



Ion exchange resin immobilised 12-tungstophosphoric acid as an efficient and recoverable catalyst for the oxidative removal of organosulfur targeting at clean fuel



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ABSTRACT

The purpose of this paper is to investigate the desulfurization of the diesel oil by immobilising 12-tungstophosphoric acid (TPA) on several ion exchange resins, and selecting the optimum resin (Amberlite-IRA900C). The studied oxidative desulfurization process (ODS) was based on a biphasic system formed by model oil containing dibenzothiophene (DBT) and extracting solvent (acetonitrile) using H_2O_2 as the oxidant. The effects of reaction temperature, O/S molar ratio and catalyst dosage on the conversion of DBT were studied. It is demonstrated that the catalyst is extremely effective for the reaction, and also, it could be easily separated from the solution and recycled three times. Under the optimal conditions, the DBT conversion efficiency is 95.8%. Moreover, very positive desulfurization efficiency is obtained for real diesel oil for catalytic oxidative desulfurization with TPA/IRA900C catalyst. The sulfur content of diesel oil is reduced from 300 ppmw to 24.9 ppmw under the following operating conditions: the dosage of catalyst, 0.222/0.500 ($mmol\ g^{-1}$ dry resin); the O/S molar ratio, 28; the pre-immersion time of the catalyst in H_2O_2 solution, 8 min; reaction temperature, 60 °C. Therefore, this immobilised catalyst TPA/IRA900C is promising for deep desulfurization in the ODS process.

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1. Introduction

Sulfur compounds such as thiols, thioethers, sulfides, disulfides, thiophenes, dibenzothiophenes and alkylated dibenzothiophenes substituted at 4 and/or 6 positions widely exist in many kinds of fuels. These sulfur species are undesirable in fuel since their combustion leads to the release of SO_x and other sulfur derivatives, which will cause the formation of acid rain and damage to human respiratory system. Environmental Protection Agency of America (EPA) has demonstrated that the benefits to environmental management and human health after ultra-deep sulfur reduction in fuels are many times higher than the costs of implementation of deep desulfurization [1]. Recently, in order to prevent problems related to environmental changes, governments have issued increasingly stringent standards to control the sulfur content of fuel oil. EU and Japan set an upper limit of the sulfur content in diesel fuel of 10 ppm in 2007 and the US EPA cut down diesel fuel sulfur to 15 ppm in 2006 [2,3].

Various efficient methods have been developed to achieve ultra-deep desulfurization of diesel. One of the most important

methods to remove organosulfur from fuel is hydrodesulfurization (HDS). HDS is easily realised in removing thiols, thioethers, sulfides and disulfides, but much higher pressure and temperature are required in the elimination of thiophenes, dibenzothiophenes and their alkyl derivatives due to the steric hindrance of the sulfur atom. Though a couple of advantages of HDS should be admitted, the shortcomings of HDS are more obvious, such as high cost and decreased octane rating. Consequently, it is imperative to find processes for higher energy-efficient and more selective ultra-deep desulfurization.

Recently, substitutive processes of deep desulfurization have been developed including oxidative desulfurization [4–6], adsorption desulfurization [7–9], bioprocesses desulfurization [10] and extraction desulfurization [11–13]. Compared with HDS, Oxidative desulfurization process (ODS) has been considered to be one of the most promising methods for desulfurization because it can be operated at room temperature and atmospheric pressure [14]. In the ODS biphasic system, the refractory sulfur species can be easily oxidised to sulfoxides and/or sulfones using H_2O_2 as an economical oxidant, and then eliminated by an extraction agent.

Owing to the green actions of earnings and high industry efficiency, heteropoly acid (HPA) catalysis has attracted considerable attention in recent years [15]. Some researchers found that 12-

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tungstophosphoric acid (TPA) is an efficient catalyst in *n*-octane/ acetonitrile (MeCN) biphasic catalyst system [16]. However, separation and reuse of TPA is extremely difficult. Here, a novel recycling system was explored, in which several ion exchange resins used as catalytic carrier to immobilise TPA were tested. And the resin of Amberlite-IRA900C was found to be the best carrier for TPA in *n*-octane/acetonitrile desulfurization system using H₂O₂ as oxidant under mild conditions.

2. Experimental

2.1. Materials

All the chemicals are reagent grade and purchased from commercial sources. Amberlite-IRA900C, Amberlite-IRA900, Amberlite-IRA400, Amberlite-IR118 and Amberlite-IR120 were purchased from Amresco, Inc. 12-tungstophosphoric acid (TPA) was purchased from Kermel Co., Ltd, China.

2.2. Preparation of immobilised TPA catalyst

2.2.1. Preparation of immobilised TPA catalyst on different resins

The resins employed in this study were macroporous strong anion exchange resins including Amberlite-IRA900C, Amberlite-IRA900, Amberlite-IRA400, Amberlite-IR118 and Amberlite-IR120. In this study, the anion exchange resins were used as carrier after pretreatment and baking. A certain amount of anion exchange resins was added to an aqueous solution containing a defined amount of TPA. The solution was adjusted to pH 7.0 and stirred at room temperature for 24 h, and then filtered through a filter paper. After that, the resulting catalyst was washed with deionized water and MeCN respectively for three times, and then immersed in MeCN. The TPA immobilising capacity of different resins was detected by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) [17].

2.2.2. Optimization of IRA900C immobilised conditions

From the results, the macroporous strongly basic anion exchange resin- Amberlite-IRA900C (IRA900C) was utilised as the suitable catalytic carrier. The preparation route of TPA/IRA900C was carried out by using the similar method. In order to select the best immobilised conditions of IRA900C, two groups of parallel experiments were designed. (1) The pH of TPA solution was kept constant at 7.0, and then IRA900C was immobilised under 20, 40, 60 and 80 °C respectively. (2) The temperature of TPA solution was kept constant at 60 °C, and then IRA900C was immobilised at pH 2.2, 7.0 and 8.5 respectively. The TPA immobilising capacity of IRA900C was detected by ICP-OES

2.3. Oxidative desulfurization process

2.3.1. Oxidation of dibenzothiophene in the *n*-octane and acetonitrile biphasic catalytic system

A certain amount of dibenzothiophene (DBT, 99%) was dissolved in 60 ml *n*-octane three-neck flask to obtain the simulated diesel oil with the sulfur content 500 mg/L (500 ppm). Then, 60 ml of MeCN was added to the *n*-octane as extraction agent. The biphasic system was heated to the required temperature in a thermostatically controlled water bath. The catalyst TPA/IRA900 was dissolved in the hydrogen peroxide with the needed mole ratio of O to S, and then the H₂O₂ containing dissolved catalyst was added into the mixed liquid.

2.3.2. Oxidative desulfurization of diesel oil

The diesel oil was purchased from Sinopec Group, with sulfur content close to 300 ppm. First, 60 ml (entry 1) or 120 ml (entry 4) of MeCN solution was added to diesel oil. Then the biphasic system was heated to 60 °C in a thermostatically controlled water bath. The catalyst TPA/IRA900C was dispersed in the hydrogen peroxide solution with O to S mole ratio 28, and then the H₂O₂ with catalyst was added into the mixed liquid.

2.4. Analysis of sulfur content

During the reactions, the total sulfur concentration in diesel oil was analysed by a micro-coulomb comprehensive analyser (WK-2E). The sulfur concentrations of diesel fuel under various times were determined in virtue of the standard materials. The standard materials for sulfur determination are obtained from Research Institute of Petroleum Processing of SINOPEC Group.

3. Results and discussions

3.1. Comparison of different resins used as catalyst carriers

In order to compare the immobilising capacity of different resins used, the prepared catalysts were applied to the oxidative desulfurization with H₂O₂ acting as oxidant. The experiments were performed at 60 °C for 180 min, the initial sulfur concentration is 500 ppm and the O/S molar ratio is 20.

From the results in Table 1, it can be seen that the resin of Amberlite-IRA900C shows the optimum load capacity. The catalytic performance of TPA/IR&A follows the order of TPA/IRA400 < TPA/IR118 < TPA/IR120 < TPA/IRA900 < TPA/IRA900C. The best desulfurization performance of TPA/IRA900C can be attributed to the macroporous strong basicity of Amberlite-IRA900C which possesses the strongly basic functional group $-N^+(CH_3)_2$, could attack the TPA's acid centre. While the other two macroporous strongly acidic anion exchange resins are lack of this kind of functional group. Compared to the other two macroporous strongly acidic anion exchange resins, Amberlite-IRA900C possesses a higher total exchanged capacity which means much more TPA could be loaded. Thus, the resin of Amberlite-IRA900C was chosen for further experiments to figure out the roles of loading factors, including temperature and pH in the desulfurization reaction.

3.2. Selection of IRA900C immobilised conditions

As the temperature increased from 20 to 80 °C, the immobilising capacity of TPA on IRA900C increased from 0.151 mmol to 0.225 mmol (Table 2). As we have known, the intensity of Brownian movement is obviously reinforced with temperature. Thus, TPAs permeates easily into the interior of macroporous anion exchange resin. As the temperature increased from 60 to 80 °C, the capacity of loading TPA nearly remained the same. From the results, the favourable immobilising temperature can be recommended as 60 °C.

Table 1
Catalytic effect of immobilised catalysts on the oxidation of DBT by H₂O₂.

Immobilized catalysts	TPA/IR&A (mmol/g dry resin)	Desulfurization efficiency (%)
Amberlite-IR118	0.031/0.500	63.4
Amberlite-IR120	0.035/0.500	65.1
Amberlite-IRA400	0.029/0.500	62.6
Amberlite-IRA900	0.043/0.500	67.7
Amberlite-IRA900C	0.151/0.500	84.9

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