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The Role of Hydrotalcite-modified Porous Alumina Spheres in

Bimetallic RuPd Catalysts for Selective Hydrogenation

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Abstract

By utilizing alumina previously modified by *in-situ* growth of varying amounts of hydrotalcites, a series of heterogeneous bimetallic catalysts with constant low loading (0.3 wt%) and identical Ru:Pd ratio (1:1) were prepared based on co-impregnation for selective hydrogenation of dimethyl terephthalate dimethyl to cyclohexane-1,4-dicarboxylate. Nanoparticles confined in the reticular structure were observed. The resulting candidates show the superior catalytic activity over that supported on the unmodified alumina, and reach the highest in the optimized sample RuPd/HT_C-Al₂O₃-1. This promotion and optimization effect could be ascribed to the improved dispersion and more supply of hydrogen and acid sites especially with medium strength.

Keywords: supported bimetallic catalysts, layered double hydroxides, selective hydrogenation, dimethyl terephthalte, dimethyl cyclohexane-1,4-dicarboxylate.

1. Introduction

Dimethyl cyclohexane-1.4-dicarboxylate (DMCD) is one important polymer modification and prerequisite intermediate in the process of dimethyl terephthalte (DMT) to 1,4-cyclohexanedimethanol (CHDM), one preferred linker candidate for highly valued polyester paints and resins, (Scheme 1) [1]. Industrially, DMCD production is carried out from DMT selective hydrogenation by sole precious Pd catalysts with high loadings under the H₂ pressure range (30-48 MPa) and reaction temperature region (160-180 °C). Hence, taking into the more severe supply of scarce sources, various alternatives have been proposed for cutting the cost and maximizing the catalytic efficiency [2-4]. For example, Pd nanoparticles with low loading (0.3 wt%) and high dispersion were reported as one promising candidate [2]; also, the low-cost metal Ru was held as one potential case [3-4].

Historically, bimetallic catalysts have attracted continuous attention potentially for the fascinating synergistic effect [5-9]; however, heterogeneous ones are generally prepared by co-impregnation of precursors containing metal elements followed by prevalent calcinations and reductions. Thus, the resulting properties are normally not satisfying for the poor reproducibility and fragile immobilization. The typical facts are partial aggregation, sintering, unevenness and leaching of particles frequently happening in preparation and applications especially for highly exothermic reactions. Accordingly, kinds of additional organic stabilizers or capping agents were employed for some essential protection of dispersed particles [10-13]; unfortunately, they are very susceptible to thermal treatments, and not gratifying from the view of "green"

synthesis [14]. Thus, it remains one challenge to build potential candidates with desirable dispersion for practical applications.

Recently, layered double hydroxides (LDHs), generally known as one class of anionic clays with brucite-like structure where cations in layer and anions in hydrated interlayer gallery can be tuned, have been of much interest [15-21]. Their distinctive flexibility offers one access to fabricate novel carriers, catalyst or relevant precursors with regulated composition, tailored structure, controlled active sites and desired properties [17-19]. For instance, by coordinating compounds with LDHs surface, Kohki et al. [18] fabricated one robust RuMnMn system with uniform composition and distribution. Recent studies reported the promotion effect of stable hydrotalcite platelets on catalytic performances in heterogeneous fields [2,20-21]. Therefore, by taking advantages of these merits, it would be one desirable strategy to immobilize bimetallic cases with high dispersion.

Here, inspired by the phenomenon that species at the perimeter of nanoparticles could strongly anchor or immobilize metal sites escaping from migration across the surface, agglomerating or coalescencing for large particles [22], *in-situ* modification by varying amounts of MgAl-LDHs was previously implemented on the surface and in the pores of θ -Al₂O₃, leading to the tailored reticular morphologies constructed by cross stacking and oriented growing of platelets; and consequently, RuPd samples with high dispersions were obtained by co-impregnation. Also, one reference with same loadings of Ru and Pd was prepared by utilizing the unmodified θ -Al₂O₃. And, for insights into the support influence, DMT selective hydrogenation tests and several

characterizations were adopted.

2. Experimental

2.1. Preparation of modified porous alumina spheres

The porous θ -Al₂O₃ spheres with purity of 99.5% and an average particle size of 20-40 mesh, previously synthesized in our laboratory, were modified by *in-situ* growth [2,23-24]. According to Mg consumption amount (wt%), modified alumina was denoted as HT-Al₂O₃-0.5, HT-Al₂O₃-1, and HT-Al₂O₃-2, respectively. After calcinations (450 °C; 6 h), the terminal supports (marked as HT_C-Al₂O₃-0.5, HT_C-Al₂O₃-1, and HT_C-Al₂O₃-2, respectively) were obtained.

2.2 Preparation of Supported Bimetallic RuPd Catalysts

Bimetallic RuPd catalysts were prepared by co-impregnation. In each case, the total loading of two metals is 0.3 wt% and the Ru:Pd ratio is 1:1. In order for understanding the effect of metals-loading on catalytic reactivity, two referenced samples (Ref 1 and Ref 2) were synthesized with total metal amounts (0.2 wt% and 0.5 wt%, respectively) and the same Ru:Pd ratio 1:1 by using the pre-prepared support HT_{C} -Al₂O₃-1. More details including compositions and nomenclatures for identification in the remainder of this paper are listed in Table 1. In addition, prior to the liquid-phase reaction, each sample was pre-reduced by NaBH₄. Specific parameters are given in Supporting Information.

2.3. Characterization

ICP-AES, XRD, SEM, BET, HRTEM, H₂-TPR/TPD, NH₃-TPD, and CO chemisorptions were applied for comprehending composition, texture, structure, morphology and surface properties. Detailed parameters are given in Supporting Information.

2.4. Selective hydrogenation test

In each test, one starting material system consists of the reactant DMT (10 mmol), the solvent ethyl acetate (80 mL) and catalyst (0.50 g), and the condition is 180 °C and 8.0 MPa for 6 h, which has been confirmed as the optimal for this reaction in our previous experiments. The catalytic reactivity of each fresh case and its reusability is investigated. Specific operations are described in Supporting Information.

The terminal products were quantified by GC-2014C (Shimadzu). Consequently, the primary product is DMCD, and the main by-products are cyclohexanecarboxylate, methyl benzecarboxylate, and trace 4-methyl-1-methyl benzecarboxylate. The specific catalytic performances are expressed by following simplified equations:

$$C = (1 - \frac{R_{DMT}A_{DMT}}{R_{DMT}A_{DMT} + R_{DMCD}A_{DMCD} + \sum_{i=1}^{n} R_{i}A_{i}}) \times 100\%$$

$$S = \frac{R_{DMCD}A_{DMCD}}{R_{DMCD}A_{DMCD} + \sum_{i=1}^{n} R_{i}A_{i}} \times 100\%$$

$$Y = \frac{R_{DMCD}A_{DMCD}}{R_{DMT}A_{DMT} + R_{DMCD}A_{DMCD} + \sum_{i=1}^{n} R_{i}A_{i}} \times 100\%$$

Where *C* represents catalytic conversion of DMT (%), *S* catalytic selectivity toward DMCD (%), *Y* catalytic yield of DMCD (%), *i* a certain by-product, *R* the relative area rectifying factor, and *A* denotes area percentage determined by GC.

3. Results and Discussion

3.1. DMT Selective Hydrogenation

Table 2 lists the test results of bimetallic RuPd catalysts for selective hydrogenation of DMT to DMCD. Obviously, under the employed conditions, three RuPd/HT_C-Al₂O₃ catalysts with total metal loading 0.3 wt% and Ru:Pd ratio 1:1 exhibit the higher DMT conversion and DMCD yield than RuPd/Al₂O₃, while DMCD selectivity in each case runs at a high value (~96.0%). And, for RuPd/HT_C-Al₂O₃ catalysts, DMT conversion and DMCD yield follow this tendency:

$$RuPd/HT_{C}-Al_{2}O_{3}-1 > RuPd/HT_{C}-Al_{2}O_{3}-0.5 > RuPd/HT_{C}-Al_{2}O_{3}-2$$

Besides, as displayed in Fig. S1, bimetallic catalysts especially for RuPd/HT_C-Al₂O₃-1 behave the improved reusability, as compared with RuPd/Al₂O₃. Also, two designed reference samples with different total metal loading amounts were tested (Table 2). Under the employed reaction condition, Ref 1 with total metal loading 0.2 wt% shows the lower DMT conversion than RuPd/HT_C-Al₂O₃-1, while Ref 2 with total metal loading 0.5 wt% exhibits a similar DMT conversion to RuPd/HT_C-Al₂O₃-1. DMCD selectivity is well preserved for each reference case. In the following sections, RuPd/Al₂O₃, RuPd/HT_C-Al₂O₃-1 and RuPd/HT_C-Al₂O₃-2, as the typical samples, were given into consideration for understanding the reaction

results mentioned above.

Very recently, we have detailedly investigated the composition regulation of bimetallic RuPd catalysts supported on porous alumina spheres for selective hydrogenation of DMT to DMCD under various conditions; [25] and consequently, the results suggest that DMT conversion shows one volcano-type tendency, and reaches the highest value in the bimetallic sample with the Ru:Pd ratio 1:1, while DMCD selectivity is well preserved in each bimetallic case despite somewhat negative influence potentially derived from the progressive Ru introduction; and, under each condition, bimetallic RuPd catalysts show higher reactivity over monometallic Ru and Pd ones.

3.2. Compositional, Structural and Textural Features of Samples

ICP-AES (Table 1) gives the exact determinations of Ru, Pd and Mg loadings, which are very similar to the feeding amounts, indicting the fine composition control. As displayed in Fig. 1, the detected peaks (002), (111), (422) and (442) of θ -Al₂O₃ in each case imply the well-preserved θ -Al₂O₃ after various treatments; characteristic peaks (003) and (006) of LDHs, which appear in HT-Al₂O₃-1 and HT-Al₂O₃-2, and disappear in HT_C-Al₂O₃-1 and HT_C-Al₂O₃-2, reveal the successful growth and subsequent structural transformation of MgAl-LDHs in θ -Al₂O₃ [25-26]. Significantly, the stronger typical peaks of MgAl-LDHs in HT-Al₂O₃-2 than in HT-Al₂O₃-1 could indicate more formation of MgAl-LDHs in the former sample. And, no obvious peaks of Ru and Pd are detected in catalysts, which might be determined by low loadings.

The textural data (Table 3) show that the specific surface area and pore volume are higher for RuPd/HT_C-Al₂O₃ catalysts than for RuPd/Al₂O₃, and reach the highest value in RuPd/HT_C-Al₂O₃-1. These alterations could be rationalized by *in-situ* growth of MgAl-LDHs, which leads to the formation of mixed oxides with higher surface area after calcinations, and somewhat inevitable blocking, stacking or covering on the surface or in the pores especially for RuPd/HT_C-Al₂O₃-2 with more hydrotalcites [2,20-21]. Thus, the catalyst textures are improved and optimized by regulated supports, which might be beneficial for dispersed deposition of metal sites.

3.3. Morphology and Dispersion of Samples

SEM images (Fig. 2) show that, compared to the bare θ -Al₂O₃ and RuPd/Al₂O₃, staggered platelets are easily observed in RuPd/HT_C-Al₂O₃-1 and RuPd/HT_C-Al₂O₃-2, illustrating the more lush surface geography. HRTEM images (Fig. 3) show the situations of sphere-like nanoparticles in each case. It is noteworthy that the reticular grid where nanoparticles are located can be roughly distinguished, implying the confined migration and mobility of nanoparticles on the surface or across the pores, while this phenomenon is absence in RuPd/Al₂O₃. Relevant histograms show the more concentrated distributions in RuPd/HT_C-Al₂O₃-1 and RuPd/HT_C-Al₂O₃-2 especially for the former than in RuPd/Al₂O₃; also, the detected largest is ~7 nm for RuPd/HT_C-Al₂O₃ cases, while it is ~9 nm for RuPd/Al₂O₃. The quantitative results from CO chemisorptions (Table 1) show that the dispersion is higher for RuPd/HT_C-Al₂O₃ catalysts than for RuPd/Al₂O₃, and reaches the highest value in

RuPd/HT_C-Al₂O₃-1. These results suggest the improved dispersion especially in RuPd/HT_C-Al₂O₃-1, which would be helpful for high catalytic activity.

3.4. Hydrogen Reducibility, Desorption, and Surface Acid Properties of Samples

H₂-TPR interprets the interaction between metals and that of metals with supports from the standpoint of reducible behavior (Fig. S2). Compared to no obvious peaks in θ -Al₂O₃, two overlapped peaks in each RuPd case could be attributed to the continual reduction of binary sites with intimate interaction. The onset temperature moves toward a lower position in RuPd/HT_C-Al₂O₃-1 than in RuPd/Al₂O₃, suggesting the facilitated reduction probably brought by the high dispersion; however, it increases for RuPd/HT_C-Al₂O₃-2, implying the delayed reduction potentially due to the intensified interaction with supports. The hydrogen consumption amounts are 0.110, 0.099 and 0.081 mmol/g for RuPd/Al₂O₃, RuPd/HT_C-Al₂O₃-1 and RuPd/HT_C-Al₂O₃-2, respectively, which indicate the occurrence of gradual inhibition for hydrogen adsorption and migration on surface during reduction process. Utilizing the hydrotalcite-modified support may lead to the formation of local confined space where nanoparticles are positioned, which should be responsible for the limited supply of accessible surface for hydrogen overflowing toward support surface.

Based on H₂-TPD results (Table 4), RuPd/HT_C-Al₂O₃ catalysts behave the higher hydrogen desorption amounts than RuPd/Al₂O₃, and reach the highest one in RuPd/HT_C-Al₂O₃-1, which could be interpreted in terms of space supply for hydrogen chemisorptions and storages [27-29]. The analysis results of NH₃-TPD (Table 4)

reveal that improved NH₃ desorption behaviors including more acid sites especially with medium intensity occur in RuPd/HT_C-Al₂O₃ catalysts, and reach the optimal in RuPd/HT_C-Al₂O₃-1. With attention to the fact that more supply of hydrogen and acid sites especially with medium intensity is conducive to the superior reactivity [30-32], these results would offer some interpretations for the enhanced catalytic activity.

4. Conclusions

A series of bimetallic RuPd catalysts with constant loading of two metals (0.3 wt%) and identical Ru:Pd ratio (1:1) were prepared based on co-impregnation on hydrotalcite-modified alumina by *in-situ* growth of MgAl-LDHs with varying amounts. The obtained cases behaved the superior catalytic activity and improved reusability over the conventional one by unmodified alumina, and reached the highest in the optimized sample RuPd/HT_C-Al₂O₃-1 for DMT selective hydrogenation. Several measurements suggest that the contribution of designed samples especially for RuPd/HT_C-Al₂O₃-1 toward structural and morphological features, and surface properties should be responsible for catalytic reactivity enhancement.

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Appendix A. Supplementary data

Supporting Information to this article is included.

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Figure Captions

Scheme 1. The industrial two-step hydrogenation process of DMT to CHDM.

Fig. 1. Powder XRD diffractions of θ -Al₂O₃ (a), HT-Al₂O₃-1 (b), HT-Al₂O₃-2 (c),

 $HT_{C}-Al_{2}O_{3}-1$ (d), $HT_{C}-Al_{2}O_{3}-2$ (e), $RuPd/HT_{C}-Al_{2}O_{3}-1$ (f), $RuPd/HT_{C}-Al_{2}O_{3}-2$ (g) and $RuPd/Al_{2}O_{3}$ (h).

Fig. 2. Representative SEM images of θ -Al₂O₃ (a), RuPd/Al₂O₃ (b), RuPd/HT_C-Al₂O₃-1 (c) and RuPd/HT_C-Al₂O₃-2 (d).

Fig. 3. Representative HRTEM images of $RuPd/Al_2O_3$ (a), $RuPd/HT_C-Al_2O_3-1$ (c) and $RuPd/HT_C-Al_2O_3-2$ (e) after NaBH₄ pre-reduction. Corresponding distribution histograms are also included.





Figure 2



K K K

Figure 3



Table 1

Comula ^{\$}	Composition* (wt%)				\mathbf{D} is a second sec
Sample	Mg	Ru	Pd	Total ^{&}	Dispersion (%)
RuPd/Al ₂ O ₃	-	0.15	0.15	0.30	56.7
$RuPd/HT_C-Al_2O_3-1$	0.96	0.14	0.15	0.29	75.8
$RuPd/HT_C-Al_2O_3-2$	2.05	0.15	0.16	0.31	62.1
Ref 1	0.98	0.11	0.10	0.21	
Ref 2	1.02	0.24	0.26	0.50	

Compositions, nomenclatures and metal dispersion of the RuPd catalysts.

[§] Sample Ref 1 and Ref 2 were prepared using pre-prepared HT_C -Al₂O₃-1 as support.

* determined by ICP.

[&] the sum of Ru and Pd.

[#] calculated based on CO chemisorptions.

Table 2

Sample	DMT Conv / %	DMCD Sel / %	DMCD Yield / %	
RuPd/Al ₂ O ₃	88.3	96.1	84.9	
$RuPd/HT_{C}-Al_{2}O_{3}-0.5$	94.3	96.0	90.5	
RuPd/HT _C -Al ₂ O ₃ -1	99.6	96.1	95.7	
RuPd/HT _C -Al ₂ O ₃ -2	90.4	95.8	87.6	
Ref 1	89.7	95.3	85.5	
Ref 2	97.8	94.8	92.7	

Catalytic performances for DMT selective hydrogenation of the RuPd catalysts.

* Reaction conditions: H₂ pressure 8.0 MPa, temperature 180 °C, reaction time 6 h,

and further details are listed in Experimental section.

Table 3

Textural properties of samples.

	Specific	Most	Total
Sample	surface area	probable pore	pore volume
	(m ² / g)	size (nm)	(cc/g)
θ -Al ₂ O ₃	83.6	32.0	1.21
RuPd/Al ₂ O ₃	85.2	30.9	0.99
$RuPd/HT_{C}-Al_{2}O_{3}-1$	94.8	30.0	1.12
RuPd/HT _C -Al ₂ O ₃ -2	91.6	29.4	1.06

Table 4

	I TD*	MTD*	IITD*	Total Desorption	
Sample		MIK*		amount*	amount [#]
	/ %0	/ %0	/ %0	(mmol/g)	(mmol/g)
RuPd/Al ₂ O ₃	6.8	41.9	51.3	2.093	0.019
$RuPd/HT_{C}-Al_{2}O_{3}-1$	8.9	50.7	40.4	2.626	0.032
RuPd/HT _C -Al ₂ O ₃ -2	12.6	48.6	38.8	2.309	0.027

Desorption behaviors of hydrogen and NH₃ for concerned samples.

* calculated by NH₃-TPD, LTR denotes the lower temperature region than 200 °C,

MTR represents the moderate one between 200 °C and 400 °C, and HTR is the higher

one than 400 °C.

[#] determined by H₂-TPD.

Highlights

New heterogeneous RuPd catalysts with high dispersion were synthesized. Activity for DMT selective hydrogenation was promoted by modified supports. RuPd/HTC-Al2O3-1 showed the highest catalytic performances. Nanoparticles located in the reticular structure were detected. Contributions of structure, morphology and surface properties were considered.

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