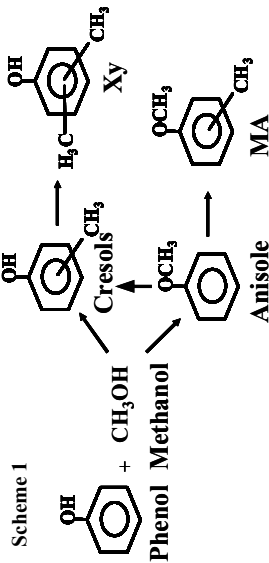


# Highly selective synthesis of *p*-cresol by gas-phase alkylation of phenol with methanol on solid acids

María E. Sad, Cristina L. Padró and Carlos R. Apóstegui\*  
*Catalysis Science and Engineering Research Group (GICIC), INCAPE (UNL-CONICET),  
 Santiago del Estero 2654, (3000) Santa Fe, Argentina*  
 \*capesteg@fiquis.unl.edu.ar

## Introduction

*p*-Cresol is widely employed for the synthesis of pharmaceuticals, herbicides, antioxidants, agrochemicals and dyes. It is commercially produced by toluene dehydration via sulfonation with sulphuric acid using a four reaction steps process that poses serious environmental concerns because of the formation of significant amounts of sodium sulfite as subproduct and the use of strong liquid acid catalysts. Thus, a number of studies have been lately devoted to explore the use of solid acids for obtaining selectively *p*-cresol via the alkylation of phenol with methanol



(Scheme 1). However, the *para-ortho*-cresol selectivity ratio on amorphous catalysts or wide pore zeolites such as HBeta, HY, and H-mordenites was always lower than 0.7. Recently, it was reported that *p:o* ratios of up to 1.2 are reached by using zeolites HZSM5 and MCM22 in liquid phase [1]. In this work, we performed a detailed study of the gas-phase alkylation of phenol with methanol on samples containing only strong Brönsted acid sites (HPA/SiO<sub>2</sub>) and catalysts containing both Lewis and Brönsted acid sites of either strong (zeolites HZSM5, HBeta and MCM22) or moderate (SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) strength. Results will show that the primary and secondary reaction pathways leading from phenol to cresols depend on both the pore microstructure and the nature, density, and strength of surface acid sites, but the reaction *para*-selectivity is only dramatically increased by using zeolite MCM22.

## Materials and Methods

Commercial zeolites HZSM5 (Zeocat PZ-2/54, Si/Al=20) and HBeta (Zeocat PB, Si/Al=12.5), and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample (Kejfen LA-LPV) were used. Zeolite MCM22 (Si/Al = 15) was synthesized according to [2]. HPA (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O) was supported on SiO<sub>2</sub> (Grace G62) by stirring a suspension of SiO<sub>2</sub> powder in an aqueous solution of HPA. Sample acidity was determined by TPD of NH<sub>3</sub> preadsorbed at 373 K. The nature of surface acid sites was determined by infrared spectroscopy using pyridine as probe molecule. The gas phase alkylation of phenol (P) with methanol (M) was carried out in a fixed bed reactor at 473 K and 101.3 kPa in continuous flow of N<sub>2</sub>. Main reaction products were cresols (*o*-, *m*- and *p*-cresols), anisole, xylenols (Xy) and methylanisoles (MA).

## Results and Discussion

Zeolites HBeta, HZSM5 and MCM22 were more active than SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or HPA/SiO<sub>2</sub>, but all the samples deactivated on stream because of coke formation. Table 1 compares the initial product selectivities obtained on all the catalysts at 20% phenol conversion. Selectivity to cresols was clearly higher on MCM22 (90%) than on HBeta, HZSM5 or SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (about 54%); HPA/SiO<sub>2</sub> formed predominantly anisole (S<sub>cresols</sub> = 32%). Production of *o*-cresol and *p*-cresol was predominant as compared to *m*-cresol. The distribution of cresol isomers on HBeta, HZSM5, and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was similar, being *o*-cresol the predominant product (*p:o* ratios between 0.7 and 0.8). In contrast, the *p:o* ratio increased to 3.4 on MCM22.

Table 1. Product selectivity for the alkylation of phenol with methanol (W/F<sub>P</sub> = 112 g h/mol, T = 473 K, M/P = 2, N<sub>2</sub>/(M+P) = 26.8)

| Catalyst   | Product selectivity, % (X <sub>P</sub> = 20%, t = 0) |                  |                  |                  |     |     |
|--|--|------------------|------------------|------------------|-----|-----|
|  | Anisole  | <i>o</i> -cresol | <i>m</i> -cresol | <i>p</i> -cresol | Xy  | MA  |
| HBeta  | 33   | 29               | 4                | 20               | 12  | 2   |
| HZSM5  | 41   | 30               | 2                | 22               | 3   | 2   |
| MCM22  | 9  | 19               | 7                | 64               | 0.5 | 0.5 |
| SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> | 34   | 28               | 3                | 23               | 9   | 3   |
| HPA/SiO <sub>2</sub>                             | 66   | 15               | 4                | 13               | 0   | 2   |

W/F<sub>P</sub> = 112 g h/mol, T = 473 K, M/P = 2, N<sub>2</sub>/(M+P) = 26.8

Cresols were formed from phenol alkylation of methanol on solid acids at 473 K via two parallel pathways: the direct C-alkylation of phenol and the transformation of anisole intermediate obtained by O-alkylation of phenol (Scheme 1). Over alkylation of *o*- and *p*-cresols lead to the formation of 2,6- and 2,4-xylenols. On the other hand, anisole may produce methylanisoles either by alkylation with methanol or by disproportionation. Cresols formation was better promoted by the simultaneous presence of strong surface Lewis and Brönsted acid sites; samples containing only strong Brönsted acid sites, such as HPA/SiO<sub>2</sub>, essentially promoted the O-alkylation of phenol forming anisole. Zeolite HBeta contained a high density of strong Brönsted and Lewis acid sites and was particularly active for producing cresols from phenol methylation. The phenol conversion rate on HZSM5 was lower than on HBeta because the narrow porous structure of HZSM5 hampered the formation of bulky intermediates involved in both the cresol alkylation to xylenols and the anisole disproportionation. However, zeolite HZSM5 did not improve the *p:o* selectivity. *p*-Cresol was the predominant product on MCM22 thereby revealing that the narrow sinusoidal channels of this zeolite is particularly suitable for improving by shape selectivity the formation of *p*-cresol.

## Significance

We report for the first time that *p*-cresol may be selectively produced by gas-phase alkylation of phenol with methanol on zeolite MCM22. In fact, *p*-cresol yields of 55% and *para-ortho*-cresol selectivity ratios of 4 are obtained on MCM22 at 473 K and contact time of 3.50 g h/mol.

## References

1. Moon, G., Böhringer, W., and O'Connor, C.T. *Catal. Today* 97, 291 (2004).
2. Rubin, M.A., and Chu, P. US Patent 4,954,325, 1990.