Catalysis Today 164 (2011) 143–147

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Synthesis of *trans*-stilbene through the hydrogenation of diphenylacetylene

Takayuki Komatsu[a,*], Kaori Takagi[b], Ken-ichi Ozawa[a]

[a] *Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1-E1-10 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*
[b] *Department of Chemistry, Tokyo Institute of Technology, 2-12-1-E1-10 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

ARTICLE INFO

Article history:
Received 1 July 2010
Received in revised form 23 October 2010
Accepted 26 October 2010
Available online 3 December 2010

Keywords:
Stilbene
Zeolite
Selective hydrogenation
Intermetallic compound
Isomerization

ABSTRACT

Trans-stilbene (*trans*-ST) was produced through the hydrogenation of diphenylacetylene (DPA). Pd-based intermetallic compounds (IMCs) supported on silica were applied to the selective hydrogenation of DPA into *cis*- and *trans*-ST. Pd_3Bi/SiO_2 showed the highest selectivity to stilbenes without accelerating the deep hydrogenation into diphenylethane (DPE), after DPA was completely converted. Proton-type zeolites were examined for the isomerization of *cis*-ST, the main product in the hydrogenation of DPA, into *trans*-ST. H-USY zeolite partially exchanged with Na^+ ions gave the highest activity owing to the appropriate acid strength and enough space inside the pores for *cis*-ST to enter. The mixture of Pd_3Bi/SiO_2 and H-USY gave *trans*-ST yield of 74 mol% through the one-pot reaction of DPA. The isomerization rate was significantly retarded by coexisting DPA and DPE molecules.

1. Introduction

Liquid crystal displays have been widely used for various applications. *Trans*-ST is one of the raw materials for the syntheses of liquid crystal molecules. In addition, *trans*-ST and its derivatives are used for the production of dyes, pigments, fluorescent whitener, electro-luminescent display, and so on. *Trans*-ST is now produced from benzene derivatives through the coupling reactions, such as Grignard reaction and Wittig reaction. These reactions usually give *cis*-ST predominantly with *trans*-ST as a by-product. In this study, we take up a new route for the production of *trans*-ST through the hydrogenation of DPA as shown in Scheme 1. In this process, the catalyst should be selective both for the partial hydrogenation of a carbon–carbon triple bond into a double bond and the stereo-selective formation of *trans*-ST instead of *cis*-ST.

The purpose of this study is to obtain an effective catalyst for the formation of *trans*-ST directly from DPA or through the partial hydrogenation of DPA into *cis*-ST followed by the isomerization into *trans*-ST. We have studied on the catalytic properties of IMCs for the selective hydrogenation and found that IMC catalysts, CoGe [1], Ni_3Sn_2/SiO_2 [2], Ni_3Ge/MCM-41 [3], Pd_3Bi/SiO_2 [4], etc., are highly selective for the partial hydrogenation of acetylene into ethylene. The high selectivity of IMCs for the partial hydrogenation of acetylene has been reported also for PdGa, Pd_3Ga_7 [5] and NiZn [6]. Therefore, we applied Pd-based IMCs to retard the deep hydrogenation into DPE, routes (4) and (5) in Scheme 1, for the selective formation of stilbenes. As shown in Scheme 2, the molecule of *trans*-ST has a plane structure, whereas that of *cis*-ST has a bending one. Therefore, the second selectivity, the stereo-selective formation of *trans*-isomer, could be achieved by the shape selective catalysis inside the pores of zeolite.

2. Experimental

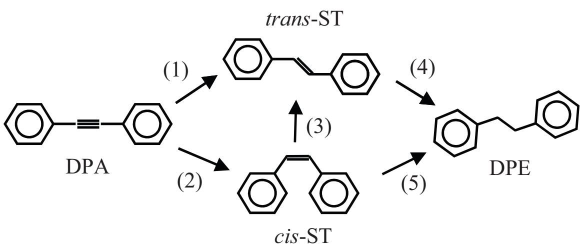
2.1. Catalyst preparation

Pd(3 wt%)/SiO_2 was prepared by a pore-filling impregnation method using an aqueous solution of $PdCl_2$ and silica gel (CARiACT G-6, Fuji Silysia). After drying the mixture at 403 K, it was reduced in flowing hydrogen at 823 K. Supported Pd-based IMC catalysts were prepared by a successive impregnation method onto Pd/SiO_2. Aqueous solutions of $Bi(NO_3)_3$, $Fe(NO_3)_3$, $TlNO_3$ were used to prepare Pd_3Bi/SiO_2, PdFe/SiO_2 and Pd_3Tl/SiO_2, respectively. Toluene solution of $Ga(acac)_3$ and benzene solution of $In(acac)_3$ were used to obtain Pd_5Ga_2/SiO_2 and PdIn/SiO_2. After the impregnation, they were reduced at 773 K (PdFe), 873 K (PdIn, Pd_3Tl), and 1073 K (Pd_3Bi, Pd_5Ga_2), respectively, to accelerate the solid-phase reaction into each IMC. Lindlar catalyst was purchased from Aldrich containing 5 wt% Pd on calcium carbonate with a small amount of lead. H-USY(Si/Al = 16) was supplied from Catalysts & Chemicals Ind. Na-Y (Y-30, Tosoh) was ion-exchanged with an aqueous solution of NH_4Cl and calcined in air at 743 K to obtain H(59%)-Y(2.9). H-ZSM-5(20), H-beta(12), H-MCM-22(19) and Al-MCM-41(19) were synthesized hydrothermally followed by the NH_4^+-exchange and calcination. H-USY was partially exchanged by Na^+ with aqueous

---

[*] Corresponding author. Tel.: +81 3 5734-3532; fax: +81 3 5734 2758.
E-mail address: komatsu@cms.titech.ac.jp (T. Komatsu).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.10.089



Scheme 1. Reaction paths in the hydrogenation of DPA.

solutions (2.4–100 mM) of NaCl at 298 or 343 K for 12–24 h to obtain Na^+-exchange levels of 12–74%.

2.2. Characterization

The crystal phases of IMC catalysts and zeolites were observed by powder X-ray diffraction (RINT 2400, Rigaku) with CuKα radiation. The bulk composition of prepared catalysts was determined by ICP (Rigaku, JY38) after dissolving samples with HF solution and aqua regia. TPD of adsorbed ammonia was measured by a flow system with a TCD detector. After dehydrating zeolite in flowing helium at 773 K, ammonia was introduced onto the sample at 423 K for 10 min. The sample was purged with flowing helium for 10 min and a TPD pattern was obtained from 298 to 1073 K at a heating rate of 10 K min^{-1}.

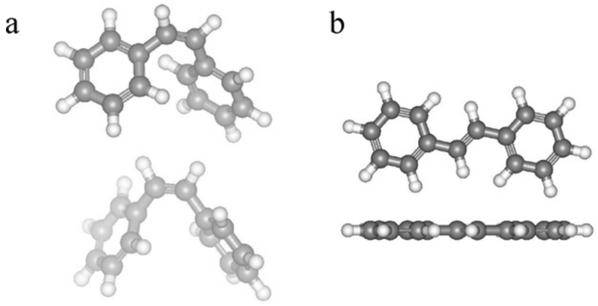
2.3. Catalytic reaction

The hydrogenation of DPA was carried out with a three-neck flask under atmospheric pressure of flowing H_2. The catalyst (0.10 or 0.50 g) was put into the flask and pretreated in situ with flowing H_2 at 673 K. After purging the flask by argon, DPA (1.0 g) dissolved in 5 ml of toluene was injected through a septum. The hydrogenation was started by flowing H_2 into the flask with agitating the reaction mixture. The isomerization of *cis*-ST was carried out with the same reaction system as that used for the hydrogenation. After the in situ pretreatment of catalyst in flowing argon at 673 K, the isomerization was started by injecting *cis*-ST (0.20 ml) diluted with 5 ml of toluene. Reaction products in both reactions were analyzed using an FID gas chromatograph (GC-14B, Shimadzu) with a column of TC-70 (0.25 mm × 60 m, GL Science).

3. Results and discussion

3.1. Direct hydrogenation of DPA into trans-ST

Direct hydrogenation of DPA into *trans*-ST, route (1) in Scheme 1, was examined with Pd-containing catalysts. Pd(0.7 wt%)/SiO_2 was first used to know the catalytic properties of Pd metal particles located on the support with relatively large pores. The hydrogenation occurred at 298 K to produce *cis*- and *trans*-ST and DPE. As shown in Table 1, DPA conversion was as high as 96% in 60 min of reaction. The main product was *cis*-ST, whereas the selectivity to *trans*-ST was only 2 mol%. Fig. 1 shows the change in DPA conversion and selectivity to each product with reaction time. When the conversion became closer to 100%, the selectivity to *cis*-ST decreased steeply, whereas that to DPE increased. DPA molecules would be adsorbed on the surface of Pd particles more strongly than *cis*-ST. When the residual amount of DPA becomes smaller at higher conversions, the adsorption of *cis*-ST would occur to be hydrogenated into DPE. The selectivity to *trans*-ST was always lower than 5 mol%. At the reaction time of 120 min, DPE was the only product. Then we carried out the reaction on Pd/zeolite catalysts, expecting the shape-selective catalysis in their micropores (Table 1). Though DPA conversion depended on the kind of zeolites, the selectivity to *trans*-ST was always lower than 15 mol%. When we extended the reaction time to obtain higher conversion, the selectivity to DPE increased to lower the selectivity to *cis*- and *trans*-ST as in the case of Pd/SiO_2 (Fig. 1). The prolonged reaction accelerated the deep hydrogenation into DPE, routes (4) and (5). Therefore, we concluded that it is difficult to obtain *trans*-ST with high selectivity through the direct hydrogenation with Pd/zeolite catalysts.



Scheme 2. Molecular structure of *cis*-ST (a) and *trans*-ST (b).

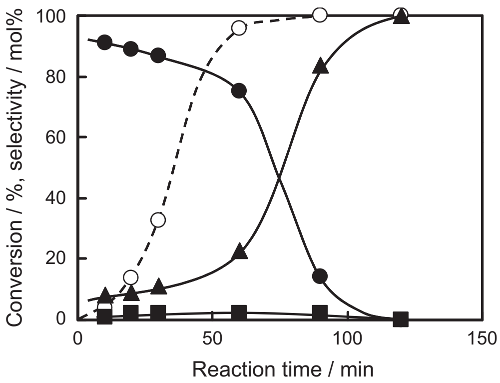


Fig. 1. Hydrogenation of DPA on Pd/SiO_2 at 298 K. DPA conversion (○), selectivity to *cis*-ST (●), *trans*-ST (■) and DPE (▲).

3.2. Selective hydrogenation of DPA into cis-ST

Next, we studied the formation of *trans*-ST through *cis*-ST by routes (2) and (3). At first, the hydrogenation of DPA into *cis*-ST, route (2), was examined on various Pd catalysts. To obtain *trans*-ST selectively, it must be important to retard the secondary hydrogenation of *cis*-ST into DPE. For this purpose, we used various Pd-based IMCs supported on SiO_2. XRD patterns showed that all the IMC catalysts gave their specific diffraction, indicating that they were composed of single-phase IMC particles supported on SiO_2. For example, Pd_3Bi/SiO_2 gave the main diffraction peaks at $2\theta = 38.2°$ and 41.0°, whereas the main peaks of Pd/SiO_2 appeared at 40.1° and 46.7°. Fig. 2 shows the change in the total selectivity to *cis*- and *trans*-ST with conversion at the reaction temperature of 333 K. The selectivity was almost 100 mol% when the conversion was low. The selectivity decreased significantly with increasing the conversion. Some IMC catalysts showed higher selectivity than Pd/SiO_2 and Lindlar catalyst at high DPA conversions. Among them, Pd_3Bi/SiO_2 gave the highest selectivity of 98 mol% at around 90% conversion. We have reported that this catalyst had exhibited the highest selectivity to ethylene in the hydrogenation of acetylene among Pd-based IMC catalysts [4].

The high selectivity of Pd_3Bi/SiO_2 for the partial hydrogenation of DPA at higher conversions was further confirmed by the reac-

Table 1
Hydrogenation of DPA[a] on Pd-supported catalysts.

Catalysts	Solvent	DPA conversion (%)	Selectivity (mol%)		
			cis-ST	*trans*-ST	DPE
Pd/SiO_2	Toluene	96	75	2	23
Pd/ZSM-5	Toluene	59	88	2	10
Pd/USY	Toluene	39	77	14	9
Pd/USY	THF	40	81	10	9
Pd/MCM-22	THF	17	79	14	7

[a] Reaction temperature: 298 K, reaction time: 60 min, catalyst weight: 0.10 g.

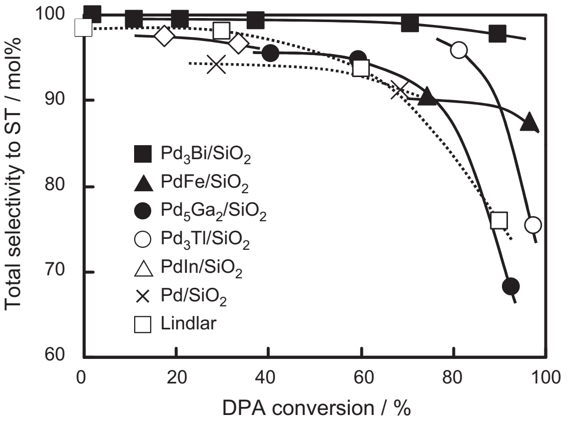


Fig. 2. Selectivity to stilbene in the hydrogenation of DPA on Pd-based catalysts at 333 K.

tion with the larger amount of catalyst (0.50 g) at higher reaction temperature (353 K). Fig. 3 shows that the conversion reached 100% at 210 min. However, the selectivity to DPE increased only slightly even after 210 min to be as low as 3 mol% at 300 min. It is revealed that Pd_3Bi/SiO_2 does not accelerate the secondary hydrogenation of *cis*- and *trans*-ST significantly even in the absence of DPA. This catalyst will be effective for the formation of *trans*-ST through the routes (2) and (3).

3.3. Isomerization of cis-ST into trans-ST

The isomerization of *cis*-ST, route (3), was next studied on acidic zeolites as catalysts. Though the photosensitized isomerization of stilbene has been studied using the stabilizing effect of zeolite pores [7,8], the catalytic isomerization of cis-ST has been reported for H-Y [9] and Ca-Y [10]. Fig. 4 shows the reaction results obtained at 333 K, the same temperature as that in the hydrogenation (Fig. 2), on various proton-type zeolites. On all the catalysts, only *trans*-ST was produced. It is clear that H-USY has the highest activity. The conversion of *cis*-ST reached 69% at the reaction time of 90 min. H-Y, however, gave the very low conversion compared with H-USY, suggesting that the weaker acid sites in H-Y are not effective for the isomerization. The very low conversion on Al-MCM-41 also indicates that the isomerization does not proceed on the weak acid sites. Though H-ZSM-5 and H-beta have stronger acid sites than H-USY, they showed lower conversion than H-USY. Their pore openings would be too small for the bending molecule of *cis*-ST to enter. The medium conversion observed on H-MCM-22 may result from the reaction in the cups on its external surface. Owing to the large pore diameter and the sufficient acid strength, H-USY would be the most effective catalyst for the isomerization of bulky *cis*-ST.

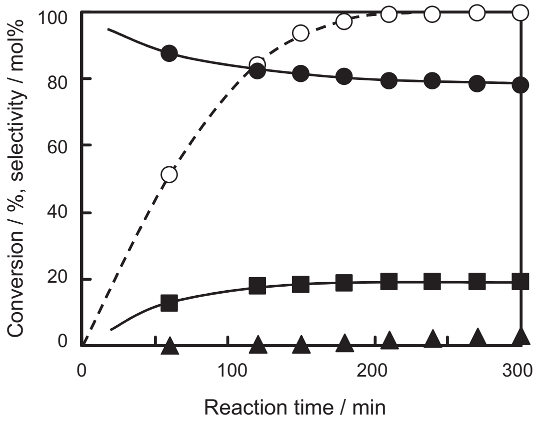


Fig. 3. Hydrogenation of DPA on Pd_3Bi/SiO_2 (0.50 g) at 353 K. Symbols are the same as those in Fig. 1.

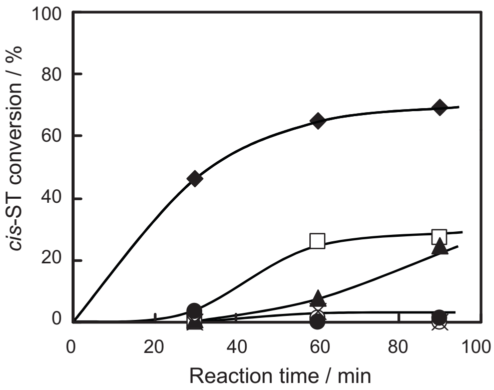


Fig. 4. Isomerization of *cis*-ST at 333 K on H-USY (♦), H-MCM-22 (□), H-beta (▲), H-Y (○), H-ZSM-5 (●) and Al-MCM-41 (×).

To clarify the role of Brønsted acid sites in H-USY, we prepared H-USY with various proton concentration by Na^+-exchange into H-USY. Fig. 5 shows the effect of Na^+-exchange level on the amount of acid sites and the conversion of *cis*-ST in the isomerization.

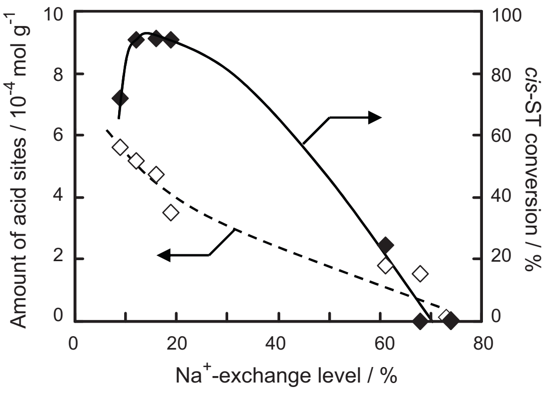


Fig. 5. Effect of Na^+-exchange on the amount of acid sites (◇) and *cis*-ST conversion in isomerization at 333 K (♦).

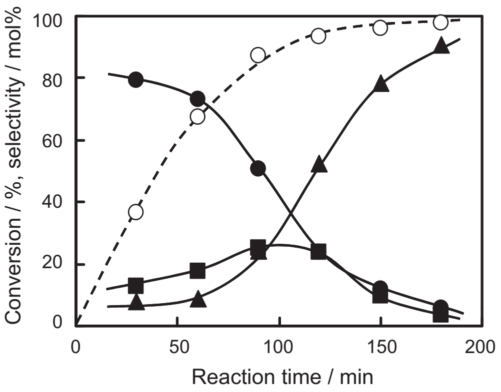


Fig. 6. One-pot reaction of DPA on the mixture of Pd-USY (0.10 g) and Na(16%), H-USY (0.50 g) at 333 K. Symbols are the same as those in Fig. 1.

The parent H-USY contained Na^+ with exchange level of 9%. The acid amount, measured by NH_3-TPD, decreased monotonously with increasing Na^+-exchange level and the acid sites which can adsorb NH_3 almost disappeared at 74% exchange level. On the other hand, a slight Na^+-exchange into the parent H-USY resulted in the increase in *cis*-ST conversion. The further Na^+-exchange decreased the conversion. The isomerization would be catalyzed by Brønsted acid sites though a small number of the strong acid sites may accelerate the oligomerization of ST resulting in the slight deactivation.

3.4. *One-pot formation of trans-ST via cis-ST*

In the hydrogenation of DPA (Table 1), Pd/USY gave *cis*-ST as the main product with selectivity of ca. 80 mol%. Then we added Na(16%), H-USY (0.50 g), having the highest activity for isomerization (Fig. 5), into Pd/USY (0.1 g) to accelerate the isomerization of primarily produced *cis*-ST for the one-pot formation of *trans*-ST from DPA. As shown in Fig. 6, the selectivity to *cis*-ST decreased with reaction time indicating the secondary reaction of *cis*-ST. However, the formation of DPE was mainly accelerated at higher conversion consuming *trans*-ST as well as *cis*-ST. The highest selectivity to *trans*-ST was only 29 mol%. To retard the secondary hydrogenation into DPE, Pd/USY was replaced by Pd_3Bi/SiO_2 (0.10 g) because of its high selectivity for the partial hydrogenation (Figs. 2 and 3). As shown in Fig. 7, *cis*-ST was the main product at the initial stage. With increasing reaction time, the selectivity to *cis*-ST decreased, whereas that to *trans*-ST increased. Though DPE formation was also observed, the isomerization of *cis*-ST was effectively accelerated by Na(16%), H-USY. The selectivity and yield of *trans*-ST reached 74 mol% through 450 min of one-pot reaction of DPA.

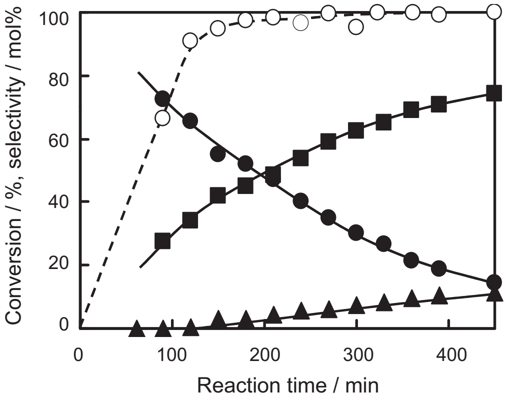


Fig. 7. One-pot reaction of DPA on the mixture of Pd_3Bi/SiO_2 (0.10 g) and Na(16%), H-USY (0.50 g) at 353 K. Symbols are the same as those in Fig. 1.

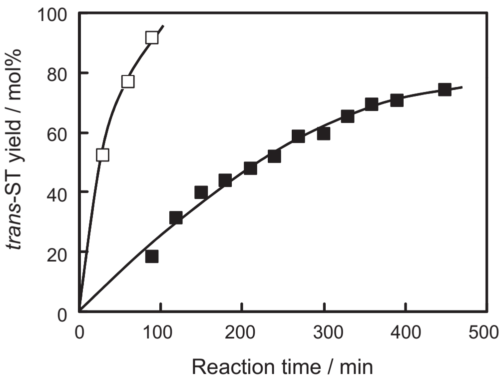


Fig. 8. Comparison between *trans*-ST yields in the isomerization of *cis*-ST (□) on Na(16%), H-USY (0.50 g) and the one-pot reaction of DPA (■) on the mixture of Pd_3Bi/SiO_2 (0.10 g) and Na(16%), H-USY (0.50 g) at 353 K.

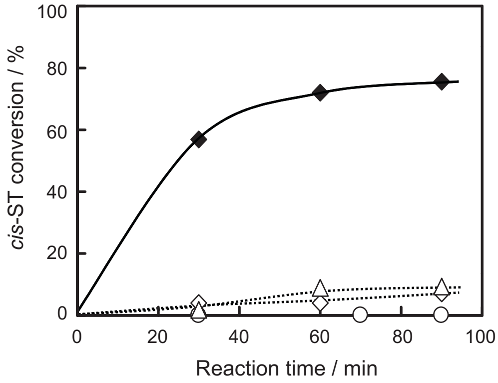


Fig. 9. Change in conversion in the isomerization of *cis*-ST without additive (♦), and with DPA (◊), DPE (○) and biphenyl (△) on Na(16%), H-USY at 333 K. Molar ratio of additive/*cis*-ST is 1.0.

Fig. 7 also indicates that the rate of hydrogenation was much higher than that of isomerization. The rate-determining step will be the isomerization of *cis*-ST. Fig. 8 shows the change in *trans*-ST yield with reaction time during the one-pot reaction of DPA (Fig. 7) and the isomerization of *cis*-ST at the same temperature of 353 K. Though we used the same amount (0.50 g) of Na(16%), H-USY for both reactions, the formation rate of *trans*-ST was much lower in the one-pot reaction. The co-existing DPA molecules may hinder the isomerization of *cis*-ST. We examined the effect of co-existing molecules on the rate of isomerization of *cis*-ST (Fig. 9). The addition of DPA with DPA/*cis*-ST molar ratio of 1.0 strongly retard the isomerization. The electronic effect of the triple bond in DPA molecule could affect the isomerization of *cis*-ST. However, the similar effect was observed when DPE or even biphenyl was added instead of DPA. The diffusion of *cis*-ST between supercages of USY may be hindered by these molecules. In the case of the one-pot reaction, therefore, the formation of DPE should be minimized to obtain *trans*-ST with higher reaction rate after DPA is completely converted into *cis*-ST.

4. Conclusions

The formation of *trans*-ST from DPA is achieved through the one-pot reaction consisting of the partial hydrogenation into *cis*-ST and the concomitant isomerization of *cis*-ST into *trans*-ST. The partial hydrogenation of DPA is catalyzed by Pd-based intermetallic compounds, such as Pd_3Bi/SiO_2, with high selectivity even after DPA is fully converted into *cis*- and *trans*-ST. The isomerization of *cis*-ST is effectively catalyzed by Brønsted acid sites of H-USY slightly exchanged with Na^+ ions. The acid strength and pore size of the Na^+-exchanged H-USY are appropriate for the isomerization. The yield of *trans*-ST exceeds 70 mol% through the one-pot reaction on the mixture of Pd_3Bi/SiO_2 and Na(16%), H-USY.

Acknowledgement

The authors would like to thank Dr. Masukawa for the valuable information and discussion on the application and analysis of *trans*-ST.

References

[1] T. Komatsu, M. Fukui, T. Yashima, Stud. Surf. Sci. Catal. 101 (1996) 1095.
[2] A. Onda, T. Komatsu, T. Yashima, J. Catal. 201 (2001) 13.
[3] T. Komatsu, T. Kishi, T. Gorai, J. Catal. 259 (2008) 174.
[4] T. Komatsu, T. Gorai, Abst. 14th Intern. Congr. Catal. OB31, Seoul, 2008, p. 69.
[5] J. Osswald, R. Giedigkeit, R.E. Jentoft, M. Armbrüster, F. Girgsdies, K. Kovnir, T. Ressler, Y. Grin, R. Schlögl, J. Catal. 258 (2008) 210.
[6] F. Studt, F. Abild-Pedersen, T. Bligaard, R.Z. Sørensen, C.H. Christensen, J.K. Nørskov, Science 320 (2008) 1320.
[7] A. Corma, V. Fornes, H. Garcia, M.A. Miranda, J. Primo, M.-J. Sabater, J. Am. Chem. Soc. 116 (1994) 2276.
[8] P.H. Laksminarasimhan, R.B. Sunoj, S. Karthikeyan, J. Chandrasekhar, L.J. Johnston, V. Ramamurthy, J. Photochem. Photobiol. A: Chem. 153 (2002) 41.
[9] M. Kojima, H. Takeya, Y. Kuriyama, S. Oishi, Chem. Lett. (1997) 997.
[10] K. Pitchumani, A. Joy, N. Prevost, V. Ramamurthy, Chem. Commun. (1997) 127.