



Hydrogenolysis of methyl heptanoate over Co based catalysts: Mediation of support property on activity and product distribution



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ABSTRACT

Co/MgO, Co/SiO₂ and Co/H β catalysts were prepared by incipient wetness impregnation. The formation of MgO–CoO solid solution and MgCo₂O₄ spinel in Co/MgO resulted in high dispersions of Co on MgO even at the low calcined temperatures and the high Co loadings. The second impregnation of Co on Co/MgO enhanced Co cations in surface/subsurface of catalysts, which led to the enlarged metallic Co particle sizes by H₂ reduction. Comparatively, the highly dispersion of Co was only observed on SiO₂ and H β at the low Co loadings owing to the Co^{δ+} species of strong interactions with these supports. The solid solution/spinel and the strongly interacted Co^{δ+} species induced the Co cations reduced at higher temperatures with obtaining the small Co particle sizes. These cases also significantly decreased the basicities of Co/MgO depending on calcined temperature and Co loadings, and increased the acidic sites of Co/SiO₂ and Co/H β with obtaining enhanced acidities, respectively. During hydrogenolysis processing, the basic sites of Co/MgO triggers the splitting of acyl C–O bond of methyl heptanoate to form heptanal and methanol, followed by further hydrogenation of heptanal to 1-heptanol. While the acidic Co/SiO₂ and Co/H β induce the cracking of ether C–O bond to heptanoic acid and CH₄. Heptanoic acid intermediate is then converted into C₆ and C₇ alkanes by the parallel decarbonylation and HDO pathways, respectively. The activity and product distribution could be facily mediated by the synergistic catalysis of metal and acid/base. Under optimal conditions, the maximal 1-heptanol and summed C₆/C₇ alkanes yields of 55% and 89% were observed over Co/MgO and Co/SiO₂ with desire Co loadings, respectively, indicating the promising applications of these catalysts in hydrogenolysis of vegetable oils.

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1. Introduction

As a unique and renewable carbon resource, vegetable oils could be effectively converted into diversified chemicals used in fine chemical industries as surfactants and plasticizers [1] and hydrocarbon fuels for sustaining our society development as fossil energy replacement [2,3]. Production of these biomass derived chemicals and fuels is considered to significantly diminish negative impacts on environment, due to that biomass hardly contains sulfur and presents the property of CO₂-neutral (CO₂ released during biomass utilization can be used for biomass growth in the next cycle) [4].

Aliphatic alcohols with long carbon chains could be produced by hydrogenolysis of fatty esters obtained via transesterification

of vegetable oils [5]. Cu–Cr catalyst was proven to be effective for this processing under severe reaction conditions of high temperatures and H₂ pressures [6]. However, the use of toxic Cr is currently discouraged and the severe reaction conditions are undesirable. Thus, exploring the catalysts without Cr to produce higher alcohols above mentioned under mild reaction conditions is of practical importance. The present catalysts used mainly focus on the supported noble metals Ru [7–9], Rh [8] and Pt [10], and the transition metals Cu [11–13], Ni [14] and Co [15–17]. The pristine metals usually show low activities as well as selectivities due to parallel side reactions. As B, Sn, Mo, Mn, Fe oxide additives are introduced, the performance can be significantly improved owing to the partially oxidic additives promote activation of fatty ester as Lewis acid and accelerates its conversion to higher alcohols [18].

On the other hand, renewable hydrocarbon fuels could be also produced by catalytic hydrodeoxygenation (HDO) of vegetable oils and/or fatty esters as model compounds [19,20]. These hydrocarbon fuels hardly contain oxygen and unsaturated C–C bonds, which shows superior fuel properties of high chemical stability,

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high caloric value and complete compatibility with gas engine to biodiesels produced by transesterification of vegetable oils with methanol [21]. Catalysts for this processing mainly contain supported sulfided Mo and W modified by Co and Ni [22–24], noble metal Pt and Pd [25,26], transition metal Ni [27,28] and metal phosphide and carbide Ni₂P [29], Mo_xC [30] and NiMoP [31]. The sulfided catalysts showed high activity and stability in HDO of vegetable oils, but the sulfur contained agents are necessary during pretreatment of catalysts and HDO processing, which inevitably brings about sulfur contamination in final products. Metal phosphide and carbide presented high selectivity for diesel ranged hydrocarbons, however, the preparation procedures of catalysts are tedious and rigorous, and transformation of active phases were usually observed during HDO of vegetable oils, leading to the limited lifetimes of such kind catalysts.

For hydrogenolysis and HDO of vegetable oils to higher alcohols and hydrocarbon fuels, acid–base properties of support played the essential role in mediating activity and product selectivity [27,32]. For example, catalysts with strong acidities showed severe cracking C₁–C₄ alkanes [27], while those with basicities have the high selectivity to heavy alkanes with carbon number of more than 35 due to significant ketonization coupling of fatty acid intermediates [32]. Co catalysts show promising performance in diversified hydrogenation/hydrogenolysis reactions. Using supported Co catalysts with mediated acid–base properties for selective conversion of vegetable oils into chemicals and hydrocarbon fuels is of scientific importance, but this is seldom reported in literature.

In this work, we prepared Co supported on basic MgO, neutral SiO₂ and acidic H β catalysts by incipient wetness impregnation and characterized their physical chemical properties by XRD, BET, H₂-TPR, CO₂/NH₃-TPD, H₂-chemisorption and TPSR techniques. The performance of supported Co catalysts were compared in hydrogenolysis of methyl heptanoate (the model compound of vegetable oils) to 1-hetpanol and hydrocarbon fuels and the hydrogenolysis pathways were discussed based on the acid–base properties of catalysts.

2. Experimental

2.1. Catalyst preparation

MgO was obtained from Aldrich Chemicals Co. Ltd., SiO₂ was gained from Aladdin Chemicals Co. Ltd. for SiO₂ and H β (Si/Al = 25) was got by Tianjin Nankai Catalyst Company. The analytical graded chemicals including Co(NO₃)₂·6H₂O, methyl heptanoate, n-hexadecane, cumene, heptanoic acid, heptanal, 1-heptanol, heptyl heptanoate, methanol, heptane, hexane and methyl acetate were purchased from Aldrich Chemicals Co. Ltd. and used without further purification.

The supported Co catalysts were prepared by incipient wetness impregnation. Co(NO₃)₂·6H₂O was dissolved in aqueous solution with the concentration of 0.1 M and a certain amount of support was added to gain a desire Co loading by weight. The resultant suspension was stirred for 10 h at ambient temperature, followed by evaporating excessive water at 353 K. The solid remained was dried at 393 K and calcined at a certain temperature for 4 h in air (for Co/SiO₂ and Co/H β , the calcined temperature was fixed at 823 K). For Co supported on MgO, a second Co impregnation was implemented by the similar procedure mentioned above. The 10%Co/MgO was calcined at 1273 K and then used as support for the sequential impregnation with different Co loadings, followed by drying at 393 K and calcining at 823 K for 4 h. All the samples were reduced at 823 K for 2 h under H₂ flow before reaction.

2.2. Catalyst characterization

XRD patterns of catalysts were obtained with using X'pert PRO MPD diffract meter (PANalytical) operated at 40 kV and 40 mA with a Cu K α ($\lambda = 0.15406$ nm) radiation. BET surface, external surface and mesoporosity of catalysts were determined by the adsorption-desorption behavior of N₂ at 77 K using a Micrometrics ASAP-2010 automated system. H₂-TPR, CO₂-TPD and NH₃-TPD experiments were carried out in a home-made instrument equipped with a thermal conductivity detector (TCD). For H₂-TPR analysis, the samples were pretreated at 673 K for 0.5 h under N₂ flow. The samples were cooled down to room temperature and then programmed to 1273 K at a ramp of 10 K/min under 5%H₂/N₂. For CO₂-TPD measurements of Co/MgO, the samples were pretreated at 823 K for 2 h, cooled down to 323 K in He and absorbed by CO₂. The CO₂ absorbed catalysts were purged by He at the same temperature to remove the physically absorbed CO₂. The samples were then heated from 323 K to 823 K at the rate of 10 K/min in He. The NH₃-TPD measurements of Co/SiO₂ and Co/H β were similar to the CO₂-TPD procedure while with the absorbing and purging temperature maintained at 393 K and the final temperature was set at 900 K. H₂-chemisorption measurements were tested with using a Quantachrome-ASIQACIV200-2 automated gas sorption analyzer. The catalysts were reduced at 823 K for 2 h under flow H₂. After reduction, the samples were further heated to 873 K in He to clean the catalyst surface, and then were cooled down to 323 K for H₂-chemisorption tests. The TPSR measurements of methyl acetate were carried out on a ChemBet Pulsar instrument (Quantachrome, USA) equipped with a mass spectrometer (Ametek DYCORLC-D200, USA). The samples were reduced at 823 K for 2 h under H₂ and were cooled down to ambient temperature for absorbing methyl acetate until saturation and then were purged by He for 0.5 h. The samples were heated to 750 K at 12 K/min under a H₂ flow of 40 ml/min.

2.3. Hydrogenolysis of methyl heptanoate

Hydrogenolysis of methyl heptanoate was conducted in a 100 ml stainless steel autoclave with a Teflon inner and a mechanical stirring. Typically, a mixture of 0.5 g methyl heptanoate dissolved in 20 g n-hexadecane was loaded into the autoclave, followed by adding 0.15 g of freshly reduced catalyst. Before reaction, the system was flushed by N₂ to remove air residue and was pressurized to 3 MPa of H₂, which was then heated to 493 K and kept at this temperature for a certain time. The liquid products of different periods were obtained via a sampling valve and the gas product was collected by a sampling bag as reaction ended and cooled down to room temperature.

The liquid product were identified by GC-MS and quantified by a gas chromatography (Agilent 6890) with a FID detector and a capillary column (INNOWax, 30 m \times 0.32 mm \times 0.25 μ m) with using cumene as the internal standard. The gas products were qualified by a GC 9800 chromatography equipped with a FID and a packed column (Porapak-Q column, 3 m \times 3 mm) for C₁–C₄ alkanes and another GC 9800 equipped with a TCD and a packed column (TDX-01 column, 3 m \times 3 mm) for CO, CO₂ and CH₄.

Conversion of methyl heptanoate (X_A) and selectivity of product i (S_i) are defined as:

$$X_A = \frac{C_0 - C_t}{C_0} \times 100\%$$

$$S_i(\text{C - mol. \%}) = \frac{n_i * a_i}{(C_0 - C_t) * 8} \times 100\%$$

Here, C_0 refers to the initial concentration of methyl heptanoate and C_t means the concentration of final methyl heptanoate after

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