Propene alkylation of biphenyl catalyzed by alumina pillared clays and related acidic oxides

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Propene alkylation of biphenyl was catalyzed by alumina pillared clays, and, for comparison, by several other oxide acids including an alumina delaminated clay, an acid washed clay (K-10 montmorillonite) and zeolites (USY and H-mordenite). Relationships between pore structures and catalytic properties were investigated. The microporous catalysts afforded high yields of meta- and para-alkylated isomers at the expense of the more spatially demanding ortho-alkylated isomer.

Keywords: Acidity; alkylation; biphenyl; pillared clay; porosity; shape selectivity.

1. Introduction

The liquid phase Friedel-Crafts alkylation of arenes over Lewis acid catalysts such as $AlCl_3$ or $FeCl_3$ is carried out on a large industrial scale. However, such catalysts are the source of several important practical problems, including corrosivity, toxicity and effluent pollution. It is desirable to replace these catalysts by regenerable solid acids. Hölderich et al. [1] reviewed the utilization of zeolites as alkylation catalysts showing outstanding activity and selectivity. Owing to their facile synthesis and adaptability, pillared clays [2] are also an attractive class of acidic microporous catalysts. However, the molecular sieving properties of these materials have not been demonstrated as clearly as for zeolites. Kikuchi et al. [3] demonstrated a relationship between pore size openings of alumina pillared clays and production of 1,2,4,5-tetramethylbenzene by disproportionation of 1,2,4-trimethylbenzene. Differences in pore structures and shape selectivity were obtained either by varying the pillars heights or varying the clay [4]. Another strategy developed by Mori and co-workers [5] was to modify the pillars density between the layers.

In order to evaluate the activity and selectivity of alumina pillared clays as alkylation catalysts, we selected the alkylation of biphenyl by propylene as a test reaction. This reaction is known to occur with exceptionally high selectivity to the 4,4′-dialkylated derivative over mordenite which has been dealuminated by reaction with mineral acid [6]. The reaction was carried out under relatively mild liquid phase conditions where coke formation was limited. Moreover, the absence of water in the reaction helped maintain a uniform acidity function throughout the reaction.

In order to better evaluate the influence of the pore structure of alumina pillared clays on catalysis selectivity, we have included in the study catalysts with very dramatically different pore structures as reference materials solid acids. The reference materials included K-10 montmorillonite, an acid washed montmorillonite with virtually no microporous structure [7], and an alumina delaminated laponite. Both of those latter materials are compositionally related to alumina pillared clays. However, in K-10 montmorillonite some of the aluminum in the octahedral sheet has been removed by the acid treatment and the material is quasicrystalline. Also, for alumina delaminated laponite the layer aggregation mechanism is mainly edge-face rather than face-face, as in pillared clays. Consequently, the delaminated card-house like structure results in substantially reduced microporosity.

USY and H^+-mordenite served as catalysts with a high degree of microporosity. The alumina pillared clays of interest were prepared from fluorohectorite with a relatively high layer charge density of 1.6 e^-/O_{20} unit and from a typical montmorillonite with a charge of 0.86 e^-/O_{20} unit.

2. Experimental

CLAY SAMPLES AND ZEOLITES

Na-montmorillonite ("Cross County" Wyoming) was purified by sedimentation. The synthetic clays Laponite (Laporte Industries Ltd.) and fluorohectorite (Corning), the acid leached montmorillonite K-10 (Aldrich) and the acid zeolite mordenite M(8)48 (molar Si/Al ratio of 48, Union Carbide) were used as obtained from the manufacturers. LZ-Y-84 as supplied by the manufacturer (Union Carbide) was inactive under our reaction conditions, even when outgassed at 350 ° C in vacuum. It was thus ammonium exchanged and steamed 3 hours at 750 ° C. The resulting catalyst is referred to as USY.

A sodium hydroxide hydrolyzed $AlCl_3$ solution (0.11 M $AlCl_3$, $OH/Al = 2.4$) was used as pillaring agent. The pillaring procedure described by Pinnavaia et al. [8] was used.

CHARACTERIZATION OF THE CATALYSTS

Elemental analyses were performed as described previously [8]. X-ray diffraction patterns (Cu-K_α) of oriented films were obtained with a Rigaku X-ray diffractometer equipped with a rotating anode. Continuous flow N_2 adsorption-desorption isotherms at 77 K were obtained on an Omnisorb 360 CX (Coulter) sorptometer. The samples were outgassed at 150 ° C for 12 hours under 10^{-4} Torr.

CATALYSIS

The alkylation of biphenyl by propene was carried out in a 300-mL batch reactor (n ° 4561 Parr instruments). Propene was CP grade (Matheson Company), and biphenyl was practical grade (Baker company). The catalysts were used without pre-activation except for the zeolites, which were pre-heated 3 hours at 360 ° C under vacuum. Biphenyl (30 g, 0.194 mole) and 0.05 g to 0.6 g of catalyst were heated to 90 ° C. The system was then purged with propene under stirring until the temperature reached 150 ° C. The temperature and propene pressure were then carefully increased until they reach the final conditions of 250 ° C and 140 psi. A temperature ramp of 3 ° /mn was used. The reaction was carried out for 20 hours. The reactor was then allowed to cool and the pressure was slowly released. Eventually, the reaction mixture was dissolved in 300 mL toluene, the catalyst was filtered, and the products were analyzed by gas chromatography. The degree of alkylation was determined by GC-MS. The monoalkyl isomers were identified according to the literature [9] on the basis of their retention times.

3. Results and discussion

The chemical compositions and basal-spacings of the alumina pillared clays prepared in this work are presented in table 1. Fluorohectorite incorporated 2.46 aluminum ions per one O_{20} unit cell whereas 1.27 aluminum ions per one O_{20} unit were intercalated in Wyoming montmorillonite. The relative amounts

Table 1
Unit cell compositions and basal spacings of alumina-clay products

Sample	Clay	Unit cell composition	d_{001} (Å) calcined
APWM	Wyoming montmorillonite	$[Al(OH)_{2.32}]_{1.27}$- $[Al_{2.98}Mg_{0.56}Fe_{0.41}]$- $(Si_{7.84}Al_{0.16})O_{20}(OH)_4$	18.7
ADL	Laponite	$[Al(OH)_{2.73}]_{1.33}$- $[Mg_{5.64}Li_{0.36}]$- $(Si_8)O_{20}(OH)_4$	amorphous
APFH	Fluorohectorite	$[Al(OH)_{2.35}]_{2.46}$- $[Mg_{4.4}Li_{1.6}]$- $(Si_8)O_{20}F_4$	18.2

Table 2
Surface area and pore size analysis obtained from N_2 adsorption-desorption isotherms

Catalyst	S_{BET} (m^2/g)	*t*-plot				Mesopore distribution (m^2/g) diameter range		
		S (m^2/g)	$S_{meso,macro}$	S_{micro}	%micro	20–75 Å	75–150 Å	150–500 Å
K-10	233	232	232	0	**0**	200	30	4
ADL	360	387	294	92	**24**	310	5	1
APFH	214	234	56	175	**75**	35	11	8
USY	652	751	93	610	**81**	69	17	3
M8(48)	725	844	119	682	**81**	71	18	22
APWM	334	377	34	327	**87**	50	2	1

of incorporated aluminum are in agreement with an ion exchange mechanism for the pillaring reaction since the layer charge is much larger for the former clay (1.6 e^-/O_{20}) than for the latter (0.86 e^-/O_{20}). It is interesting however, that the unit cell composition of alumina delaminated laponite (1.33 Al per O_{20} unit) is comparable to that obtained for montmorillonite, eventhough laponite has a low layer charge of only 0.36 e^-/O_{20} unit. Basal-spacings for the two alumina pillared clay materials after calcining at 350 ° C were similar (around 18.5 Å).

The pore structures of the non-porous acid catalysts, pillared clays, and microporous zeolites were studied by N_2 adsorption-desorption measurements. The adsorption data were treated by the BET equation in its linearity range and by the *t*-plot method [10]. Several classes of porosity can be distinguished (table 2). As expected, alumina delaminated laponite (ADL) and K-10 exhibit few or no micropores. Pillared clays (APWM and APFH) are microporous materials, but the fraction of the total surface area due to the micropores varies somewhat with the clay layer (75% for APFH vs. 87% for APWM). Acid treated mordenite and USY are microporous materials with more regular pores.

Mesopore distributions were determined by treating the desorption data using either a slit shape [11] or cylindrical [12] pore model. The data reported in table 2 are those which best fit the *t*-plot results. For non-microporous ADL, K-10, and M8(48), the cylindrical pore model was the more appropriate model, whereas for the other catalysts the slit shape model gave better agreement with *t*-plots, which is somewhat surprising for USY. K-10 exhibited a broad distribution of mesopores. In contrast, the mesopores of ADL were more or less uniformly centered around 25 Å. Differences in mesopore distribution were also noted for the two pillared clays. APWM exhibited fewer mesopores of large diameter than APFH. An average mesoporosity near 100 Å was well developed for USY.

The catalytic activities of the non-porous, pillared clays and zeolite catalysts were compared for the alkylation of biphenyl by propylene at 250 ° C using the

Table 3
Biphenyl conversion and product isomer distribution obtained for different solid acid catalysts

Catalyst:	APFH	K-10	ADL	USY	M(8)48	APWM
%conversion:	98	96	89	78	77	67
%monoalkyl:	11	16	29	45	50	60
%dialkyl:	33	36	39	40	47	32
%trialkykyl:	38	37	25	14	3	7
%tetraalkyl:	17	11	7	2	0	1

same mass of catalyst (0.2 g, 100–200 mesh fraction) (table 3). The biphenyl conversion was reproducible to +/− 5%. Pretreatments were carried out in order to obtain the best activity for a given catalyst. A three-optimum hour outgassing period at 350 ° C under vacuum was necessary to observe activity with the zeolites. Water is less tightly bonded in pillared clays. Thermal pretreatments of the pillared clays had no effect on the conversion obtained with these catalysts, probably because the water present was removed during the purge of the reactor at 100–150 ° C. The non-microporous K-10 and ADL catalysts were among the most active. This could be a consequence of low diffusional limitations for these materials. On the other hand, zeolites and pillared Wyoming montmorillonite are very microporous and access to the acid sites within the micropores may be limited. The acid properties of these materials, as judged by pyridine and ammonia adsorption are currently under investigation and will be reported later. We can, however, already observe that alumina pillared clay catalysts are almost as active as zeolites, yet substantially more convenient to utilize for this reaction.

The product selectivity towards the three possible mono-alkylated isomers was studied in the range 50–80% of conversion. In this range, the total concentration of monoalkylated products is nearly constant. The desired conversions were obtained by using different amounts of a 100–200 mesh fraction of catalyst. Table 4 provides the monoalkylated product distributions for the different catalysts. Since the twist angle between the two benzene rings increases from 20 ° in biphenyl to 60.7 ° in ortho-isopropylbiphenyl in the solid state [13], spatial factors should favor the meta and para isomers at the expense

Table 4
Distribution of monoalkylated products

Catalyst:	K-10	ADL	APFH	APWM	USY	M(8)48
weight (g):	0.1	0.1	0.06	0.2	0.2	0.2
%conversion:	76	63	50	67	78	77
%monoalkyl:	48	58	73	60	45	50
%ortho:	**33**	**32**	**23**	**17**	**20**	**6**
%meta:	27	30	34	39	36	34
%para:	40	37	43	43	44	61

of the ortho isomer. It is thus possible to interpret the higher meta and para yields for the microporous materials in terms of a shape selectivity effect on product distribution. Materials with few or no micropores, such as ADL and K-10 montmorillonite, afforded approximatively 32% of ortho isomer. For microporous materials, the fraction of meta- and para-monoalkylated products seems to parallel the microporosity of the catalyst. The exceptional selectivity of acid mordenite toward para alkylation have been interpreted by Lee et al. [6] as a consequence of shape selectivity of the two channels structure of this material. The aromatic nuclei are believed to occupy the larger channel and propylene fills the smaller channel. In pillared clays the pore structure should be more uniform and less likely to distinguish between meta and para isomers.

4. Conclusion

Propene alkylation of biphenyl appears to be a useful reaction for probing the pore size selectivity of pillared clays relative to other solid acids with non-porous or microporous structure. The preliminary results suggest a relationship between pore structure of the catalysts and selectivity towards meta and para monoalkylated biphenyl products. Further characterization of the solids should enable us to improve our understanding of pore size effects on the distribution of alkylated aromatic products.

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