

# Unconventional coke composition originating from Catalytic fast pyrolysis model reaction

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## Highlights

- Anisole disproportionation on zeolite catalyst was studied.
- The reaction produces at high temperature, an unconventional coke (oxygenated).
- Effects of zeolite structure and acidity were studied on coke composition and content.
- The usual coke formation mechanisms are probably impaired by the feed and reaction products.

## 1. Introduction

Petrochemical products are pervasive in our daily lives as plastics, packaging, clothing, digital devices, medical equipment, tires... and provide substantial benefits to society, including a growing number of applications in various cutting-edge, clean technologies critical to sustainable energy systems. They are set to account for more than a third of the growth in oil demand by 2030 and nearly half by 2050. Hence, the landscape for both petrochemical, oil, and gas industries is evolving to develop more “high-value chemicals” (HVCs) as aromatics.

The majority of BTX aromatics originate from catalytic reforming and FCC units located in refineries. The catalytic fast pyrolysis (CFP) of biomass represents an interesting route for producing green aromatics and olefins by mimicking the fluid catalytic cracking of crude oil[1,2]. The pyrolysis is conducted in a dual fluidized bed on a zeolite catalyst; the latter shifts the chemical composition of bio-oils to petroleum compatible products. The oxygenated volatiles formed by biomass pyrolysis diffuse within the catalyst particles and contact the catalytic acid sites to form the targeted products (aromatics, olefins) but also coke and gas (mainly CO, CO<sub>2</sub>). Despite the growing interest in biomass CFP, this process is still in its infancy compared with other thermochemical technologies (gasification or combustion). It requires the development of more stable catalysts, with increased BTX selectivity. The most significant economic and technical concern of this emerging process remains the zeolite deactivation. Thus, mastering catalyst stability has become as essential as regulating selectivity and activity. There is, therefore, a strong incentive to understand the mechanisms of coke formation, the major factor leading to catalyst deactivation.

Biomass has abundant compounds containing methoxy functional groups (anisole, guaiacol, syringol, and derivatives). Since the methoxy group is the only functionality of the molecule, anisole (or methoxybenzene) is used as a model compound to investigate the reactivity of methoxy-based compounds present in the gas phase during the fast pyrolysis of lignin.

## 2. Methods

Anisole disproportionation was carried out in a continuous flow fixed bed reactor over HZSM-5 (MFI structure, Si/Al = 43), HBEA (Si/Al = 12.5 and 13.7) and HFAU (Si/Al = 6, 15, 30) catalysts at 400 °C under atmospheric pressure (N<sub>2</sub>) with partial anisole pressure of  $\approx 0.048$  atm. Physicochemical properties (acidity, porous volume, crystal size, etc.) of the catalysts were assessed with a range of techniques (Pyridine

Structure	Pore opening (Å)	Si/Al	V <sub>micro</sub> cm <sup>3</sup> .g <sup>-1</sup>	V <sub>meso</sub> cm <sup>3</sup> .g <sup>-1</sup>	[PyH <sup>+</sup> ] μmol.g <sup>-1</sup>	[PyL] μmol.g <sup>-1</sup>	Coke (wt.%)
MFI	{5.1x5.5 5.3x5.6}***	43	0.16	0.05	281	42	8
*BEA	6.6x6.7* 5.6x5.6*	12.5	0.16	0.86	315	316	11
		13.7	0.16	0.27	641	93	15
FAU	7.4x7.4***	6	0.27	0.15	481	186	11
		15	0.31	0.21	270	101	10
		30	0.34	0.20	88	18	7

chemisorption-desorption followed by FTIR, N<sub>2</sub>-physisorption, SEM, etc. **Table 1**). The coke accumulation in the spent catalysts was studied with TGA and extracted via dissolution of the zeolite framework in HF, then, after neutralization of the acid, extracted in an organic solvent. The solution was injected in a GC-MS and GC-FID, for identification and quantification of the coke components.

### 3. Results and discussion

Previous work on anisole disproportionation on MFI zeolites showed a steady-state activity was achieved after a short time, and that it was caused by the nature of the deactivating species, being methylated phenolics, i.e. the main reaction products: (CH<sub>3</sub>)<sub>x</sub>-Phenol, with 0 < x < 4 [3]. No polyaromatics were found after extraction of the coke species, which was ascribed to the steric hindrance of the 10-MR channels in MFI.

In the present study, anisole disproportionation was carried out on 12-MR zeolites in addition to the previous MFI. Again, no polyaromatic coke was found after extraction, instead the previously mentioned methylphenols were found, with higher selectivities than previously for the pentamethylphenol, due to the lower steric constraints in the 12-MR zeolites (**Figure 1a**). The unusual absence of polyaromatic species in the coke extract can be explained by the inhibition of the paring mechanism[4], usually found in hydrocarbon transformation processes, by the electronic effects induced by the hydroxyl group of the phenolics (**Figure 1b**).

### 4. Conclusions

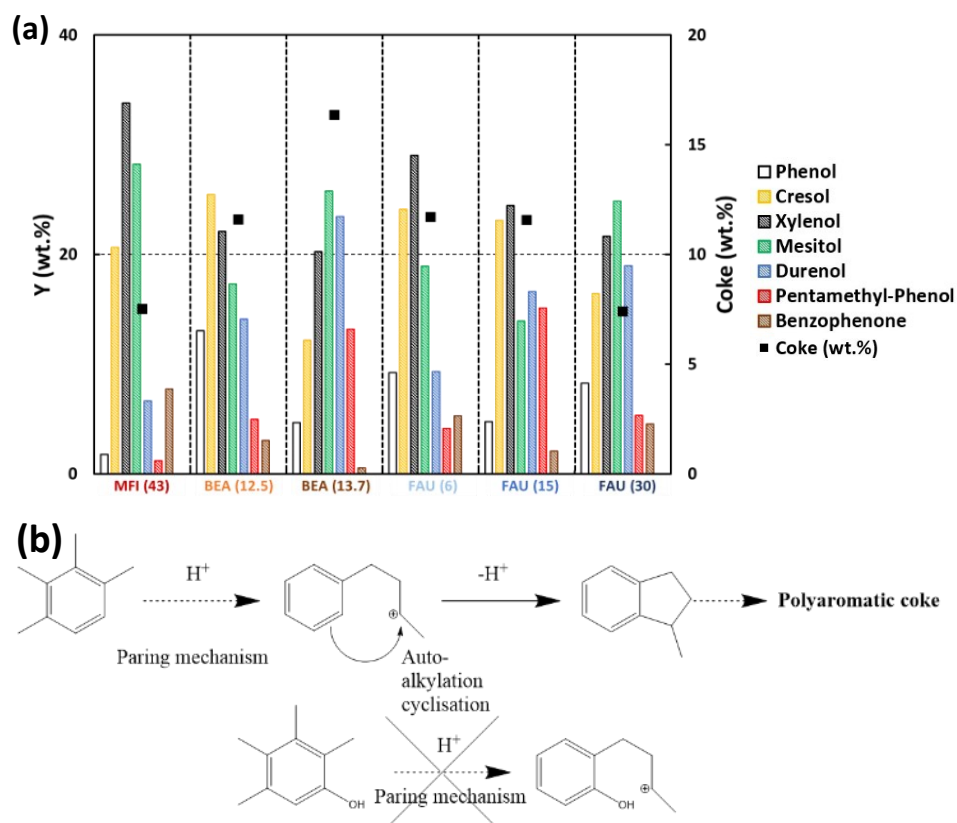
Anisole disproportionation presents a steady-state activity on zeolites after 20 minutes, due to the lack of formation of polyaromatic coke, which would normally (in all well-known industrial processes involving organic compounds) be produced, grow and have its shape heavily influenced by the porosity and structure of the zeolite involved. None of this happens, due to the inhibiting effect of Phenol (and the mesomeric effect of hydroxyl) on the usual coke formation mechanism.

### References

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### Keywords

Catalytic Fast Pyrolysis; model reaction; coking species study; zeolites.



**Figure 1:** (a) Main coke components on different zeolite structures and acidities; (b) Inhibition of the paring mechanism by the hydroxyl group.