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Effect of alkali metal promoters on catalytic performance of Co-based catalysts in selective hydrogenation of aniline to cyclohexylamine

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In this study, a series of Co-based catalysts with alkali metal carbonate promoters were prepared to investigate the interrelation between promotion effect of these carbonates and catalytic performance for aniline hydrogenation to cyclohexylamine in vapour phase. The chemical promoters Li_2CO_3 and Na_2CO_3 leading to decrease in catalytic activity of cobalt catalysts for aniline hydrogenation. Catalysts with K_2CO_3 and Cs_2CO_3 loadings have practically no catalytic activity for hydrogenation of aniline. Results of TPD of aniline proved that presence of alkali metals carbonates restricts the adsorption of aniline on the surface of cobalt catalysts. Further, it was found that the addition of Na_2CO_3 greatly enhances the catalytic selectivity towards the cyclohexylamine and inhibits the consecutive reactions of cyclohexylamine leading to formation of by-products such as dicyclohexylamine and *N*-phenylcyclohexylamine.

Keywords: Aniline, Cyclohexylamine, Hydrogenation, Cobalt catalyst, Alkali metal carbonate.

INTRODUCTION

Cyclohexylamine (CHA) is an important basic intermediate, used for the production of artificial sweeteners, dyestuffs, plasticizers, metal corrosion inhibitors, surfactants, agricultural chemicals and antiseptics[1–3]. In addition, CHA is applied in the making of pharmacological stuffs, gas adsorbents and this cycloaliphatic amine is useful in synthesis of vulcanization accelerator *N*-cyclohexyl-2-benzothiazole sulphonamide[4]. The reactions of CHA with 1,5-naphtalenedisulphonic acid or 3,5-dinitrosalycilic acid are used for the synthesis of nonlinear optical materials for application in the field of photonics[5]. Conventionally, the CHA is obtained by traditional methods as catalytic hydrogenation of aniline[1, 2], reductive amination of cyclohexanol or cyclohexanone[6, 7], much less ammonolysis of chlorocyclohexane[8] or reduction of nitrocyclohexane[8, 9]. Also, it is possible to synthesize CHA by catalytic hydrogenation of nitrobenzene[10, 11]. Still, the catalytic hydrogenation of aniline is most simple and atom-efficient route for production of CHA[1]. Hydrogenation of aniline (AN) can be performed in vapour phase as well as in liquid phase over a variety of metal catalysts as cobalt, nickel, platinum, palladium, rhodium and ruthenium[12]. However, the catalytic hydrogenation of AN to CHA is accompanied by several side reactions. As illustrated in Figure 1, the hydrogenation of AN is leading to stepwise formation of cyclohex-1-enamine (CH-enA) and cyclohexanimine (CHI) intermediates which are hydrogenated to main product, primary cycloaliphatic amine CHA. Condensation reaction of CHA and intermediate CHI proceed to formation of imine *N*-cyclohexylidenecylohexanamine (NCCHA), which is subsequently hydrogenated, thus giving arise in concentration of major by-product, the secondary cycloaliphatic amine dicyclohexylamine (DCHA)[13]. In the same way, condensation of molecules of AN and intermediate CHI resulting in *N*-cyclohexylideneaniline (NCAN) and by its sequential hydrogenation is afforded the aromatic amine *N*-phenylcyclohexylamine (NPCHA) as second major by-product[14]. The formation of NPCHA is likewise the outcome of catalytic dehydrogenation of DCHA[15]. Thereunto, on smaller extent, the hydrogenolysis reactions of AN to benzene (BZ) and CHA to cyclohexane (CH-an) take place during the catalytic hydrogenation of AN[15, 16]. Moreover, the presence of water leading to formation of

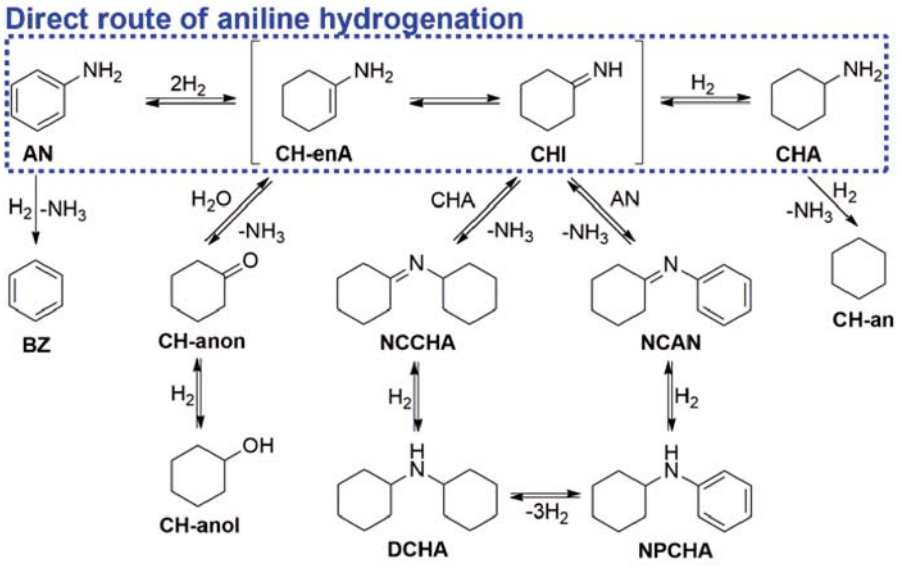


Figure 1. Reaction routes of the hydrogenation of aniline to cyclohexylamine

cyclohexanol (CH-anol), *i.e.* hydrolysis of intermediate CH-enA to cyclohexanone (CH-anon), which is by the hydrogen converted to CH-anol[13, 17]. Thus, is an effort to enhance selectivity of catalytic hydrogenation of aniline unto major product, CHA.

One way to suppress the formation of undesirable secondary amines is the addition of ammonia into reaction mixture. However, the addition of ammonia results in considerable decrease in the catalytic activity of used metal catalysts, especially the ones of ruthenium and rhodium[11, 13]. The alternative is the rational choice of catalyst for hydrogenation of AN. High yields are achieved with the use of nickel and cobalt catalysts[18], but nickel catalysts also show high selectivity for the secondary products NPCHA and DCHA[15, 19]. For the hydrogenation of AN towards CHA are more appropriate less active, yet more selective cobalt catalysts in preference to nickel catalysts[19]. It has been found that the addition of alkali hydroxides into reaction mixture has a positive effect on the reactivity of the hydrogenation of AN in liquid phase as well as on the selectivity, due to the suppressing formation of undesirable side products[20, 21]. The presence of alkali hinders the condensation of molecules of CHA and CHI, thus prevents the formation of DCHA[21]. Likewise, the nickel catalysts promoted with sodium hydroxide and used in hydrogenation of AN to CHA in vapour phase significantly increased the selectivity of the title reaction[17].

As summarized above, there are published works dealing with the study of addition of alkali metal hydroxides into reaction mixture or their loading in heterogeneous catalysts on the performance of hydrogenation of aniline, particularly from the perspective of the reaction selectivity. However, the question then arises, about the effect of alkali metal cations in the form carbonate salts on the catalytic hydrogenation of AN. Hence, focus of this work lies in the study of influence of presence of alkali metal carbonates in matter of cobalt catalyst on the catalytic activity and selectivity for the selective hydrogenation of aniline to cyclohexylamine in vapour phase.

MATERIALS AND METHODS

Chemicals

Aniline (99.9%) and cyclohexylamine (99.9%) were provided by BorsodChem MCHZ and aniline was additionally distilled. Methanol (> 99.9 %) was purchased from Penta Chemicals. Gas chromatography (GC) standards: dicyclohexylamine (99.9%), *N*-cyclohexylidenecyclohexanamine (>50%), and *N*-phenylcyclohexylamine (>50%) were obtained from BorsodChem MCHZ as well. All solid chemicals were used without further purification. $CoCO_3.Co(OH)_2$ (>99%) was purchased from Freeport Cobalt Oy, Co_3O_4 (>99%) from Umicore and the $CaCO_3$ (>99%), Li_2CO_3 (>99%), Na_2CO_3 (>99%), K_2CO_3 (>99%) and Cs_2CO_3 (>99%) were acquired from local suppliers. Electrolytic hydrogen (grade 3.0), nitrogen (grade 4.0) and helium (grade 5.5) were purchased from SIAD Czech spol., and additionally catalytically purified.

Distillation of aniline

The commercial AN with content of *ca.* 0.02 wt% of water was distilled to reach final concentration of water of < 0.01 wt%. The necessity to use dry aniline lies in the fact that the content of water affects the catalytic properties and performance of Na_2CO_3-promoted cobalt catalyst during the AN hydrogenation[22]. Distillation of commercial AN was carried out in distillation column of length of 1.4 m, inner diameter of 30 mm and with column structured packing Sulzer DX with efficiency of 18 theoretical plates. Distillation was performed under reduced pressure of 9.0-9.8 kPa and temperature range of reboiler of 65–86 °C. As a distillate fractions of AN-H_2O were removed, the residue AN with 0.005 wt% of H_2O was used as reactant for hydrogenation experiments.

Catalysts preparation

The model cobalt catalysts for the catalytic tests were prepared by the two-stage homogenization of solid components, first cobalt precursors $CoCO_3{\cdot}Co(OH)_2$ and Co_3O_4, with chemical promoter Me_2CO_3 (Me = Li, Na, K and Cs) and after that with diluent material $CaCO_3$ in agate mill. The molar ratios of solid components for their physical mixing were as follows: $CoCO_3.Co(OH)_2/Co_3O_4$ 0.71, Co-precursors/Me_2CO_3 9.0 and Co-precursors/$CaCO_3$ 0.7. Thereafter, homogeneous catalyst matter was compressed into cylindrical tablets of diameter of 10 mm. Then tablets were crushed and the granulate fractions were sorted. For the catalytic tests was used fraction of 0.80–1.25 mm. For the chemisorption measurements the model cobalt catalysts were prepared pursuant to above-described procedure but only from one cobalt precursor, *i.e.* $CoCO_3{\cdot}Co(OH)_2$, and chemical promoter Me_2CO_3 (molar ratio Co-precursor/Me_2CO_3 23.0). For the chemisorption measurements was used granulate fraction of 25–45 μm.

Catalytic tests

Catalytic hydrogenation of AN was performed in glass tubular continuous-flow U-shaped reactor of an inner diameter of 7 mm. The used experimental apparatus[15] for the catalytic hydrogenation reactions in gaseous phase (Fig. 2) is described as follows: Inlet of hydrogen (or hydrogen + nitrogen mixture) (**1**) into catalytic purifier with copper catalyst (**2**) and subsequently to column with molecular sieve (**3**) for the additional depuration of trace amount of oxygen and water in gases. The aniline (**4**) was fed into reactor (**5**) by a piston pump. The reactor was placed in bath of heat transfer medium, *i.e.* Rose's metal alloy (**6**). The side arm of reactor was still heated by the infrared lamp (**7**) in order to supress premature condensation of outlet gaseous reaction mixture. The outlet reaction mixture was condensed in Liebig condenser (**8**) cooled by water (**9**) and absorbed into methanol in freeze trap (**10**) placed in a cooling bath of ice-water mixture (**11**) tempered at 0 °C. Waste gases such as hydrogen and ammonia were disposed (**12**).

The experiments were preceded by the reduction of individual cobalt catalysts. The conditions of catalysts reduction were as follows: 230 °C for 2 hours under a flow of mixture H_2+N_2 (30 mol% + 70 mol%) at rate of 50 l h^{-1} and 230 °C for 8 hours under a flow of pure H_2 at rate of 50 l h^{-1}. In the final step, the cata-

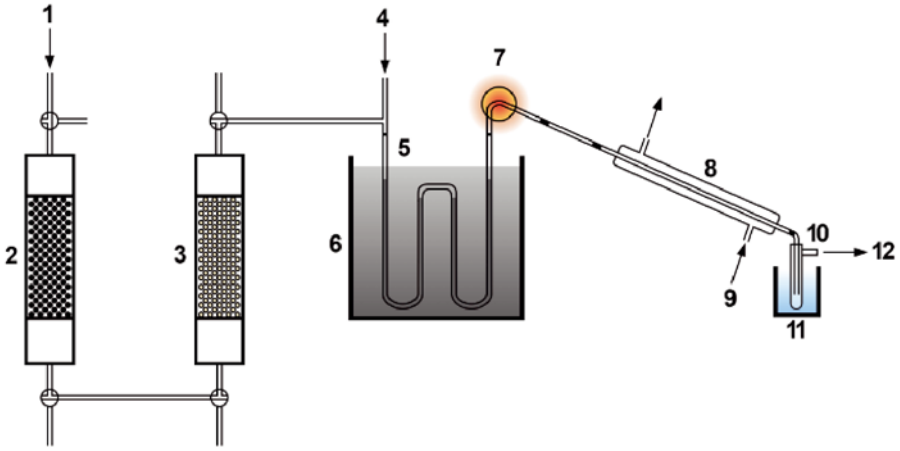


Figure 2. Schematic diagram of the experimental apparatus for the catalytic hydrogenation of AN to CHA in vapour phase

lysts were reduced at 330 °C for 0.5 hour under a flow of pure H_2 at rate of 50 l h^{-1}. Duration of reduction of cobalt catalysts with K_2CO_3 and Cs_2CO_3 loadings was in final step at 330 °C 1.5 and 2.5 hour respectively, because of effect cation radius of alkali metal carbonate promoters on the rate of reduction of the cobalt catalyst precursor[23–25]. The both cobalt precursors, *i.e.* Co_3O_4 and $CoCO_3{\cdot}Co(OH)_2$ are completely transformed to active cobalt only in hexagonal-closed packed (hcp) phase under the aforesaid reduction conditions[26]. Specific surface area of cobalt Co^0 originating from Co_3O_4 reduction is 5.0 m^2 g^{-1}, and from $CoCO_3{\cdot}Co(OH)_2$, 6.7 m^2 g^{-1}[26]. Thereupon, after reduction, the hydrogenation of AN over a 14.5 g of cobalt catalyst was carried at temperature 165 °C, atmospheric pressure, molar ratio of AN/H_2 of 0.09 and feed of AN of 6–15 g_{AN} h^{-1}, *i.e.* catalyst contact time of 2.42–0.97 $g_{cat}/(g_{AN}$ $h^{-1})$. The samples of reaction mixtures were analysed by a GC technique with FI detector.

Temperature programmed desorption

The aniline and cyclohexylamine temperature programmed desorptions (TPD) were performed on AutoChem II 2920 (Micromeritics) equipped with TC detector. 90 mg of cobalt catalyst was filled in a quartz tubular U--reactor and *in situ* reduced at 260 °C for 3 hours under a flow of H_2 at rate of 50 ml min^{-1}. Then temperature was increased to 330 °C and reduction continues for 0.5 hour under a flow of H_2 at rate of 50 ml min^{-1}. After the temperature was cooled down to 150 °C, on the surface of catalyst was pulse dosed AN or CHA (1.60 kPa) through the loop (5 ml), pulse frequency 1 pulse min^{-1} (overall 30 pulses), under a flow of He at rate of 30 ml min^{-1}. In the next step, the flow rate of He was increased to 50 ml min^{-1} to remove physically adsorbed amine for 1.5 hour at 150 °C. Finally, the catalyst was heated from 150 to 600 °C with a heating rate of 10 °C per min in flow of He (50 ml min^{-1}) and the desorbed species were detected.

Analytical

Quantitative GC analyses of chemicals and samples of reaction mixtures were performed using a Shimadzu GC-2010 chromatograph with FI detector. Using a Rxi®-624Sil MS column (30 m x 0.25 mm x 1.40 μm) and He as a carrier gas. The column temperature regime was set as follows: Initial temperature 80 °C for 2 min, heating with the temperature ramp of 15 °C per min up to the temperature of 210 °C. The injector and detector temperatures were set to 250 °C. The reaction products were identified by GC standards.

The concentration of water in samples of aniline was determined by the coulometric Karl-Fischer titration on Titrator C 30 Mettler Toledo.

Data processing

The results of GC analyses, *i.e.* area percent units (area %) were converted to mass fractions (wt%) and subsequently to mole fractions (mol%). The reaction system of hydrogenation of AN was characterized by conversion of AN and reaction (percentage) selectivity, which are defined by Eqs. 1 and 2.

$$X_{AN} = \left[\frac{x_{AN,in} - x_{AN,out}}{x_{AN,in}}\right] \cdot 100 \quad (1)$$

$$S_i = \left[\frac{x_{i,out}}{x_{AN,in} - x_{AN,out}}\right] \cdot 100 \quad (2)$$

Here X_{AN} is conversion of aniline, x_{AN} molar fraction of AN, S_i reaction (percentage) selectivity of species i and x_i molar fraction of species i. The catalytic activity of each cobalt catalyst for hydrogenation of AN to CHA was evaluated by comparative, simplified kinetic method at the constant conversion of AN expressed as follows:

$$\text{rel.}\, a_w = \left[\frac{(W/F_{AN})_{ref}}{(W/F_{AN})}\right]_{X_{AN}} \cdot \text{rel.}\, a_{w,ref} \quad (3)$$

where rel.a_w corresponds to relative (weight) activity, W to weight of the catalyst, F_{AN} to mass flow rate of aniline and the rel.$a_{w,ref}$ is the reference relative (weight) activity which is equal to one. It means, the greater value of rel.a_w the more active is catalyst sample. The catalysts performance was also described by value of the relative selectivity, which is defined by following Eq. 4.

$$\text{rel.}\, S = \left[\frac{(x_i)_{ref}}{x_i}\right]_{X_{AN}} \cdot \text{rel.}\, S_{ref} \quad (4)$$

Here rel.S is the relative selectivity of catalyst towards the main product (CHA), but from the perspective of formation of by-products. As in the case of previous case, the greater the value of rel.S the catalyst is more selective towards CHA.

RESULTS AND DISCUSSION

Catalytic activity of Me_2CO_3 promoted $Co/CaCO_3$ catalysts in aniline hydrogenation

It was studied the catalytic activity of each prepared $Co/CaCO_3$ and $Co/CaCO_3$-Me_2CO_3 (Me = Li, Na, K and Cs) catalysts (henceforward abbreviated as Co and Co-Me) for the hydrogenation of AN to CHA. Figure 3 shows that the activity of cobalt catalysts drops stepwise with increasing alkali metal cation of Me_2CO_3 promoter. The highest activity for hydrogenation of aniline has unpromoted cobalt catalyst. Then the catalytic activity decreases abruptly. In the first instance, the Co-Li and then Co-Na cat. Both cobalt catalysts with promoters K_2CO_3 and Cs_2CO_3 are entirely inactive for the hydrogenation of AN. Table 1 summarized the results of performance of each cobalt catalyst through the values of relative (weight) reactivity with the Co as reference catalyst. The values of relative (weight) reactivity were evaluated at the constant conversion of AN of 57.1, 69.5, 83.2 and 91.5% and the obtained results made into arithmetic mean. The Co-Li catalyst reaches only half of the activity of the reference cobalt catalyst free of Me_2CO_3 promoter for the AN hydrogenation. Whereas the activity of Co-Na catalyst for the self-same hydrogenation reaction is 83% lower than in the case of reference Co catalyst.

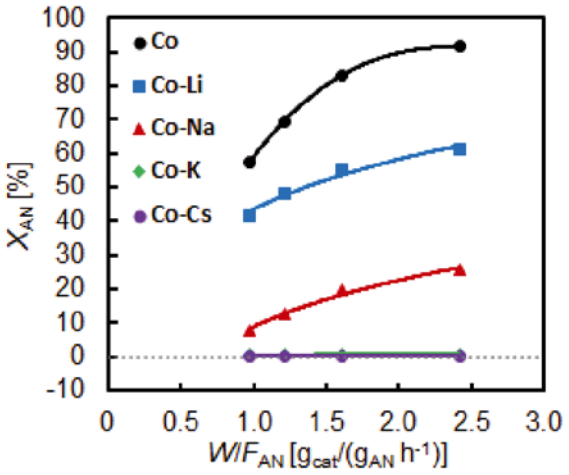


Figure 3. The effect of alkali metal carbonate doping of cobalt catalyst on its activity for hydrogenation of AN to CHA

Catalyst	rel.a_w [–]
Co	1.00
Co-Li	0.50
Co-Na	0.17
Co-K	<0.01
Co-Cs	<0.01

Table 1. Comparison of catalytic activity of used cobalt catalysts for hydrogenation of AN

According to TPD results of the AN adsorption the alkali metal carbonate promoters significantly affects the chemisorption of AN on the cobalt catalysts surface. It was further discovered that the AN is partially transformed to benzene and ammonia under the conditions of TPD. From Table 1 can be seen that the activity of cobalt catalysts for the AN hydrogenation dropped in accordance with addition of alkali metal carbonate promoters, which can be further explained by the TPD results. As can be seen in Figure 4, at the temperature range of 450–600 °C occurs desorption of species of the TPD of aniline. With the promotion of cobalt catalysts by alkali metal carbonates decreased AN adsorption, which resulted in a decrease of relative concentration rel.*c* of chemisorbed species (amount in area %) in reference to unpromoted Co catalyst (Table 2) whence implies the resultant low hydrogenation activity. Possible explanation may be the geometric effect of the alkali metal of Me_2CO_3 molecule. The hydrogenation activity of catalysts is in the order Co > Co-Li > Co-Na > Co-K ~ Co-Cs because the larger alkali metal cations may impede the adsorption of AN on the cobalt catalyst surface. An interesting finding is that the desorption peak maximum of AN-TPD for the Co-Li and Co-Cs catalysts is considerably dissimilar (*ca.* 541 °C for Co-Li and 501 °C for Co-Cs) from the rest of used cobalt catalysts (*ca.* 512–520 °C). Explanation of this observed phenomenon may lie in the aspect of the electronic effect, *i.e.* polarization of Li^+ ion, which is the strongest among the rest of alkali metal ions due to its higher electronegativity compared to rest of the alkali metals. From this viewpoint the Li^+ ion results in boosting electron density at interface between active Co and Li_2CO_3 and thus affect the adsorption of AN, which makes a stronger interaction of AN with catalyst surface[27, 28]. Compared to that, the Cs has the lowest electronegativity amongst the alkali metals and for this reason, there is weaker bonding of AN on the Co-Cs catalyst surface.

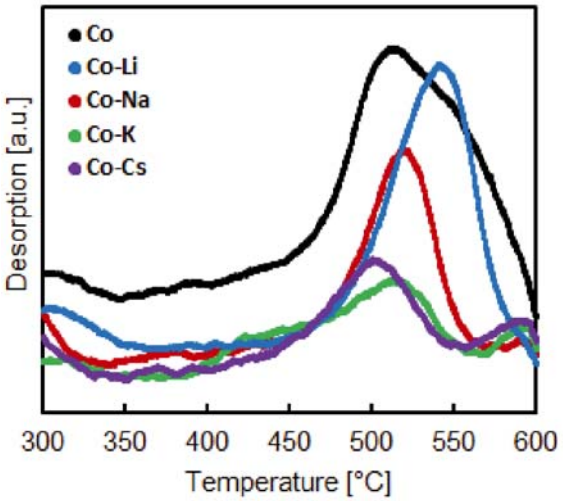


Figure 4. AN-TPD profiles of various cobalt catalysts after reduction

Catalytic selectivity of Me_2CO_3 promoted $Co/CaCO_3$ catalysts in aniline hydrogenation

Conjointly with the activity of cobalt and alkali metal-doped cobalt catalysts, their efficiency for the formation of the main product CHA and undesirable by-products DCHA, NPCHA and NCCHA was studied. Nevertheless, selectivity was evaluated only for Co, Co-Li and Co-Na catalysts due to the poor activity of Co-K and Co-Cs catalysts for AN hydrogenation. To reliably compare each cobalt catalyst in the perspective of selectivity, it was chosen Co as reference catalyst. The values of relative selectivity and reaction (percentage) selectivity were evaluated at the constant conversion of AN of 50% (for the Co-Na cat. the composition of the reaction mixture at the

Table 2. Summary of data obtained from temperature programmed desorption of AN

Catalyst	Temperature maximum		Area %[a]	rel.*c* [–]
	T_1 [°C]	T_2 [°C]		
Co	512	–	0.1039	1.00
Co-Li	541	–	0.0876	0.84
Co-Na	520	590	0.0446	0.43
Co-K	514	596	0.0231	0.22
Co-Cs	501	590	0.0243	0.23

[a]Sum of the desorbed amount (T_1 + T_2).

conversion of 50 % was obtained by extrapolation (Fig. 5–7). The results of relative selectivity of each catalyst and reaction (percentage) selectivity are summarized in Table 3. In absence of Me_2CO_3, AN is in small extent converted to both secondary amines DCHA (*ca.* 0.6% selectivity at conv. 50%) and NPCHA (*ca.* 0.5% selectivity at conv. 50%). However, when alkali metal carbonates were added, the consecutive reactions leading to DCHA and NPCHA were supressed. As shown in Table 3, Co-Na catalyst has superior catalytic selectivity because AN is converted almost just to CHA. It may be steric hindrance by Me_2CO_3 for the formation of DCHA and NPCHA, which is the reason for improved selectivity towards CHA[11]. Nevertheless, it's interesting that the addition of Li_2CO_3 slightly worsens the selectivity of cobalt catalyst towards CHA, *i.e.* promotes the formation of NCCHA (*ca.* 2.3% selectivity at conv. 50%).

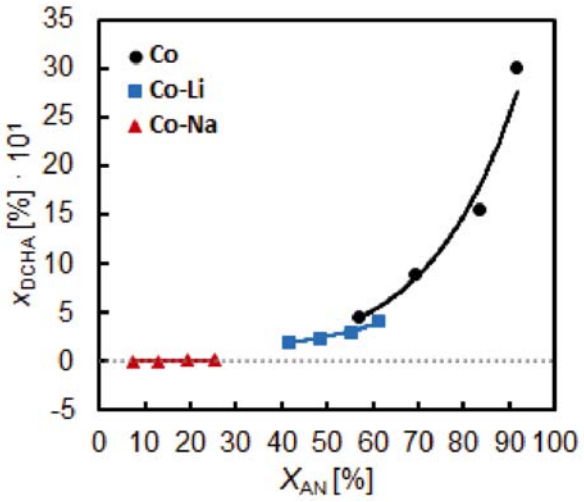


Figure 5. Concentration profiles of DCHA (mol%) during the AN hydrogenation over a cobalt catalysts

As in the case of the previous chapter, results of the effect of alkali metal carbonate promoters on selectivity were supported by TPD measurement (Fig. 8). It was discovered that the TPD of adsorbed CHA over Co, Co-Li and Co-Na resulted in conversion to aniline (and subsequently to benzene and ammonia) under the condition of TPD of CHA. As can be seen in Figure 8, the addition of alkali metal carbonate promoters, especially Na_2CO_3, limits the adsorbed amount of CHA. Interesting finding is that TPD results of adsorption of AN

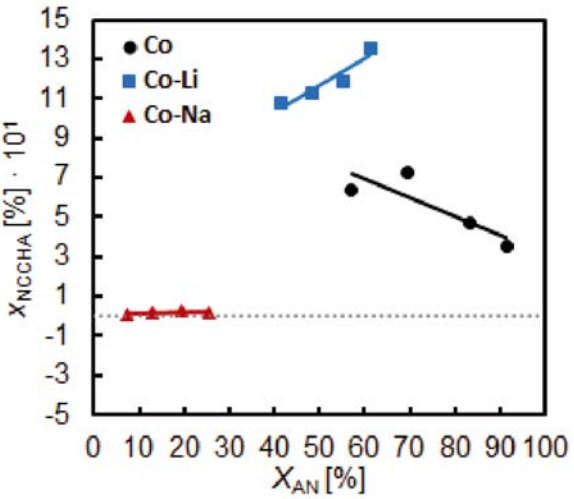


Figure 6. Concentration profiles of NCCHA (mol%) during the AN hydrogenation over a cobalt catalysts

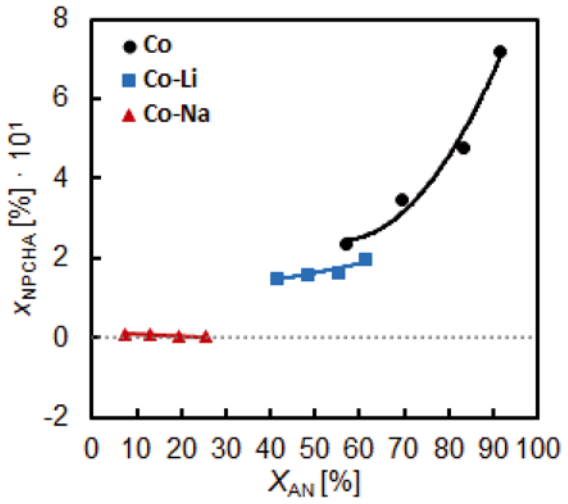


Figure 7. Concentration profiles of NPCHA (mol%) during the AN hydrogenation over a cobalt catalysts

and CHA over Co and Co-Na catalysts share the almost the same values of temperature maxima of desorption peaks (Table 2, Table 4), however, this is not the case of Co-Li catalyst. From the adsorption of CHA, the temperature maximum of desorption peak of product is now 491 °C which is differs by 50 °C. In the case of both AN-TPD and CHA-TPD the reproducible of experiments, *i.e.* peak temperature maxima is 5%. Most certainly, Li_2CO_3 loading supply additional active sites

Table 3. Effect of alkali metal carbonate promoter on the selectivity of cobalt catalysts and distribution of major by-products

Catalyst	DCHA		NCCHA		NPCHA	
	rel.*S* [-]	*S* [%]	rel.*S* [–]	*S* [%]	rel.*S* [–]	*S* [%]
Co	1.00	0.62	1.00	1.56	1.00	0.51
Co-Li	1.19	0.52	0.67	2.33	1.56	0.33
Co-Na	11.42	0.05	24.02	0.07	50.49	0.01

At the constant conversion of AN of 50%.

to the cobalt catalyst[29] or affects the properties of the active sites of cobalt catalyst itself. It's a possible that the CHA preferably adsorbs on these active sites, but with increasing temperature of TPD measurement the desorbed CHA, more precisely desorbed species does not re-adsorbs on the surface of cobalt catalyst.

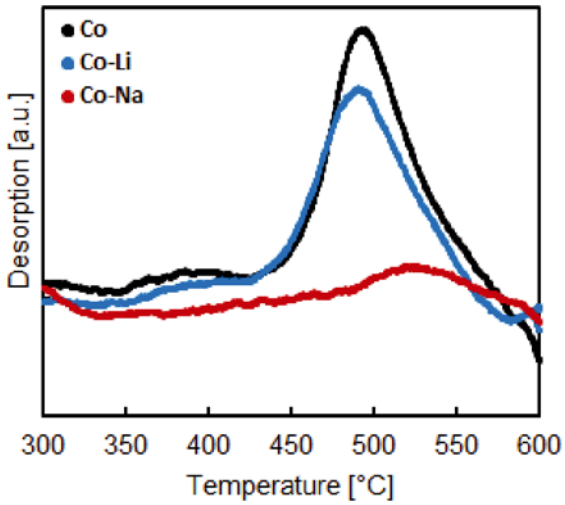


Figure 8. CHA-TPD (AN-TPD) profiles of various cobalt catalysts after reduction

Table 4. Summary of data obtained from temperature programmed desorption of CHA

Catalyst	Temp. max. *T* [°C]	Area %	rel.*c* [–]
Co	495	0.0630	1.00
Co-Li	491	0.0456	0.72
Co-Na	524	0.0124	0.20

CONCLUSION

In summary, a series of $Co/CaCO_3$ catalysts promoted by various alkali metal (Li, Na, K and Cs) carbonates were prepared by physical mixing. The cobalt catalysts were evaluated for direct hydrogenation of aniline to cyclohexylamine in vapour phase. The results show that the Li_2CO_3 loading leading only to 50% of catalytic activity of alkali free $Co/CaCO_3$ catalyst and Na_2CO_3 loading merely to 17% of catalytic activity of the reference catalyst. Besides, introduction of K_2CO_3 and Cs_2CO_3 in matrix of cobalt catalyst results in utter loss of catalytic activity for hydrogenation of aniline. As a result, gradual loss of catalytic activity is consistent with the experiments of temperature programmed desorption of aniline, which exhibited that with the presence of Me_2CO_3 promoters there is a decrease of adsorbed amount of aniline on the surface of cobalt catalyst. It is noteworthy that the addition of Na_2CO_3 into cobalt catalyst exceedingly enhances the selectivity towards desired product cyclohexylamine. The Na_2CO_3-promoted cobalt catalyst significantly inhibits the consecutive reactions of cyclohexylamine to *N*-cyclohexylidenecyclohexanamine (selectivity of 0.07%), dicyclohexylamine (selectivity of 0.05%) and *N*-phenylcyclohexylamine (selectivity of 0.01%). This work can provide guidance for the design of cobalt catalysts to modulate balance between the catalytic activity and selectivity for the hydrogenation reactions in vapour phase similar to hydrogenation of aniline.

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