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A Pd–Fe/α-Al_2O_3/cordierite monolithic catalyst for CO coupling to oxalate

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A novel Pd–Fe/α-Al_2O_3/cordierite monolithic catalyst was prepared for the synthesis of diethyl oxalate from CO and ethyl nitrite. The palladium-based monolithic catalyst with an optimal thickness (15 μm) of Al_2O_3 washcoat showed excellent catalytic activity and selectivity in a continuous flow, fixed-bed microreactor. The physicochemical properties of catalyst were studied by a variety of characterization techniques. Catalytic performances of Pd–Fe/α-Al_2O_3/cordierite monolithic catalysts were dependent on particle size of alumina-sol, thickness of Al_2O_3 washcoat, pore structure, surface acidity of carrier, and distribution of active metal component on the Al_2O_3 washcoat. Under the mild reaction conditions, CO conversion was 32% and the space–time yield of diethyl oxalate was 429 g/(L h). Pd efficiency (DEO(g)/Pd(g)/h) of the monolithic catalyst (274 h^{-1}) was much higher than that of a reference pellet catalyst (46 h^{-1}), probably due to high dispersion of the Pd nanoparticles on the surface of the monolithic catalyst.

1. Introduction

Synthesis of ethylene glycol (EG) from syngas (derived from coal, natural gas, or biomass) has become considerably competitive as a result of the depletion of petroleum resource, and the constantly increased demand of EG (Celik et al., 2008; Metzner and Ehrreich, 1959; Tahara et al., 1984a, b; Miyazaki et al., 1986; Bartley and Charleston, 1987). Considering limited crude oil supplies and from economical points of view, a two-step technique of EG synthesis stemmed from syngas has been developed to complement traditional ones, in which oxalate is used as an intermediate (Xu et al., 1995a, b; Thomas et al., 1992; Chen et al., 2008a, b; Li et al., 2005a, b). This indirect synthesis process includes the CO coupling with nitrite esters to oxalates such as diethyl oxalate (DEO) followed by the hydrogenation of oxalates to EG (Jiang, 1990; Gao et al., 2005; Jiang et al., 2001).

Oxalic ester has typically been synthesized via esterification between oxalic acid and alcohol. Using inorganic acids as catalysts, both the crystal water in oxalic acid and water produced from the reaction can be removed by utilizing low-boiling point solvent or excessive alcohol. However, traditional processes for production of oxalate and oxalic acid have caused serious problems of pollution, required high capital input, and high energy consumption (Fable, 1980; Chilba, 1964; Kirk, 1980). Synthesis of dialkyl oxalate by oxidative carbonylation of ethanol with O_2 in the presence of $PdCl_2$–$CuCl_2$ in liquid phase was originally discovered by Fenton et al. (1974). Subsequently, Ube Industries Ltd. built the first plant to prepare dibutyl oxalate using alkyl nitrite in liquid phase (Uchiumi et al., 1999; Matsuzaki and Nakamura, 1997). Major drawbacks for the systems involved with liquid phase include: (1) easy deactivation of the catalyst due to metal leaching or poisoning, and (2) difficulty in separating the catalyst due to the intrinsic nature of the homogeneous system. Therefore, gas phase reactions employing heterogeneous catalysts have attracted considerable attention recently, for example, the synthesis of diethyl oxalate by CO coupling with ethanol in the presence of an oxidizer (Eq. (1)). Indeed, as mentioned earlier, this reaction can be considered as a two-step process: a coupling reaction (Eq. (2)) and a regeneration reaction (Eq. (3)).

$$2CO+2C_2H_5OH+1/2O_2\rightarrow(COOC_2H_5)_2+H_2O \tag{1}$$

$$2CO+2C_2H_5ONO\rightarrow 2NO+(COOC_2H_5)_2 \tag{2}$$

$$2C_2H_5OH+1/2O_2+2NO\rightarrow 2C_2H_5ONO+H_2O \tag{3}$$

Nitrite is usually introduced at the beginning of this process to facilitate the completion of the reaction cycle. Particularly, the coupling reaction of carbon monoxide for producing diethyl oxalate takes place under moderate reaction conditions, while the coupling and regeneration reactions occur simultaneously, ideally leading to a self-closing, non-waste, catalytic cycling process and the corresponding process flowsheet was shown in Scheme 1 (Franco and Ugo, 1978; Kenji et al., 1980; Miyazaki et al., 1983, 1985; Tahara et al., 1984a, b; Shiomi et al., 1989; Ohdan et al., 1997).

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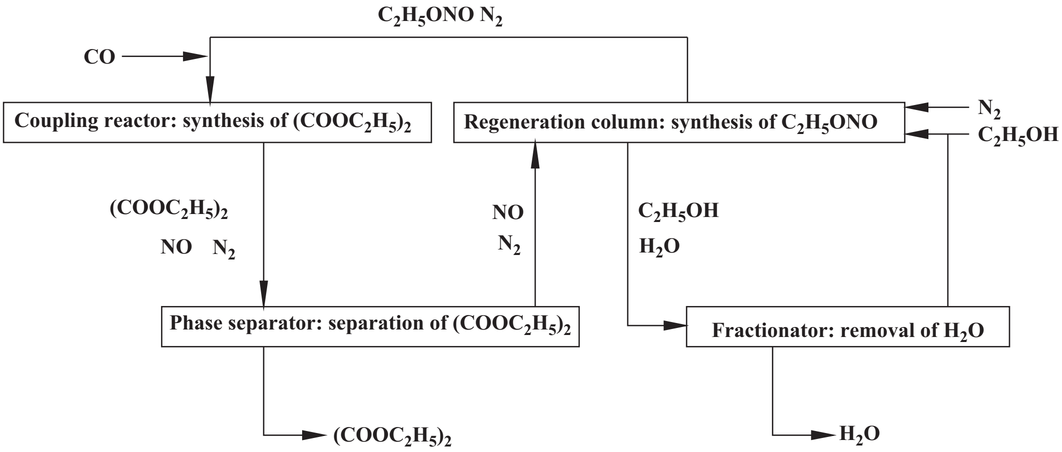

Scheme 1. Diagram for the synthesis of $(COOC_2H_5)_2$ from carbon monoxide.

The synthesis of dialkyl oxalate via gas-phase CO coupling reaction over palladium catalysts has attracted great interest. The catalyst structure (Jiang, 1990; Gao et al., 2005; Xu et al., 1995a, b), support (Jiang et al., 2001; Zhao et al., 2005), operating conditions and process (Fang et al., 2003; Li et al., 2001), kinetics (Li et al., 2003, 2005a, b; Ma et al., 1995; Meng et al., 2003, 2004), and mechanism (Gao et al., 2002; Jiang et al., 2001; Xu et al., 1995a, b) of a Pd–Fe/α-Al_2O_3 catalytic system (Eq. (2)) have been studied; it has been concluded that a Pd/α-Al_2O_3 pellet catalyst exhibited good catalytic activity, selectivity, and stability. We scaled up this process into commercial production of DEO with a capacity of 300 tons per year in 2002, and it is extending to a capacity of 10,000 tons per year as of 2010. One disadvantage of this system is the high loading amount of Pd, which could substantially affect the cost of DEO production. Therefore, developing low loading, but still efficient palladium-based catalysts, is desirable from a practical point of view.

The monolithic catalyst is well known for its application in automotive as an exhaust gas converter (Kapteijn et al., 1999, 2001; Centi and Perathoner, 2001; Williams, 2001; Geus and van Giezen, 1999). In general, a monolithic catalyst comprises a honeycomb-like ceramic structure, washcoat, active component, and promoter. Alternative catalytic materials, supports or their precursors can be coated on a monolithic support in 'washcoating' process (Cybulski and Moulijn, 1998). The traditional catalyst washcoated on the channel walls forms a high cell density of the monoliths with high surface area. Moreover, the monolithic catalyst is identical to the pellet one in terms of efficiency of mass transportation. Monolithic catalyst, however, offers several advantages over pellet catalysts in fixed-bed reactor such as low pressure drop, less diffusion limitations, and ease of scaling-up (Chen et al., 2008a; Kapteijn et al., 1999). This, in turn, spurs many investigations on how to improve other gas phase reactions using monolithic catalysts. Such applications include catalytic combustion, oxidation, hydrogenation or dehydrogenation, and methanation (Heck et al., 2001).

To obtain a high catalytic efficiency with low loading amount of Pd, this study focuses on the design and characteristic of the monolithic catalyst for the CO coupling reaction. We report on the synthesis and characterizing of a series of Pd–Fe/α-Al_2O_3/cordierite monolithic catalysts for the synthesis of diethyl oxalate from ethyl nitrite and carbon monoxide in a continuous fixed bed. We made monolithic catalyst using a dip-coating process to obtain Al_2O_3 washcoat followed by active phase impregnation, where the Al_2O_3 washcoat was used as a secondary carrier on monolithic support. Through detailed characterization by LPSA, BET, MIP, XPS, XRD, SEM, Energy Dispersive X-ray (EDX), and NH_3-TPD, the physicochemical properties of catalysts such as pore structure, surface acidity, and distribution of active metal component were studied. We also compared the catalytic performance of our monolithic catalyst with that of conventional catalyst in a fixed-bed reactor under the same conditions.

2. Experimental

2.1. Preparation of washcoated monolithic catalysts

The cylindrical (length 25.0 mm, diameter 25.0 mm) cordierite monoliths were used, which have square channels, a cell density of 62 cells cm^{-2} (400 cpsi), and a wall thickness of 0.11 mm (4.5 mil) (Corning Shanghai Inc.). The apparent monolith density and its geometric surface are 0.57 g/cm^3 and 26.4 cm^2/cm^3, respectively. In order to remove organic impurities pre-adsorbed on the surfaces, the monoliths were calcined in air at 973 K before we carry out the coating procedure. Since bare cordierite monolith is not an ideal support due to its low BET surface area (<1 m^2/g), we coated Al_2O_3 washcoat with high surface area by the slurry-coating method (Nijhuis et al., 2001) on the cordierite monolith as a carrier of active component. The slurry was prepared by wet-milling of the Al_2O_3 precursor. Ensuring the adhesive performance between monolith and washcoat, the slurry was ball-milled for various periods of time until batches with the desired particle size distribution were obtained. The monolith was kept with respect to channels' direction perpendicular to the surface of the slurry during the whole dipping and withdrawing processes. Each dipping was followed by removal of the excess slurry using dry air and a subsequent aging for a period of time. The washcoat quality was investigated under four different drying conditions: (1) natural drying at room temperature, (2) static drying in an oven at 393 K, (3) vacuum freeze-drying at 233 K and 10 Pa, and (4) microwave drying at 500 W. The washcoating and drying procedures were repeated several times until the desired loading was obtained. Finally, the washcoated monoliths were calcined in air at temperatures ranging from 773 to 1473 K for 4 h, and the loading of the washcoat of 5.0–50.0 wt% was obtained. The catalyst was then prepared by wet impregnation using palladium chloride and ferric chloride as precursors and the Pd/Fe atomic ratio was 1/1. The loading of 0.1–5.0 wt% Pd on the washcoated monolith was obtained. Before activity test, the catalysts were treated under flowing hydrogen at 773 K for 4 h to reduce Pd(II) to Pd(0).

A reference Pd/Al_2O_3 pellet catalyst (∅ 2×2 mm) was also prepared via incipient-wetness impregnation. The monolithic and