Catal Lett (2012) 142:87–94
DOI 10.1007/s10562-011-0693-0

Selective Hydrogenation of Cinnamaldehyde over Cobalt Supported on Alumina, Silica and Titania

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Received: 2 May 2011 / Accepted: 28 August 2011 / Published online: 16 September 2011

Abstract The liquid phase selective hydrogenation of cinnamaldehyde has been investigated on cobalt (15 wt%) impregnated on alumina, silica and various phases of titania supports. The multiple reduction stages observed in the TPR studies suggest the presence of cobalt aluminate/silicate/titanate species, and DRIFT spectra results seem to corroborate this observation. An optimum level of conversion and selectivity to cinnamyl alcohol was observed at 120 °C and 10 kg/cm^2 hydrogen pressure. Co/TiO$_2$ exhibited a greater conversion (47.4%) and selectivity to cinnamyl alcohol (58%) than Co/Al$_2$O$_3$ and Co/SiO$_2$, which may be attributed to the presence of TiO$_x$ ($x < 2$) species on the catalyst surface and to the preferential adsorption of C=O on the catalyst surface. The stability of Co/TiO$_2$ was found to be better than Co/Al$_2$O$_3$ and Co/SiO$_2$. Between the various phases of titania (high surface area, anatase and rutile), the crystalline phases exhibited a better conversion and selectivity to cinnamyl alcohol, while the stability was found to be better for high surface area titania.

Keywords Selective hydrogenation · Cobalt supported catalysts · Cinnamaldehyde · Cinnamyl alcohol

1 Introduction

The selective hydrogenation of α,β-unsaturated carbonyl compounds is a key step in the manufacture of chemicals for pharmaceuticals, flavors and fragrances. At present, reduction by hydrides (LiAlH$_4$ and NaBH$_4$) and aluminum isopropoxide [1] is used for the preparation of unsaturated alcohols. These procedures necessitate the use of minimal quantity of reducing agents since it leads to the generation of considerable hazardous waste. The selective catalytic hydrogenation method is superior in economizing resources, reducing waste disposal and protecting the environment [2].

Zhao et al. [3] investigated the reduction of cinnamaldehyde over Pt/SiO$_2$ and reported a conversion of 27% and selectivity of 88.1% for cinnamyl alcohol. Breen et al. [4] examined the hydrogenation of cinnamaldehyde on graphite supported Ir catalyst and showed a conversion of about 58% and selectivity of 98% for cinnamyl alcohol. Giroir-Fendler et al. [5] studied Ir supported on carbon and reported greater selectivity for cinnamyl alcohol than the other noble metal catalysts. Ir, Os, and Pt based catalysts were proved to be suitable for the process for producing cinnamyl alcohol [6–13]; however, the cost effectiveness of these catalysts is a cause of concern. There are reports [14–16] on the reduction of cinnamaldehyde over Co/B with 87.6% yield of cinnamyl alcohol. While there are reports focused on the Ni-based amorphous catalysts and their effect in the hydrogenation of olefinic compounds [17–20], Co based amorphous catalysts have not been studied in great detail [21]. It was reported that the selectivity to unsaturated alcohol is governed by the nature of supports [22, 23], the presence of promoters [24], metal particle size [25] and the reaction medium [26].

The hydrogenation of the C=C bond of α,β-unsaturated carbonyl compounds to yield saturated carbonyl compounds is thermodynamically favoured and the selective hydrogenation of the C=O bond to yield unsaturated alcohols is difficult to accomplish. Gallezot and Richard

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[27] remarked on the paucity of systematic studies on the influence of reaction parameters such as pre-reduction of the catalyst, temperature, solvent, agitation, catalyst support and hydrogen pressure for the selective hydrogenation. In view of their wide utility in perfumery, cinnamyl alcohol, an unsaturated alcohol, and their esters are of great interest. The present work aims to systematically study the selective hydrogenation of cinnamaldehyde (CMA) employing cobalt catalysts supported on alumina, silica, and (high surface area) titania. This paper also compares the activity of amorphous titania with crystalline one in the CMA selective hydrogenation.

2 Experimental

2.1 Chemicals

Rutile TiO_2 (Aldrich), anatase TiO_2 (Aldrich), $Co(NO_3)_2\cdot 6H_2O$ (Qualigens), fumed silica (Aldrich), Catapal-B (74% alumina, Sasol,), cinnamaldehyde (Qualigens), methanol (Qualigens) and high surface area TiO_2 [28] were used without further purification. Water used as solvent in the study is doubly distilled.

2.2 Preparation of Catalysts

Co/Al_2O_3, Co/SiO_2 and various Co/TiO_2 samples were prepared by the conventional impregnation method with $Co(NO_3)_2\cdot 6H_2O$ as the precursor for cobalt. The typical synthesis of Co/Al_2O_3, is given below. Catapal-B, 2.78 g was mixed with 20 g of distilled water. To this mixture, 1.48 g of $Co(NO_3)_2\cdot 6H_2O$ was added and stirred for 5–6 h at 80 °C. The slurry was filtered and dried at 110 °C for 12 h. The dried samples were calcined at 500 °C in air for 2 h. The cobalt content of all the catalysts is 15 wt%. Similarly fumed silica was employed to prepare Co/SiO_2, and high surface area titania, anatase and rutile were employed to prepare, respectively, Co/TiO_2, Co/anatase and Co/rutile catalysts.

2.3 Characterization

Wide-angle XRD patterns for the calcined materials were obtained on Rigaku Miniflex II, with CuKα irradiation with a scan range of $2\theta = 5$–$60°$ and a scan rate of 5°/min. The composition of the catalysts was analyzed using a Rigaku XRF spectrometer. The metal-support interaction was determined by DRIFT spectra and recorded using a Bruker Tensor-27 instrument. The BET-surface area of the samples was measured on Micromeritics ASAP-2020 analyzer by nitrogen adsorption at -195.6 °C after the samples were degassed in vacuum at 300 °C for 3 h. Hydrogen temperature programmed reduction (H_2-TPR) was performed in a quartz reactor using Micromeritics autochem II chemisorption analyzer. The reduction of the samples was performed using 10 mol% H_2/Ar flowing at a heating rate of 10 °C/min.

2.4 Catalytic Studies

Liquid phase hydrogenation of cinnamaldehyde was performed at 100–140 °C and 10–20 kg/cm^2 of hydrogen pressure in a 100 mL Parr autoclave. Prior to charging the reactants, the autoclave was purged with nitrogen and then pressurized with hydrogen. The autoclave was charged with 0.2 g of Co/TiO_2 catalyst, 2 g of cinnamaldehyde and 40 mL of methanol. The reaction was performed for 1 h while stirring the reaction mixture at 600 rpm. After each reaction, the autoclave was cooled to 30 °C. The catalyst and reaction products were separated by filtration and analyzed on PerkinElmer Clarus-500 GC equipped with ZB-1 capillary column and FID. The reaction products were identified by GC–MS.

3 Results and Discussion

3.1 X-ray Diffraction

The XRD patterns of cobalt (15 wt%) supported on Al_2O_3, SiO_2 and TiO_2, calcined at 500 °C are shown in Fig. 1. The peaks obtained at 2θ of 31.3 and 36.9 on the samples are characteristic of CoO. The intensity of CoO peaks on SiO_2 is greater than that obtained on Al_2O_3 and TiO_2. This could be attributed to the higher concentration of CoO on the surface of Co/SiO_2 than on Co/Al_2O_3 and Co/TiO_2, without much interaction with the support. A higher dispersion of CoO manifests in the broad peaks observed for Co/TiO_2. The peaks obtained at 2θ of 15.6, 18.6, 20.3, 23.5 and 27 for Co/Al_2O_3 are characteristic of Al_2O_3. Similarly, the peaks observed for Co/TiO_2 at 25.3, 37.9 and 48.1 are attributed to anatase form of TiO_2.

The XRD patterns of cobalt supported on anatase and rutile TiO_2 calcined at 500 °C and thereafter reduced under flowing hydrogen at 400 °C for 2 h are shown in Fig. 2. Co/anatase calcined at 500 °C for 2 h showed peaks for anatase titania ($2\theta = 25.3$, 36.9, 37.9, 38.5, 48.2, 54.0 and 55.1) and CoO ($2\theta = 31.4$, 36.9 and 45). When this sample is reduced at 450 °C under flowing hydrogen for 4 h, anatase is converted to rutile titania ($2\theta = 27.3$, 36.2, 39.3, 41.3, 54.3 and 56.7). This could be attributed to the presence of cobalt and reducing atmosphere. The reduced samples of cobalt supported anatase (Co/anatase) and rutile (Co/rutile) showed characteristic peaks for cobalt at 2θ of 44.2 and 51.5.

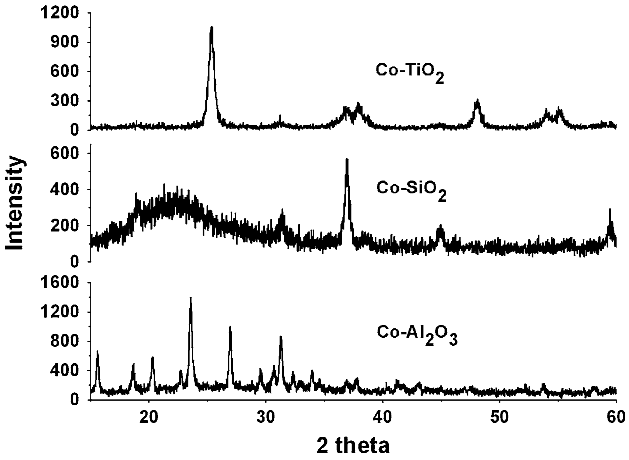

Fig. 1 XRD patterns of cobalt impregnated samples calcined in air at 500 °C for 2 h

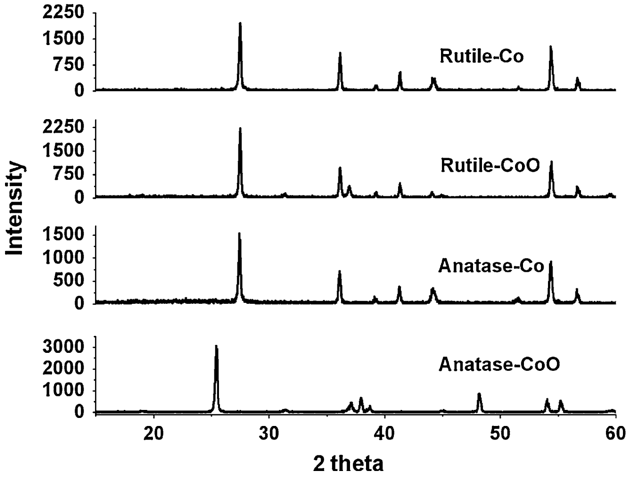

Fig. 2 XRD patterns of cobalt impregnated on anatase and rutile calcined in air at 500 °C and reduced in hydrogen at 400 °C for 4 h

3.2 Temperature Programmed Reduction

The temperature programmed reduction profiles of Co/Al_2O_3, Co/SiO_2 and Co/TiO_2 are shown in Fig. 3. The Co/Al_2O_3 sample showed a three step reduction at 336, 363 and 380 °C. The Co/SiO_2 showed a two stage reduction at 400 and 421 °C. The Co/TiO_2 demonstrated a four stage reduction with 506 °C being the maximum. The evaluation of the TPR profiles revealed that Co/Al_2O_3 could be reduced at lower temperature than Co/SiO_2 and Co/TiO_2. The trend of reduction temperature of the samples can be given as $Co/Al_2O_3 < Co/SiO_2 < Co/TiO_2$. It may be noted that various phases of titania impregnated with Co displayed a broader TPR profile relative to Co/SiO_2 and Co/Al_2O_3. The cobalt modified anatase and rutile showed three stage reduction with a peak reduction at 347 and 349.5 °C, respectively. The observation of multiple stages of reduction for the Co present in Al_2O_3, SiO_2 and various phases of TiO_2 in the TPR profile is essentially attributed to the formation of cobalt aluminate, cobalt silicate and cobalt titanate, respectively. The TPR profiles of cobalt supported on various phases of titania showed that Co/TiO_2 could be fully reduced at 599 °C while Co/anatase and Co/rutile reduced at 473 and 457 °C respectively. This suggested a stronger metal-support interaction between cobalt and high surface area titania than Co/anatase and Co/rutile. It may be noted here that the XRD patterns obtained for the calcined samples did not suggest the formation of cobalt aluminate, cobalt silicate or cobalt titanate, Similarly, the XRD patterns of the cobalt supported anatase and rutile did not show the formation cobalt titanates. Nevertheless, the TPR profiles showed reduction in multiple stages for the Co/anatase and Co/rutile.

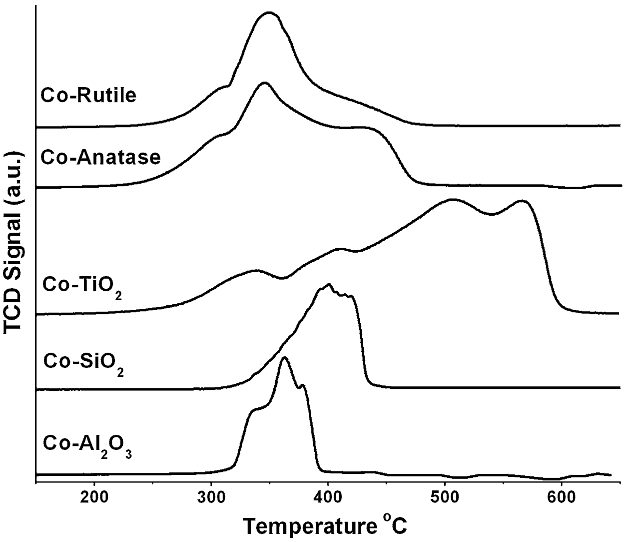

Fig. 3 TPR profiles of cobalt impregnated on various supports calcined at 500 °C

3.3 DRIFT Spectra and BET-Surface Area

The DRIFT spectra obtained for the unmodified supports such as Al_2O_3, SiO_2 and TiO_2 (Fig. 4a, c, e) did not show significant absorptions in the region of 720–1700 cm^{-1} while cobalt modified supports (Fig. 4b, d and f) showed absorptions in this region. This could be due to the formation of cobalt aluminates, cobalt silicates and cobalt titanates. The Co/anatase and Co/rutile samples showed DRIFT spectra similar to that of Co/TiO_2 (Fig. 4b).

The BET-surface area of the unmodified supports of Al_2O_3, SiO_2 and TiO_2 were, respectively, 248, 230 and 275 m^2/g. The cobalt supported on Al_2O_3, SiO_2 and TiO_2 lowered the surface area to 52, 45 and 66 m^2/g respectively. The decrease in the surface area could be due to

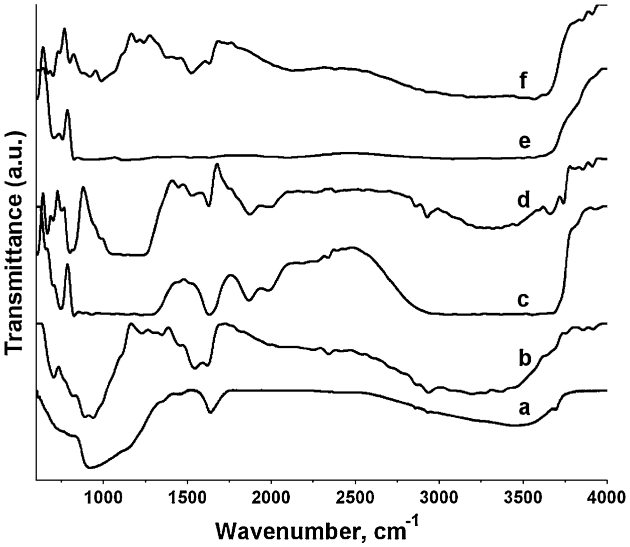

Fig. 4 DRIFT spectra of the samples calcined at 500 °C: (*a*) TiO_2 (*b*) Co–TiO_2 (*c*) SiO_2 (*d*) Co–SiO_2 (*e*) Al_2O_3 (*f*) Co–Al_2O_3

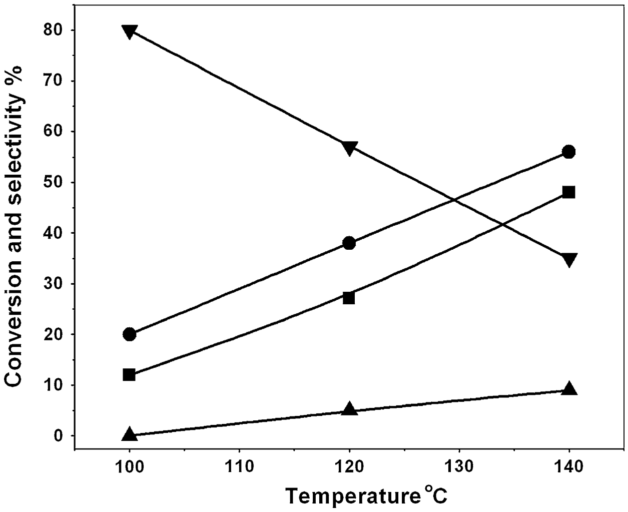

Fig. 5 Effect of temperature on the conversion of cinnamaldehyde on Co/TiO_2 (H_2 pressure = 10 kg/cm^2; rpm = 600) (*filled square*) % conversion; (*filled circle*) % HCMA selectivity; (*filled triangle*) % HCMO selectivity; (*inverted filled triangle*) % CMO selectivity

aggregation of particles leading to lowering of porosity of the samples.

3.4 Effect of Temperature

Liquid phase hydrogenation of CMA was performed at 100, 120 and 140 °C and at 10 kg/cm^2 of hydrogen pressure on Co/TiO_2 as per the conditions outlined in Sect. 2.4. The effect of temperature on the conversion is shown in Fig. 5. The conversion is found to increase with temperature and attained a maximum at 140 °C. However, the selectivity for cinnamyl alcohol (CMO) was found to decrease with increasing temperature. Although, a higher selectivity for CMO was obtained at 100 °C, the conversion was lower. The conversion and selectivity for CMO were found to be optimum at 120 °C. Consequently, 120 °C was chosen as the temperature for the catalyst activity studies. The selectivity for hydrocinnamaldehyde (HCMA) and hydrocinnamic alcohol (HCMO, also known as 3-phenylpropanol) was found to increase with the temperature. At higher temperatures, the C=C is more activated than C=O which is thermodynamically favored and this could possibly account for the higher selectivity to HCMA and HCMO.

3.5 Effect of Hydrogen Pressure

The effect of hydrogen pressure on the conversion of CMA was studied for Co/TiO_2 at 120 °C and hydrogen pressures of 10, 15, and 20 kg/cm^2, and the results are shown in Fig. 6. An increase in conversion was observed with increase in hydrogen pressure. However, there was a steep drop in selectivity to CMO with the formation of HCMA and HCMO favored. This necessitated maintaining a hydrogen pressure of 10 kg/cm^2 in the rest of this investigation.

3.6 Effect of Amount of Catalyst

The amount of the Co/TiO_2 catalyst was changed in order to study its effect on the conversion of CMA. The experimental conditions employed are: temperature = 120 °C; hydrogen pressure = 10 kg/cm^2; reaction time = 1 h. The conversion was found to increase from 27 to 49 wt% when the catalyst amount was increased from 0.2 to 0.8 g. The enhanced conversion with the amount of catalyst is attributed to the improved contact of the catalyst with reactants.

3.7 Effect of Co Loading

The effect of Co content in titania on the conversion of CMA was also studied. The experimental conditions employed are: temperature = 120 °C; hydrogen pressure = 10 kg/cm^2; reaction time = 1 h.; catalyst amount = 0.2 g. The Co content in the catalyst samples used was 2.5, 5, 10 and 15 wt%. A conversion of 3, 7.2, 18.8% was observed when the Co content was 2.5, 5 and 10 wt%, respectively, which increased to 27.1% when the Co content was enhanced to 15 wt%. A higher conversion at Co loading of 15 wt% dictated maintaining this Co concentration in this investigation. The enhanced conversion is attributed to higher concentrations of Co on the surface of the catalyst.

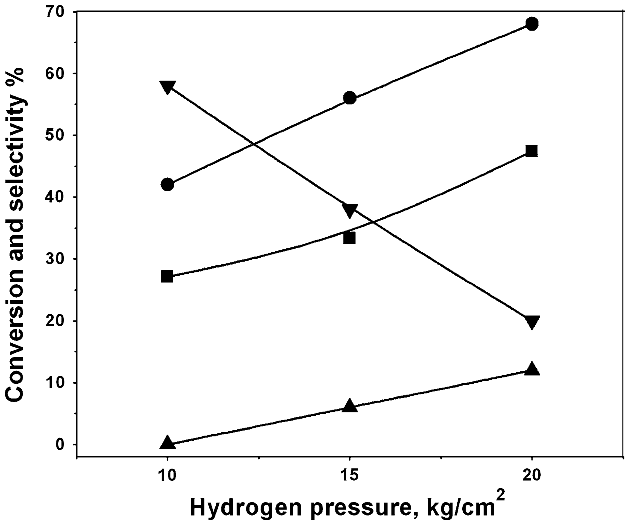

Fig. 6 Effect of conversion of cinnamaldehyde with H_2 pressure on Co/TiO_2 (Temp. = 120 °C; rpm = 600) (*filled square*) % conversion; (*filled circle*) % HCMA selectivity; (*filled triangle*) % HCMO selectivity; (*inverted filled triangle*) % CMO selectivity

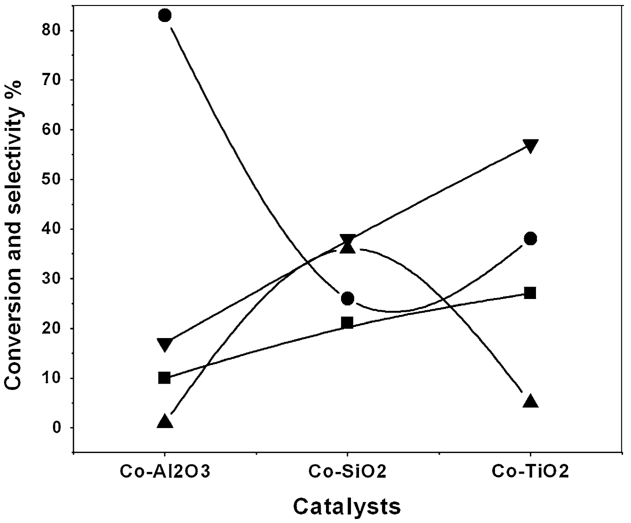

Fig. 7 Effect of conversion of cinnamaldehyde on various catalysts (Temp. = 120 °C; H_2 pressure = 10 kg/cm^2; rpm = 600) (*filled square*) % conversion; (*filled circle*) % HCMA selectivity; (*filled triangle*) % HCMO selectivity; (*inverted filled triangle*) % CMO selectivity

3.8 Effect of Catalyst Reduction Temperature

The cobalt supported on titania was reduced at various temperatures of 300, 400, 500 and 600 °C for 4 h under flowing hydrogen and their activity was evaluated for the hydrogenation of CMA at 120 °C. The catalyst reduced at 300 °C showed a conversion of 20% while the catalysts reduced at 400, 500 and 600 °C showed a conversion of 27, 19 and 8% respectively. The observed trend suggests that the reduction performed at 300 °C is not effective in reducing all the cobalt present in the catalyst. The reduction performed beyond 400 °C showed lower conversion which could be due to sintering of cobalt. This study suggests that the reduction temperature of 400 °C is optimum for cobalt modified catalysts

3.9 Effect of Cobalt Impregnated on Alumina, Silica and High Surface Titania Supports

The conversion and selectivity of CMA on cobalt impregnated on Al_2O_3, SiO_2 and high surface TiO_2 were investigated at 120 °C and the results are shown in Fig. 7. The conversion of CMA was found to increase from 10 to 27% on going from Co/Al_2O_3 to Co/TiO_2, with Co/SiO_2 exhibiting an intermediate conversion. The hydrogenation mechanism of CMA over Co/Al_2O_3, Co/SiO_2 and Co/TiO_2 catalysts is shown in Fig. 8. An inspection of the data revealed the following: The selectivity for CMO followed the order Co/TiO_2 > Co/SiO_2 > Co/Al_2O_3, and a maximum selectivity of 58% was observed over Co/TiO_2. Co/Al_2O_3 was found to have a greater tendency to saturate the olefinic bond relative to the other supports, as discerned from 83% selectivity for HCMA. The selectivity for HCMO found to be lower for both Co/TiO_2 and Co/Al_2O_3 in comparison with Co/SiO_2 which exhibited a selectivity of 36%. From these results, it is conspicuous that the conversion and selectivity to CMO is greater for Co/TiO_2 than Co/Al_2O_3 and Co/SiO_2. This may be because the C=O bond is more activated than C=C bond when the reaction was performed on the reducible support of TiO_2 in Co/TiO_2. It is suggested that in case of titania support, TiO_x ($x < 2$) species present in the support which are oxygen deficient. They tend to coordinate with the oxygen atom of C=O bond in CMA with the resultant polarization of C=O bond leading to hydrogenation of C=O by hydrogen species. The higher selectivity of HCMA on Co/Al_2O_3 than the other catalysts shows the preferential interaction and activation of C=C on Co/Al_2O_3 than C=O. CMO and HCMO showed similar selectivity on Co/SiO_2 this may be due to the equivalent activation of C=O and C=C with the cobalt supported on SiO_2.

3.10 Catalyst Stability

The conversion of CMA with time was evaluated by performing the reaction at 120 °C and 10 kg/cm^2 hydrogen pressure (Fig. 9) with a view to measure the stability of the catalysts. The reaction was performed for 4 h and samples were withdrawn at every hour and analysed on GC. It was observed that the conversion increased with time on stream for Co/TiO_2 and conversions of 27, 36, 43 and 50.3% were obtained for 1, 2, 3 and 4 h, respectively. This shows that there is no loss of catalytic activity and the conversion can

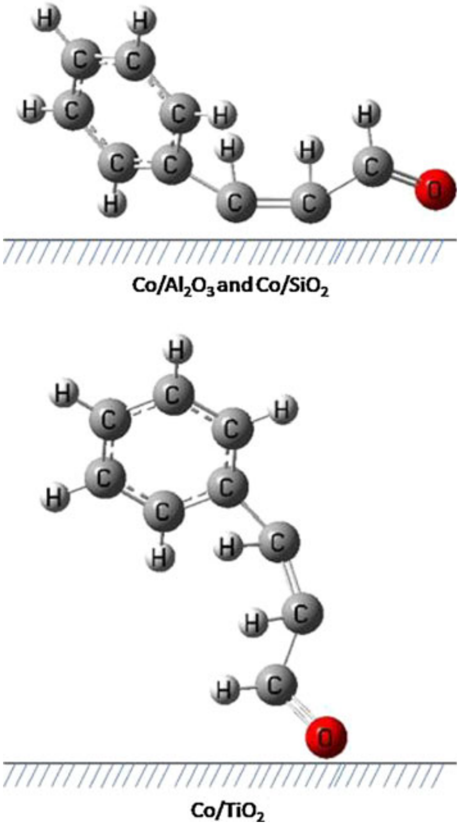

Fig. 8 Hydrogenation mechanism of cinnamaldehyde over Co/Al_2O_3, Co/SiO_2 and Co/TiO_2 catalysts

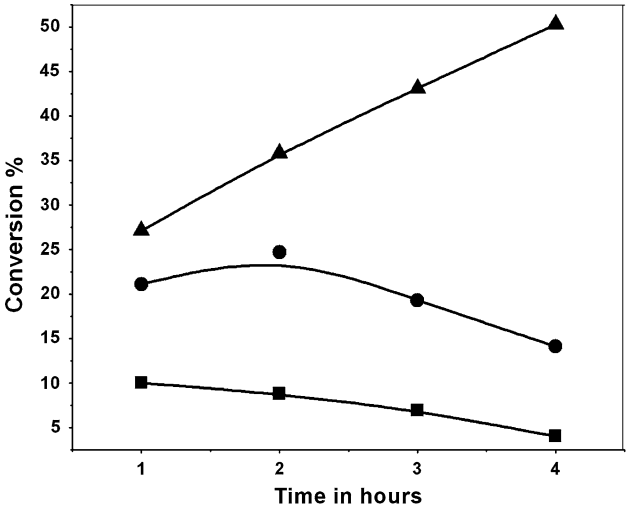

Fig. 9 Effect of conversion of cinnamaldehyde with time on various catalysts (Temp. = 120 °C; H_2 pressure = 10 kg/cm^2; rpm = 600) (*filled square*) Co/Al_2O_3; (*filled circle*) Co/SiO_2; selectivity; (*filled triangle*) Co/TiO_2

be enhanced by increasing the contact time up to 4 h on Co/TiO_2. However, the conversion could not be obtained beyond 50.3 wt% at higher TOS. In case of Co/SiO_2 an increase in conversion was observed for the second hour and conversion decreased thereafter. On the other hand, conversion for Co/Al_2O_3 declined from the first hour itself. It is assumed that titania is a reducible support in that Ti(IV) is reduced to Ti(III) under reducing conditions and the structure is stabilized by migration of Ti(III) over metal surface, typifying a strong metal support interaction. On the other hand, the alumina and silica supports being non-reducible in nature are simply deactivated with time.

3.11 Studies on Co Impregnated on Various Titania Phases

Cobalt (15 wt%) was supported on high surface area titania (275 m^2/g), anatase (12 m^2/g) and rutile (11 m^2/g). The experimental parameters for the catalytic activity are described under Sect. 2.4. The conversion of CMA on Co supported on various phases of titania is shown in Fig. 10. The CMA hydrogenation showed the formation of products in the order of CMO > HCMA > HCMO. Furthermore, the conversion of CMA on the Co supported on crystalline phases of titania, viz., anatase and rutile (36–39 wt%) is considerably higher than that of the Co supported on high surface titania (27 wt%). The possible reason for the higher conversion of CMA with crystalline phases of titania (which are non-porous) is that the concentration of Co present on the surface are greater than high surface titania.

While the crystalline phases exhibited a better selectivity for CMO, the HSA titania showed a longer life than the crystalline phases. The Co supported on crystalline

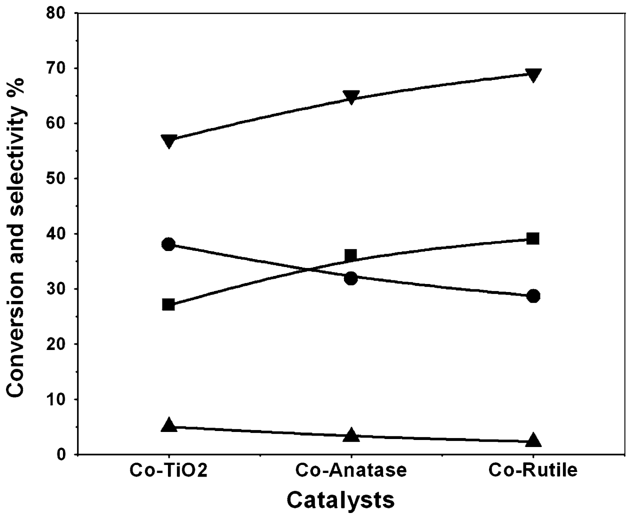

Fig. 10 Effect of conversion of cinnamaldehyde on various phases of titania (Temp. = 120 °C; H_2 pressure = 10 kg/cm^2; rpm = 600) (*filled square*) %conversion; (*filled circle*) %HCMA selectivity; (*filled triangle*) %HCMO selectivity; (*filled inverted triangle*) %CMO selectivity

phases deactivated in less than three hours while the Co supported on high surface titania was active beyond 4 h.

It is noted that during the course of the reaction, the products formed also compete for active sites on the catalyst for adsorption. The formation of HCMO requires the adsorption of HCMA or CMO. The observation that HCMO is formed in lower amounts (2.3–5%) suggested the adsorption of these species on catalyst surface is limited.

The crystalline phases of titania showed a stronger influence on the hydrogenation of CMA than the Co supported on the high surface titania. The results suggested that anatase and rutile enhance the synergistic effect between Co and titania support. During the hydrogenation, the CMA can possibly adsorb on the surface of the catalyst through C=C or C=O bond. As the hydrogenation progresses, the products can also compete for the adsorption on the catalyst surface. The adsorption of HCMA is suppressed due to steric hindrance while CMA and CMO continues to adsorb through a vertical C=O atop geometry. This mechanism is also supported by the product distribution obtained on these samples. The higher selectivity of HCMO obtained on Co supported on titania requires more adsorption of HCMA on the catalyst surface however the lower selectivity of HCMO obtained on Co supported titania shows the negligible adsorption of HCMA on these catalysts. The hydrogenation reaction could have occurred through the activation of cabonyl function with angular variation on the bridge site consisting of metal centre and reduced support on the metal support periphery.

4 Conclusion

In summary, the liquid phase selective hydrogenation of CMA has been investigated on cobalt impregnated on diverse supports. The supports employed are alumina, silica and various phases of titania. The Co modified catalysts were prepared by impregnation method and the cobalt concentration was maintained at 15 wt%. The XRD patterns are characteristic of these catalysts. The anatase phase was converted into rutile phase when calcined extensively. The multiple reduction stages observed in the TPR studies suggest the presence of cobalt aluminate/silicate/titanate species, and DRIFT spectra results seem to corroborate this observation. Loading of Co on these supports was found to lower the BET-surface area. A reduction temperature of 400 °C was found to be optimum for Co/TiO_2. An optimum level of conversion and selectivity to CMO was observed at 120 °C. An increase in hydrogen pressure lowered the selectivity to CMO in case of Co/TiO_2. Co/TiO_2 exhibited a higher conversion (47.4 wt%) than Co/Al_2O_3 and Co/SiO_2. The selectivity to CMO followed the order Co/TiO_2 (58 wt%) $>$ $Co/SiO_2 > Co/Al_2O_3$. The greater conversion observed for Co/TiO_2 may be attributed to the presence of TiO_x ($x < 2$) species on the catalyst surface. The higher selectivity for CMO seems to suggest preferential adsorption of C=O bond to the titania surface. Co/TiO_2 catalyst displayed a better stability with no loss of activity up to 4 h, while Co/Al_2O_3 and Co/SiO_2 simply deactivated with time on stream. Between the various phases of titania (high surface, anatase and rutile), the crystalline phases exhibited a better conversion and selectivity to CMO. On the other hand, the stability was found to be better for high surface area titania.

Acknowledgement The authors acknowledge the Department of Science and Technology, Government of India for funding the National Centre for Catalysis Research (NCCR) at IIT-Madras.

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