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Isobutene oligomerization on MCM-41-supported tungstophosphoric acid

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ABSTRACT

Oligomerization offers a broad potential for converting light olefins into liquid fuels. Here, tungstophosphoric acid, TPA, was impregnated on a mesoporous silica support, MCM-41, at varying loadings from 1 to 90 wt%. The IR and XRD results indicated the presence of interactions between the TPA clusters and MCM-41, especially at loadings below 50 wt%. These interactions led to variations in acid site density and their corresponding strength as evidenced by the results of temperature programmed desorption of ammonia measurements. Consequences of these changes were investigated on isobutene oligomerization. Results obtained at 393 K and 15 bar indicated that the TPA/MCM-41 catalysts provide more than 75 wt% isobutene conversions at a weight hourly space velocity (WHSV) of 46 h^{-1}. Results further showed that the catalysts were more selective towards distillate range products especially at very low TPA loadings. The relative selectivity of trimers over dimers in the oligomerization product pool was approximately four at a TPA loading of 1 wt% and it decreased to 1.5 with increasing TPA loading. Ruling out the presence of any strong correlations between acid strength and catalytic performance, the data presented a strong dependence of the product selectivity on the availability and vicinity of the acid sites.

1. Introduction

The refineries are now forced to process heavier crude oil as they are relatively cheaper compared to their lighter counterparts [1]. Technologies, such as delayed coking and fluid catalytic cracking, are widely used to upgrade these heavier feedstocks. These technologies produce lots of valuable products ranging from gasoline to diesel fuel components along with gaseous products containing a significant amount of olefins. However, the market demand for these gaseous unsaturated hydrocarbons is mostly limited with the utilization in LPG fractions and petrochemicals. A recent trend is to convert these undervalued light olefins into more valuable liquid hydrocarbons that are more suitable for gasoline and diesel pool, or for middle distillate. This approach is also needed for the utilization of the cracked shale gas components. The conversion can be done by several different technologies, such as alkylation and oligomerization [2]. Among these technologies, alkylation is used to produce mostly gasoline range products by using very strong acids, such as HF or H_2SO_4, to process a feedstock containing isobutane and isobutene [2]. Oligomerization, on the other hand, is more flexible in terms of both feed (C_2–C_4 range olefins) and product composition [3,4]. This technology requires a solid acid catalyst [5], such as solid phosphoric acid [6–8], zeolites [9–15], cation exchange resins [16–19], and metal oxides with acidic function [20]. The structure, location, and the strength of active sites in these catalysts determine the product selectivity. For instance, the solid phosphoric acid (SPA) has been used commercially since 1930s (Catpoly process developed by Universal Oil Products Company (UOP)) for the production of high-octane olefinic motor gasoline by the oligomerization of C_2–C_5 olefins [7,21,22]. Zeolites, on the other hand, are a widely studied group of catalysts offering various advantages, such as high degree of regenerability, thermal stability, and shape selectivity [23]. They are also applied in industrial applications. For instance, the COD-9 catalyst (Süd-Chemie), mostly based on ZSM-5, provides 95–97% olefin conversion in a commercial process called “Conversion of Olefins to Distillate” (COD) operating at 473–573 K and 45 bar. This process is highly selective to diesel fraction because of the shape selectivity of ZSM-5 catalyst [24]. Ion-exchange resins, on the other hand, have macroporous structures with strong acidity and high acid capacity offering long lifetime (low tendency to deactivation by pore blockage) and high trimer selectivity for C_4 olefins [25]. For instance, Nafion-NR50

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provides 95% conversion for propene oligomerization at 423 K and 8 bar at a space velocity of 10 h^{-1}, while SPA offering only 6% conversion under identical conditions [25].

Although all of these catalysts can be used commercially, there are some drawbacks regarding their utilization. For instance, SPA catalysts produce only gasoline range products, and they have a limited catalytic lifetime. Besides, they generate corrosion problems, and are difficult to dispose [21]. Zeolites require higher operating temperatures and pressures compared to other solid acid catalysts; and this requirement leads to some side reactions, such as cracking and aromatization, directly influencing the product quality [24]. Ion-exchange resins cannot be regenerated because of their low thermal stability [26]. These limitations in solid acid catalysts suggest a strong need for a new type of catalyst. A good alternative in this respect is the Keggin type heteropolyacids (HPAs). These relatively new class of catalysts offer unique physicochemical and catalytic properties suitable for various reactions including oligomerization of light olefins [3,27–32]. One of the main advantages of these catalysts is that their redox and acidic properties can be tuned by varying their chemical composition [27,30,33]. These materials have a general formula of $H_{8\text{-}x}MX_{12}O_{40}$, where M and X are the central- and hetero-atoms, respectively. Typically, M can be either P or Si, and X can be W or Mo [30,31,34,35]. The structure of the heteropoly anion consists of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedral MO_6. Among a wide range of available HPAs, tungstophosphoric acid ($H_3PW_{12}O_{40}$), silicotungstic acid ($H_4SiW_{12}O_{40}$), phosphomolybdic acid ($H_3PMo_{12}O_{40}$), and silicomolybdic acid ($H_4SiMo_{12}O_{40}$) are the most commonly used ones with a variation of acid strength in the following order: $H_3PW_{12}O_{40}$ (TPA) > $H_4SiW_{12}O_{40}$ (TSA) > $H_3PMo_{12}O_{40}$ (MPA) > $H_4SiMo_{12}O_{40}$ (MSA) [32,37,38]. Because of this variation in acid strength, the HPAs with a tungsten hetero-atom are usually the choice of material for various reactions requiring strong acidity, high thermal stability, and low oxidation capability [34–39]. These materials are, in general, more active catalysts than other conventional solid acid catalysts because of their strong Brønsted acidity. Their strong acidity allows operation at mild conditions [34,40–42]. However, these materials offer a very low surface area, generally in the range of < 10 m^2/g. Such low surface area limits the availability of the acid sites for surface-type reactions. Therefore, they are usually dispersed on high surface area supports, such as silica, titania, and carbon [29,42]. Among these, silica is the most widely used support because it interacts weakly with Keggin anions preserving the heteropolyacid structure [30,39,43,44]. The acidic properties of HPAs on these supports can be varied simply by changing the corresponding HPA loading. For instance, Sushkevich et al. tested the effect of HPA loading on the selectivity of amorphous silica-supported TPA for isoprene synthesis from formaldehyde and isobutene. Their results illustrated that a catalyst with 20 wt% TPA loading provides the best performance with an isoprene yield of 48%. The effect of HPA loading on the catalytic performance was inferred to be associated with the high content of weak Brønsted acid sites [45]. Zhang et al. studied the relation between the changes in surface acidity and loadings for SiO_2-supported TSA. They performed temperature-programmed desorption of benzonitrile (BN-TPD) complemented by an infrared (IR) spectroscopy investigation on BN- and pyridine-adsorbed catalyst. Their results illustrated that the formation of medium strength Brønsted acid sites occurred until the surface of SiO_2 covered with a single layer of TSA and reached a maximum at an HPA loading of 30 wt%. The formation of sites with different acid strength was accompanied by the direct interactions between TSA and SiO_2 [46].

Applications of HPAs for light olefin oligomerization is quite limited [5]. One of the few studies on this reaction was reported by Zhang et al. on the selective oligomerization of isobutene in the presence of 1-butene (with a molar ratio = 1:1 in the feed). They illustrated that 40 wt% TSA loading on SiO_2 provides the highest activity for isobutene oligomerization, while the selectivity to isobutene oligomerization reaches a maximum of 95 wt% on a TSA/SiO_2 catalyst with a TSA loading of 10 wt% [38]. Here, we extend this approach to a family of another HPA catalyst supported on a support with a significantly high surface area. For this purpose, TPA was selected as the HPA because of its higher acid strength than that of TSA. And as a support, we used a mesoporous silica, MCM-41. This support has hexagonal mesoporous arrays, thus it is superior to the conventional silica supports because of its high surface area (in the range of 800-1000 m^2/g), porosity, and high thermal stability [3,37,47]. With these properties, MCM-41 is a promising support for HPAs because it enables a high degree of dispersion of TPA and ease of diffusion for the reactants and products [48–50]. There are some reports on HPA/MCM-41 catalysts on various reactions, such as alkylation, hydrodesulphurization, esterification, and oxidation [31,41,43,44,51–54]. However, to the best of our knowledge, MCM-41-supported HPA catalysts have not been studied for olefin oligomerization. This report illustrates their potential utilization for this reaction.

2. Experimental

2.1. Materials and catalyst preparation

TPA (reagent grade, 99.95%, Sigma Aldrich) loaded MCM-41(A grade, > 850 m^2/g, ACS Materials) catalysts were prepared by the impregnation method. MCM-41 was calcined in air at 793 K for 5 h before use. TPA was first dried at 363 K under vacuum for 3 h and then impregnated on freshly calcined MCM-41. The loading amounts of TPA on MCM-41 were varied from 1 to 90 wt% and water was used as solvent. For 1 wt% TPA loading, TPA/MCM-41 (1 wt%), for instance, 0.01 g of TPA was dissolved in 3 g of water and mixed on a magnetic stirrer at 100 rpm at room temperature for 15 min. After mixing, 0.99 g of MCM-41 was added into the solution. The solution was then mixed for 24 h and dried at 383 K for 5 h. The dried powder was calcined in air at 523 K for 4 h. The same procedure was applied to prepare catalysts at different TPA loadings using the corresponding amounts of TPA and MCM-41.

2.2. Catalyst characterization

Fourier Transform Infrared (FTIR) Spectroscopy. A Bruker Vertex 80v IR spectrometer was used with a platinum diamond attenuated total reflection (ATR) cell. Spectra in a range of 600 to 3000 cm^{-1} were collected at a spectral resolution of 2 cm^{-1} in air at room temperature. Before each sample scan, 64 scans of background signal were collected and averaged. Approximately 10 mg of each sample was loaded into the ATR cell for each measurement. 256 scans were collected and averaged for each sample. Because the peak positions of TPA and MCM-41 features overlap, the MCM-41 spectrum is subtracted from the corresponding TPA/MCM-41 catalysts' spectra for detailed analysis.

Brunauer-Emmet-Teller (BET) Surface Area. BET surface area measurements were performed using a Micrometrics ASAP 2020–Physisorption Analyzer. Samples (300 mg) were degassed at 523 K for 4 h. N_2 adsorption was applied at 77 K using t-method between 0.091 and 0.4 P/P_0 to determine surface areas.

Thermal Gravimetric Analyses (TGA). TGA analyses were performed on a TA Instruments TGA Q500 model instrument. Platinum pans were weighed before sample loading (15 mg). TGA analyses were performed under N_2 flow (60 ml/min). Samples were heated up to 373 K with a heating rate of 10 K and isothermally treated for 4 h at that temperature to allow desorption of any water molecules. Temperature was then increased up to 973 K with heating rate of 2 K/min.

X-Ray Diffraction (XRD). XRD analyses were performed using a Bruker D8 Discover X-Ray Diffraction having a Cu Kα1 radiation source with wavelength of 1.5418 Å. A Vantec-1 detector with a slit-size of 1 mm was used. The power rating of X-ray generator was set to 40 kV and 40 mA. The 2θ range of the measurements was from 1 to 70° with a step size of 0.00985°. Approximately 10 mg of sample was loaded on a double sided tape on a glass slide. Then, the glass slide was placed on a