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MgO–SBA-15 Supported Pd–Pb Catalysts for Oxidative Esterification of Methacrolein with Methanol to Methyl Methacrylate☆

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ABSTRACT

Novel MgO–SBA-15 supported catalysts were prepared for oxidative esterification of methacrolein (MAL) with methanol to methyl methacrylate (MMA). The MgO–SBA-15 supports were synthesized with different magnesia loadings from different magnesium precursors and hydrochloric acid molar concentrations. The MgO–SBA-15 supports and Pd–Pb/MgO–SBA-15 catalysts were characterized by several analysis methods. The results revealed that the addition of MgO improved the ordered structure of SBA-15 supports and provided surface alkalinity of SBA-15 supports. The average size of the Pd_3Pb particles on magnesia-modified Pd–Pb/MgO–SBA-15 catalysts was smaller than that on the pure silica-based Pd–Pb/SBA-15 catalysts. The experiments on catalyst performance showed that the magnesia-modified Pd–Pb/MgO–SBA-15 catalysts had higher activity than pure silica-based Pd–Pb/SBA-15 catalysts, showing the strong dependence of catalytic activity on the average size of active particles. The difference of activity between Pd–Pb/SBA-15 catalysts and Pd–Pb/MgO–SBA-15 catalysts was due to the discrepant structural properties and surface alkalinity provided by MgO, which led to the different Pd_3Pb particle sizes and then resulted in the different number of active sites. Besides magnesia loadings, other factors, such as hydrochloric acid molar concentration and magnesium precursors, had considerable influences on the catalytic activity.

1. Introduction

Methyl methacrylate (MMA) is one of the most important chemicals to produce plexiglass, acrylic coatings, polymeric dispersants for paints and so on. Oxidative esterification of methacrolein (MAL) with methanol to MMA in the presence of oxygen has the advantages of short routes and high atom efficiency. In general, the catalysts for oxidative esterification of aldehydes are mainly supported noble metal catalysts. Among them, palladium catalysts are one of the most active catalysts. In general, the most commonly used support is alumina, but the pore of alumina is irregular and the specific surface area is relatively small. Mesoporous silica materials have some advantages over alumina such as reproducible and scalable synthesis, and significantly larger surface areas and more flexible pore architectures [1–3]. The large surface area of mesoporous silica materials helps in attaining higher metal dispersions compared with lower surface area non-ordered supports. Additionally, the regular and tunable pore size offered by ordered mesoporous silica materials can impart this uniformity to the hosted catalytic nanoparticles under controlled synthesis conditions [4–7]. Above all, the introduction of mesopores can strongly affect mass transport to in-pore active sites and increase palladium dispersion [8–10]. There are so many advantages of mesoporous silica materials over alumina, and thus, we want to use them in oxidative esterification of MAL with methanol to MMA.

SBA-15 is one of the most popular mesoporous silica materials due to its high surface area and large tunable pores [11]. Its thick pore walls provide enhanced mechanical stability, and can be modified to tailor their properties and achieve specific purposes [12–14]. However, the inherent lack of adequate acid and basic sites limits their applications in catalysis. Several metals such as Al, Zr, Ti, Cr and B [15–18] have been incorporated into SBA-15 to broaden its applications. SBA-15 based solid bases have been widely studied including amino [19], magnesium [20,21], and calcium [22] modified SBA-15. MgO is regarded as a typical solid base material due to its electron donation ability. It is found that MgO accelerates the reaction rate of oxidative esterification of MAL with methanol in the presence of oxygen [23]. By adding magnesium salts into the initial mixture of raw materials, basic mesoporous silica materials can be achieved. The addition of magnesium salts will lead to a better order, either in structure or morphology [2]. It is believed to be related to the special interaction between surfactant head groups and magnesium [2]. As far as we know, the investigations on MgO–SBA-15 supported Pd–Pb catalysts for oxidative esterification of MAL with methanol have not been reported so far.

In this work, a series of MgO–SBA-15 supports was prepared with different magnesia loadings, hydrochloric acid molar concentration and precursors of magnesium salts. MgO–SBA-15 supported Pd–Pb

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catalysts, prepared by co-impregnation methods, were applied to oxidative esterification of MAL with methanol (Fig. 1). The effects of magnesia loadings on the structural properties of supports, surface alkalinity of catalysts and the particle size distribution of active sites were investigated. The effects of hydrochloric acid molar concentration on the particle size distribution of active sites and the influences of precursors on the structural properties of supports and catalysts were also studied. Finally, the catalytic activity of catalysts prepared from the above factors was examined.

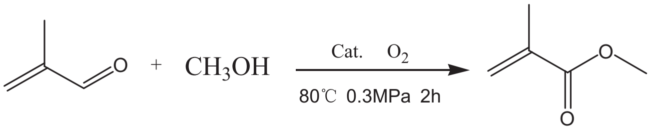

Fig. 1. Oxidative esterification of MAL with methanol to MMA.

2. Experimental

2.1. Preparation of supports and catalysts

MgO–SBA-15 supports were synthesized according to the literature with some modifications [2]. Typically, 4.0 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich) and a calculated amount of magnesium salts from one of $MgCl_2$, $Mg(NO_3)_2$ and $Mg(CH_3COO)_2$ (AR, Sinopharm Chemical Regent Co., Ltd.) were dissolved in 150 g hydrochloric acid solution (AR, Beijing Chemical Works). Then, 8.5 g of tetraethoxysilane (TEOS, Xilong Chemical Co., Ltd.) was added. The molar ratio of the mixture TEOS:P123:Mg^{2+}:HCl:H_2O was 1:0.02:X:Y:192, where X was 0, 0.015, 0.075, 0.150, 0.300 and 0.450 for the preparation of samples with the mass ratio of MgO/SBA-15 of 0%, 1%, 5%, 10%, 20%, and 30% and Y was 6, 3, and 1.5 with the hydrochloric acid molar concentrations of 1.6 $mol \cdot L^{-1}$, 0.8 $mol \cdot L^{-1}$, and 0.4 $mol \cdot L^{-1}$. It was denoted as MgO–SBA-15(X-Cl)-Y, MgO–SBA-15(X-N)-Y and MgO–SBA-15(X-A)-Y respectively. The resulting mixture was stirred for 24 h at 313 K and then heated at 373 K for another 24 h without stirring. The liquid was evaporated with stirring at 353 K. Finally, the solids were dried at 353 K and calcined at 823 K for 6 h to remove the template. Palladium chloride (Beijing Cuibolin Non-Ferrous Technology Developing Co., Ltd.) and lead nitrate (AR, Xilong Chemical Co., Ltd.) were impregnated simultaneously. The loading value of Pd and Pb was both 5% (by mass) of MgO–SBA-15 supports. The obtained samples were reduced by hydrazine hydrate.

2.2. Experiments on catalytic performance

The reaction was performed at 353 K and 0.3 MPa of oxygen for 2 h over 0.013 $g \cdot ml^{-1}$ of the supported catalysts under stirring. The molar ratio of methanol to MAL was 20. Catalytic results were expressed as conversion (x, %) and selectivity (S, %) determined by gas chromatography (GC) using ethanol as external standard. Parameters were defined as

$$x = \left(1 - \frac{C_{MAL}}{C_{MAL}^0}\right) \times 100\% \tag{1}$$

$$S = \left(\frac{C_{MMA}}{C_{MAL}^0 - C_{MAL}}\right) \times 100\% \tag{2}$$

where C_{MAL}^0 ($mol \cdot L^{-1}$) was the molar concentration of MAL at the beginning mixture, C_{MAL} ($mol \cdot L^{-1}$) the molar concentration of MAL after 2 h and C_{MMA} ($mol \cdot L^{-1}$) was the molar concentration of MMA after 2 h.

2.3. Catalyst characterization

Several analysis methods were applied to characterize the supports and catalysts in this work. The nitrogen adsorption and desorption isotherms were measured using a TriStarII3020 system at 77 K. The samples were degassed at 473 K for 6 h. The Brunauer–Emmett–Teller (BET) specific surface area was calculated using adsorption data in the relative pressure range of 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The mean pore diameter was calculated by the Barrett–Joyner–Halenda (BJH) method using the desorption curves. X-ray diffraction patterns (XRD) were recorded in the 2 theta range of 0.5° to 5.0° and 10° to 90° respectively on a X'Pert PRO diffractometer equipped with a copper anode generating Cu K_α radiation ($\lambda = 0.15418$ nm). Transmission electron microscopy (TEM) measurements were obtained on a JEM2010 electron microscope operated at 120 kV. MgO contents of catalysts were determined by an inductively coupled plasma optical emission spectroscopy (ICP-OES) (IRIS Intrepid II XSP). In CO_2–TPD experiments, 30 mg samples were heated in a flow of helium at a rate of 10 $K \cdot min^{-1}$ to 773 K and kept for 2 h, then cooled to 323 K to adsorb CO_2. After the physically adsorbed CO_2 was purged by helium for 2 h, the sample was then heated at the rate of 10 $K \cdot min^{-1}$ up to 773 K and the liberated CO_2 was detected by a thermal conductivity detector (TCD).

3. Results and Discussion

3.1. Characterization

3.1.1. Textural characteristics

The textural characteristics of Pd–Pb/MgO–SBA-15 catalysts and MgO–SBA-15 supports were characterized by the N_2 adsorption–desorption method. The specific surface area (S_{BET}), pore volume (V_{total}) and mean pore diameter (d_p) of supports and catalysts are summarized in Tables 1 and 2, respectively. Firstly, the specific surface area, pore

Table 1
Textural characteristics of supports

Entry	Support	The mass ratio of MgO to SBA-15①/%	S_{BET}/$m^2 \cdot g^{-1}$	V_{total}/$cm^3 \cdot g^{-1}$	d_p/nm
a	MgO–SBA-15(0-A)	0	540.6	0.95	6.3
b	MgO–SBA-15(0.015-A)	1	638.1	1.00	6.3
c	MgO–SBA-15(0.075-A)	5	610.3	0.96	6.3
d	MgO–SBA-15(0.150-A)-1.6 $mol \cdot L^{-1}$	10	560.8	0.96	6.3
e	MgO–SBA-15(0.300-A)	20	459.1	0.82	6.2
f	MgO–SBA-15(0.450-A)	30	353.4	0.64	6.0
g	MgO–SBA-15(0.150-A)-0.8 $mol \cdot L^{-1}$	10	596.7	0.85	5.7
h	MgO–SBA-15(0.150-A)-0.4 $mol \cdot L^{-1}$	10	590.5	0.75	5.1
i	MgO–SBA-15(0.150-Cl)	10	529.2	0.86	6.0
j	MgO–SBA-15(0.150-N)	10	529.4	0.89	6.3

① Theoretical mass ratios of MgO/SBA-15 were calculated by the added amounts of magnesium precursors and TEOS.