

Chemical grafting of coal surface with mixed alkyl-aryl layers

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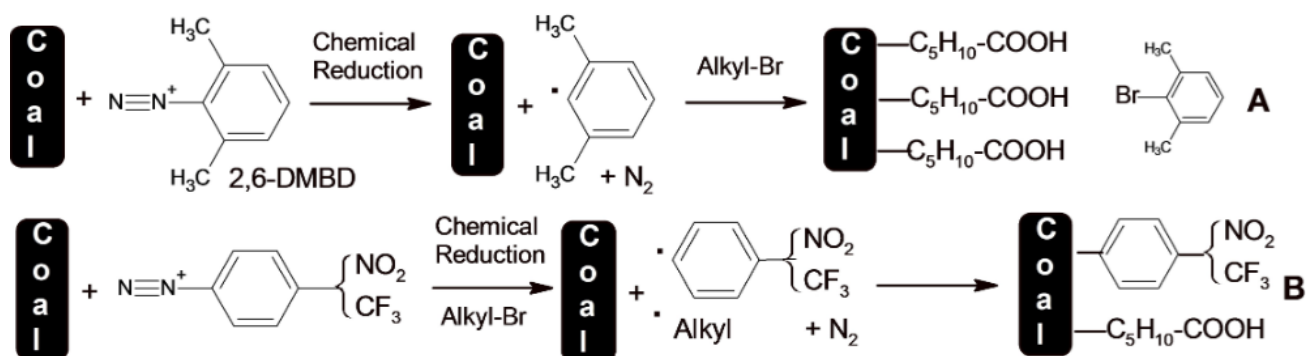
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The use aryl diazonium salts to attach the surface of many materials is now considered a successful alternative to create nanocomposite materials. [1] Their reduction reaction can be triggered in several ways, including electrochemical, chemical and spontaneous reduction which allows the generation of very reactive species, aryl radicals, part of which react with the surface of material and forms an organic layer strongly attached. Another part of these radicals can initiate other reactions in the solution, such as the removal of hydrogen atom from the solvent or halogen atoms from alkyl halides and allow the formation of alkyl radicals, which, at their turn, attach to the material surface. [2,3,4] In this case, mixed alkyl-aryl layers are grafted onto the material surface. When aryl diazonium salts bearing methyl groups ortho to the position to the diazonium group are used, the aryl radicals generated are particularly important because they do not attach to the material surface but can remove halogen atoms from alkyl halides and allow the grafting of alkyl layers. Here we show the results we have obtained with 2,6-dimethylbenzen diazonium salt (2,6-DMBD), which is used to generate 2,6-dimethylphenyl radicals that do not attach to the coal surface due to steric hindrance but are prone to remove bromine atoms from 6-bromohexanoic acid and tether the coal surface with hexanoic groups, scheme 1A. [5] When other diazonium salts are used, we have modified the coal surface with alkyl-aryl layer, scheme 1B. The presence of organic layer is attested with IR and XPS Spectroscopies while DFT calculations are used to calculate the bond dissociation energy.



Scheme 1. A) Chemical reduction of 2,6-DMBD and the formation of aryl radicals that attach to the lignite surface; B) Reduction of an aryl diazonium salt without steric hindrance i) leads to aryl radicals and ii) also create alkyl radicals, Alkyl*, both radicals attack the lignite surface to give a mixed. [5]

References

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