

ORIGINAL PAPER

Effect of valence of copper on adsorption of dimethyl sulfide from liquid hydrocarbon streams on activated bentonite

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Samples of activated bentonite and activated bentonite modified with CuCl and CuCl₂, separately, were tested as dimethyl sulfide (DMS) adsorbents. The adsorption and desorption behaviours of DMS on the adsorbents were studied systematically. The adsorbents were characterised by nitrogen adsorption, XRD, and DMS-TPD tests. The addition of CuCl and CuCl₂ to the activated carbon significantly enhanced the adsorption capacity of DMS, despite a notable decrease in the specific surface area and total pore volume of the activated bentonite. It is presumed that copper cation species may act as an adsorption site for DMS. The adsorption capacity of Cu(II)-bentonite was better than that of Cu(I)-bentonite. The DMS-TPD patterns indicate that the stronger electrophilicity of Cu(II) compared to that of Cu(I) caused it to interact with the DMS molecules more strongly, thus contributing to a better adsorptive performance. The Cu(II)-bentonite calcined at 150°C had the best DMS removal performance with a high sulphur capacity of 70.56 mg S g⁻¹ adsorbent. The DMS removal performance became much lower with the increase in the calcination temperature, which appeared to be due to the decrease in the CuCl₂ · 2H₂O phase and the formation of the monoclinic Cu(OH)Cl phase.

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Introduction

Dimethyl sulfide (DMS), as one of the important volatile organic sulphur compounds, has an important impact on the global sulphur cycle, climate change and odour occurrence processes (Nishikawa & Takahara, 2001; Iliuta & Larachi, 2007). Due to the deterioration in the quality of crude oil in recent years, the DMS content in the liquid hydrocarbon streams especially in light hydrocarbons (i.e. C_{5~6} fractions), which are valuable petrochemical feedstocks, has become much higher (Lee et al., 2011). The presence of DMS in the liquid hydrocarbon streams will reduce the purity of petrochemical products, deteriorate the process performance, and severely poison the noble metal catalyst used in subsequent processing (Hernández-Maldonado & Yang, 2004; Lee et al., 2011); accordingly, it should be removed in a pre-treatment process.

Much effort has been directed towards removing

sulphur compounds from liquid hydrocarbon streams using the adsorptive method on a variety of adsorbents such as activated carbons (Marín-Rosas et al., 2010; Tang et al., 2011a), zeolites (Yang et al., 2003; Subhan & Liu, 2011), and modified composite oxides (Ma et al., 2005; Ryzhikov et al., 2008). However, the vast majority of these efforts have focused on thiophene and thiophene derivatives. For gas hydrocarbon compounds, several efforts have sought to remove DMS, regarded as the most difficult sulphur compound to remove from pipeline gas by adsorption. Activated carbons are porous sorbents that can be used in removing sulphur compounds but which offer a relatively low sulphur adsorption capacity at ambient temperature (Cui et al., 2009). Cui & Turn (2009) reported that using activated carbon modified with FeCl₃ as the adsorbent could improve the adsorptive capacity for DMS compared with the parent-activated carbon. Wakita et al. (2001) studied the adsorption of DMS and

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