heating	52.9	1.3	0.7	3h (strated with N2+O2 Heating)
2/17/2011			Lower zone heating	45.7	3.9	1.8	3rh-8th hr
2/17/2011			Lower zone heating	47.2	1.7	0.8	
1/26/2011	10wt% NaBr/KZSM5	361-26A	Lower zone heating	63.3	4.5	2.8	at 3h, N2+O2 start up heating
1/26- 1/27/2011			Lower zone heating				Dark heavy oil forming overnight
2/21/2011	10wt% NaBr/KZSM5	361-26A	Lower zone heating	62.2	0.6	0.4	at 3h, N2 start up heating rerun
2/21/2011			Lower zone heating	54.2	0.4	0.2	3th-8th hr, Dark heavy oil start forming
2/22/2011	10wt% NaBr/KZSM6	361-29 (SiO2/Al2O3=80)	Lower zone heating	45.7	3.1	1.4	3hr
2/22/2011			Lower zone heating	48.3	4.1	2.0	3rd-8th h
2/10/2011	Air calcined NaBr/KZSM5	361-21A	Lower zone heating	75.6	0.5	0.4	3hr
2/10- 2/11/2011			Lower zone heating	55.6	3.1	1.7	overnight
2/9/2011	6wt% NaBr/KZSM5	370-38	Lower zone heating	52.4	13.5	7.1	0-3h (strated with N2 Heating)
2/9/2011			Lower zone heating	51.4	16.2	8.3	3rd-9th hr
2/10/2011	6wt% NaBr/KZSM5	370-38	Lower zone heating	56.9	15.6	8.9	3h (started with O2+N2 Heating)
2/10/2011			Lower zone heating	53.6	7.2	3.9	3rd-7th hour
3/1/2011	10wt% NaBr/KZSM5	370-37-1	Lower zone heating				Dark heavy oil formed
2/12/2011	6wt% NaBr/KZSM5	370-40-2 (same as 370-38)	Lower zone heating	52.6	2.7	1.4	Dried at 120°C overnight in 50cc/min N2, 4h run
2/12/2011			Lower zone	68.8	2.8	1.9	4th-8th hr

			heating				
3/17/2011	6wt% NaBr/KZSM5	370-40-2	Lower zone heating	33.8	3.7	1.3	3 hr (without pretreatment)
4/5/2011	6wt% NaBr/KZSM5	380-5	Lower zone heating	42.4	15.8	6.7	3hr dark heavy oil formed (mostly PAHs and their oxygenated derivatives)
4/5/2011			Lower zone heating				3-6h dark heavy oil formed (mostly PAHs and their oxygenated derivatives)
4/6/2011			Lower zone heating				3hr dark heavy oil formed (mostly PAHs and their oxygenated derivatives)
4/7/2011			Lower zone heating	34.5	10.8	3.7	N2 diluted feed, dark oil formation persists
4/8/2011			Lower zone heating				3hr, 740-750oC, dark Heavy Oil formation persists
4/19/2011			HZSM5	378-23	Lower zone heating	68.6	1.3
4/20/2011	378-24	Lower zone heating		80.7	0.8	0.6	3h
4/20/2011		Lower zone heating		60.7	1.2	0.7	3-6h
1/12/2011	10wt% NaBr/KY (SiO2/Al2O3=80)	361-51A	Lower zone heating	38.4	9.5	3.6	6hr
2/18/2011	6wt% NaBr/KY (SiO2/Al2O3=5)	370-42-2	Lower zone heating	62.7	0.8	0.5	3 hr
2/18/2011			Lower zone heating	68.1	1.2	0.8	3th - 8 th hour
3/15/2011	MgO	370-52	Lower zone heating	57.2	1.7	1.0	3h
1/10/2011	Li/MgO (15/85mol%)	361-49	Lower zone heating	76.8	22.6	17.4	3h
1/10-1/11/2011			Lower zone heating	68	19.2	13.1	3-6h
2/7/2011	Li/MgO (25/75mol%)	370-36	Lower zone heating	48.8	43	21.0	710-720°C, 3h
2/7/2011			Lower zone heating	52.1	27.8	14.5	740-750°C, 4th-9th hr
2/7-			Lower	49	21.4	10.5	740-750°C, next day

2/8/2011			zone heating				
3/25/2011	CaO	380-4A	Lower zone heating	70.1	12.3	8.6	3h
3/25/2011			Lower zone heating	74.3	4	3	3-6h
3/2/2011	Li/MgO (25/75mol%, LT run)	370-36	Lower zone heating	31.5	6.8	2.1	680-690°C, 3hr
3/2/2011			Lower zone heating	27.5	8.7	2.4	680-690°C, 3rd-8th h
3/7/2011	Na/MgO (25/750 mol%)	370-46A	Lower zone heating	50.6	16.3	8.2	3h
3/7/2011			Lower zone heating	66.9	11.7	7.8	3rd-8th h
3/7- 3/8/2011			Lower zone heating	58.3	10.7	6.2	overnight
4/18/2011	Li/MgO (25/75mol%, remake)	380-6	Lower zone heating	32.1	20.5	6.6	Lower activity than previous sample
4/25/2011			Lower zone heating	31.8	7.7	2.4	contaminated by acidic ZSM5
1/6/2011	Ni/Li/MgO (5/15/80 mol%)	370-2	Lower zone heating	65.4	16.5	10.8	
1/17/2011	Ni/Li/MgO (5/15/80 mol%)	370-2	Lower zone heating	68.6	15.6	10.7	With steam
1/25/2011	Ni/Li/MgO (5/15/80 mol%)	370-2	Lower zone heating	65.4	17	11.1	2nd fresh run
1/25- 1/26/2011			Lower zone heating	60.7	14.7	8.9	Half the oxygen used
1/26/2011	Ni/Pb/Li/MgO (5/2/13/80 mol%)	370-31	Lower zone heating	49.9	13.4	6.7	Confirmed Pb effect for C14 formation
1/26- 1/27/2012			Lower zone heating	56.3	10	5.6	Confirmed Pb effect for C14 formation
3/3/2011	Ni/La/Li/MgO (3/1/16/80 mol%)	370-46	Lower zone heating	75.8	21.6	16.4	3h
3/3/2011			Lower zone heating	62.4	21.4	13.4	3rd-8th h
3/3- 3/4/2011			Lower zone heating	59.7	18.3	10.9	overnight

3/28/2011	Ni-La-Li/MgO (4-1-25-70 mol%)	370-51	Lower zone heating	44.7	15.7	7.0	3h
3/28/2011			Lower zone heating	57.7	17.5	10.1	3-6h
2/8/2011	Ni-Pb-La-Li/MgO (3-1-1-15-80mol%)	361-49	Lower zone heating	64.1	24.3	15.6	
2/8-2/9/2011			Lower zone heating	68.8	28.1	19.3	
1/3/2011	Pb/Li/MgO (5/15/80mol%)	361-50A	Lower zone heating				Reactor plugged by C14 crystals
1/13/2011	Pb/Li/MgO (1/15/84mol%)	361-50B	Lower zone heating	66.1	14.7	9.7	Higher C14 sel% than w/o Pb
2/28/2011	La/MgO (0.05/1 mol/mol)	370-45	Lower zone heating	38.2	2	0.8	3h
2/28/2011		370-45	Lower zone heating	59.4	1.7	1.0	3rd-6th h, yellow crystal forming
2/24/2011	1.9wt% La ₂ O ₃ /MgO	370-41	Lower zone heating	59.3	1.3	0.8	3h
2/24/2011		370-41	Lower zone heating	44.5	1.5	0.7	3rd-6th h
3/25/2011	CaO		Lower zone heating	70.1	12.3	8.6	3h
3/25/2011	CaO		Lower zone heating	74.3	4	3.0	3-6h
2/23/2011	K/Na/CaO (5/5/90mol%)	370-43	Lower zone heating	71	20.5	14.6	3h
2/23/2011			Lower zone heating	66.8	14.2	9.5	3rd-6th h
2/25/2011	La/CaO (0.05/1 mol/mol)	370-44	Lower zone heating	65.2	5.7	3.7	3h
2/25/2011			Lower zone heating	47.5	10.1	4.8	3rd-6th h, yellow crystal forming
3/31/2011	25mol% Li/CaO	380-4	Lower zone heating	42.3	35.5	15.0	3h
3/31/2011			Lower zone heating	34	41	13.9	3-6h
4/1/2011			Lower zone	51.1	30.8	15.7	3h, rerun 1

			heating				
4/4/2011			Lower zone heating	52.5	25.1	13.2	3h, rerun 2
4/10/2011			Lower zone heating	47.8	35.6	17.0	3h, rerun 3
4/10/2011			Lower zone heating	44.8	27.2	12.2	3-6h
1/11/2011	Na-superbeta	361-34	Lower zone heating	57.4	2.8	1.6	3h
1/18-1/19/2011	Rb-superbeta	361-37	Lower zone heating	67.5	1.5	1.0	3h
1/19-1/20/2011	MgO/Na-superbeta	370-3	Lower zone heating	57.8	2.2	1.3	3h
1/24/2011	Drysyn Na-Y	370-10	Lower zone heating	68.9	1.4	1.0	3h
1/24-1/25/2011			Lower zone heating	59.4	1.9	1.1	3h
4/27/2011	6wt% Cs / KZSM5	380-7	Lower zone heating	46.7	5.5	2.6	3h
4/27/2011	6wt% Cs / KZSM6	380-7	Lower zone heating	43.1	7.5	3.2	3-6h
5/2/2011	25mol% K/MgO	370-48	Lower zone heating	77.8	4.4	3.4	3h
5/3/2011	Blank (contaminated)		Lower zone heating	24.3	6.2	1.5	3h, contaminated tube (HZSM5 fused on tube wall)
5/16/2011	5wt% Na ₂ WO ₄	380-9	Lower zone heating	38.6	7.3	2.8	3h, contaminated tube (HZSM5 fused on tube wall)
5/17/2011			Lower zone heating	43.7	9	3.9	3h
5/18/2011	Li ₂ O	380-10	Lower zone heating	44.6	4.9	2.2	3h
5/19/2011	Li ₂ O	380-10	Lower zone heating	42.3	7.6	3.2	3-6h, 750-760°C