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Trimerization of isobutene over WO_x/ZrO_2 catalysts

Ji Sun Lee [a], Ji Woong Yoon [a], Shiva B. Halligudi [a], Jong-San Chang [a,**], Sung Hwa Jhung [b,*]

[a] Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology, P.O. Box, 107, Yuseong, Daejeon 305-600, Republic of Korea
[b] Department of Chemistry, Kyungpook National University, Daegu 702-701, Republic of Korea

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ABSTRACT

Trimerization of isobutene to produce isobutene trimers has been investigated over WO_x/ZrO_2 catalysts that were obtained by wet-impregnation and successive calcination at high temperatures. Very stable isobutene conversion and high selectivity for trimers are attained over a WO_x/ZrO_2 catalyst obtained by calcination at 700 °C. From the XRD study it can be understood that tetragonal ZrO_2 is beneficial for stable performance; however, monoclinic ZrO_2 is not good for trimerization. Nitrogen adsorption and FTIR experiments suggest that amorphous WO_x/ZrO_2 is inefficient catalyst even though it has high surface area and high concentration of acid sites. The observed performance with the increased selectivity and stable conversion demonstrates that a WO_x/ZrO_2 having tetragonal zirconia, even with decreased porosity and acid sites, is one of the best catalysts to exhibit stable and high conversion, high selectivity for trimers and facile regeneration.

1. Introduction

In the petrochemical industry, C_4 stream including isobutene is an important raw material that can be upgraded. Recently, oligomerization, especially trimerization, of light olefins has attracted considerable attention as a method for the production of fuel additives [1] and separation of isoolefins from other olefins [2]. Triisobutenes, for example, are considered to be highly useful for the synthesis of specialty chemicals including neo-acids [2]. Triisobutenes, after hydrogenation, can be used as premium solvents (odorless solvents without aromatics) and additives for kerosene and jet fuel [3].

The blending of MTBE (methyl-*tert*-butyl ether) in gasoline has been banned in California [4] since 2004 due to contamination caused by the dissolution of MTBE in underground water. The surplus of isobutene is, therefore expected because it is one of the main raw materials for the synthesis of MTBE.

Hence, the trimerization is a very promising reaction not only for the utilization and separation of isobutene but also for the production of isobutene oligomers such as trimers. Nevertheless, the trimerization of isobutene has not received adequate attention in comparison with the dimerization of olefins [5–11]. Several solid acid catalysts such as a sulfated titania [1,12,13], a cation exchange resin [2,14], a heteropoly acid [15], a zirconia [16] and zeolites [17–19] have been suggested for the trimerization reaction.

To the best of our knowledge, there has been no report for the utilization of solid acids such as mixed metal oxides consisting of WO_x/ZrO_2 in the isobutene trimerization reaction even though these are well-known acid catalysts [20–24]. We, therefore, presenting our results in this paper on the catalytic performance of a highly active and stable WO_x/ZrO_2 solid acid catalyst in trimerization of isobutene under mild liquid phase conditions. We believe that the reported catalyst could find its use in commercial scale production of trimers of olefins (such as isobutene to triisobutenes) since the performance is superior or equal to other catalysts and WO_x/ZrO_2 catalyst has several advantages over conventional solid acid catalysts.

2. Experimental

2.1. Chemicals

Zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, Alfa), ammonia water (35%, v/v, Samchun), and ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$, Sigma–Aldrich) were used without further purification for the synthesis of the catalysts. Amorphous zirconia was obtained from MEL corp. (UK) for the catalyst supports. Amorphous WO_x/ZrO_2 (16 wt% WO_3) was also procured from MEL for a reference catalyst without high temperature calcinations.

2.2. Catalyst preparation

WO_x/ZrO_2 catalysts were prepared by following the standard method reported in the literatures [23,24] using the required precursors. In short, zirconium oxychloride was added to

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[*] Corresponding author. Fax: +82 53 950 6330.
[**] Co-Corresponding author. Fax: +82 42 860 7676.
E-mail addresses: jschang@krict.re.kr (J.-S. Chang), sung@knu.ac.kr (S.H. Jhung).

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deionized water and precipitated into zirconium oxyhydroxide ($ZrO(OH)_2$) by the dropwise addition of ammonia water. Zirconium oxyhydroxide was recovered by filtration, washing and drying. Zirconium oxyhydroxide was added in the water solution of ammonium metatungstate hydrate and mixed well. WO_x/ZrO_2 catalysts were recovered by evaporation, drying and calcinations at 550–800 °C. The amount of zirconium oxychloride and ammonium metatungstate hydrate was adjusted to prepare the catalysts supported with 15 wt% of WO_3. Depending on the calcinations temperature, WO_x/ZrO_2 catalysts were designated as WZ-temp (temp means the calcination temperature). WZ-amorphous catalyst represents the amorphous WO_x/ZrO_2 catalyst supplied by MEL. To understand the effect of zirconia phase on the isobutene trimerization, WO_x/ZrO_2 catalysts were prepared by the impregnation of ammonium metatungstate hydrate on the zirconia precalcined at different temperatures. The WO_x/ZrO_2 catalysts were obtained by calcination at low temperature of 400 °C in order to minimize the conversion of tetragonal phase into monoclinic phase. The WO_x/ZrO_2 prepared using precalcined zirconia was designated as WZ-400/temp (temp means the precalcination temperature of zirconia).

2.3. Characterization

WO_x/ZrO_2 catalysts were characterized for their physicochemical properties by XRD, nitrogen adsorption and FTIR techniques. The nitrogen adsorption and desorption isotherms were obtained at −196 °C with an adsorption unit (Micromeritics, Tristar3000) after evacuation at 300 °C. The surface area was calculated from nitrogen adsorption isotherms using the BET equation. Powder X-ray diffraction patterns of all the samples were obtained by a Rigaku diffractometer (D/MAX IIIB, 2 kW) using Ni-filtered CuKα-radiation (40 kV, 30 mA, $\lambda = 1.5406$ Å) and a graphite crystal monochromator. FTIR spectra of adsorbed pyridine (Aldrich, 99.8%) were obtained at room temperature using a Nicolet FTIR spectrometer (MAGNA-IR 560). The catalysts were pelletized to a wafer and evacuated for 6 h at 300 °C under vacuum ($\sim 10^{-5}$ Torr). After the adsorption of pyridine at room temperature, the physisorbed pyridine was evacuated for 1 h.

2.4. Isobutene trimerization

Trimerization of isobutene (99.0%, 1-butene < 0.3%, n-butane < 0.3%, Rigas Korea) was carried out in liquid phase using a fixed bed continuous flow reactor (stainless steel 316, OD 3/8 inch, thickness 0.035 inch) equipped with a back pressure regulator (Tescom). Catalysts (0.5 g on dry base, together with five times of quartz beads for dilution) were loaded in the reactor after pelletizing. Prior to the commencement of the reaction, the catalyst loaded in the reactor was dehydrated under the flow of nitrogen at 300 °C for 10 h. The aged catalyst, because of long operation, was regenerated by calcination at 400 °C under air flow (flow rate ~100 cc/min, without the flow of isobutene and n-butane).

The reaction temperature and pressure used for the reaction were 70 °C and 15 bar, respectively. The selected conditions were chosen for facile comparison of catalytic performances and considerable conversion and trimers selectivity based on previous results [14]. The reactor temperature was controlled by a water jacket in which water, at constant temperature, was flowing continuously with the help of a circulator. The reactant (isobutene) and a diluent (n-butane, 99.5%, Rigas Korea), without further purification, were continuously fed by using liquid mass flow controllers (Bronkhorst HI-TEC). The space velocity of isobutene, WHSV (weight-hourly space velocity, g of isobutene fed per g of catalyst per hour) was maintained at 5–20 h^{-1} by controlling the flow rates of isobutene and n-butane. The feeding rates of the isobutene and the diluent were the same (50 wt%/50 wt%).

The conversion of isobutene was determined by analyzing periodically the composition of the off-gas stream, after condensing liquid products, by using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and an alumina column (J&W SCIENTIFIC, 30 m × 0.53 mm). The conversion was cross-checked by measuring the total flow rates of isobutene and the diluent with a mass flowmeter (Brooks, 5850 E). Liquid products were analyzed by GC equipped with a flame ionization detector (FID) and a PONA column (HP, 50 m × 0.2 mm). The detailed analysis conditions were reported elsewhere [14]. In this study, the selectivity of dimers, trimers and tetramers is described in wt%. The contribution of pentamers or higher oligomers was neglected in this work since their concentrations were less than 0.5 wt%. The isobutene conversion and selectivities were calculated with following equations.

$$\text{conversion}_{\text{IB}}\,(\%) = [1 - \frac{\text{concentration}_{\text{IB}}\,(\text{off gas})}{\text{concentration}_{\text{IB}}\,(\text{feeding gas})}] \times 100$$

$$\text{selectivity}_{\text{Dimer}}\,(\text{wt\%}) = \frac{\text{concentration}_{\text{Dimer}}}{\text{concentration}_{\text{Dimer}} + \text{concentration}_{\text{Trimer}} + \text{concentration}_{\text{Tetramer}}} \times 100$$

$$\text{selectivity}_{\text{Trimer}}\,(\text{wt\%}) = \frac{\text{concentration}_{\text{Trimer}}}{\text{concentration}_{\text{Dimer}} + \text{concentration}_{\text{Trimer}} + \text{concentration}_{\text{Tetramer}}} \times 100$$

$$\text{selectivity}_{\text{Tetramer}}\,(\text{wt\%}) = \frac{\text{concentration}_{\text{Tetramer}}}{\text{concentration}_{\text{Dimer}} + \text{concentration}_{\text{Trimer}} + \text{concentration}_{\text{Tetramer}}} \times 100$$

3. Results and discussion

Fig. 1 shows the isobutene trimerization results over WO_x/ZrO_2 catalysts according to time-on-stream. After 20 h of time-on-stream, the isobutene conversion is in the order of WZ-700 > WZ-800 > WZ-550. The isobutene conversion decreases steadily with reaction time over the WZ-800 or WZ-550. By contrast, the WZ-700 catalyst shows stable activity compared with other two catalysts. Interestingly, the conversion over WZ-amorphous (without calcination) is negligibly low (less than 2% at 6 h of time-on-stream).

The selectivity for trimers after 20 h of reaction is similarly in the order of WZ-700 > WZ-800 > WZ-550, which is in line with the order of decrease in the isobutene conversion over the catalysts. The high selectivity of trimers with WZ-700 can be ascribed to its high activity and catalyst stability considering that their selectivity generally increases with increasing conversion [14,18]. Similarly, it is noted that the concentration of dimer in the products increases with decrease in isobutene conversion because the oligomerization reaction is a consecutive reaction (from monomer to dimer, dimer to trimers, and trimers to tetramers) [14,18].

It is hard to explain why the WZ-700 shows the best performance among the catalysts, so the catalysts were analyzed