



Short communication

## Sulfated zirconia as a novel and recyclable catalyst for removal of olefins from aromatics



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### ABSTRACT

A novel sulfated zirconia ( $ZrO_2/SO_4^{2-}$ ) catalyst was prepared and the catalytic property of this catalyst was compared with active clay and zeolite (USY) in removing olefins from aromatics. Pyridine-FTIR indicated that the abundance of Lewis acid centers on sulfated zirconia is a vital factor for its excellent catalytic activity.  $N_2$  adsorption analysis shows that sulfated zirconia is a promising mesopore catalyst material. The superior catalytic performance as well as efficient reusability demonstrated that sulfated zirconia possesses bright application prospects in industry.

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### 1. Introduction

Benzene, toluene and xylene (BTX) are basic organic chemical raw materials in the petrochemical process. Naphtha reforming and thermal cracking are the main processes to obtain these aromatics [1]. However, BTX streams produced by naphtha are accompanied by the formation of undesirable non-aromatic olefinic impurities. Inevitably, these impurities include styrene, diene, and hexene. These chemically active contaminations will cause a series of adverse effects on subsequent separation. In paraxylene (PX) adsorptive separation device, even trace amount of olefins will lead to the deactivation of the adsorbent. Because compared with PX, olefins are easier to adsorb in the adsorbent. Therefore, it's quite necessary to remove these trace impurities from aromatics.

As suggested by Liu [2] et al. and Pu [3] et al., these harmful olefins can be removed via acid-catalyzed alkylation of specific aromatic hydrocarbons. Conventionally, olefins are removed by acid-treated clay in industrial plants [4]. However, as the lifetime of clay is quite limited, the discharge of deactivated clay is a key problem for this method. Increasing demands from environmental protection and consequent trend towards clean process force us to develop an eco-friendly catalyst alternative. Effective catalysts can increase olefin removal rate and at the time optimize products distribution without arene loss. In fundamental researches, novel catalysts have been continually studied and developed for removing olefins from aromatics. Several relatively green acid-catalyzed alkylation catalysts such as ionic liquids [5], organic-inorganic hybrid silica [6] and modified zeolites [7] have been studied in removal of olefins from aromatics. Among the above

mentioned catalysts, modified zeolites such as USY is a considerable material that may gradually replace the industrial application of clay in the future, as initial activity of USY is very high. Nevertheless, the biggest disadvantage of zeolites is their rapid deactivation and the regeneration is not satisfactory. So far, there has been no proper modification method to overcome it.

As eco-friendly and promising catalysts, solid superacid catalysts by incorporation of superacidity in solids have received considerable interest in recent years, especially in the petroleum field. Solid superacid catalysts like zeotypes, ion-exchange resins and metal oxides have been extensively studied in many areas. Besides the strength of acidity, the appropriate distribution of Lewis and Bronsted acid sites matter for catalyzing kinds of industrial reactions with excellent activity and selectivity [8]. Among these catalysts, sulphated zirconia (SZ) exhibits a great application prospect in many industrially important reactions, which is attributed to its distinctive surface acidic properties.

Despite several reports of Friedel-Crafts alkylation studies over SZ catalysts [9,10], little available attention has been paid to the removal of trace olefins from aromatics over SZ catalysts. In the present investigation, a recyclable SZ catalyst was prepared and used to remove trace olefins from aromatics in a fixed-bed micro reactor. The catalytic property of SZ was compared with commercial clay and modified zeolites. The physico-chemical properties of the catalysts were studied by  $N_2$  adsorption analysis and py-IR measurements.

### 2. Experiment section

#### 2.1. Materials

Aromatics used for experiment were industrial streams without clay treatment. They were obtained from reforming p-xylene (PX)

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**Table 1**  
Composition of the aromatic materials with a BI of 1109.

Component	Content (wt%)
Non-aromatics	0.238
Toluene	0.238
Ethylbenzene	7.885
p-Xylene	52.207
C9	32.622
C10+	6.81

combination units of Sinopec Zhenhai Refining & Chemical Company. USY zeolite modified with citric acid was obtained from XinNian Petrochemical Additives Company (China). The commercial acid activated clay was produced in Anhui, China. The aromatics hydrocarbons components (C8–C10) with a Bromine Index (BI) of 1109 mg Br/100 g are listed in Table 1. All other reagents were commercially available from the market, and they are of analytical grade without any further purification.

## 2.2. Catalyst preparation and regeneration

Zirconium hydroxide was prepared by adding ammonia solution (25%–28%) dropwise to dichlorooxozirconium ( $ZrOCl_2 \cdot 8H_2O$ ) solution while stirring well at temperature of 60 °C until pH = 9.5. After aging at room temperature for 12 h, the colloidal solution was filtered, washed adequately to remove chloride ion and subsequently oven dried at 393 K for 24 h. The above dried  $Zr(OH)_4$  was sulfated by impregnating in aqueous ammonium sulfate solution (1.0 mol/L) for 1 h. Then, the suspension was filtrated, followed by drying for 12 h and calcined in air at 650 °C for 3 h. The prepared catalyst is denoted as SZ. The deactivated SZ catalyst was regenerated “in-situ” at 550 °C for 3 h under air flow.

## 2.3. Catalytic activity evaluation

The catalyst evaluation experiments were performed in a laboratory fixed-bed micro-reactor system at a pressure of 1.0 MPa and a liquid hourly space velocity (LHSV) of  $30 \text{ h}^{-1}$ . The reaction system was equipped with a metering pump to keep the flow rate and a temperature control instrument to maintain the required temperature. The constant temperature segment of the tubular micro-reactor was charged with the catalyst (20–40 mesh) and spare spaces loaded with quartz sand (40–60 mesh). The Bromine Index (BI) of the feedstock and products obtained was analyzed using a Bromine Index Analyzer. Olefin removal rate  $X$  was determined using the equation

below:  $X = [(n_0 - n_i) / n_0] * 100\%$ , where  $n_0$  represents the content of olefins of the feedstock and  $n_i$  represents the content of olefins after reaction. It's notable here that ASTM standard D2710-92 defined the Bromine Index as the number of milligrams of bromine consumed by 100 g of hydrocarbon sample, so Bromine Index can be seen as an indicator of olefins content.

## 2.4. Characterization of catalyst

Using pyridine as a probe molecule, surface acidity of the catalysts was determined by Fourier transform infrared (FT-IR) spectroscopy. The finely ground self-supported sample wafer (16.5–16.9 mg) loaded into the in-situ cell was pretreated to eliminate the moisture at 653 K under vacuum condition (under 0.1 Pa), followed by pyridine adsorption after cooling down to 353 K. Finally, the wafers were thermally desorbed at 473 K and 723 K for 2 h. Fourier transform infrared (FT-IR) spectra were collected using an FTIR (Nicolet-6700) spectrometer ( $4000\text{--}400 \text{ cm}^{-1}$ ) on sample wafers. The specific pore volume and surface area were estimated by  $N_2$  adsorption–desorption at 77.3 K (ASAP 2010 N, Micromeritics, America).

## 3. Results and discussion

### 3.1. Catalytic performance

Catalytic properties of different catalysts for removing olefins from aromatics are presented in Fig. 1. As optional reaction temperature in industrial process is between 160 and 180 °C, the experimental temperature in Fig. 1I was set at 175 °C. As can be seen, the initial removal of olefins catalyzed by active clay was appreciable, but the rapid inactivation rate made the whole performance unsatisfactory. More seriously, the deactivated clay can't be regenerated, thus massive deactivated clay has to be buried. This burning problem accounts for the dominant motivation of this paper – to develop eco-friendly alternatives of active clay.

The initial activity of USY was also high, and the removal of olefins for the first two points even reached 100%. However, there's a sharp deactivation after 4 h. Herein it still needs further improvement for USY to replace active clay. With regard to SZ, practically total olefins were catalytically reacted at this temperature after running for 8 h, which is nearly 3 times as long as that of USY. Even 12 h later, the removal of olefins still remained as remarkable as 80%.

To obtain more comparable olefin removal rates on these catalysts, a lower reaction temperature (125 °C) was set for SZ in comparison with USY and active clay (Fig. 1II). It's noteworthy here that SZ exhibited a

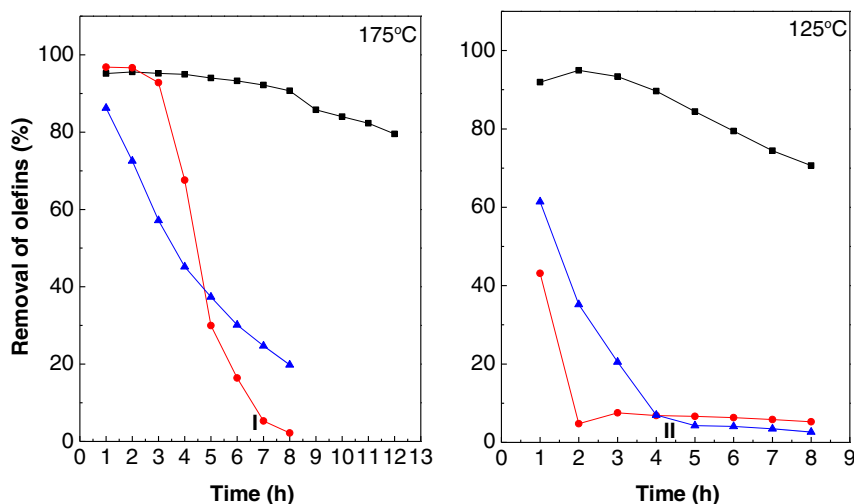


Fig. 1. Olefin removal rates of different catalysts at 175 °C (I) and 125 °C (II). (■) SZ, (●) USY zeolites, (▲) Active clay.

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