cient condition for establishing these constituents as phenols.

The procedures employed here are likely to simplify and enhance the use of mass spectrometry alone in the analysis of complex mixtures. Screening for particular functional groups seems to be as readily achieved as screening for individual compounds.[12] Most of all, the results demonstrate the exceptional versatility of mass spectrometers in chemical analysis.

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Para-Directed Aromatic Reactions over Shape-Selective Molecular Sieve Zeolite Catalysts

Sir:

We have found that it is possible to alkylate or disproportionate certain monosubstituted benzene compounds to achieve nearly 100% selectivity to para-disubstituted derivatives with the molecular sieve zeolite catalyst ZSM-5[1,2] by modification of the latter with certain chemical reagents. An example is the alkylation of toluene with methanol to give primarily *p*-xylene and water. Toluene was also disproportionated to give *p*-xylene and benzene. This is in sharp contrast to results obtained with a variety of Friedel–Crafts catalysts and other solid acidic catalysts, including silica-alumina and zeolites where initial ortho-para substitution was observed, and where some subsequent isomerization usually occurred under the conditions of reaction to give a mixture of all isomers.[3-5]

Table I. Results with Large-Crystal ZSM-5

	alkylation	disproportionation	thermodynamic equilibrium
temp, °C	500	550	
WHSV[b]	6.6	30	
feedstock	2:1 mol ratio of toluene/methanol	toluene	
conversion, wt %			
toluene	39	13.2	
methanol	99		
product distribution,[c] wt %			
C_1–C_5	2.6	<0.1	
benzene	1.9	5.5	
toluene	54.0	86.8	
xylenes			
para	17.9	2.6	
meta	14.0	3.5	
ortho	7.0	1.4	
others	3.3	0.1	
% xylenes			
para	46	35	23
meta	36	46	51
ortho	18	19	26

[a] Weight hourly space velocity, (g of feed)/(g of catalyst) h^{-1}. [b] Organic phase.

Table II. Results with Chemically Modified ZSM-5

modification element	P	Mg
temp, °C	600	550
WHSV[a]	10	3.5
feedstock	2:1 mol ratio of toluene/methanol	toluene
conversion, wt %		
toluene	21	10.9
methanol	92	
product distribution,[b] wt %		
C_6^-	1.7	0
benzene	0.1	4.9
toluene	74.1	89.2
xylene		
para	20.7	5.2
meta	0.4	0.6
ortho	0.2	0.1
others	2.2	
% xylene		
para	97	88
meta	2	10
ortho	1	2

[a] See footnote *a*, Table I. [b] Organic phase.

Chemical reactions catalyzed by crystalline zeolites occur primarily within the catalysts' internal pore structure, which has precise dimensions characteristic of the individual zeolite species. By selection among the different zeolite species available, a variety of different pore and channel sizes are available. The interconnected channels formed by ten-membered rings of oxygen, such as in ZSM-5,[2] are especially interesting because certain benzene derivatives fit rather closely, are able to diffuse into the pores, reach a catalytic site, and undergo a reaction and the product may diffuse out. Other compounds or isomers may be too large to be formed easily or may diffuse out at greatly reduced rates.

When methanol is reacted over ZSM-5,[6,7] a hydrocarbon product mixture containing aromatic and aliphatic components is produced, the boiling range of which ends abruptly at compounds possessing ~10 carbon atoms. This molecular weight limitation is a result of the reactions occurring in a confined

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space limiting the sizes of the product molecules.

Molecular shape-selective catalysis was first reported by Weisz and Frilette in 1960.[8] With zeolite A, which has a pore opening of ~5 Å in diameter, straight-chain molecules such as normal paraffins, normal olefins, straight-chain primary alcohols, etc., were selectively converted in the presence of their branched isomers. The latter, because their molecular dimensions exceeded those of the catalyst's pore openings, could not enter the zeolite and react. Similarly, only straight-chain molecules small enough to diffuse out of the zeolite appeared as products.

ZSM-5 has pore openings made of 10-membered oxygen rings[2] with dimensions intermediate between the 8- and 12-membered rings in zeolite A and faujasite, respectively. The fact that ZSM-5 sorbs monocyclic hydrocarbons and excludes molecules with critical dimensions larger than that of 1,3,5-trimethylbenzene[9] suggests the possibility of shape-selective reactions among aromatic molecules.

Although all three xylene isomers can enter the pore of ZSM-5, diffusion measurements indicate that the diffusivity of *p*-xylene is $>10^3$ times faster than that of *o*- and *m*-xylenes. With the regular ZSM-5 crystals, which are $<0.5\ \mu$m in size, the isomer distribution of C_8 aromatics produced catalytically from the alkylation of toluene with methanol and the disproportionation of toluene showed essentially an equilibrium distribution of the xylene product composed of 54% meta, 23% ortho, and 23% para at 500 °C.[10] When the crystal size of ZSM-5 was increased to 3 μm, the diffusional path length was increased, and *p*-xylene was produced in excess of its equilibrium yield as shown by the data in Table I.

The diffusional characteristics of ZSM-5 could be modified even more significantly by treatment with a variety of chemical reagents. With these chemically modified zeolites we have achieved para selectivity as high as 97% for the toluene alkylation reaction. Similarly, high para selectivity has been achieved in the toluene disproportionation reaction to produce benzene and *p*-xylene as the principal products.

Selected results summarized in Table II show 88–97% concentrations of the para isomer in the xylene product. Modification with phosphorus was made by impregnating the zeolite crystals with aqueous phosphoric acid. Elemental analysis showed that 8.5% phosphorus was present. The magnesium-modified catalyst was prepared by impregnating with aqueous magnesium acetate and had a magnesium content of ~11% by weight. It is proposed that these chemical treatments function in part by reducing the pore openings and channel dimensions of the ZSM-5 crystals, favoring the formation of the para isomer and permitting it and small molecules to diffuse out of the catalyst at a rapid rate.

These results provide the basis for the development of a new class of stereospecific catalytic processes for the production of para-substituted aromatic hydrocarbons of importance to the petrochemical industry. *p*-Xylene, for example, with an annual production capacity exceeding 5 billion pounds in the United States, is oxidized to terephthalic acid, a major component of polyester fibers. Presently, *p*-xylene is produced by isomerizing a C_8 aromatic concentrate to an equilibrium mixture of xylene isomers, separating a portion of the para isomer from the mixture, and recycling the remaining ortho/meta rich stream back through the isomerization step to reach equilibrium again, etc. The process is complex and costly. Direct production of the desired para isomer offers a potentially simpler process.

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Intriguing Aspects of 1,2-Dialkyldimolybdenum and -ditungsten (M≡M) Chemistry

Sir:

Both historically[1] and commercially[2] σ-alkyl complexes have played a prominent role in the development of mononuclear organo transition metal chemistry. Our syntheses[3] of *anti*-1,2-dichlorotetradimethylamido compounds, $M_2Cl_2(NMe_2)_4$ ($M\equiv M$, M = Mo, W), affords the opportunity of attempting to prepare 1,2-dialkyltetradimethylamido compounds by use of the general metathetic reaction

$$M_2Cl_2(NMe_2)_4 + 2LiR \xrightarrow[-78\ ^\circ C]{\text{toluene}} M_2R_2(NMe_2)_4 + 2LiCl \qquad (1)$$

Compounds of the form $M_2R_2(NMe_2)_4$ allow an investigation of the reactivity patterns of σ-alkyl groups bonded to the simplest of metal clusters, namely dimetal centers. We here report our extended[4] syntheses of compounds of the general formula $M_2R_2(NMe_2)_4$ and, in particular, describe their reactivity patterns toward carbon dioxide and *tert*-butyl alcohol with special attention being given to the labeled compounds $M_2(CH_2CD_3)_2(NMe_2)_4$.

From reaction 1 we have obtained $M_2R_2(NMe_2)_2$ compounds for both M = Mo and M = W where R = CH_3, CH_2CH_3, CH_2CD_3, $CH_2CH_2CH_2CH_3$, $CH(CH_3)_2$, CH_2CMe_3, CH_2SiMe_3, and CMe_3.[5] Purification of these compounds followed the following general procedure: (1) the reaction mixture was warmed slowly to room temperature whereupon the solvent was stripped; (2) hexane was added and the solution was filtered using a medium frit with standard Schlenk techniques; (3) the hexane solvent was again stripped and the residue was purified by sublimation (80–100 °C, 10^{-6} cm Hg) to give yellow-orange (M = Mo) or orange-red solids (M = W). When R = *n*-butyl, the compounds were liquids at room temperature and were purified by vacuum distillation.

In all cases the ^1H NMR spectra of the $M_2R_2(NMe_2)_4$ compounds obtained in toluene-d_8 solution at −60 °C (100 or

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