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Methylation of cyclopentadiene on solid base catalysts with different surface acid–base properties

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ABSTRACT

The methylation of cyclopentadiene with methanol has been studied over Al_2O_3 and KOH promoted MgO and unpromoted MgO. The dehydrogenation of methanol to formaldehyde was found to be a key-step in the generation of the active methylating species on these solid bases. The modification with Al_2O_3 or KOH favors the formation of methylcyclopentadienes and elevates the activity of MgO based on different reasons: introduction of acidic sites for Al_2O_3/MgO and superbasic effect for KOH/MgO. These catalysts present different deactivation behaviors due to the different surface acid–base properties. The heavy coking of cyclopentadiene on basic sites is responsible for the rapid deactivation of KOH/MgO along the catalytic test at 773 K. However, the coking can be well suppressed at 723 K, and KOH/MgO exhibits the catalytic performance apparently superior to MgO and Al_2O_3/MgO.

1. Introduction

The gasoline with high quality is extremely demanded with the development of transportation vehicles manufacturing and stricter regulations on environmental protection. The leaded antiknock additive, which used to be an important component in gasoline, should be replaced by unleaded antiknock additive. Methylcyclopentadienyl manganese tricarbonyl (MMT), as one of the alternate antiknock additives, has the advantage of low cost, improving the octane number and combustion efficiency of gasoline as well as reducing emission pollution [1]. As the precursor of MMT, methylcyclopentadienes (MCPD) can be formed from the petroleum cracking, however, the yield is quite limited. Contrarily, cyclopentadiene (CPD) is a more abundant product, and thus many researchers have endeavored to produce MCPD from the methylation of CPD.

In the earlier studies, the methylation of CPD is realized through the following procedure: CPD reacts first with alkali metal sodium, and the formed cyclopentadienyl sodium then reacts with methyl halides to produce MCPD [2,3]. This method has the advantages of high yield (76–85%) and relative simple post-treatment procedure. It has been used for producing commercial MCPD [4]. However, this process concerns the expensive reactants, such as metal sodium and methyl halides (usually methyl iodide), and must be carried out in liquid ammonia in order to disperse and stabilize sodium. Some researchers attempt to prepare alkylcyclopentadiene with alcohol in the presence of a liquid strong basic catalyst such as potassium or sodium hydroxide or alkoxide [5]. It should be noted that this reaction is still carried out in liquid-phase and only a tarry product can be obtained when methanol is involved. Yoshida et al. [6] report a vapor-phase reaction of CPD with an aliphatic lower alcohol in the presence of a catalyst containing oxides such as an alkaline earth metal oxide or alkali metal oxide. They also utilize the basic zeolites in this process but mainly for producing the multi-alkylated CPD derivatives [7]. Compared with liquid base, the use of solid base has apparent advantages in many aspects, e.g. noncorrosive and environmentally benign. The replacement of liquid-phase catalysis with vapor-phase catalysis allows easier separation of the products as well as the possibility of catalysts regeneration and reuse. Therefore, the vapor-phase methylation of CPD is a very attractive route to prepare MCPD.

Although the catalysts concerned in the patent [6] cover most of the conventional oxide or mixed oxide solid bases, little work has focused on the reaction process. In the previous work, we found

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that the base strength of catalysts plays a key role in vapor-phase methylation of CPD with methanol [8,9]. In the present work, we have investigated the catalytic behaviors and the deactivation of unpromoted, KOH and Al_2O_3 promoted magnesium oxides in the vapor-phase methylation of CPD with methanol. Our aim is to correlate the catalytic performance in CPD methylation with the nature of catalysts and explore the possible reaction and deactivation mechanisms.

2. Experimental

2.1. Catalyst preparation

KOH and Al_2O_3 promoted MgO catalysts were prepared by impregnation of potassium hydroxide and aluminum nitrate from their aqueous solution, respectively. Typically, a calculated amount of potassium hydroxide or aluminum nitrate was dissolved in 20 mL of distilled water, and then 2 g commercial MgO (Shanghai Chemical Reagent, China, ⩾97.0%) was added into this solution. After stirring at room temperature for 24 h, the mixture was evaporated to remove most of the water in a water bath and then dried at 373 K overnight. The resulting solid was further calcined at 873 K for 2 h to form KOH- or Al_2O_3-modified MgO. These prepared solid bases were denoted as *x*%KOH/MgO and *x*%Al_2O_3/MgO, respectively, where *x*% indicated the mass percentage of KOH or Al_2O_3 in the whole catalysts. For comparison, pure Al_2O_3 was prepared by calcining aluminum nitrate at 873 K for 2 h, and portions of these prepared Al_2O_3 powders were mechanically mixed with MgO powders according to the mass ratio of 10%Al_2O_3 in the whole catalyst, which was denoted as 10%Al_2O_3/MgO(mix).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku, D/max-RA diffractometer with Cu Kα radiation in the 2θ range from 10° to 80°. N_2 adsorption at 77 K was measured using a Micromeritics ASAP 2020 system. Sample was evacuated at 573 K for 4 h prior to testing. Specific surface area of MgO was determined using the Brunauer–Emmett–Teller (BET) equation with adsorption data in the relative pressure range from 0.04 to 0.2. The base strength (H–) of samples was determined using Hammett indicators [10], and sample was activated at 873 K for 1 h in the flow of N_2 (30 mL/min) before contacting with the indicators. Acidity of sample was determined by using temperature-programmed desorption (TPD) of NH_3. Sample (100 mg) was treated in He (50 ml/min) at 873 K for 1 h and 40 ml of NH_3 was injected at room temperature. Weakly adsorbed NH_3 was removed by flowing He at 30 ml/min for 1 h. Temperature was then increased to 873 K at 8 K/min, and the liberated NH_3 was detected by an on-line gas chromatograph with a thermal conductivity detector (TCD) and quantitatively measured by the external standard method. CO_2-TPD measurements were performed in the manner similar to NH_3-TPD measurements, except that CO_2 was injected instead of NH_3. Inductively coupled plasma-optical emission spectrometric (ICP-OES) analysis was performed in JA1100 ICP instrument. X-ray photoelectron spectra (XPS) were acquired from Thermo Fisher scientific K-Alpha spectrometer using a nonmonochromatized Al Kα X-ray source (1486.6 eV). Base pressure in the analysis chamber was maintained in the range of 10^{-9} mbar. Energy resolution of the spectrometer was set at 0.9 eV. The error in the reported binding energy (BE) values is ±0.1 eV. Solid-state ^{13}C MAS nuclear magnetic resonance (NMR) spectrum of spent catalyst was performed on a Bruker advance III NMR spectrometer, operating at a frequency of 100.62 MHz for ^{13}C. To obtain quantitative data, single pulse excitements (SPEs) were used with a 90° pulse length $p_1 = 3.5$ s and a delay time $d_1 = 5.0$ s. The sample was spun in a 7-mm zircon rotor at 6 kHz and 4200 scans. Adamantane was used as external reference for the chemical shift.

2.3. Catalytic testing

The catalytic decomposition of isopropanol or methanol was measured in a conventional flow reactor at atmospheric pressure. The sample (50 mg, 20–40 mesh) was activated at 873 K in the flow of N_2 (30 mL/min) for 1 h and then was cooled to the reaction temperature. The reactant isopropanol (Nanjing Chemical Reagent, China, ⩾99.7%) or methanol (Nanjing Chemical Reagent, China, ⩾99.7%) was introduced using a syringe pump with the space velocity of 1.9 or 0.9 h^{-1} in the flow of N_2 (20 mL/min). The reaction mixture was analyzed by on-line gas chromatography, using a Varian 3700 instrument equipped with a flame ionization detector (FID) and a Propark-T column or a thermal conductivity detector and a TDX-01 column. Conversion was defined as C_i = (moles of substrate reacted per mole of reactant in the feed); yields of H_2, dimethylether (DME) and other product i were defined as Y_{H2} = (-moles of product H_2 formed per 2 moles of reactant in the feed), Y_{DME} = (moles of product DME formed per 0.5 moles of reactant in the feed), Y_i = (moles of product *i* formed per mole of reactant in the feed), respectively; selectivity was defined as S_i = (moles of product *i* formed per mole of reactant reacted).

The vapor-phase methylation of CPD with methanol was carried out in a conventional flow reactor at atmospheric pressure [11]. The catalyst (50 mg, 20–40 mesh) was thermally activated at 873 K for 1 h in N_2 and then was cooled to the reaction temperature. CPD was obtained by thermal depolymerization of dicyclopentadiene (Aldrich) at 873 K, and the reactants CPD and methanol (Nanjing Chemical Reagent, China, ⩾99.7%) were introduced by syringe pumps with a molar ratio of 0.9 or 1.8 (space velocity of 1.6 or 2.5 h^{-1}) in the flow of N_2 (20 mL/min). The reaction was carried out in two modes: (1) the reaction was performed at various temperatures with the same reaction time of 10 min, in order to study the effect of temperature on the catalytic activity and (2) the reaction was performed at various times with the same reaction temperature, in order to compare the deactivation rate on different catalysts. The reaction mixture was analyzed by on-line GC (Varian 3700). In situ poisoning experiments were carried out by doping methanol with a certain amount of acetic acid or pyridine, and were ended by repumping pure methanol for reaction. In order to study the regeneration of the deactivated catalyst, the catalyst after reaction was calcined at 873 K for 1 h in the flow of air, and then cooled to the reaction temperature for further reaction. The coking was observed on these catalysts at higher reaction temperatures, and the coking amount varied with the difference in catalysts, temperatures and even the time. In order to better compare the activity of these catalysts in CPD methylation, the calculations of the conversion and product selectivity were irrespective of the contribution of the coking. Thus conversion and selectivity in this reaction were defined as C_i = (moles of substrate reacted per mole of CPD in the feed except what was transformed to the coke deposit) and S_i = (moles of product *i* formed per mole of CPD reacted), respectively. Carbon balance measurement indicated that this treatment has little effect on the calculated values of conversions in the temperature range of 673–723 K; however, the calculated value is lower than that including the contribution of the coking in the temperature range of 773–823 K, especially for KOH/MgO at a lower reaction time. For example, when the reaction was carried out at 773 K for 10 min on 10%KOH/MgO, 41% of conversion was calculated irrespective of the contribution of the coking, while 68% of conversion was obtained including the contribution of the coking.