Palladium catalyzed synthesis of methylamines from carbon dioxide, hydrogen and ammonia

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The synthesis of methylamines from carbon dioxide, hydrogen, and ammonia has been studied over two palladium–alumina catalysts with palladium loadings of 2.8 and 7.6 wt%, respectively. Catalytic tests were performed in a fixed-bed microreactor at 0.6 MPa total pressure in the temperature range 473–573 K. The catalysts showed high activity for methylamine formation at low temperatures and produced monomethylamine with selectivities higher than 80%, besides of smaller amounts of di- and trimethylamine. Other carbon containing products observed were carbon monoxide, formed by the reverse water–gas shift reaction, and methane, which was the prevailing product above 573 K. In situ diffuse reflectance FTIR studies were performed to identify the species present on the catalyst surface under reaction conditions. Ammonia and methylamines are adsorbed on Brønsted and Lewis acid sites on the catalyst. Evidence is given that surface formate and isocyanate species are present on palladium–alumina under reaction conditions.

Keywords: methylamine synthesis, carbon dioxide, palladium–alumina, FTIR

1. Introduction

The use of carbon dioxide as a C_1-building block for the manufacture of fuels and chemicals is a research area of much current interest. CO_2 can be efficiently reduced to methanol, methane and hydrocarbons, as well as to formic acid and its derivatives, in the presence of suitable catalysts [1–4]. Methanol synthesis by the hydrogenation of CO_2 has been the subject of intensive investigations [2,3]. Various catalysts have been reported to be active for this reaction, among which copper and palladium proved to be most suitable [3].

Catalytic reactions of ammonia or amines and alcohols to the corresponding N-alkylated products have been in the focus of a number of investigations [5–7]. Among the numerous catalysts tested for this reaction, supported copper and group VIII metal catalysts such as nickel, cobalt, and palladium were most suitable [5,7]. For the synthesis of lower amines such as methylamines from methanol and ammonia, zeolites and mixed oxide based solid acid catalysts are applied successfully [8]. The thermodynamic equilibrium composition of this reaction favors the formation of trimethylamine (TMA), whereas the commercially demanded products are monomethylamine (MMA) and dimethylamine (DMA) [8]. Methylamines can also be prepared by the reaction of CO/H_2 synthesis gas in the presence of ammonia over modified Fischer–Tropsch or copper based catalysts [9–12]. Depending on catalyst and reaction conditions, a broad range of products is produced. Recently we demonstrated, that methylamines can be synthesized by the reaction of $CO_2/H_2/NH_3$ mixtures over copper–alumina catalysts [13,14], with MMA being the main methylamine product formed. Other metal (Fe, Co, Ni, Pt, and Ag)–alumina catalysts showed inferior activity and selectivity for methylamine synthesis [15]. For both the CO [10] and the CO_2 [13,14] based reaction an intermediate of the methanol synthesis reaction has been proposed to react with ammonia to the methylamine product over copper based catalysts.

In this work we report the catalytic behavior of palladium–alumina catalysts in the reaction of carbon dioxide, hydrogen and ammonia. In situ FTIR measurements are used to identify surface intermediates in the reaction of $CO_2/H_2/NH_3$ to methylamines and a reaction pathway is proposed.

2. Experimental

The investigated palladium–alumina catalysts were prepared from a palladium nitrate ($Pd(NO_3)_2{\cdot}2H_2O$) solution, aluminum hydroxide and KOH, as described in detail elsewhere for copper/alumina catalysts [16]. In brief, a slurry of aluminum hydroxide gel in aqueous palladium nitrate solution was mixed with a solution of potassium hydroxide (2 mol KOH per mol Pd^{2+}) at 353 K. The resulting precipitate was aged for 40 min at 353 K. After cooling to room temperature, the residue

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was filtrated and washed with distilled water until the filtrate was neutral. The wet precipitate was dried at 423 K for 12 h, crushed and sieved.

Catalytic tests were performed using a continuous tubular fixed-bed microreactor. The feed gas, containing 60 mol% H_2, 20 mol% CO_2, 0–20 mol% NH_3 and N_2 as a balance, was mixed from pure gases using mass flow controllers. Feed and product gas analysis was performed using a Hewlett-Packard 5890A gas chromatograph equipped with two thermal conductivity detectors. Product separation was achieved with an SPB-1 fused silica capillary column (60 m, 0.53 mm i.d., 5 μm film) and a Porapak QS column (5 m, 1/8 in. o.d., 80–100 mesh), arranged in parallel. Standard experiments at a total pressure of 0.6 MPa and in the temperature range 473–573 K were carried out using 3 g catalyst under a reactant flow rate of 150 cm^3(STP) min^{-1} (GHSV $= 2250\ h^{-1}$) $H_2 : CO_2 : NH_3 = 3 : 1 : 1$. Before use the catalysts were reduced at 453 K in a H_2/N_2 mixture by increasing the mole fraction of hydrogen stepwise (30 min per step) in the sequence 10/20/50 to 100%. After increasing the temperature to 473 K for 10 min, hydrogen was replaced by the reaction gas mixture and the temperature was brought to 513 K.

BET surface areas of catalysts, degassed to 0.1 Pa at 473 K, were measured by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 instrument, and assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule.

Palladium surface areas were measured by CO-chemisorption at 308 K using a Micromeritics ASAP 2010C instrument. Prior to measurements the samples were treated in flowing oxygen at 308 K for 30 min, followed by reduction in flowing hydrogen at 523 K for 2 h. A stoichiometric factor of 2 and a cross-sectional area of 0.0787 nm^2 for the palladium atom were assumed [17].

DRIFT spectra (4 cm^{-1} resolution) were recorded using a Perkin-Elmer 2000 FTIR spectrometer equipped with a controlled environmental chamber fitted with CaF_2 windows within a diffuse reflectance unit (both Spectra-Tech). Prior to experiments the samples were pretreated with hydrogen at 523 K for 2 h, and at 573 K for 10 min. Subsequently, a flow of 20 mol% H_2 in Ar (100 $cm^3\ min^{-1}$) was passed over the catalyst. Pulses of ammonia (4 cm^3) and of MMA (0.1 cm^{-3}, 40% MMA/H_2O) were injected at 303 K and 10^5 Pa into the carrier gas. After 10 min, the temperature was increased stepwise (50 K) to 573 K and DRIFT spectra were recorded.

For the in situ DRIFT measurements, 100 $cm^3\ min^{-1}$ of the reaction gas mixture ($H_2 : CO_2 : NH_3 = 3 : 1 : 1$) was passed over the pretreated catalyst sample under 0.6 MPa total pressure at a temperature of 523 or 593 K, respectively. After the system reached steady state, a first spectrum was recorded. Subsequently, the gas flow was changed to argon (100 $cm^3\ min^{-1}$, 0.6 MPa) and a second spectrum was taken. After cooling to 323 K, a third spectrum was recorded under argon flow at atmospheric pressure.

3. Results

3.1. Catalytic tests

Two catalysts with palladium contents of 2.8 wt% (Pd-3) and 7.6 wt% (Pd-8) were used. Table 1 lists the textural and catalytic properties of the palladium catalysts in the synthesis of methylamines from $H_2/CO_2/NH_3$ mixtures under the specified standard conditions. No indication for catalyst deactivation was observed throughout the catalytic tests. The pure alumina component possessed no catalytic activity, neither for amine synthesis nor for any other reaction under all experimental conditions. Thus palladium was the catalytically active component.

The temperature dependence of the product distribution measured for Pd-3 is shown in figure 1. Over the whole temperature range only small amounts of DMA and TMA were detected, reaching a maximum concentration of 0.081 and 0.049 mol%, respectively, at 533 K. At temperatures above 553 K, the amine production rate decreased as a consequence of enhanced methane production. CO formation via the reverse water–gas shift (RWGS) reaction increased with higher temperature. No other carbon containing products were detected with 20% NH_3 in the feed.

Without ammonia in the feed, traces of methanol (0.010 mol%) were detected, besides carbon monoxide. Methane formation was not observed at 513 K. Upon addition of ammonia to the feed, methanol production disappeared completely. The influence of the ammonia concentration in the feed on the amine production is illustrated for catalyst Pd-3 in figure 2. With increasing ammonia concentration the amount of MMA increased,

Table 1
Textural and catalytic properties of palladium–alumina catalysts

	Pd-8	Pd-3	Al_2O_3
Pd loading (wt%)	7.6	2.8	–
S_{BET} (m^2/g)	261	384	291
$\langle d_P \rangle$ (nm) [a]	4	15	23
$S_{(Pd)}$ (m^2/g) [b]	8.0	4.0	–
$d_{(Pd)}$ (nm) [b]	6	4	–
$rate_{(MA)}$ (mol amines $kg_{cat}^{-1}\ h^{-1}$) [c]	0.55	0.67	0
MMA : DMA : TMA [c]	88 : 9 : 3	80 : 12 : 8	–
TOF × 10^3 (MA $Pd^{-1}\ s^{-1}$)	1.10	1.81	–

[a] Mean pore diameter $\langle d_P \rangle$ ($4V_P/S_{BET}$).

[b] $S_{(Pd)}$, palladium surface area measured by CO chemisorption; $d_{(Pd)}$, palladium crystallite size calculated from $S_{(Pd)}$, assuming hemispheric particles.

[c] Rate of methylamine (MMA) production, methylamine distribution, and turnover frequency (TOF) of methylamine formation, respectively. (Standard conditions: 3 g catalyst, 513 K, 0.6 MPa, 150 $cm^3\ min^{-1}$ $CO_2 : NH_3 : H_2 = 1 : 1 : 3$).

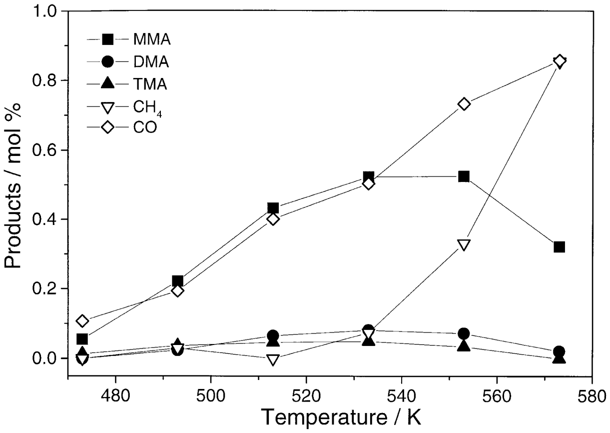

Figure 1. Temperature dependence of formation of methylamines, CO, and methane from CO_2, H_2, and NH_3 over catalyst Pd-3. Conditions: 3 g catalyst, 0.6 MPa, 150 cm^3 min^{-1} $CO_2 : NH_3 : H_2 = 1 : 1 : 3$.

whereas CO formation decreased up to 5 mol% NH_3. For higher ammonia concentrations CO formation reached its initial value and MMA formation continuously increased. Up to an ammonia concentration of 20 mol%, only trace amounts of DMA and TMA were observed.

Catalyst Pd-8, with higher palladium content, was less active for methylamine synthesis (table 1), reaching a maximum MMA concentration of 0.39 mol% at 513 K. DMA and TMA were only produced in trace amounts over the whole temperature range. At higher temperature methane formation increased strongly, whereas MMA production dropped, and at 573 K no amines could be observed anymore. The formation of CO, the main carbon containing product over the whole temperature range, increased continuously with increasing temperatures. Without ammonia in the feed, traces of methanol (0.004%), methane, and carbon monoxide were found in the product stream at 513 K. As with catalyst Pd-3 methanol formation was completely suppressed in the presence of ammonia in the feed, and MMA production increased with increasing ammonia concentration, whereas the formation of methane and carbon monoxide remained on the same level.

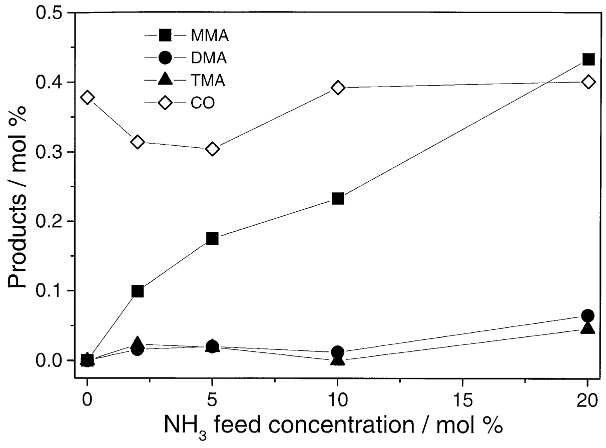

Figure 2. Influence of NH_3 feed concentration on formation of products from CO_2, H_2, and NH_3 over catalyst Pd-3. Conditions: 3 g catalyst, 0.6 MPa, 513 K, 150 cm^3 min^{-1} $CO_2 : H_2 = 1 : 3$.

3.2. Thermodynamics

The equilibrium product distribution of methylamines, starting from a $CO_2/H_2/NH_3$ (1 : 3 : 1) gas mixture, was calculated taking into account the following reactions:

$$CO_2 + 3H_2 + NH_3 \rightleftharpoons CH_3NH_2 + 2H_2O \tag{1}$$

$$2CO_2 + 6H_2 + NH_3 \rightleftharpoons (CH_3)_2NH + 4H_2O \tag{2}$$

$$3CO_2 + 9H_2 + NH_3 \rightleftharpoons (CH_3)_3N + 6H_2O \tag{3}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{4}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{5}$$

Taking into account methane formation as an additional reaction pathway,

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{6}$$

indicated that the hydrogen present in the feed is completely consumed by this reaction, and consequently reactions (1)–(5) became irrelevant.

The free standard reaction enthalpies, $\Delta G^0_{r,x}$, of the reactions (1)–(5) were calculated for different temperatures using literature values [18,19] for corresponding enthalpies and entropies of formation, and assuming ideal gas mixtures. Using the Van't Hoff relation, the equilibrium constants K_x of the reactions (1)–(5) were calculated for a total pressure of 0.6 MPa. The equilibrium composition of the product gas mixture at standard conditions (0.6 MPa, $H_2 : CO_2 : NH_3 = 3 : 1 : 1$) was derived from the system equations using a numerical method. The corresponding amine distribution, depicted in figure 3, indicates that MMA is the thermodynamically favored amine product when starting from a $CO_2/H_2/NH_3$ mixture.

3.3. Diffuse reflectance infrared Fourier transform (DRIFT) measurements

DRIFT measurements were performed to elucidate the nature of possible intermediates present on the catalyst surface under reaction conditions. For all experiments catalyst Pd-3 was used. Spectra are presented as difference spectra, which were obtained by subtracting the spectra measured for the catalyst before and after exposure to the adsorbing gas.

Ammonia adsorption. Figure 4A shows the spectra measured at different temperatures after adsorption of

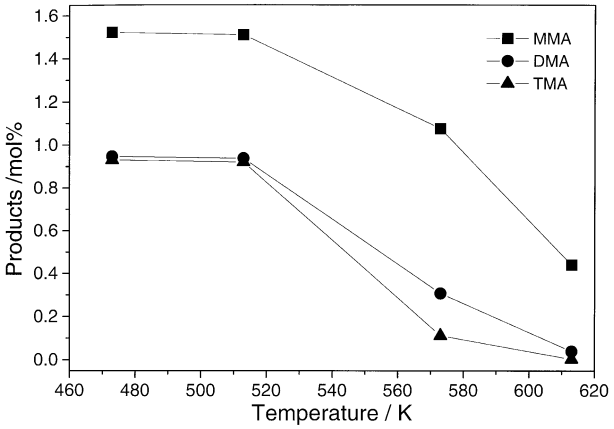

Figure 3. Equilibrium distribution of methylamines calculated for different temperatures.

ammonia at 303 K. At 373 K, prominent bands at 1692, 1470 and 1397 cm^{-1}, assigned to Brønsted bound ammonia, and weaker bands of ammonia adsorbed on Lewis acid sites were observed at 1270 and 1622 cm^{-1} [20,21]. In the N–H stretch region, four bands were observed at 3095, 3155 cm^{-1} (Brønsted bound ammonia) and at 3360, 3405 cm^{-1} (Lewis bound ammonia). The negative bands in the range 3670–3770 cm^{-1} are due to the loss of surface hydroxyl groups on alumina upon adsorption of NH_3 on Brønsted acid sites. When the temperature was increased, ammonia desorbed progressively from the surface and finally, at 573 K, only weak signals due to Lewis and Brønsted bound ammonia remained, whereas the hydroxyl groups of the alumina regenerated almost completely.

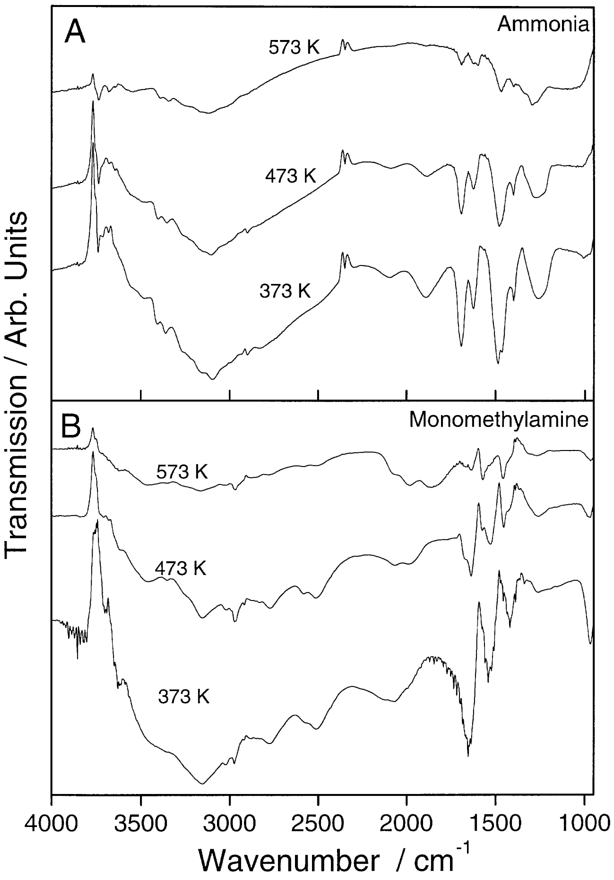

Figure 4. FTIR spectra of (A) ammonia and of (B) monomethylamine adsorbed at 303 K on Pd-3, measured at different temperatures. Carrier gas: 20 mol% H_2 in Ar; 100 cm^3 min^{-1}. (Spectra after subtracting the background spectra of the sample recorded before exposure to the adsorbing gas.)

Monomethylamine (MMA) adsorption. DRIFT spectra of MMA adsorbed on Pd-3 at 303 K are depicted in figure 4B. The spectrum recorded at 373 K is superimposed by strong absorptions due to the presence of water. The disappearance of surface hydroxyl groups, characterized by negative bands around 3750 cm^{-1}, indicated the adsorption of MMA on Brønsted acid sites of alumina. In the N–H stretch region broad, weak bands were observed at 3355, 3260 and 3158 cm^{-1}, which overlapped with bands originating from water. The band at 3355 cm^{-1} was assigned to MMA adsorbed on Lewis acid sites, whereas the latter two bands originated from Brønsted bound MMA [21]. The spectral range below 2000 cm^{-1} is dominated by a strong band at 1640 cm^{-1}, which results from a superposition of the deformation band of water with the asymmetric bending vibration of $-NH_3^+$ groups of MMA on Lewis and Brønsted acid sites, respectively [22,23]. The band at 1540 cm^{-1} was assigned to Brønsted bound MMA [22,23]. In the C–H stretch region bands were observed at 3016, 2975, 2916 and 2763 cm^{-1}, resulting from adsorbed MMA and from oxidation products of MMA. Upon increasing the temperature, the bands due to the adsorption of MMA decreased, and the hydroxyl groups of the alumina regenerated almost completely.

In situ amine synthesis. The in situ FTIR measurements, shown in figure 5, were carried out at 523 K (top) and 593 K (bottom), respectively. Spectra A in figure 5, measured under a flow of $CO_2/H_2/NH_3$, represent a combination of gas phase and surface spectra, whereas spectra B and C, recorded under argon atmosphere, are more specific for surface species. The spectral range below 2000 cm^{-1} (not shown in figure 5) was superimposed by bands originating from adsorbed water, ammonia, and possibly methylamines as well as from surface carbonate and formate species, rendering a straightforward interpretation difficult. Spectra A (figure 5) showed a doublet at 2363/2338 cm^{-1} and two additional doublets in the region of 3730 to 3550 cm^{-1}, characteristic for gas phase and physisorbed carbon dioxide. The band at 3334 cm^{-1} with the surrounding multiplet was caused by gas phase ammonia.

In the region of C–H stretch vibrations (2700–3000 cm^{-1}) two broadened bands with maxima at about 2960 and 2880 cm^{-1}, and two weak signals at 2765 and 2740 cm^{-1} were observed at 523 K. These signals mainly originated from adsorbed formate species, which show

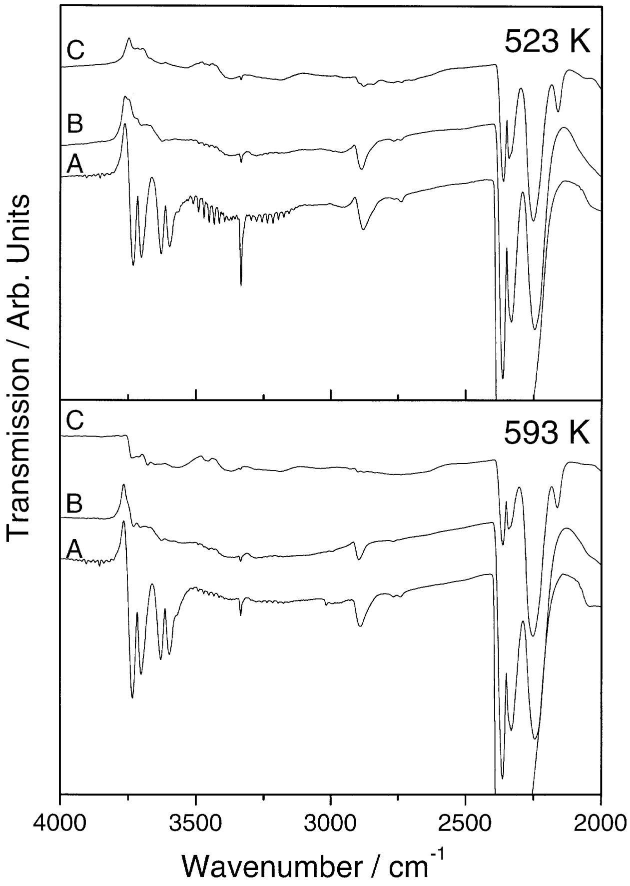

Figure 5. In situ FTIR measurements at 523 K (top) and at 593 K (bottom) of catalyst Pd-3 during methylamine synthesis from CO_2, H_2, and NH_3. (A) Spectrum under reactant gas atmosphere and 0.6 MPa pressure; (B) spectrum recorded under argon (100 cm^3 min^{-1}) flow at 0.6 MPa pressure and reaction temperature; (C) spectrum recorded under argon (100 cm^3 min^{-1}) flow at atmospheric pressure after cooling to 323 K.

characteristic bands around 2960, 2880 and 2750 cm^{-1} [24]. The asymmetry and the broadening of the bands at 2880 (shoulder at 2840 cm^{-1}) and 2960 cm^{-1} could be indicative for an overlapping with bands originating from adsorbed methylamine or methylate species. The spectra of the in situ measurements carried out at 593 K (figure 5, bottom) were similar, except for the C–H stretch region, where an additional narrow band at 3016 cm^{-1}, assigned to gas phase or physisorbed methane [24], was observed. Moreover, no broadening of the band at 2880 cm^{-1} was detected, and the band at 2960 cm^{-1} disappeared.

In addition to the bands described above, a shoulder was observed at 2250 cm^{-1} for both temperatures in spectra A (figure 5), which developed to an isolated band for spectra B and C. Upon cooling to 323 K at atmospheric pressure under argon, a new band appeared at 2161 cm^{-1} (spectrum C). Bands around 2250 cm^{-1} are assigned in the literature to surface isocyanate species, whereas bands around 2161 cm^{-1} are indicative for surface cyanide species [25,26].

4. Discussion

4.1. Catalytic behavior

Methylamines are industrially produced by the reaction of ammonia with methanol. The thermodynamic equilibrium composition of this reaction favors the formation of TMA, whereas the commercially demanded products are MMA and DMA [8]. This renders the high MMA selectivity obtained in methylamine synthesis from $CO_2/H_2/NH_3$ over palladium–alumina catalysts particularly interesting. Both catalysts produced the monoalkylated product MMA with selectivities $> 80\%$ at 513 K (table 1). This value also exceeds the selectivity (45% MMA) calculated from the thermodynamic equilibrium concentrations (figure 3), indicating that the methylamine distribution may not be thermodynamically controlled. The results indicate that the disproportionation of the MMA product, which is also catalyzed by palladium–alumina catalysts [5], seems to have little influence on the methylamine distribution. Comparing the palladium–alumina catalysts with other metal–alumina catalysts [15], shows the former to be most active for methylamine synthesis at temperatures up to 533 K. Turnover frequencies based on moles of methylamines produced at 533 K under standard conditions per hour and per mol of surface metal are clearly higher for Pd-3 ($\mathrm{TOF} = 9.4\ \mathrm{h}^{-1}$) compared to copper–alumina ($\mathrm{TOF} = 2.9\ \mathrm{h}^{-1}$) [14]. At higher temperatures, methane formation becomes dominant and methylamine production declines, but with the palladium based catalysts being still more selective towards MMA than the highly loaded copper–alumina catalysts, which showed highest activity at temperatures exceeding 553 K [15].

As to the role of the support, methylamine synthesis studies [27] performed on various copper–metal oxide catalysts revealed that the metal oxide component has some influence on the catalytic performance. Similar behavior is also expected for the palladium based catalysts.

4.2. DRIFT measurements

DRIFT measurements with ammonia and monomethylamine revealed, that both molecules are adsorbed on Brønsted and Lewis acid sites. Upon heating to 573 K the Brønsted bound ammonia and MMA are almost completely desorbed. In situ experiments with a $CO_2/H_2/NH_3$ feed at 523 K show that predominantly formate species are present on the catalyst surface under reaction conditions, as indicated by the main band at 2880 cm^{-1} and the additional weaker absorptions at 2960, 2765, and 2740 cm^{-1}. The observation, that the bands at 2960 and 2880 cm^{-1} are broadened and asymmetric suggests overlapping with bands originating from adsorbed methylamine or methylate species. Methylamines show bands in this region (figure 4) and

CH_3O^--species possess characteristic vibrational absorptions at 2930 and 2820 cm^{-1} [24].

At a reaction temperature of 593 K mainly carbon monoxide and methane are produced (figure 1) in the catalytic tests. The corresponding DRIFT measurements at 593 K clearly show the presence of methane by a sharp band at 3016 cm^{-1}. In addition, the asymmetric component of the band at 2880 cm^{-1} disappeared and the band shifted to 2890 cm^{-1}, whereas the broadened band at 2960 cm^{-1} was not detected anymore (figure 5, bottom). This finding is in accordance with the fact that methylamine production is very low at 593 K.

The NCO band at 2250 cm^{-1}, observed in the in situ experiments, was also found on the pure alumina support under analogous conditions, indicating that palladium is not necessary for the formation of NCO on the surface. NCO can be formed according to the surface reactions (7) and (8) or (9) and (10):

$$NH_3 + -OH_{ads} \rightleftharpoons -NH_{2ads} + H_2O \quad (7)$$

$$CO_2 + -NH_{2ads} \rightleftharpoons -NCO_{ads} + H_2O \quad (8)$$

$$NH_3 + CO_2 \rightleftharpoons H_2NCOOH \rightleftharpoons HNCO + H_2O \quad (9)$$

$$HNCO + -OH_{ads} \rightleftharpoons -NCO_{ads} + H_2O \quad (10)$$

These reactions were described by Unland [25] in the opposite direction as decomposition reactions of NCO species on Pt/Al_2O_3.

The band at 2161 cm^{-1}, observed in the FTIR experiments on Pd-3 after cooling to 323 K at atmospheric pressure under argon, is assigned to surface cyanide species. Over several metal–alumina catalysts (Cu, Ag and Fe) HCN was produced as a by-product [15], but on palladium–alumina no HCN was observed in the product gas under the conditions tested.

As regards the reaction pathway for the formation of methylamines from CO_2, H_2 and NH_3, a mechanism has been proposed for copper–alumina catalysts, which involves the reaction of an aldehydic surface intermediate formed from CO_2 and H_2 with adsorbed ammonia. The mechanism was proposed on the basis of findings in the amination of alcohols with ammonia, and of methanol synthesis from CO_2 and H_2. It was suggested, that methylamine formation occurs mainly by the reaction of ammonia with a methanol precursor and not via methanol when starting from a $CO_2/H_2/NH_3$ mixture [14]. However, with palladium–alumina catalysts, a reaction pathway involving surface isocyanate species in the synthesis of methylamines cannot be excluded. Isocyanate species could be hydrogenated to MMA, thus requiring the metal component of the catalyst to activate hydrogen. This would be in agreement with earlier results [15], which showed that over the pure alumina support no methylamines can be formed from $CO_2/H_2/NH_3$ mixtures.

5. Conclusions

The catalytic reaction of carbon dioxide, hydrogen, and ammonia over palladium–alumina produces methylamines with high rates and selectivity to monomethylamine $> 80\%$ at low temperatures. Other carbon containing products formed are di- and trimethylamine, carbon monoxide (reverse water–gas shift reaction), and methane, which becomes the main product at temperatures above 573 K.

FTIR investigation showed that ammonia and monomethylamine are adsorbed on Brønsted and Lewis acid sites on palladium–alumina. Surface formate and isocyanate species are prevailing on the catalyst surface under reaction conditions. At higher temperatures methane formation is clearly evidenced in the FTIR spectra.

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