

Direct syntheses of a promising industrial organic–inorganic hybrid silica containing methanesulphonate

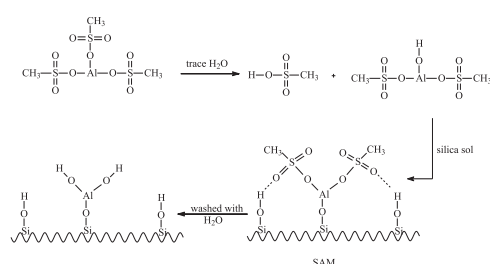
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HIGHLIGHTS

- Sulphonic groups are anchored on silica by the Si–O–Al–O–S covalent bond.
- Tetraethoxysilane is hydrolysed by formic acid in the absence of water.
- No structure-directing agents are used, and no wastewater is discharged.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple procedure was developed for the synthesis of sulphonic group-functionalised silica material (SAM) under formic acid conditions without the presence of surfactant species or precursors. The organic–inorganic hybrid materials exhibited high catalytic activity and excellent thermal stability in the alkylation of aromatics with olefins. Pyridine-FTIR indicated that SAM has abundant Lewis acid sites, especially weak acid sites. ^{29}Si and ^{27}Al MAS NMR confirmed that aluminium methanesulphonate was anchored on the surface of the silica matrix by the covalent bond of Si–O–Al.

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1. Introduction

Organic–inorganic hybrid materials have attracted a great deal of interest due to their outstanding properties in catalysis, sensing and adsorption (Aguado et al., 2000; Bao et al., 2004; Hoffmann et al., 2006). As a type of composite, they offer the advantages of both inorganic and organic components such as high surface areas, high thermostability, good mechanical strength and easy processability (Fernandes et al., 2014; Gong et al., 2014; Pirez et al., 2014). The biggest advantage of these materials is that their structure can

be designed and controlled on the molecular level, so hybrid materials can be functionalised according to a specific application request and be widely applied.

Organic–inorganic hybrid materials can be prepared in the following three ways: grafting, co-condensation or one-pot synthesis and production of periodic mesoporous organosilicas (Hoffmann et al., 2006). Each method has advantages and disadvantages. The advantages of grafting are that mesostructured silica phases can be mass-produced, and the properties can be standardised. The disadvantage of this method is that the modification usually affects the mesostructure of the silica phase and can subsequently reduce the porosity of the hybrid materials, which is a very important property for some reactions in hybrid materials

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(Cagnol et al., 2004; Lim and Stein, 1999). Bulky molecules are not usually considered grafting species; instead they are blocked at the pore-opening sites, impairing further diffusion of subsequent molecules. In extreme cases, these molecules could completely close the pores. Another method for preparing hybrid materials is co-condensation (Van et al., 1998). In this method, tetra-alkoxysilanes (TEOS or TMOS), functional reagents and structure-directing agents are co-condensed to make materials with functional groups anchored on the surface. The functional reagent is one part of the matrix and does not need to diffuse into the pores through the pore opening, so pore blockage is not a problem in this method of co-condensation. Furthermore, the distribution of functionalities on the matrix is more homogeneous than that of materials synthesised through the grafting method. However, the structure-directing agents are simultaneously condensed in the matrix with the functionalities. Considering the thermal decomposition of the functionalities, the removal of surfactant is usually by extraction. Periodic mesoporous organosilicas (PMOs) are highly promising candidates for large numbers of technical applications (Cornelius et al., 2005; Hunks and Ozin, 2004; Kang et al., 2004; Osegovic and Drago, 2000). The breakthrough of PMOs is the selectivity of the bridged organosilica precursors, $(R'O)_3Si-R-Si(OR')_3$ (Wahab et al., 2004). The organic functionalities are incorporated on the bridged R and anchored in the three-dimensional network structure through covalent bond with the silica matrix. The greatest challenge for PMOs is that analysis has only been performed in the laboratory, and the synthesis of the precursors and structure-directing agents is complex, costly and strenuous, particularly on an industrial scale. Therefore, whether it is necessary to convert PMOs into real application or not should be carefully considered.

Sulphonic groups are frequently utilised as modifiers to functionalise the surface of hybrid materials because they generate abundant strong acid sites, forming a good heterogeneous solid acid catalyst (Karimi and Vafaeezadeh, 2013; Salis et al., 2005; Usai et al., 2013; Zheng et al., 2005). Depending on the source of sulphonic group, it could be separated into two main classes of materials. One class is fluoro-alkylsulphonics such as perfluoroalkylsulphonic resin and triflic acid; the other class is non-fluorinated reagents such as H_2SO_4 , alkylsulphonics and reagents with thiol groups (El et al., 2013; Ganesan and Walcarius, 2004; Hunks and Ozin, 2004; Shimizu et al., 2005; Van et al., 1998; Yang et al., 2004). These modified materials show high catalytic activity in acid-catalysed reactions like condensation and esterification (Drelinkiewicz et al., 2014; Satoh et al., 2013). However, it is difficult to find industrial applications for these excellent catalysts. One important reason for this difficulty is that their preparation requires the use of a large amount of precursors and structure-directing agents, such as 3-mercaptopropyltrimethoxysilane (MPTMS), cetyltrimethylammonium bromide (CTAB), P123 (EO20PO70EO20), F127 (EO106PO70EO106) and B50-6600 (EO39BO47EO39) (Ganesan and Walcarius, 2004). These reagents are expensive and must be removed after synthesis. Because calcination may destroy the functional organic groups, solvent extraction is preferred. Considering waste emission and fundamental questions of their utility, these materials are difficult to use on a large scale.

To overcome the above problems and produce a practical organic–inorganic hybrid material, the novel catalyst aluminium methanesulphonate/SiO₂ was prepared. The catalytic activity of this new catalyst is outstanding; more importantly, the whole process is environmental friendly, economic and relatively quick. No precursors or structure-directing agents are used, and no wastewater is discharged. One of the highlights of this study is the anchoring of the sulphonic groups by Si–O–Al covalent bond rather than using organosilanes, which were first reported as a bridge to anchor sulphonic groups. Another important innovation is that no water is added to the system, and formic acid is used as catalyst for the hydrolysis and condensation of TEOS.

The catalyst activity was investigated using an alkylation reaction, which is one of the most important industrial reactions. Products from almost every sector of the chemical industry are prepared using this methodology (Alimardanov et al., 2012; Yoon et al., 2007). In this paper, olefins are reacted with aromatics through alkylation to reduce the olefin concentration in aromatic fluid because the olefins have some adverse effects on the purity of aromatics and some later processes are sensitive to olefins even at very low concentrations. Currently, the primary method to reduce olefins is clay treatment; however, frequent replacement of clay caused by rapid deactivation results in high labour and monetary costs and causes environmental problems.

2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS) and formic acid (purity > 98%) were purchased from Shanghai Chemical Reagent Co. Ltd., Shanghai, China. Methanesulphonic acid, aluminium methanesulphonate (AM), copper methanesulphonate (CM) and zinc methanesulphonate (ZM) were obtained from Sigma-Aldrich Shanghai Trading Co. Ltd. (Shanghai China). All reagents were of analytical grade and used without any purification. To accurately compare laboratory and industrial experimental results, aromatic hydrocarbons, a real industrial material, were obtained from PX combination units in Sinopec Shanghai Refining and Chemical Co. Ltd. The aromatic hydrocarbons components had a Bromine Index (BI) of 1187 mgBr/100 g and are shown in Table 1.

2.2. Preparation of catalyst

The silica support was synthesised by the sol-gel method. TEOS (20.82 g) and formic acid (55.24 g) were added into a beaker (150 mL). After stirring for 25 min at 30 °C, aluminium methanesulphonate (AM) was added to the silica sol. After aging for 2 h at room temperature and dried for 6 h at 200 °C under vacuum, the organic–inorganic hybrid catalyst (SAM) was obtained. The catalyst was named SAM-X, where the X represents the additive amount of AM; for example, SAM-5% means that the additive amount of AM in the final dried catalyst was 5% (wt%). When the active component is copper methanesulphonate or zinc methanesulphonate, the corresponding catalyst is called SCM and SZM, respectively.

2.3. Reaction procedures and analysis

The activity of the catalysts was investigated in a fixed-bed tubular microreactor equipped with a constant-flow pump to control the flow rate and a heating system to maintain the required temperature. Two millilitres of the catalyst was loaded

Table 1
Components of aromatic hydrocarbons with a BI of 1187 mgBr/100 g.

Component	Content (wt%)
Non-aromatics	2.18
Benzene	0.05
Toluene	0.06
Ethylbenzene	6.75
p-Xylene	10.92
m-Xylene	19.98
o-Xylene	11.25
C9	34.12
C10+	14.69

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