TRANSITION METAL TETRACHLOROALUMINATE CATALYSTS FOR PROBE REACTIONS SIMULATING PETROLEUM RESIDS UPGRADING

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INTRODUCTION

In current commercial practice for catalytic upgrading of heavy oil and resids, there are two approaches. One is hydrocracking to obtain light and middle distillates, and the other is hydrotreating followed by FCC to produce gasoline components. While commercial hydroprocessing uses metal sulfide catalysts, an alternative approach would be to convert resids into lower-molecular-weight hydrocarbons with Lewis acidic catalysts. The present work deals with petroleum resid upgrading using Lewis acidic dual-functional salts as catalysts, which contain transition metal halides(1,2). Dual-function here refers to cracking via acid-catalyzed C-C bond cleavage for molecular weight reduction, and hydrogenation of reactive intermediates (from bond cleavage) and polyaromatics for production of stable molecules of low molecular weight. Plummer(3) suggested that sodium and hydrogen tetrachloroaluminates ($NaAlCl_4$ and $HAlCl_4$) was effective as catalyst for molecular weight reduction of resids. The $NaAlCl_4$ was the major molecular weight reduction and synthesis component, and $HAlCl_4$ added a hydrogenation function. Historically, such catalysts have been used in synthesis-type reactions such as isomerization, alkylation and polymerization(4,5).

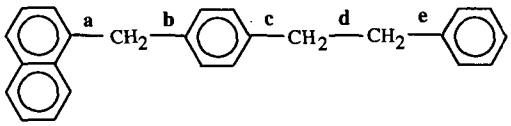
The present work examines the potential of transition metal tetrachloroaluminates as resid upgrading catalysts. This is a fundamental applied research using model compounds as probe molecules. The MClx in the alkali metal or transition metal tetrachloroaluminate $MClx\text{-}(AlCl_3)x$ includes three kinds of alkali metal chlorides, LiCl, NaCl and KCl, and six transition metal chlorides, VCl_3, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $MoCl_3$. We selected four compounds as models, including 4-(1-naphthlymethyl) bibenzyl (NMBB), eicosane (n-C_{20}), dibenzothiophene and pyrene. Batch tests with model compounds were carried out at 425 °C for 20 min in autoclave under hydrogen pressure. The catalytic performance was evaluated in the reaction of model compounds with respect to bond cleavage reaction of C-C bond, hydrogenation, methylation and ring opening of aromatics.

EXPERIMENTAL

Catalyst Precursor and Compound

Three kinds of alkali metal chlorides, LiCl, NaCl and KCl, and six transition metal chlorides, VCl_3, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $MoCl_3$ and $PdCl_2$, were used for preparing the $MClx\text{-}(AlCl_3)_x$ catalysts. Ammonium tetrathiomolybdate (ATTM) also was used as catalyst precursor.

4-(1-naphthylmethyl)bibenzyl (NMBB), eicosane (n-C_{20}), dibenzotiophene and pyrene were used as a model compound. The structure of NMBB is



An intriguing feature of the NMBB structure is the presence of five different C_{ar}-C_{al} or C_{al}–C_{al} bonds. Following the system established by earlier workers, these bonds are denoted as **a** through **e** in the structure shown above. (Some authors refer to this compound as naphthylbibenzylmethane and use the abbreviation NBBM; the system of labeling the bonds remains the same.) ATTM and these model compounds were used without further purification.

Catalyst Preparation

Before catalyst preparation, the precursors were dried at 210 °C for 6 h in vacuum. Catalyst were prepared by using a quartz tube insert, which was placed in a vertical microautoclave reactor with a capacity of 25 mL. Precursor loading amount depends on its valence number, x, for example, $CoCl_2\text{-}(AlCl_3)_2$ was $CoCl_2/AlCl_3$=0.5. The reactor was heated at 400 °C for 20 min, including heat-up time for about 6 min, under nitrogen pressure (300 psig-cold). The combination of LiCl, NaCl, KCl and $ZnCl_2$ with $AlCl_3$ were melt at 400 °C, which indicated these catalysts made molten salt. Other combinations did not become molten salts even at 400 °C. However, strong interactions between MCl_x and $AlCl_3$ may occur even if the combination $MCl_x\text{-}(AlCl_3)_x$ is not in molten state at the reaction temperature.

Model Compound Reaction

A horizontal microautoclave reactor with a capacity of 25 mL was loaded with the reactant and 10 mol% of catalyst based on molar number of reactant. The amounts of reactants were as follows; NMBB: 0.78 mmol; eicosane : 1.8 mmol; DBT : 2.0 mmol; pyrene: 2.0 mmol. After loading reactant and catalyst, the reactor was sealed and purged three times with hydrogen, then pressurized with 800 psig-H_2 at room temperature. A preheated fluidized sand bath was used as a heating source, and the reactor was vertically agitated to provide mixing (about 240 strokes / min). Most of the reactions were carried out at 425 °C for 20 min including heat-up time for about 6 min. After the reaction the reactor was quenched in a cold water bath. Gaseous products were collected into a sample bag. The solid and liquid products were washed out with about 20 mL CH_2Cl_2, then

filtered to separate to solid and liquid products. The solid material was dried at 50 °C for 6 h in vacuum. The CH_2Cl_2 insoluble product was defined as coke.

Analysis

Gaseous products were analyzed by GC-FID using a Parkin Elmer AutoSystem GC for C_1 to C_6 hydrocarbon gases.

Liquid products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971 A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30 m x 0.25 mm, coated with 50 % phenyl - 50 % methylpolysiloxane with a coating film thickness of 0.25 μm. For quantification, a Perkin Elmer 8500 GC with flame ionization detector and the same type of DB-17 column used. Both GC and GC-MS were programmed from 80 to 280 °C at a heating rate of 6 °C/min, and a initial holding time of 0 min and a final holding time of 2 min (or 22 min for NMBB as a reactant). The response factors for all the reactant and 8 of the products were determined using pure compounds(6,7).

RESULTS AND DISCUSSION

NMBB conversion over MClx-($AlCl_3$)x catalyst

Table 1 shows the results of non-catalytic and catalytic runs of NMBB at 425 °C for 20 min. Complete conversion of NMBB was achieved with significant coke formation with $CoCl_2$, $NiCl_2$, $ZnCl_2$ and $PdCl_2$ containing catalyst. For coke formation, the yield with the fourth row in periodic table metal containing catalysts were much higher than that with the fifth raw ones. It was with $MoCl_3$ containing catalyst that there was no coke formation.

For liquid products distribution, the main products in liquid were naphthalene, methylnaphthalene, bibenzyl and methylbibenzyl. Using transition metal MCl_x-$(AlCl_3)_x$ enhanced hydrogenation activity (yield of tetralin), especially $NiCl_2$, $ZnCl_2$ and $PdCl_2$. Table 1 also gave the results of ATTM as a catalyst precursor, which produces MoS_2 in situ. For the reaction with ATTM, there was no dimethylated products in liquid, for example DiMe-naphthalene and DiMe-bibenzyl. It means that methylation activity of molybdenum sulfide catalyst is much lower than that of MCl_x-$(AlCl_3)_x$ catalysts. However, molybdenum sulfide catalyst showed much higher hydrogenation activity (yield of tetralin).

Computer-aided reaction pathway analysis(8) indicated that bond cleavage in catalytic reaction of NMBB may occur favorably in bond **a** (between naphthyl and methylene) with Mo sulfide catalyst, in bond **b** (between the two methylene carbon in bibenzyl part) with Lewis acidic Mo chloride catalyst, and bond **d** (between naphthyltolyl and methylene) in noncatalytic thermal reaction. These results suggested that the main cracking products for catalytic reaction can be represented by Me-bibenzyl and bibenzyl. Therefore, we introduced the molar ratio Me-bibenzyl / bibenzyl as an index of bond cleavage of NMBB, as summarized in Table 2. For thermal cracking of NMBB, the yields of these compounds were very low, because bond cleavage reaction mainly occurred at **d**. In this case, the main cracking products were naphthyltolymethane and toluene. For catalytic reaction with MCl_x-$(AlCl_3)_x$, a/b values for transition metals were lower than those with alkali metal, but in all cases, a/b values were less than 1. It means bond cleavage reaction at **b** position was significant for MCl_x-$(AlCl_3)_x$ catalyst. On the other hand, a/b value with ATTM is much higher than the others (over 1). This higher value indicated that bond cleavage reaction mainly occurred at **a** position. These experimental data of bond cleavage reaction are consistent with the results of computational analysis.

In addition, we also determined the ratio of i-C_4 / n-C_4 as an index, which is a relative measure of the acidity of the catalysts. Figure 1 shows the relation between a/b value and i-C_4/n-C_4 ratio. From this figure, the selectivity of bond cleavage (a/b) decrease with increasing i-C_4/n-C_4 ratio. This result suggests that the selectivity of bond cleavage of NMBB depends on catalyst acidity for MCl_x-$(AlCl_3)_x$ catalysts.

Table 2 also specified the result with Na tetrachloroaluminate catalyst at 400 °C. There was no remarkable difference in conversion between reaction at 400 °C and that at 425 °C, conversion value was 91.5 and 91.7 wt%, respectively. At 400 °C, the degree of bond cleavage reaction at **a** position was almost same as that at **b** position(selectivity: 1.12). On the other hand, bond cleavage reaction at **b** was dominant reaction at 425 °C(selectivity: 0.48). These results indicated that bond cleavage reaction of NMBB with binary catalyst is sensitive to reaction temperature. On the other hand, it should be noted that demethylation reaction and some hydrocracking reaction also occurred, as can be seen from the C_1-C_4 products shown in Table 1.

Eicosane conversion over MClx-($AlCl_3$)x catalyst

Table 3 shows the results of non-catalytic and catalytic runs of eicosane (n-C_{20}) at 425 °C for 20 min. Using transition metal in MCl_x-$(AlCl_3)_x$[MClx=VCl_3, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $PdCl_2$] caused great enhancement in long-chain paraffin hydrocracking. In these cases, C_3 and C_4 hydrocarbons were main products. Complete conversion of eicosane was achieved without any coke formation with $NiCl_2$, $ZnCl_2$ and $PdCl_2$. $MoCl_3$-$(AlCl_3)_3$ catalyst was not very active for eicosane hydrocracking among the transition metal-containing catalysts.

On the other hand, alkali metal-based MCl_x-$(AlCl_3)_x$ [MClx = LiCl, NaCl, KCl] catalysts were not as effective as transition metal-containing ones. The order of conversion was : LiCl > NaCl > KCl.

Table 4 shows a selected group distribution of liquid products. Here the liquid products are divided into two groups for convenience, one is C_9 to C_{11} and the other is C_{12} to C_{19}. The value of A/(A+B) (the fifth column) indicates the degree of hydrocracking of eicosane molecule. In all cases, the values of transition metal are higher than that of alkali metal, which means transition metal catalyst has higher hydrocracking activity for eicosane molecule. In addition, this value is closely related to total conversion.

Table 1 NMBB Conversion at 425 °C for 20 min.

Exp. #	393	336	340	344	348	352	374	360	364	368	420
MClx-(AlCl3)x	None	LiCl	NaCl	KCl	VCl3	CoCl2	NiCl2	ZnCl2	MoCl3	PdCl2	ATTM
Conv. (wt%)	17.1	82.8	64.3	36.2	81.0	100.0	100.0	100.0	72.9	100.0	96.8
Gas yield (wt%)	6.1	0.0	2.2	0.0	2.4	1.5	12.4	10.5	3.4	13.5	2.8
Liquid yield (wt%)	5.8	48.8	45.1	13.1	54.2	62.6	52.3	48.1	43.8	52.0	77.7
Coke yield (wt%)	0.0	7.3	2.9	0.0	8.9	15.1	20.0	20.3	0.0	10.3	0.0
Liquid products (mol%)											
toluene	2.4	5.1	4.3	1.2	4.3	6.5	4.5	6.4	2.9	6.5	1.4
p-, m-xylene	0.6	2.9	2.7	0.4	3.2	5.0	5.5	8.1	1.9	9.7	6.9
o-xylene	1.1	0.3	0.2		0.3	0.5	0.5	0.6	0.2	0.7	
1,3,5-trimethylbenzene		0.4	0.3		0.5	0.9	1.1	1.6	0.2	2.0	0.9
1,2,4-trimethylbenzene					0.1	0.1	0.2	0.3		0.3	
1,2,3-trimethylbenzene						0.2	0.2	0.3		0.4	
tetralin	0.7	2.0	0.7		1.8	2.3	7.6	13.7	0.8	20.6	34.4
Me-tetralin*		0.5			0.4	0.6	2.0	3.3		4.7	3.2
naphthalene	1.0	41.0	44.5	19.0	45.7	46.4	32.3	20.7	47.7	11.3	37.3
1-Me-naphthalene		3.6	3.9	0.7	4.8	4.2	3.3	2.3	3.7	2.1	4.0
2-Me-naphthalene		7.0	4.9		6.4	8.0	5.8	4.0	4.8	3.5	0.6
1,2-DiMe-naphthalene		0.1				0.2		0.2		0.3	
1,3-DiMe-naphthalene		0.5			0.3	0.4	0.2	0.2		0.2	
1,4-DiMe-naphthalene		0.3	0.2		0.2	0.4	0.3	0.2	0.1	0.2	
1,5-DiMe-naphthalene		0.6	0.4		0.5	0.8	0.6	0.5	0.3	0.6	
1,6-DiMe-naphthalene		0.3				0.1		0.2		0.2	
2,6-DiMe-naphthalene					0.4	0.4					
2,7-DiMe-naphthalene						0.4	0.1	0.6		0.5	
bibenzyl	0.2	36.0	29.0	4.7	36.1	43.9	40.5	34.0	25.7	36.2	12.5
4Me-bibenzyl	1.6	5.9	12.6	3.0	14.9	11.7	7.4	2.7	13.0	3.1	54.8
Me-bibenzyl		3.5	1.3		2.7	4.3	4.2	3.5	1.2	4.2	0.7
DiMe-bibenzyl*					0.4	1.1	0.5	0.5		1.5	
1-benzylnaphthalene	0.5			0.2							
naphthyltolylmethane	2.3			1.1							
4H-NMBB	0.3	0.0									
NMBB isomer		1.9	6.9	38.0	5.0				6.1		
NMBB	82.9	15.3	28.8	25.8	16.8				21.0		3.2
Gaseous Products (mol%)											
CH4	35.9	0.0	13.8	0.0	6.1	5.0	15.0	22.9	14.4		8.0
C2H6	3.1	0.0	2.8	0.0	3.3	2.4	14.5	18.3	1.8		2.7
C3H8	14.3	0.0	1.5	0.0	5.8	3.8	22.5	20.9	1.8		1.7
iso-C4H10	0.0	0.0	2.2	0.0	2.0	1.3	18.1	18.3	3.1		1.5
n-C4H10	1.3	0.0	0.5	0.0	0.8	0.4	5.8	2.0	1.0		1.5
i-C4 / n-C4	0.0		3.8		2.8	2.9	5.9	9.1	2.9		1.0

* including isomers

Table 2 Selectivity bond cleavage of binary catalyst system at 425 °C for 20 min.

Exp #	Catalyst	Cleavage at (a), Me-Bibenzyl		Cleavage at (b), Bibenzyl		Selectivity	i-C4 / n-C4
	MClx-(AlCl3)x	(mmol)(1)	(mol %)(2)	(mmol)	(mol %)(2)	(a)/(b)	
393	None	0.012	1.6	0.004	0.5	3.21	0.00
336	LiCl	0.073	9.3	0.282	36.0	0.26	n/a
340	NaCl	0.109	13.9	0.228	29.0	0.48	3.84
313*	NaCl	0.128	16.3	0.114	14.6	1.12	n/a
344	KCl	0.024	3.0	0.037	4.7	0.64	n/a
348	VCl3	0.138	17.6	0.284	36.1	0.49	2.78
352	CoCl2	0.127	16.1	0.346	43.9	0.37	2.92
374	NiCl2	0.092	11.6	0.320	40.5	0.29	5.86
360	ZnCl2	0.048	6.2	0.267	34.0	0.18	9.05
364	MoCl3	0.111	14.2	0.201	25.7	0.55	2.88
368	PdCl2	0.057	7.2	0.284	36.2	0.20	n/a
425	ATTM	0.456	55.5	0.098	12.5	4.65	1.00

(1): 4Me-Bibenzyl + iosmer

(2): Based on feed molar number of NMBB

*: Reaction temperature 400°C

n/a : not available

Table 3 Eicosane Conversion at 425 °C for 20 min.

Exp. #	392	333	337	341	345	349	371	357	361	365
MClx-(AlCl3)x	None	LiCl	NaCl	KCl	VCl3	CoCl2	NiCl2	ZnCl2	MoCl3	PdCl2
Conv. (wt%)	21.8	36.0	26.9	23.0	88.7	83.2	100.0	100.0	37.2	100.0
Gas yield (wt%)	7.7	15.7	4.7	3.6	59.0	47.9	85.4	71.6	22.6	81.5
Liquid yield (wt%)	7.8	7.1	5.9	8.8	2.9	2.6	0.8	2.1	5.2	1.2
Coke yield (wt%)	0.0	0.0	0.0	0.0	4.9	6.0	0.0	0.0	0.0	0.0
Liquid products (mol%)										
n-nonane	1.0	2.4	0.7	4.5	1.9	0.5	0.6	3.7	0.8	0.5
C9H18	0.7			0.2		0.2			0.6	
C9H18 or C9H20 isomer		0.1	1.4	0.5	0.4	0.6			1.7	
n-decane	0.9	0.5	1.2	1.1	0.7	0.3	0.7	0.2	0.9	0.8
C10H20	0.7		0.1	0.1		0.1			0.1	
C10H20 or C10H22 isomer	0.3	0.2	0.2	0.9	0.6	0.7	0.0	0.5	0.9	0.7
n-undecane	0.9	0.5	1.2	1.1	0.3	0.2	0.2	0.1	0.8	0.0
C11H22	0.6			0.1					0.2	
C11H22 or C11H24 isomer		0.2	0.3	0.4	0.8	0.9	0.1		0.3	0.4
C12H24	0.6		0.1	0.1	0.1	0.1		0.0	0.0	
C12H24 or C12H26 isomer				0.4	0.3	0.4			0.1	
n-tridecane	0.8	0.5	1.0	1.0	0.2	0.2			0.7	
C13H26	0.5		0.1	0.1						
C13H26 or C13H28 isomer				0.4		0.0				
n-tetradecane	0.8	5.6	0.9	1.0	0.1	0.4			0.6	
C14H28	0.5			0.1						
C14H28 or C14H30 isomer				0.2						
n-pentadecane	0.7	0.4	0.9	0.9	0.1	0.1			0.6	
C15H30	0.4			0.1						
C15H30 or C15H32 isomer				0.1						
n-hexadecane	0.7	0.4	0.7	0.8	0.1	0.1			0.5	
C16H32	0.4			0.1						
C16H32 or C16H34 isomer				0.1						
n-heptadecane	0.6	0.4	0.7	0.8	0.1	0.1			0.5	
C17H34	0.3									
C17H34 or C17H36 isomer				0.1						
n-octadecane	0.2	0.1	0.1	0.1					0.1	
C18H36	0.3									
C18H36 or C18H38 isomer				0.1						
n-nonadecane	0.1									
C19H38	0.1									
C19H38 or C19H40 isomer									0.0	
n-eicosane	78.3	64.0	73.1	77.0	11.3	16.8			62.8	
Gaseous Products (mol%)										
CH4	3.3	5.0	2.9	2.0	27.3	16.7	17.4	26.4	6.1	19.9
C2H6	12.0	6.4	10.2	8.1	19.9	13.6	18.5	20.4	11.1	28.4
C3H8	12.9	29.9	10.4	7.4	140.3	99.3	148.0	170.4	37.2	180.2
iso-C4H10		42.6	1.2	1.2	123.8	112.7	161.8	160.6	46.4	157.0
n-C4H10	7.0	2.1	1.6	1.7	31.3	25.7	34.0	31.7	13.2	39.4
i-C4 / n-C4	0.0	20.7	0.7	0.4	4.0	4.4	4.1	5.1	3.5	4.0

Table 4 Degree of Hydrocracking of eicosane with MClx-(AlCl3)x Catalysts

Exp.#	MClx-(AlCl3)x	A: C9-C11(mmol)	B: C12-C19(mmol)	A/(A+B)	i-C4 / n-C4	Conv.(wt%)
392	None	0.1016	0.1162	0.466	0.00	21.8
333	LiCl	0.0706	0.1314	0.350	20.65	36.0
337	NaCl	0.0964	0.0790	0.550	0.72	26.9
341	KCl	0.1693	0.1035	0.621	0.41	23.0
345	VCl3	0.0918	0.0082	0.918	3.96	88.7
349	CoCl2	0.0696	0.0159	0.814	4.39	83.2
371	NiCl2	0.0289	0.0000	1.000	4.11	100.0
357	ZnCl2	0.0804	0.0000	1.000	5.07	100.0
361	MoCl3	0.1124	0.0528	0.680	3.52	37.2
365	PdCl2	0.0427	0.0000	1.000	3.99	100.0

* With transition metal catalyst, more cracking occures, giving A / (A+B) ratio of close to or equal to 1.0.

DBT conversion over MClx-($AlCl_3$)x catalyst

The results of DBT reaction with MCl_x-$(AlCl_3)_x$ catalyst are summarized in Table 5. It was observed that transition metal-based catalysts gave higher conversion compared with alkali metal-based ones. From the liquid products distribution, $MoCl_3$ containing catalyst afforded higher biphenyl yield compared with others. This result suggests that Mo containing catalyst has high hydrodesulfurization activity and selectivity. In addition there was no coke formation with Mo containing catalyst. Other transition metal catalyst showed good methylation activity of DBT molecule and significant coke formation. On the contrary, alkali metal-containing catalysts showed much less activity for DBT conversion. Their order of activity (DBT conversion) was LiCl > NaCl > KCl, which is the same as that observed for eicosane conversion.

Pyrene conversion over MClx-($AlCl_3$)x catalyst

Table 6 shows the results of pyrene reaction with MCl_x-$(AlCl_3)_x$ catalyst. Hydrogenation and ring opening and subsequent dealkylation were more remarkable with VCl_3-$(AlCl_3)_3$, $NiCl_2$-$(AlCl_3)_2$ and $ZnCl_2$-$(AlCl_3)_2$. The yield of C_2H_6 appears to be the most important dealkylation product. $MoCl_3$ containing catalyst showed high hydrogenation activity (higher yield of hydrogenated pyrene) and selectivity, and there was no coke formation. Other transition metal containing catalysts resulted in significant amount of coke formation. The alkali metal containing catalysts displayed an order of activity (LiCl > NaCl > KCl) which is consistent with those observed in other reactions.

CONCLUSION

From the results of model compounds reactions, transition metal containing catalysts showed higher activity in most cases, especially with eicosane and DBT as reactants. The selectivity of bond cleavage of NMBB molecule appears to be related to i-C4 / n-C4 ratio which is a relative measure of the acidity of the catalysts. In addition, this selectivity was sensitive to reaction temperature. $MoCl_3$-$(AlCl_3)_3$ catalyst has a specific character for model compound reaction compared with other transition metal containing catalysts, for example, higher activity and selectivity of desulfurization of DBT and higher activity of hydrogenation of pyrene. The most important feature with $MoCl_3$-$(AlCl_3)_3$ is no coke formation in all cases. In the present paper there was no remarkable difference than can be attributed to the molten state of the catalyst, such as that between molten $ZnCl_2$-$(AlCl_3)_2$, and a mixture of MCl_x-$(AlCl_3)_x$ catalyst that do not become molten salt at the reaction temperature. The activity of alkali metal tetrachloroaluminate catalysts was found to decrease in the order of LiCl > NaCl > KCl in all the reactions examined.

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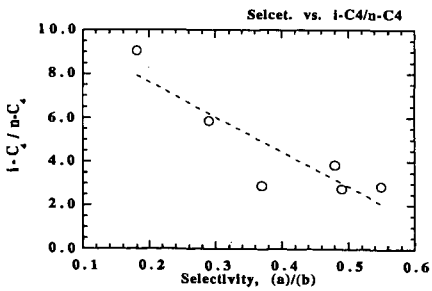

Figure 1 Relation between i-C_4 / n-C_4 ratio and selectivity of bond cleavage

Table 5 DBT Conversion at 425 °C for 20 min.

Exp. #	334	337	341	346	350	372	358	362	366
MClx-(AlCl3)x	LiCl	NaCl	KCl	VCl3	CoCl2	NiCl2	ZnCl2	MoCl3	PdCl2
Conv. (wt%)	23.8	15.4	10.2	79.5	46.5	82.0	76.2	83.5	87.6
Gas yield (wt%)	0.0	1.3	0.0	13.8	7.0	12.8	13.8	25.0	22.5
Liquid yield (wt%)	3.6	2.0	1.2	9.3	10.4	14.3	11.0	33.1	18.4
Coke yield (wt%)	0.0	0.0	0.0	25.9	3.6	26.4	36.8	0.0	3.9
Liquid products (mol%)									
toluene	0.0	0.3		0.9	0.3	0.8	1.0	0.6	3.6
p-, m-xylene	0.1			1.0	0.3	1.0	0.7	0.8	3.0
o-xylene	0.5	0.1		0.1		0.1	0.1	0.1	0.6
1,3,5-trimethylbenzene				0.2		0.2	0.1		0.7
1,2,4-trimethylbenzene	0.7								
1,2,3-trimethylbenzene									
biphenyl	1.7	1.5	1.0	1.1	1.5	1.3	1.7	29.8	1.4
2-Me-biphenyl						0.1	0.1		0.1
3-Me-biphenyl				0.2	0.1	0.3	0.3	0.3	0.3
4-Me-biphenyl				0.1	0.1	0.2	0.1	0.2	0.2
4H-DBT*	1.3	0.6	0.3	0.8	2.2	1.0	1.4	1.8	1.8
Me-DBT*	0.1			3.5	3.6	5.1	3.6		3.4
DiMe-DBT*				1.5	1.7	3.2	1.8		2.6
DBT	76.2	84.6	89.8	20.5	53.5	18.0	23.8	16.5	12.4
Gaseous Products (mol%)									
CH4	0.0	0.7	0.0	5.2	1.9	2.5	5.3	12.6	3.5
C2H6	0.0	0.6	0.0	5.9	1.5	3.3	4.4	9.5	5.6
C3H8	0.0	0.4	0.0	18.3	7.0	8.3	18.2	25.9	21.1
iso-C4H10	0.0	0.9	0.0	17.5	10.8	12.1	19.2	27.0	25.8
n-C4H10	0.0	0.3	0.0	4.2	1.1	3.4	4.7	4.2	7.2
i-C4 / n-C4		3.3		4.2	10.0	3.0	4.1	6.4	3.6

* including isomers

Table 6 Pyrene Conversion at 425 °C for 20 min.

Exp. #	335	339	343	347	351	373	359	363	367
MClx-(AlCl3)x	LiCl	NaCl	KCl	VCl3	CoCl2	NiCl2	ZnCl2	MoCl3	PdCl2
Conv. (wt%)	73.5	69.3	9.0	85.7	69.5	86.7	93.9	44.4	89.7
Gas yield (wt%)	0.0	0.0	0.0	2.8	0.2	3.4	2.2	4.8	7.2
Liquid yield (wt%)	19.6	18.6	6.5	15.0	17.3	12.6	9.4	17.9	12.4
Coke yield (wt%)	31.6	19.9	0.0	50.4	33.2	53.6	64.9	0.0	49.1
Liquid products (mol%)									
toluene	0.2	0.2		0.1	0.1	0.2	0.1	0.1	0.1
p-, m-xylene	0.2	0.1		0.2	0.2	0.2	0.2	0.1	0.2
o-xylene	0.1	0.1			0.0	0.1			
2H-fluorene	0.7	0.5		0.7	0.4	0.9	0.9		1.1
2H-Me-fluorene	0.2	0.1		0.1	0.1	0.2	0.2	0.1	0.2
4H-pyrene*	2.2	2.5	0.2	1.7	1.7	0.9	0.6	2.1	0.8
6H-pyrene*	1.9	2.2	0.2	1.5	1.2	0.8	0.5	1.5	0.8
2H-pyrene*	8.3	9.1	5.3	5.0	8.1	3.9	1.9	13.2	3.1
Me-pyrene*	1.1	0.7		1.0	1.2	1.2	1.1	0.1	2.0
DiMe-pyrene*	3.3	1.8		2.9	3.1	2.9	2.3	0.3	2.1
pyrene	25.6	30.6	91.0	14.3	30.5	13.3	6.1	55.6	10.3
Gaseous Products (mol%)									
CH4	0.0	0.0	0.0	3.1	0.3	3.3	3.6	2.9	7.3
C2H6	0.0	0.0	0.0	9.4	0.9	9.8	8.8	3.6	19.9
C3H8	0.0	0.0	0.0	2.0	0.2	2.4	1.7	1.5	4.7
iso-C4H10	0.0	0.0	0.0	0.7	0.1	1.2	0.3	2.8	2.0
n-C4H10	0.0	0.0	0.0	0.3	0.1	0.7	0.2	1.0	1.6
i-C4 / n-C4				2.1	2.0	4.3	1.5	3.0	1.2

* including isomers