Applied Catalysis B: Environmental 148–149 (2014) 80–90

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Catalytic decomposition of benzothiophenic and dibenzothiophenic sulfones over MgO-based catalysts

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ARTICLE INFO

Article history:
Received 28 July 2013
Received in revised form
28 September 2013
Accepted 15 October 2013
Available online 23 October 2013

Keywords:
Oxidative desulfurization
Sulfone decomposition
MgO
Solid base catalysts
Hydrocarbon fuel

ABSTRACT

Bulk and supported MgO based catalysts with weight loadings from 3 to 30 wt% were prepared by wet impregnation (WI) and sol–gel (SG) methods and tested for sulfone decomposition to sulfur-free hydrocarbon in real and surrogate liquid hydrocarbon fuels. The catalysts were characterized by BET analysis, XRD measurements,CO_2–chemisorption and XPS. Among bulk MgO, MgO/Al_2O_3 (WI) and MgO/SiO_2 (WI) catalysts, activity for sulfone decomposition was greatly influenced by crystallite size of MgO. Increasing calcination temperature increased MgO crystallite size which adversely affected catalytic activity. $30MgO/SiO_2$ (WI) showed the highest activity for decomposition of sulfones both in real jet and diesel fuels. The effect of temperature on decomposition of benzothiophenic and dibenzothiophenic sulfones over $30MgO/SiO_2$ (WI) was examined from 320 to 450 °C using (pre-oxidized) JP-5 jet fuel and BP-325 diesel fuel to elucidate the difference in decomposition activity of two and three ring sulfones. At 450 °C, about 77% of the dibenzothiophenic sulfones in BP-325 diesel fuel were decomposed over $30MgO/SiO_2$ catalysts. Benzothiophenic sulfones were more active for decomposition and about 97% of the sulfones in JP-5jet fuel were decomposed at 400 °C. In contrast to bulk MgO, MgO/Al_2O_3 (WI) and MgO/SiO_2 (WI) catalysts; MgO/TiO_2 (WI) and MgO/SiO_2 (SG) promoted undesired conversion of sulfones back to sulfur compounds by oxygen removal. The difference in selectivity was attributed to the effect of support and synthesis procedure potentially resulting in catalyst with different surface properties. Model compounds decomposition of dibenzothiophenic sulfone and 3-methyl benzothiophene sulfone were also studied to evaluate the potential pathway from sulfones to sulfur-free hydrocarbons.

1. Introduction

The stringent sulfur regulation has motivated intensive research in non-conventional desulfurization techniques of liquid hydrocarbon fuels [1–3]. For example, oxidative desulfurization (ODS) has been extensively studied on diesel fuel because of the increased reactivity of alkylated dibenzothiophenes for oxidation which are hard to remove by conventional hydrodesulfurization (HDS) [4–11]. Unlike HDS, oxidation of sulfur compounds does not result in the formation of sulfur-free hydrocarbon and therefore requires post-oxidation steps for effective removal of oxidized sulfur compounds to yield low sulfur product.

Most studies on ODS have, however, focused on catalyst and oxidant development for selective oxidation [12–18] with fewer efforts on treatment of oxidized sulfur compounds or sulfones obtained after oxidation [19–26].By theory, sulfones can be easily extracted or adsorbed because of their increased polarity in comparison to the parent sulfur compounds. Although liquid extraction of sulfones by polar solvents is feasible and has been demonstrated, the loss of whole hydrocarbon containing the sulfone can be an issue. A study by Otsaki et al. quantified the loss of hydrocarbon in straight run gas oil and vacuum gas oil when the oxidized sulfur is extracted by polar solvents [25].The authors showed that dimethyl formamide extraction of sulfones from oxidized vacuum gas oil (2.17 wt% S) to < 0.1 wt% S results in 35% feed loss and requires multiple extraction steps [25]. Like extraction, adsorption can be used for removal of sulfones but rapid saturation of the bed and the need for regeneration of the sorbent are some of the limitations. Further disposition of the effluent containing sulfones after regeneration can be an issue.

To overcome the limitations involved with post-separation techniques based on adsorption and extraction, we report in this paper the decomposition of benzothiophenic and dibenzothiophenic sulfones to sulfur-free hydrocarbon using real and model hydrocarbon feeds in the presence of MgO-based catalysts. The potential reaction scheme of the decomposition process is presented in Fig. 1.

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http://dx.doi.org/10.1016/j.apcatb.2013.10.033

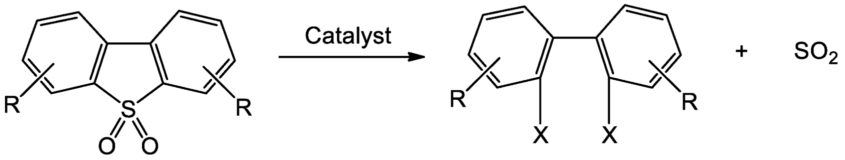

Fig. 1. Reaction scheme for catalytic decomposition of alkylated dibenzothiophenic sulfones (R:H or alkyl group, X: H or alkyl group from other hydrocarbons in the feed).

Decomposition of oxidized sulfur compounds using model compounds has been demonstrated in previous studies, but most of the efforts used large amounts of molten NaOH or KOH which are corrosive and tend to produce products of complex nature [27–29]. To avoid the limitations associated with NaOH based chemistry, heterogeneous catalysts have been proposed in some recent studies [19,20,30,31]. For example, Kocal and Brandvold postulated that decomposition of dibenzothiophene sulfone over heterogeneous catalyst results in the formation of hydroxybiphenyl and volatile sulfur compounds (sulfur dioxide) [26].Heterogeneous NaOH based, sodium aluminate was shown to be effective for decomposition of sulfones in liquid hydrocarbon and addressed the handling issue of molten alkali by impregnating NaOH on alumina [31]. Even though heterogeneous system has been shown to be effective, the nature of the products obtained from decomposition of dibenzothiophenic sulfones is unknown. Also very limited work has been carried out on decomposition of benzothiophenic-type sulfones over heterogeneous catalysts.

This paper discusses the catalytic decomposition of benzothiophenic and dibenzothiophenic sulfones over a series of MgO based catalysts viz., MgO, MgO/SiO_2 prepared by sol–gel method, MgO/SiO_2, MgO/Al_2O_3 and MgO/TiO_2 catalysts prepared by wet impregnation procedure. Catalysts were characterized by BET, XRD, CO_2-chemisorption (TPD-MS and FTIR) and XPS to understand the influence of physical and chemical properties of the catalysts for decomposition of sulfones. Both real and surrogate liquid hydrocarbons containing different types of oxidized sulfur compounds were tested for sulfone decomposition chemistry.

2. Experimental

2.1. Catalysts synthesis and characterization

Catalyst used in this study were prepared by wet impregnation of magnesium ethoxide (98%, Sigma Aldrich) from its methanol solution onto γ-Al_2O_3 (UOP LaRoche VGL-15), fumed SiO_2 (Cabosil M5) and TiO_2 (Degussa P25) supports. A catalyst based on MgO/SiO_2 was also prepared by sol–gel method. A typical sol–gel synthesis involves premixing of magnesium ethoxide dissolved in methanol and tetraethyl orthosilicate (98%, Sigma Aldrich) in ethanol, followed by drop wise addition of water which results in the formation of a gel. The gel is then dried overnight at 80 °C followed by calcination at the desired temperature. Typical MgO loading of all the supported catalysts was 30 wt%. Unsupported MgO catalysts, MgO–ME (obtained by direct calcination of magnesium ethoxide) and MgO–SA obtained from Sigma Aldrich were also tested for their catalytic activity. All catalyst samples were calcined at the desired temperature between 450 and 650 °C for 5 h in a muffle furnace.

N_2 adsorption–desorption was carried out at liquid-N_2 temperature (−196 °C) to measure the BET (Brunauer–Emmett–Teller) surface area and pore volume on a Micromeritrics ASAP 2020 analyzer. All samples were degassed at 200 °C under vacuum prior to measurement.

Temperature-programmed desorption of CO_2 (CO_2-TPD) was conducted in a flow mode on a Micrometrics Autochem 2910 TPR/TPD analyzer. In a typical CO_2-TPD experiment, about 150 mg of the sample was loaded in U-shaped quartz cell above a small amount of quartz wool. The sample was dried under argon flow at 200 °C for 60 min. After the treatment, the temperature was cooled to 50 °C. CO_2 adsorption was facilitated by passing a 50% CO_2-helium mixture at 40 mL/min. After CO_2 adsorption, the CO_2-TPD profile of the sample was recorded by increasing the temperature from 50 to 900 °C at a heating rate of 10 °C/min under 50 mL/min of UHP He flow. The desorbed CO_2 was identified on the basis of the intensity of the mass fragment with $m/e = 44$ which was analyzed by AMETEK Dycor DM200M mass spectrometer.

Powder X-ray diffraction (XRD) patterns of the calcined catalysts were obtained on a Scintag (Thermo Scientific) PAD V Powder Diffractometer using Cu *K*a radiation (l = 0.154 nm) operated at 30 mA and 35 kV with a scanning speed of 1°/min. The diffractograms were analyzed using MDI JADE 8.0 software and the standard JCPDS files.

Fourier transform infrared spectrometry (FTIR) was carried out on a Bruker Optics IFS 66/S equipped with diffuse reflectance IR Fourier transform spectrometry (DRIFTS), Thermo Spectra-Tech Collector II. The catalyst samples were analyzed using a micro sampling cup and all spectra were referenced to KBr. Samples were dried in-situ at 250 °C under a flow of argon at 40 mL/min and then temperature was reduced to 50 °C followed by exposure to CO_2 at 40 mL/min for analysis of type of basic sites of the catalyst. The spectra before and after CO_2 adsorption were recorded in diffuse reflectance model and the difference spectrum obtained was used for further analysis.

XPS analysis of the spent catalysts was performed on a Kratos Analytical Axis Ultra using a monochromatized Al $K\alpha$ X-ray source (1486.6 eV) at 280 W, with pass energy of 20 eV and a step size of 0.1 eV. Charge referencing of the features was done relative to the aliphatic carbon peak in C 1s spectrum at 285 eV. Spent catalysts were analyzed without any further treatment after sulfone decomposition reaction.

Spent catalyst from sulfone decomposition reaction were analyzed by thermogravimetric analysis on a TGA 2050 (TA Instruments) analyzer with argon and the sample was heated from room temperature to 1000 °C at 20 °C/min. Gaseous effluent from the TGA was analyzed by a Thermostar GSD 301T mass spectrometer (Pfeiffer Vacuum Inc.).

2.2. Catalytic Reaction

The sulfone decomposition reactions were carried out in a downflow fixed-bed reactor at atmospheric pressure and temperatures between 320 and 450 °C with constant weight hourly space velocity (WHSV) of 10 h^{-1}. On top of the catalyst bed was a pre-heating zone, about 4 in. in length filled with glass beads of 2 mm in diameter. A high-pressure liquid chromatography pump was used to measure and pump the liquid hydrocarbon feedstock. A gas–liquid separator was employed to separate the reaction products into gas and liquid phases. The gaseous effluents were scrubbed in a basic solution before being vented out and were not analyzed in this study except in a few cases. Three K-type thermocouples were used to measure and maintain the temperature of the reactor unit. The first was used to measure the temperature of the tubular furnace and the second was placed on the outer wall of the reactor tube. The third thermocouple was placed at the center of