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Author(s)	Fujita, Shin-ichiro; Yoshida, Hiroshi; Asai, Kouki et al.
Citation	The Journal of Supercritical Fluids, 60, 106-112 https://doi.org/10.1016/j.supflu.2011.02.016
Issue Date	2011-12
Doc URL	https://hdl.handle.net/2115/48154
Type	journal article
File Information	JSF60_106-112.pdf

Selective hydrogenation of nitrostyrene to aminostyrene over Pt/TiO_2 catalysts: Effects of pressurized carbon dioxide and catalyst preparation conditions

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Abstract

The present work has studied the influence of CO_2 pressurization on the hydrogenation of nitrostyrene (NS) using Pt/TiO_2. With CO_2 pressurization up to 12 MPa (CO_2-dissolved expanded liquid (CXL) phase), the over-all reaction rate and the selectivity to aminostyrene (AS) increased. At higher CO_2 pressures where all NB dissolved in scCO_2 (scCO_2-homogeneous phase), both of them decreased with increasing the CO_2 pressure. The phase behavior was an important factor for the present reaction system. It was also found that the presence of pressurized CO_2 gave higher selectivity to AS than in its absence at any conversion level. This was ascribed to retardation effects of dense phase CO_2 on the hydrogenation of AS to ethylaniline. Competitive adsorption of nitro and vinyl groups was suggested to determine the product selectivity. FTIR measurements showed that the pressurized CO_2 lowers the reactivity of the nitro group, and this effect is stronger in scCO_2-homogeneous phase than in CXL phase, resulting in the lower AS selectivity in the former phase. Lower Pt loadings and higher catalyst reduction temperatures gave Pt/TiO_2 catalysts more selective for the AS formation. FTIR measurements of adsorbed CO over the catalysts suggested that the presence of less-coordinated Pt atoms on edge, corner and kink sites was significant for the selective hydrogenation of NS to AS.

Keywords: carbon dioxide, hydrogenation, platinum catalyst, molecular interaction, SMSI.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is an attractive alternative to conventional organic solvents, due to its environmentally benign, non-toxic, and non-flammable nature, complete miscibility with gases, adjustable dissolving power, and easy separation from liquid/solid products after reactions [1-4]. In addition, $scCO_2$ can have several advantages, which are the absence of gas-liquid mass transfer limitations, relatively high rates of molecular diffusion and heat transfer, and the possibility of molecular interactions with the dissolved reacting species (substrates or catalysts). These can result in interesting effects of enhancing reaction rates and modifying product selectivity.

When a large quantity of substrates or solvents is used for reactions under pressurized CO_2, dissolution of CO_2 into the liquid phase causes an increase in the volume of the liquid phase. Such phases are called CO_2-expanded liquids (CXLs). The extent of expansion depends on the nature of the liquid used as well as CO_2 pressure and temperature. In recent years, several reviews demonstrated that CXLs are also promising reaction media [5-8]. Promotional features of CO_2 can also appear under CXL conditions. Dissolved CO_2 will facilitate the dissolution of other coexisting gases such as O_2, CO, or H_2, and hence may accelerate the reactions involving these gaseous reactants although CO_2 is not a reactant but rather a diluent. It can also interact with substrates and/or catalysts, resulting in the modification of the reaction selectivity. Co-exiting organic solvents in CXLs easily dissolve substrates and catalysts whose dissolution into $scCO_2$ is difficult. This would be another advantage of CXL compared to $scCO_2$.

The catalytic hydrogenation of nitrobenzenes is commonly used to manufacture anilines, which are important intermediates for polyurethanes, dyes, pharmaceuticals, explosives, and agricultural products. Industrially, the reaction is operated in gas phase with Cu or Ni catalysts using H_2 near or slightly above atmospheric pressure (0.1-0.5 MPa) at high temperatures around 523 K [9-13]. It can also be performed in the liquid phase by using supported metal catalysts (Pt, Pd, and Ni) and organic solvents with H_2 of higher pressures (1-4 MPa) at temperatures around 323 K [14-20]. However, these catalysts sometimes show low selectivity to anilines because of the formation of several poisonous reaction intermediates such as nitrosobenzenes, phenylhydroxyamines, azoxybenzenes, and azobenzenes whose formation and accumulation should be avoided for the green production of anilines. The present authors reported that, when the hydrogenation of nitrobenzene to aniline was carried out in/under pressurized CO_2, the selectivity to aniline was much higher than that obtained in conventional organic solvents [21-25]. The higher selectivity is ascribed to interactions of CO_2 with the substrate and the intermediates. When nitrobenzenes have another reducible group, their chemoselective hydrogenation to corresponding substituted anilines is another important issue. Corma et al. reported the selective hydrogenation of nitrostyrene to aminostyrene using TiO_2 supported metal catalysts in toluene [26,27]. For these catalysts, high-temperature reduction was required to obtain the high selectivity to aminostyrene [26]. This would sometimes cause lower hydrogenation activity because of strong support-metal interaction (SMSI).

The present authors studied the effects of pressurized CO_2 on the selective hydrogenation of α,β-unsaturated aldehydes (cinnamaldehyde and citral) to unsaturated alcohols [28-30], and the interactions of pressurized CO_2 with aldehyde compounds were also studied by in situ FT-IR spectroscopy and computational calculations [28,29,31,32]. Pressurized CO_2 enhanced the selectivites to the unsaturated alcohols, and this was ascribed to the interactions of CO_2 with the carbonyl C=O bond of the aldehydes; however, the interaction between CO_2 and the C=C bond was absent. On taking account of these results, in the case of nitrostyrene hydrogenation, pressurized CO_2 may interact with the vinyl and nitro groups of nitrostyrene in different modes, and hence may improve the overall reaction rate and/or the selectivity to aminostyrene. To our knowledge, no one has so far studied the influence of pressurized CO_2 on the title reaction. In the present work, this reaction was carried out with Pt/TiO_2 in the presence of pressurized CO_2. It has been shown that pressurized CO_2 improves the overall reaction rate and the selectivity to aminostyrene under CXL conditions. The influence of a few catalyst preparation conditions (Pt loading and the catalyst reduction temperature) on the reaction has also been examined.

2. Experimental

Pt/TiO_2 catalysts whose nominal Pt contents were 2.0, 1.0 and 0.5 wt.-% were prepared by impregnation of TiO_2 (JRC-TiO-4, supplied by the Catalyst Society of Japan) with aqueous solutions of H_2PtCl_6. TiO_2 was immersed in the solution of H_2PtCl_6, dried at 373 K for 5 h, and reduced with a hydrogen stream (4 vol.-%) diluted with nitrogen at 473 K for 3 h. The Pt loading was adjusted by changing the H_2PtCl_6 concentration. Two 0.5 wt.-% Pt/TiO_2 catalysts were also prepared by the H_2 reduction at 573 and 723 K. The Pt crystallite sizes of the catalysts prepared were measured by transmission electron microscopy (TEM).

The hydrogenation of 3-nitrostyrene (NS) was carried out in a 50 cm^3 autoclave. The reactor was charged with 0.5 cm^3 of NS (3.6 mmol) and 20 mg of the catalyst, purged with CO_2, and heated to 323 K by a water bath. Then, 4 MPa of H_2 was introduced into the reactor, followed by the introduction of compressed liquid CO_2 to the desired pressure with a high-pressure liquid pump. The reaction mixture was stirred with a magnetic stirrer for 1 h. After the reaction, the reactor was cooled below room temperature by ice-water and carefully depressurized. The reaction mixture was then analyzed by a gas chromatograph attached with a flame ionization detector using decane as an internal standard.

For investigating molecular interactions of CO_2 with NS, FTIR spectra of CO_2-dissolved NS liquid phase and those of NS dissolved in pressurized CO_2 were measured by ATR and transmission modes, respectively. The measurements were carried out by a FTIR spectrometer (JASCO FTIR-620) with a triglycine sulfate (TGS) detector at a wavenumber resolution of 2 cm^{-1} at 323 K. The ATR spectra were collected in an *in situ* high-pressure ATR cell (Fig. 1), which was made in cooperation with JASCO Co. It has an inner volume of 1.18 cm^3, and is attached with a ZnSe rod (3ϕ x 63 mm, 5-7 reflections). The temperature of the cell was controlled by a temperature controller and a heating jacket containing rod heaters. A small volume (about 1 cm^3) of NS was introduced into the cell and it was purged with CO_2 three times. The cell was heated up to 323 K. Then, the pressure was increased slowly by introduction of liquid CO_2 by a pressure pump while stirring by a Teflon coated magnetic stirrer. A spectrum of the empty cell was used as the background. The FTIR transmission spectra of NS dissolved in pressurized CO_2 were also measured with an *in situ* high pressure cell whose volume and optical path length were 1.5 cm^3 and 4 mm, respectively. The procedures for measurements in the transmission mode were given elsewhere [29,31].

Diffuse reflectance FTIR (DRIFT) spectra of CO adsorbed on the catalysts prepared were obtained with the same FTIR spectrometer to which an *in situ* diffuse reflectance instrument (JASCO DR-500H) was attached. The catalyst was set in the IR cell, reduced at 323 K with flowing H_2 at 0.1 MPa for 1 h, and cooled to ambient temperature in a He flow. Then, a spectrum of the catalyst was taken as the background, and a 4 vol.-% CO-He mixture was fed over the catalyst for 30 min. After the gaseous CO was purged with flowing He, a spectrum of the catalyst was collected.

Phase behavior of the reaction mixture was investigated by a 10 cm^3 high-pressure reactor attached with two sapphire windows in a similar way to previous works [24,25,29].

3. Results and discussion

Under the present reaction conditions, products observed for nitrostyrene (NS) hydrogenation over Pt/TiO_2 were aminostyrene (AS), ethylnitrobenzene (ENB), and ethylaniline (EA) (Scheme 1). The product distribution was changed by the reaction and catalyst preparation conditions.

3.1. Influence of pressurized CO_2

At first, the influence of pressurized CO_2 on the title reaction was investigated using 0.5 wt.% Pt/TiO_2 prepared by the reduction at 473 K. Table 1 lists the reaction results obtained without solvent and with $scCO_2$ (10 MPa), toluene or ethanol. Compared to the reaction under the neat condition, the reaction in toluene gave almost the same conversion of NS; however, the selectivity to AS obtained in toluene was lower. Although ethanol gave the highest conversion, the selectivity to AS obtained was not high. In contrast to these solvents, $scCO_2$ improved both the conversion and the selectivity.

Fig. 2 represents the influence of CO_2 pressure on the reaction. The conversion of NS was increased with increasing the CO_2 pressure up to 12 MPa; however, it was decreased with further increase of the pressure (Fig. 2a). To elucidate the reason for the pressure dependence, the states of NS liquid phase at different CO_2 pressures were visually investigated. The NS liquid phase gradually expanded with introducing CO_2, and the liquid-gas two phases transformed into a single phase at 13.5 MPa, revealing that NS was completely dissolved in CO_2 at the pressure where the decrease of the NS conversion was observed to start. Thus, the phase behavior was significant for the reaction. Under CXL conditions, dissolved CO_2 can promote the dissolution of H_2 into the liquid phase. This may be a possible reason for the increase of the NS conversion observed below 12 MPa. On the other hand, the decrease in the conversion above 13.5 MPa would be explained by simple dilution effects. Under the CXL conditions (solid-liquid-gas three-phase), the catalyst would exist in the liquid phase and, hence, the reaction would proceed in the liquid phase whose volume was below 1 cm^3. Above 13.5 MPa, the reaction mixture is solid-gas two-phase, and the reaction would proceed in the whole of the reactor (50 cm^3). Thus, the volume where the reaction proceeds and, consequently, the catalyst concentration therein are significantly changed at the pressure around 13.5 MPa. This would be the reason for the decline of the conversion. The product distribution was also affected by the CO_2 pressurization (Fig. 2b). The selectivity to AS was increased slightly with increasing CO_2 pressure up to 10 MPa. Above this pressure, the selectivity to AS decreased. In a reverse manner, the selectivity to ENB increased in the higher CO_2 pressure region. The selectivity to EA was decreased by the presence of CO_2, but it was not changed by the CO_2 pressure. The gas-liquid-solid three-phase system gave higher selectivity to AS than in the neat reaction, but the gas-solid two-phase system did not. Thus, the CXL conditions are better than $scCO_2$ homogeneous conditions for the selective hydrogenation of NS to AS.

The relationship between the NS conversion and the product selectivity was investigated by carrying out the reaction for various periods of time in the presence of 10 MPa CO_2 (Fig. 3). The selectivity to AS did not change in the whole range of conversion, while that to EA increased in compensation for the decrease of the ENB selectivity with increasing the conversion. These results show that NS is hydrogenated to AS and ENB, and ENB is further hydrogenated to the final product of EA but AS is not. Similar results were obtained in the absence of pressurized CO_2; however, slight decrease in the AS selectivity was observed at conversions above 70% (Fig. 4). The selectivity to EA was slightly higher than the one expected from the decrease in the ENB selectivity, revealing that a part of AS formed was further hydrogenated to EA. The decrease in the selectivity to AS was not observed in the presence of CO_2 (Fig. 3). According to Scheme 1, these results suggest that CO_2 retards the further hydrogenation of AS to EA. To confirm this, the hydrogenation of AS was carried out. As shown in Table 2, the conversion of AS was decreased about one forth by pressurizing the reaction system by CO_2. Thus, one can conclude that pressurized CO_2 suppresses the hydrogenation of AS, resulting in the higher selectivity to AS at high conversion levels. Thus, the presence of pressurized CO_2 again improves the selectivity to the desired product of AS under CXL conditions.

To study the reactivities of vinyl and nitro groups of NS separately, reaction runs were also conducted using nitrobenzene (NB), styrene (ST) or an equimolar mixture of them (Table 3). When pure NB was used as the substrate (entries 1-4), the conversion of NB increased with increasing CO_2 pressure up to 10 MPa. But it decreased at 12 MPa where the reaction mixture changed from solid-liquid-gas three phases to solid-gas two phases. These results consist with those in the previous work on the hydrogenation of NB with Ni/Al_2O_3 [24]. In contrast to the reaction with NB, when pure ST was used as the substrate (entries 5-7), the conversion simply declined with increasing the CO_2 pressure. It is also seen that the conversion of ST was much larger than that of NB irrespective of the presence and the absence of pressurized CO_2, strongly suggesting that the reactivity of the vinyl group of ST is much higher than the nitro group of NB. When the substrate was changed from ST alone to the mixture of ST and NB (entries 8-10), the conversion of ST was lowered, while such decrease in the NB conversion by ST was not observed. These results suggest that NB retards the hydrogenation of ST by competitive adsorption on Pt/TiO_2. Probably, in the course of the hydrogenation of NS, the nitro group of NS would preferentially be adsorbed on the catalyst surface, resulting in the selective hydrogenation of the nitro group.

Interactions of pressurized CO_2 with the substrate of NS were investigated by FTIR. The NS liquid phase in the absence of pressurized CO_2 exhibited three absorption bands at 1347, 1525, 1633 cm^{-1}. The former two bands can be assigned to symmetric and asymmetric stretching bands of the nitro group of NS, respectively, and the last one is assignable to the C=C stretching band of the vinyl group. When the NS liquid phase was pressurized with CO_2 (CXL conditions), the peak positions of the absorption bands of the nitro group blue-shifted. The blue-shift became slightly larger as the CO_2 pressure was increased (Fig. 5). On the other hand, no shift by the CO_2 pressurization was observed for the peak position of the band of the vinyl group. FTIR measurements were also done for NS gas phase and that dissolved in pressurized CO_2. The gas phase NS showed the two absorption bands of the nitro group at 1349 and 1530 cm^{-1} and the one of the vinyl group at 1636 cm^{-1}. The peak positions of the former two bands again blue-shifted respectively to 1357 and 1547 cm^{-1}, when NS was dissolved in CO_2 at 6 MPa (Fig. 5). At higher pressures, these two bands red-shifted but only marginally. Thus, the extent of the blue-shift for NS dissolved in dense CO_2 was larger than that for NS in the CXL conditions. No shift was observed for the band of the vinyl group. Based on these results, one can conclude that pressurized CO_2 interacts only with the nitro group of NS, and the interaction is stronger in dense CO_2 phase than in CXL phase. The interaction may occur between the oxygen atom of NS and the carbon atom of CO_2 and between the nitrogen atom of NS and the oxygen atom of CO_2. The blue-shift observed for the bands of the nitro group should mean that the reactivity of NO bond is lowered [33]. The absence of the peak shift for the C=C bond suggests that the reactivity of the vinyl group is unchanged by the presence of pressurized CO_2. Thus, the interaction between CO_2 and the nitro group should explain the lower AS selectivity at higher CO_2 pressures where all the substrate of NS was dissolved in dense phase CO_2 (Fig. 2). Under such conditions, the reactivity of the nitro group would be much lowered by pressurized CO_2 compared with that of the vinyl group, resulting in the lower AS selectivity.

3.2. Influence of Pt loading and catalyst reduction temperature

Effects of Pt loading and the catalyst reduction temperature on the catalytic performance of Pt/TiO_2 were also investigated for the reaction in the presence of 10 MPa CO_2. Table 4 presents the average crystallite sizes of Pt on the catalysts prepared by the reduction at 473 K with different Pt loadings and the reaction results obtained with them. With increasing the Pt loading, the Pt crystallite size was slightly increased and the activity of the catalyst was enhanced, as expected. The reaction selectivity was also changed by the Pt loading. The catalyst with higher Pt loading showed lower AS selectivity. The selectivity to AS was only 34% with 2.0 wt.-% Pt/TiO_2, and this low selectivity was unchanged even at a lower conversion (entries 3, 4).

Fig. 6 illustrates FTIR spectra of adsorbed CO over the catalysts with different Pt loadings. Over 0.5 wt.-% Pt/TiO_2 catalyst (spectrum a), the spectrum displayed an absorption band at 2065 cm^{-1}, revealing the presence of Pt atoms on edge sites [34-38]. The shape of this band was asymmetry toward the lower wavenumber side, suggesting the presence of another band around 2035 cm^{-1}, which could be assigned to CO adsorbed on corner and/or kink sites [36-38]. In addition to these bands, the one of bridge-type adsorbed CO was observed at 1845 cm^{-1} (not shown). The increase in the Pt loading resulted in the appearance of a band at 2125 cm^{-1} and of a shoulder one at 2088 cm^{-1} (spectra b and c). The latter band was assigned to CO adsorbed on Pt atoms on terrace sites [34-38], while the former one was ascribable to CO adsorbed on oxidized Pt atoms [35,39]. These observations showed that increasing the Pt loading caused the decrease in the relative quantity of unsaturated Pt atoms on edge and corner sites over Pt/TiO_2.

Combining the results of the reaction experiments and those of the FTIR measurements, it is strongly suggested that the higher selectivity of 0.5 wt.-% Pt/TiO_2 for AS formation results from the larger relative quantity of less-coordinated Pt atoms on edge, corner and kink sites. Such Pt sites were previously proposed to be the active sites for the selective hydrogenation of NS to AS by Corma et al. who carried out the NS hydrogenation using several Pt/Al_2O_3 catalysts of different Pt loadings and measured FTIR spectra of adsorbed CO over them [26]. Probably, the hydrogenation of the nitro group would preferentially proceed on such less-coordinated Pt sites as edge, corner, and kink, whereas that of the vinyl group would occur on the terrace sites.

Table 5 compares the reaction results obtained with three 0.5 wt.-% Pt/TiO_2 prepared by the H_2 reduction at different temperatures. The catalysts reduced at higher temperatures instead of 473 K showed better selectivity for the AS formation, although their activities were lower. The catalyst reduced at 723 K gave the AS selectivity of 94%. Probably, the relative activities of the nitro and the vinyl groups depended on the catalyst reduction temperature. To confirm this, the hydrogenation of equimolar mixture of NB and ST was again carried out using those catalysts (Fig. 7). The conversions of both NB and ST declined over the catalysts reduced at higher temperatures. But, the extent of the decrease in the conversion was much larger for ST that for NB. The activity of the catalyst reduced at 723 K was marginal for the hydrogenation of ST. Therefore, one can say that the reduction at higher temperature makes the catalyst more selective for the hydrogenation of the nitro group of NS.

FTIR spectra of adsorbed CO over the catalysts reduced at 573 and 723 K revealed the absence of bridge-type adsorbed CO, which was observed at 1845 cm^{-1} over the catalyst reduced at 473 K (Fig. 8). It is well known that partially reduced TiO_2 (TiO_x) decorates metal surface when TiO_2 supported metal catalysts are reduced at high temperatures. In the cases of Pt/TiO_2, the decoration of TiO_x preferentially occurs over Pt crystallite terrace sites where bridge-type adsorbed CO is formed [40,41]. This would be the reason of the disappearance of bridge-type adsorbed CO by the high temperature reduction. Hence, in conformity with the results for the influence of Pt loading on the reaction, the larger relative quantity of less-coordinated Pt atoms would again be the possible reason for the higher selectivity to AS observed over the catalysts reduced at the higher temperatures.

4. Conclusions

In the present work, the hydrogenation of NS was carried out with Pt/TiO_2 in the presence of pressurized CO_2. Phase behavior was significant for the reaction. Pressurized CO_2 enhanced the overall reaction rate and the selectivity to AS under CXL conditions. On the other hand, lower selectivity to AS was obtained under the conditions where all NS was dissolved in $scCO_2$. This lower selectivity was ascribed to stronger interaction between CO_2 molecule and the nitro group of NS, which lowered the reactivity of the nitro group. It was also found that pressurized CO_2 retarded the hydrogenation of AS to EA, resulting in the higher selectivity to AS in the presence of pressurized CO_2 than in its absence at any conversion level. Competitive adsorption of nitro and vinyl groups was also suggested to determine the product selectivity. Lower Pt loadings and higher catalyst reduction temperatures gave Pt/TiO_2 catalysts more selective for the AS formation. FTIR measurements of adsorbed CO over the catalysts suggested that the presence of less-coordinated Pt atoms on edge, corner and kink sites was significant for the selective hydrogenation of NS to AS.

The combination of the dense phase CO_2 and the surface-tailored Pt catalyst is very effective for the selective hydrogenation of NS to AS and would be promising for the selective transformations of substrates with two or more functional groups.

Acknowledgement

This work was supported by the Japan Society for the Promotion of Scienec (JSPS) with Grant-in-Aid for Scientific Research (B) 22360327 and also by JSPS and CAS (Chinese Academy of Science) under the Japan-China Research Cooperative Program. The authors express sincere thanks to Prof. F. Zhao of Changchun Institute of Applied Chemistry for TEM measurements.

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Captions for Tables, Scheme and Figures.

Table 1 Influence of solvents on the hydrogenation of NS with Pt/TiO_2.

Table 2 Influence of CO_2 pressure on the hydrogenation of AS to EA with Pt/TiO_2.

Table 3 Hydrogenation of ST, NB and an equimolar mixture of them with Pt/TiO_2.

Table 4 Influence of Pt loading and reduction temperature on the performance of Pt/TiO_2 for the hydrogenation of NS.

Table 5 Influence of reduction temperature on the performance of 0.5 wt.-% Pt/TiO_2 for the hydrogenation of NS.

Scheme 1. Hydrogenation of nitrostyrene.

Fig. 1. A diagram for high-pressure in situ ATR cell.

Fig. 2. Influence of CO_2 pressure on (a) the conversion of NS and (b) the product distribution. Reaction conditions were the same as those for Table 1 except for CO_2 pressure.

Fig. 3. Relationship between the product distribution and the conversion of NS under pressurized CO_2. Reaction conditions: NS, 3.6 mmol; 0.5 wt.% Pt/TiO_2, 20 mg; H_2, 4 MPa; CO_2, 10 MPa; temperature, 323 K.

Fig. 4. Influence of CO_2 on the relationship between NS conversion and AS selectivity. Reaction conditions: NS, 3.6 mmol; 0.5 wt.% Pt/TiO_2, 20 mg; H_2, 4 MPa; temperature, 323 K.

Fig. 5. Peak-shifts of symmetric (circles) and asymmetric (squares) NO_2 stretching bands by CO_2 pressurization in liquid (closed symbols) and gas (open symbols) phases at 323 K.

Fig. 6. FTIR spectra of adsorbed CO over (a) 0.5, (b) 1.0, and (c) 2.0 wt.-% Pt/TiO_2.

Fig. 7. Hydrogenation of equimolar mixture of NB and ST with Pt/TiO_2 reduced at different temperatures. Open and closed symbols represent the conversions of NB and ST, respectively. Reaction conditions: NB, 2.45 mmol; ST, 2.45 mmol; 0.5 wt.% Pt/TiO_2, 20 mg; H_2, 4 MPa; CO_2, 10 MPa; temperature, 323 K; time, 10 min.

Fig. 8. FTIR spectra of adsorbed CO over 0.5 wt.-% Pt/TiO_2 reduced at (a) 473, (b) 573, and (c) 723 K.

Table 1

Influence of solvents on the hydrogenation of NS with Pt/TiO_2.

Solvent	Conversion (%)	Selectivity (%)		
		AS	ENB	EA
Neat	41	70	8	21
scCO_2	64	75	11	14
Toluene	43	55	33	13
Ethanol	99	48	3	49

Reaction conditions: NS, 3.6 mmol; 0.5 wt.% Pt/TiO_2, 20 mg; H_2, 4 MPa; organic solvent, 10 cm^3; CO_2, 10 MPa; temperature, 323 K; time, 1 h.

Table 2

Influence of CO_2 pressure on the hydrogenation of AS to EA with Pt/TiO_2.

CO_2 pressure (MPa)	Conversion (%)
0	21
10	5.3
16	5.6

Reaction conditions: AS, 4.4 mmol; 0.5 wt.% Pt/TiO_2, 20 mg; H_2, 4 MPa; temperature, 323 K; time,30 min.

Table 3

Hydrogenation of ST, NB and an equimolar mixture of them with Pt/TiO_2.

Entry	Substrate	CO_2 pressure (MPa)	Conversion (%)		Number of phases
			NB	ST	
1	NB	0	43	–	3
2		8	48	–	3
3		10	57	–	3
4		12	37	–	2
5	ST	0	–	95	3
6		8	–	88	3
7		12	–	72	2
8	NB + ST[a]	0	58	33	3
9		8	46	24	3
10		12	47	23	2

Reaction conditions: NB, 4.9 mmol; ST, 4.9 mmol; 0.5 wt.% Pt/TiO_2, 20 mg; H_2, 4 MPa; temperature, 323 K; time, 10 min.

[a] NB, 2.45 mmol; ST, 2.45 mmol.

Table 4

Influence of Pt loading and reduction temperature on the performance of Pt/TiO_2 for the hydrogenation of NS.

Entry	Pt loading (wt.%)	Crystallite size of Pt (nm)[a]	Conversion (%)	Selectivity (%)		
				AS	ENB	EA
1	0.5	2.0	64	75	11	14
2	1.0	2.8	72	58	18	24
3	2.0	3.0	97	34	20	46
4[b]	2.0	3.0	56	31	49	20

Reaction conditions: NS, 3.6 mmol; Pt/TiO_2, 20 mg; H_2, 4 MPa; CO_2, 10 MPa; temperature, 323 K; time, 1 h. The catalysts were reduced at 473 K.

[a] Determined by TEM.

[b] Reaction time was for 10 min.

Table 5

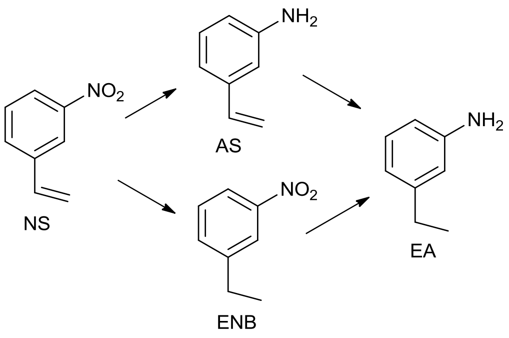
Influence of reduction temperature on the performance of 0.5 wt.-% Pt/TiO_2 for the hydrogenation of NS.

Entry	Reduction Temp. (K)	Crystallite size of Pt (nm)[a]	Conversion (%)	Selectivity (%)		
				AS	ENB	EA
1	473	2.0	64	75	11	14
2	573	2.2	59	82	7	11
3	723	–[b]	30	94	3	3

Reaction conditions: NS, 3.6 mmol; Pt/TiO_2, 20 mg; H_2, 4 MPa; CO_2, 10 MPa; temperature, 323 K; time, 1 h.

[a] Determined by TEM.

[b] Not determined.



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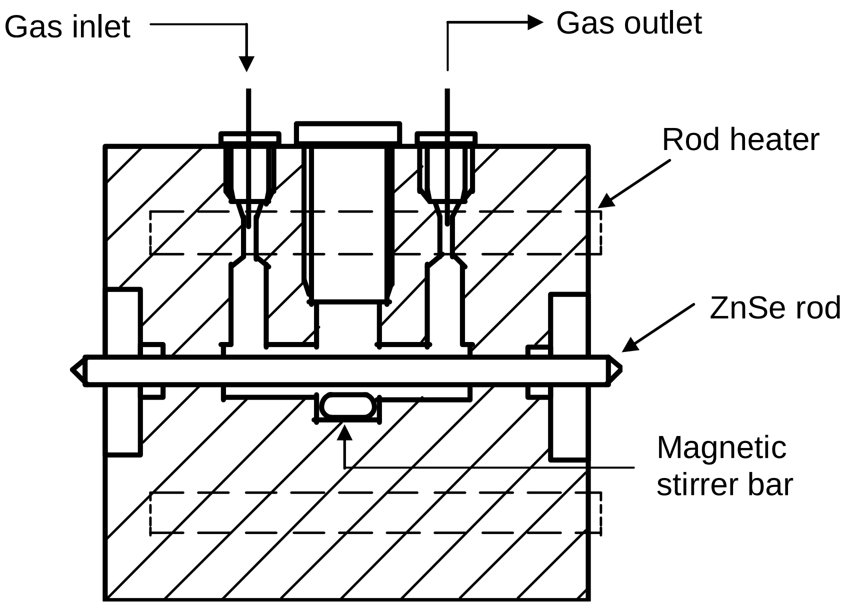

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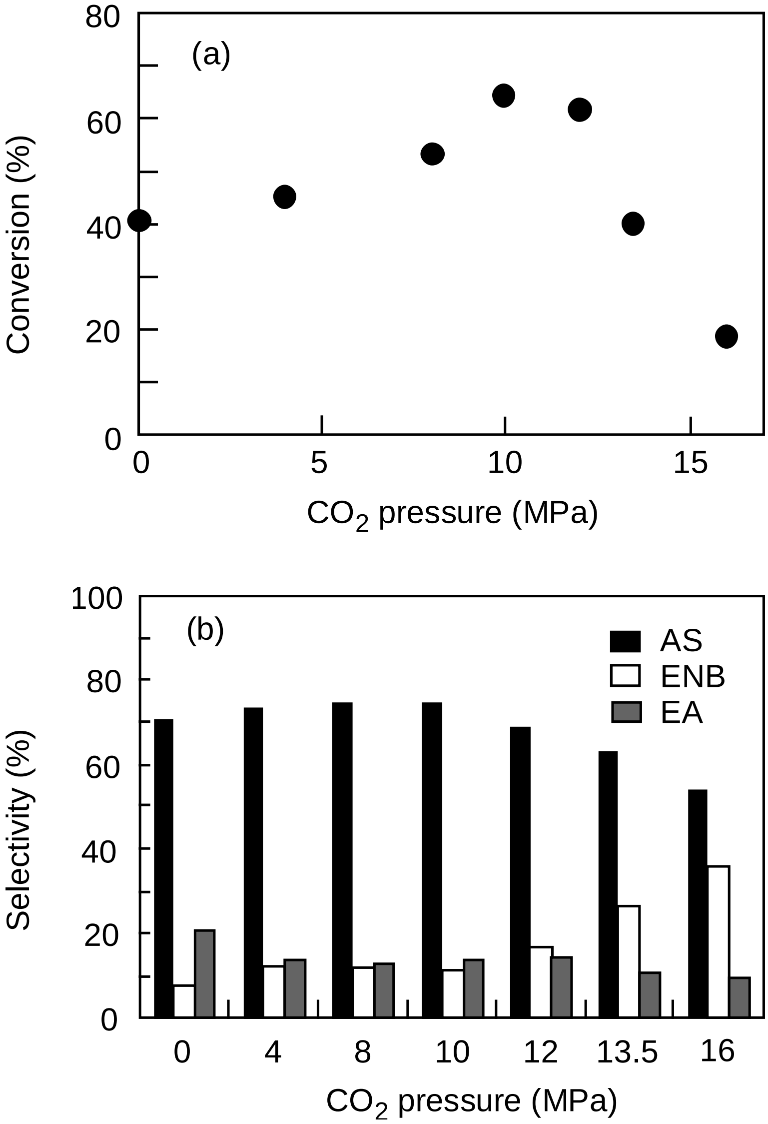

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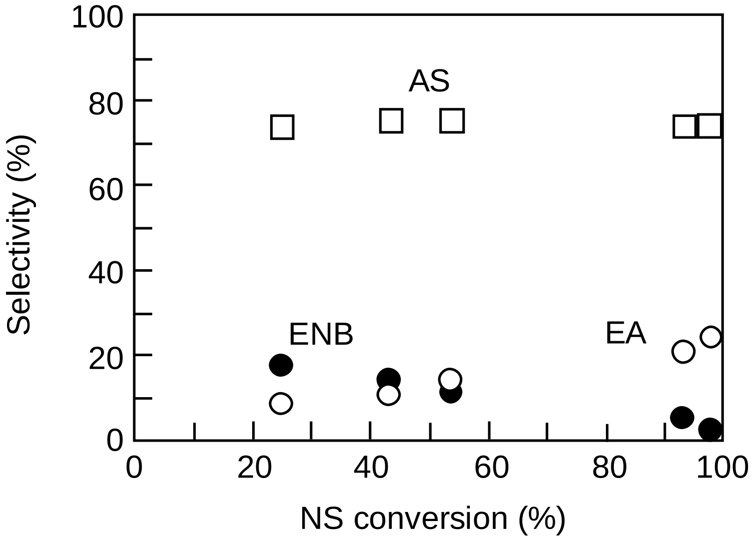

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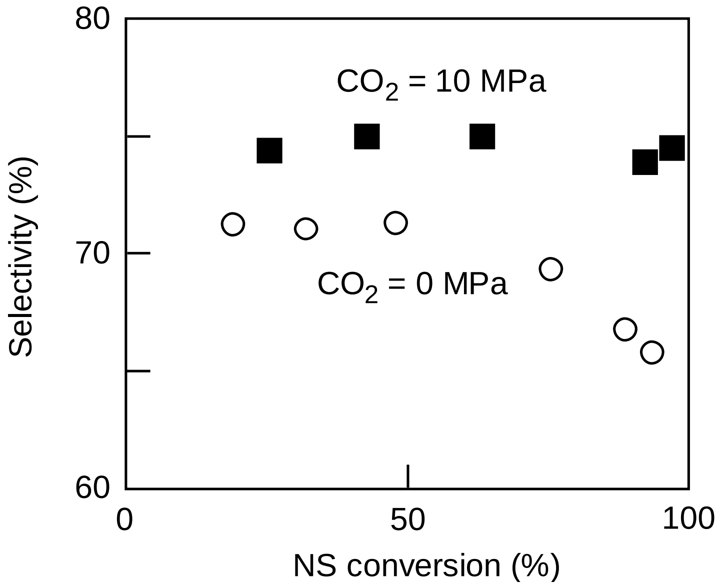

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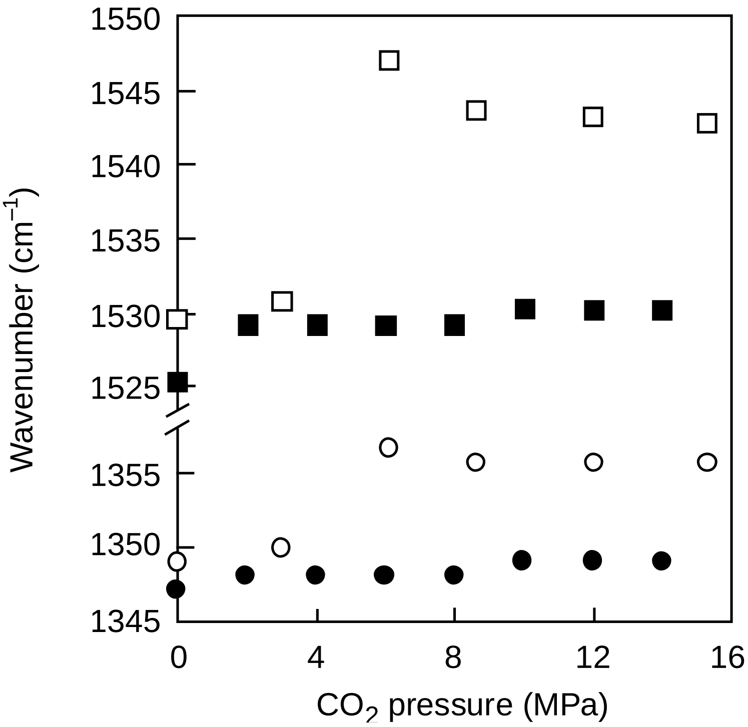

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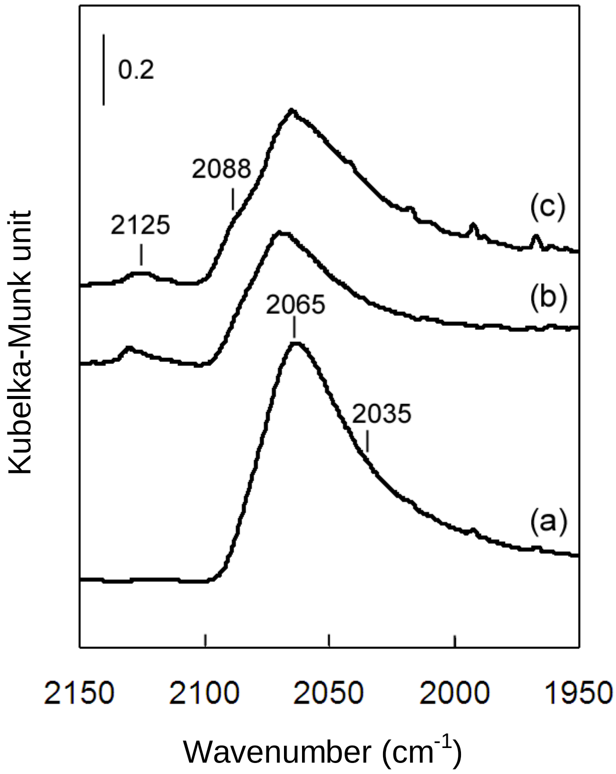

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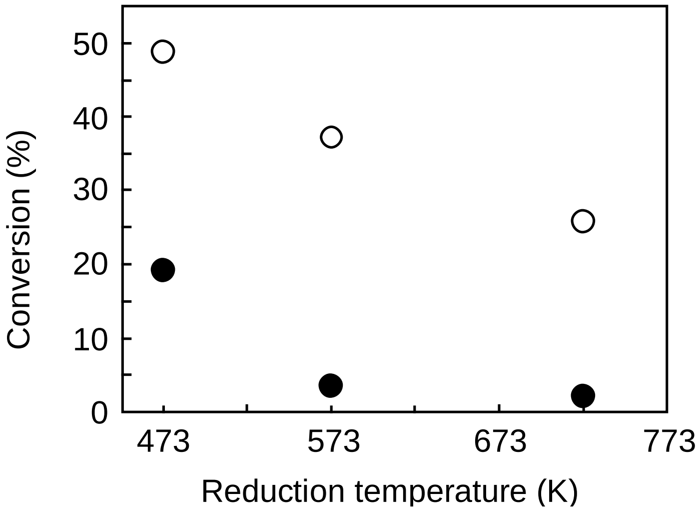

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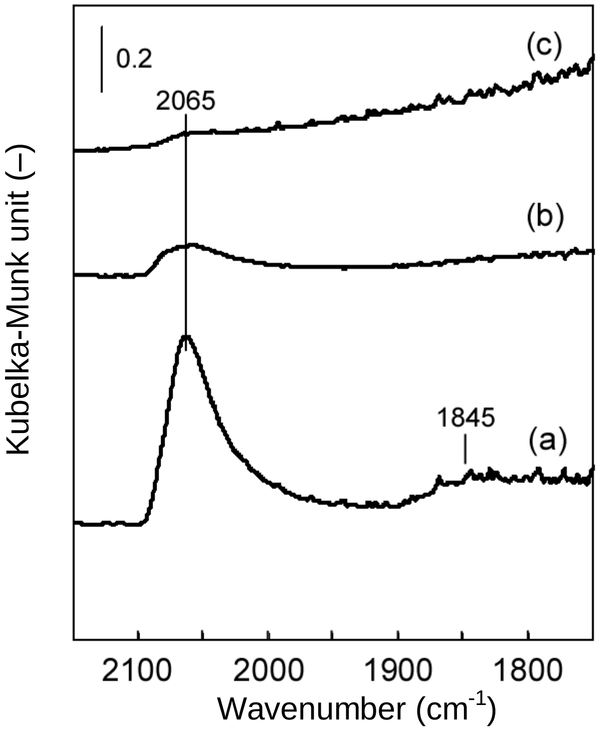

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