

Chemically activated ruthenium mono(bipyridine)/SiO₂ catalysts in water–gas shift reaction

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Abstract

Chemical activation of supported ruthenium mono(bipyridine) carbonyls was found to be an effective route to highly active water–gas shift catalysts. Catalysts were activated by treating silica supported [Ru(bpy)(CO)₂Cl₂], [Ru(bpy)(CO)₂ClH], [Ru(bpy)(CO)₂Cl(C(O)OCH₃)] or [Ru(bpy)(CO)₂Cl]₂ with dilute NaOH or KOH solution. Ruthenium mono(bipyridine) carbonyls were deposited onto the support by impregnation from organic solvent or by pulse impregnation technique. In a typical experiment, catalysts achieved the final activity during WGS reaction. This induction period could be reduced by carrying out the hydroxide treatment under CO atmosphere. Catalytic activity was tested in the continuous flow WGS reaction at the temperature range 100–170°C. The non-activated supported complexes showed at most moderate activity. Chemical treatment with NaOH or KOH solution increased the turnover frequency at the whole temperature range. The highest activities were obtained with NaOH treated [Ru(bpy)(CO)₂Cl]₂/SiO₂, which gave turnover frequencies as high as 14 500 (mol CO₂ (Ru mol)⁻¹ (24 h)⁻¹) at 150 °C. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Chemical activation; Water–gas shift reaction; Ruthenium mono(bipyridine)/SiO₂ catalysts

1. Introduction

Commercial water–gas shift reaction (WGS) catalysts are typically metal oxides, which require relatively high reaction temperatures [1–3]. The search for the active catalysts operating at low temperatures has been concentrated mainly on homogeneous systems. Among the most widely studied systems are group VIII transition metal carbonyls including ruthenium catalysts such as [Ru₃(CO)₁₂], [Ru₃(CO)₁₂]/amine, [Ru₃(CO)₁₂]/([PPN]Cl) and [Ru(bpy)₂-

(CO)Cl](PF₆) [4–9]. Less attention has been paid to supported molecular-based ruthenium catalysts. One of the most promising heterogeneous systems is Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ [10,11].

Ruthenium bis(bipyridine) carbonyls are known to be active in WGS reaction. The reaction route for ruthenium bis(bipyridine) catalyzed WGS reaction has been well documented, including isolation and characterization of the key intermediates [9,12–16]. However, catalytic behavior of ruthenium mono(bipyridine) derivatives has been much less studied. In the present work catalytic activity and effects of chemical activation with alkalimetal hydroxides

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have been studied using silica supported ruthenium mono(bipyridine) carbonyls $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ and $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]$.

2. Experimental

2.1. Preparation of chemically activated catalysts

$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]$ $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ and $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]$ were synthesized by a literature method [17]. Impregnation, activation and catalyst manipulation was carried out in nitrogen or CO atmosphere. Catalyst precursors were impregnated onto calcinated (600 °C, 24 h or 100 °C 17 h) silica (silica-gel 60, Merck) from CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ or THF to obtain 1.5–3.0 wt.% initial Ru loading. Poorly soluble $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]$, which could not be dissolved, was merely mixed with the support in THF. After impregnation organic solvents were removed under vacuum and catalysts were activated with NaOH or KOH solutions (0.1 mol/dm³). Activation was carried out either by mixing supported catalyst in hydroxide solution, or the catalyst was packed into a modified column-type pulse-impregnation reactor [18] and activated by passing hydroxide solution through the catalyst bed. In the former method, the effectiveness of activation reaction could be

improved by refluxing the catalyst under CO or nitrogen atmosphere. The advantage of the latter method was that preliminary WGS tests could be carried out in situ in the modified pulse-impregnation reactor at low temperatures (110–113°C). Hydroxide activation led to formation of air-sensitive dark-blue, nearly black, catalyst surface. After activation, all catalysts were washed with water to remove residues of NaOH. Activation caused some leaching of the supported metal complex, which lowered the final Ru loading. This was noticeable especially when the activation was carried out in pulse impregnation reactor. The final ruthenium content of the activated catalysts was analyzed by AAS. Final ruthenium loading varied between 1.3–2.3 wt.%.

2.2. WGSR experiments

The catalysis experiments were carried out in a stainless steel continuous flow reactor (Fig. 1). The inner diameter of the reactor tube was 4 mm and the length was 20 cm. The total flow rate was controlled by adjusting inlet pressure of CO. Both water reservoir and the reactor could be heated separately (Fig. 1), allowing the control of the partial pressure of water. The total loading of the supported catalyst was typically 1.4–1.6 g and reaction time was 1–5 days. Reaction conditions: inlet pressure of CO $p_{\text{CO}} = 1\text{--}12$ bar, partial pressure of water $p_{\text{H}_2\text{O}} = 1\text{--}11$ bar, total flow rate 1.5–195 cm³/min,

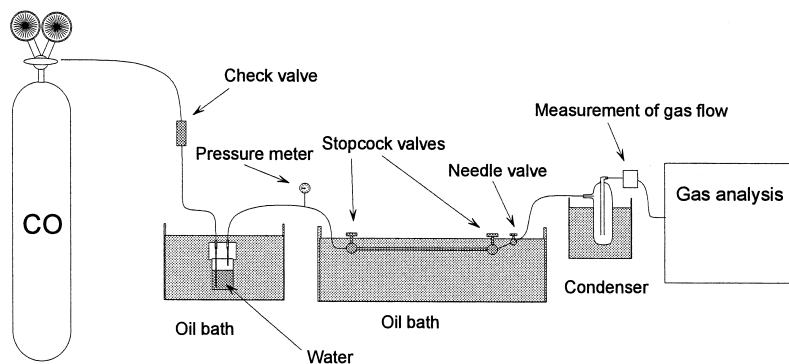


Fig. 1. WGS reactor system.

reactor temperature $T = 100\text{--}185^\circ\text{C}$. In all temperatures, the flow rate and inlet pressures were adjusted to obtain maximum turnover frequencies [$\text{mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$]. Reaction products H_2 and CO_2 were analyzed by GC. With all catalysts, the ratio of H_2 and CO_2 in the reaction product was determined in separate experiments and found to be ca. 1:1. During continuous flow reactions, only the formation of carbon dioxide was monitored.

Catalytic activity of non-activated $[\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})\text{-(CO)}_2\text{ClH}]/\text{SiO}_2$ was tested only in pulse impregnation reactor (inner diameter ca. 10 mm) at constant temperature ($110\text{--}113^\circ\text{C}$) and low pressures (inlet $p_{\text{CO}} = 1\text{--}1.1 \text{ bar}$). In these experiments, the typical loading of the supported catalyst was 2.5 g.

3. Results and discussion

Alkalimetal hydroxides are known to improve catalytic activity of ruthenium carbonyl-based catalysts in WGS. However, hydroxides have been previously used in homogeneous catalysis to achieve alkaline reaction conditions. In these systems, the hydroxide ion is proposed to act as a nucleophilic group, which attacks the carbon of a carbonyl ligand producing $-\text{COOH}$ group, an intermediate in the WGS cycle [9]. In the case of present hydroxide-activated ruthenium mono(bipyridine) derivatives, the role of hydroxide is solely to activate the catalyst. After activation, ruthenium mono(bipyridine) carbonyls do not require alkaline reaction conditions.

3.1. Catalytic behavior of non-activated ruthenium mono(bipyridine) carbonyl / SiO_2 catalysts

Compared to the NaOH - or KOH -activated catalysts, the non-activated ruthenium mono(bipyridines) showed considerably poorer activities in tested temperature range between $100\text{--}170^\circ\text{C}$

(Figs. 2 and 3, Table 1). However, the activity improved with increasing temperature. The turnover frequencies of non-activated $[\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}_2]/\text{SiO}_2$ increased from about $5 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$ at 100°C up to $850 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$ at 170°C . At low temperatures, the non-activated dimer $[\{\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}_2\}]/\text{SiO}_2$ was even less active. Turnover frequencies increased slowly from ca. 2 to $250 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$ in the temperature range from 100 to 150°C . Over 150°C , temperatures increased the activity of the dimer, rapidly giving maximum turnover frequencies of $2100 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$ at 170°C .

During the WGS reaction, the color of the non-activated catalysts tended to darken to dark blue or bluish black, which indicates that activation of the catalysts probably occurred to some extent. However, since the turnover frequencies remained relatively low, the activation during WGS reaction was obviously insufficient. Furthermore, the catalyst surface was not uniform. Especially in the case of $[\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}_2]/\text{SiO}_2$, the color of the catalyst varied throughout the catalyst bed containing dark blue and dark brown regions. Another problem with inactivated $[\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}_2]/\text{SiO}_2$ and $[\{\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}_2\}]/\text{SiO}_2$ was that the flow rate varied strongly during the WGS reaction. This could be due to surface reactions of the supported

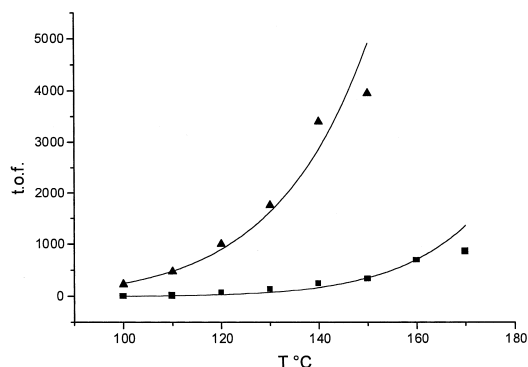


Fig. 2. Turnover frequencies ($\text{mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$) of activated (▲) and non-activated (■) $[\text{Ru}(\text{bpy})\text{-(CO)}_2\text{Cl}_2]/\text{SiO}_2$ catalysts. Solid lines: corresponding Arrhenius plots.

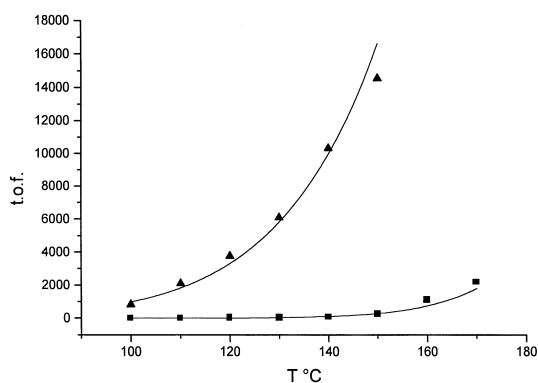


Fig. 3. Turnover frequencies ($\text{mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$) of activated (\blacktriangle) and non-activated (\blacksquare) $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$ catalysts. Solid lines: corresponding Arrhenius plots.

ruthenium compound during the catalysis process.

Catalytic behavior of non-activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ was tested only in pulse impregnation reactor at low temperatures and inlet pressures (see Section 2). The turnover frequencies are therefore not completely comparable with the experiments in the actual continuous flow reactor. At these milder conditions, the turnover frequencies of non-activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ remained below $20 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$. Activation with NaOH solution increased activities considerably giving turnover frequencies over $200 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$.

3.2. Maximum activities and thermal behavior of activated ruthenium mono(bipyridine) carbonyl / SiO_2 catalysts

With all tested catalysts, NaOH (or KOH) activation turned the catalyst to dark blue or bluish black in color. The color change was faster with $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ and slower with dimeric $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2\}]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$, indicating poorer reactivity of the latter compounds. Especially with these less reactive precursors, the effectiveness of the activation process could be improved by refluxing the catalyst in the alkalimetal hydroxide solution under nitrogen or preferably under CO atmosphere. Typically, the hydroxide-activated catalysts obtained their final activity after several hours of continuous WGS reaction, suggesting that the activation was completed only under CO/ H_2O pressure. Similar induction period is also required to obtain final activity with $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine catalyst [10].

It has been proposed that treatment of chlorine containing ruthenium mono(bipyridine) carbonyls with alkalimetal hydroxides leads to dechlorination of the parent compound accompanied with oligomerization [19] or, under suitable conditions, polymerization [20]. Especially when the activation is carried out under CO atmosphere, the activation process may also in-

Table 1
Maximum activities of the silica supported ruthenium mono(bipyridine) carbonyls

Catalyst precursor	Ru (wt.%)	T ($^{\circ}\text{C}$)	Turnover frequency ^a
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2^{\text{b}}$	1.4	170	860
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$	1.5	150	4000
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$	1.3	150	6800
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$	1.3	160	10 500
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$	2.3	150	4100
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$	2.3	160	6600
$[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2\}]/\text{SiO}_2^{\text{b}}$	1.6	170	2200
$[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2\}]/\text{SiO}_2$	1.6	150	14 500
$[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2\}]/\text{SiO}_2^{\text{c}}$	1.6	150	7500

Reaction conditions: $p_{\text{CO}} = 1\text{--}12 \text{ bar}$, $p_{\text{H}_2\text{O}} = 1\text{--}11 \text{ bar}$, flow rate $1.5\text{--}195 \text{ cm}^3/\text{min}$, $T = 100\text{--}185^{\circ}\text{C}$.

^at.o.f. = $\text{mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$.

^bNon-activated catalyst.

^cActivated with 0.1 mol l^{-1} KOH solution, other catalysts were activated with 0.1 mol l^{-1} NaOH solution.

clude reduction of the ruthenium compound. If the role of the alkalimetal hydroxide, or hydroxide/CO, is to act as a dechlorination agent, the presence of CO in WGS reaction could enhance the reduction process, further improving the activity during the induction period.

The chemically activated ruthenium mono(bipyridine) carbonyls were active in the whole temperature range from 100 to 185°C (Figs. 2–4). The highest activities were obtained with NaOH-treated dimer $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$ (Table 1). The activity of the dimer-derived catalyst increased rapidly with increasing temperature, giving maximum reproducible turnover frequency of $14\,500 \text{ mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$ at 150°C (Fig. 3). Even higher activities were observed at higher temperatures, but the catalyst was no longer stable. The activity of the KOH-activated dimer was lower than the activity of corresponding NaOH activated $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$, giving maximum turnover frequency of $7500 \text{ mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$ at 150°C. However, it shows that both NaOH and KOH can be used in activation.

In the temperature range of 100–140°C, NaOH-treated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$, $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})-$

$(\text{CO})_2\text{Cl}_2]$ showed comparable activities with each other, but at higher temperatures, activities varied depending the parent compound (Figs. 2 and 4). The turnover frequency of activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]$ was 6600 at 160°C, and it increased up to $10\,000 \text{ mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$ at 170°C. However, at 170°C, the stability of the catalyst started to deteriorate, and at higher temperatures, the stability was completely lost. Above 140°C, the catalytic efficiency of activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ was somewhat higher compared to $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ or $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$, yielding 6800 and $10\,500 \text{ mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$ at 150°C and 160°C, respectively. With activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$, the reproducible maximum turnover frequency of $4000 \text{ mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$ was obtained at 150°C (Fig. 2). At this temperature, the catalytic efficiency was thus lower than the activity of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$, but still comparable with the activity of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$. At higher temperatures (over 150–160 °C) also, the stability of the activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$ was lost.

Variations in activity of activated ruthenium mono(bipyridine) carbonyl/ SiO_2 catalysts is most probably due to differences in reactivity of the ruthenium compounds with alkalimetal hydroxides. Both $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ react rapidly even at room temperature, yielding a uniform dark blue catalysts. Reaction of $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$ requires several hours heating by refluxing under N_2 or CO atmosphere to obtain the final catalyst, and even such thermal treatment may be insufficient to obtain completely uniform catalyst surface. Although the dimeric $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$ is also poorly reactive at room temperature the activation, can be carried out effectively by refluxing under N_2 or CO atmosphere. This may be due to the fact that the ruthenium center in the dimer is already at lower oxidation state than in monomers.

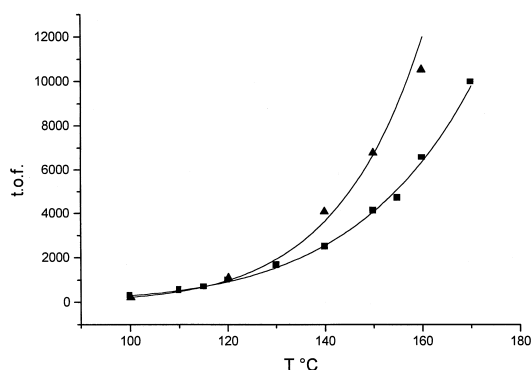


Fig. 4. Turn-over frequencies ($\text{mol CO}_2 (\text{mol Ru})^{-1} (24 \text{ h})^{-1}$) of activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ (▲) and activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ (■) catalysts. Solid lines: corresponding Arrhenius plots.

With all activated catalysts, turnover frequencies increased nearly exponentially with increasing temperature. In order to estimate the apparent activation energy of the catalysis reaction, Arrhenius plots (Arrhenius expression $r = A \exp(-E_a/RT)$, where A is the preexponential frequency factor and E_a the apparent activation energy) were fitted in the experimental data. Preexponential factors and activation energies are summarized in Table 2. Activated $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$ gave good fit with the exponential curve up to 140°C , but at higher temperatures, the calculated curve overestimates the activity. Similar overestimation occurs also with activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$ catalysts at higher temperatures (over 150 and 130°C , respectively). Activated $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$ gave good fit at a whole temperature range of 100 – 170°C . Overestimation is probably due to thermal instability of the activated catalysts at higher temperatures. Close to maximum operating temperature, where the catalysts remain stable, the observed activity increase is no longer exponential, but starts to curve, resembling more closely to Gaussian-shaped plot.

The Arrhenius fit was poorer for non-activated $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$ and $[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$, indicating that the thermal behavior of non-activated catalysts were not strictly exponential.

The apparent activation energies calculated for activated mono(bipyridine) carbonyl/ SiO_2

catalysts are close to those reported by Grenoble et al. [21] for a series of alumina-supported metal catalysts. Compared to $\text{Ru}/\text{Al}_2\text{O}_3$, the activated ruthenium mono(bipyridine) carbonyl/ SiO_2 catalysts give superior activity at low temperatures. At 150°C , the activity of $\text{Ru}/\text{Al}_2\text{O}_3$ is $15 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$, which is nearly a thousand times lower than the activity of $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$. In fact, the activity of the $[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]/\text{SiO}_2$ is close to the activity of $10\% \text{ Cu}/\text{Al}_2\text{O}_3$. According to Grenoble et al., the calculated activity for alumina supported copper catalysts is ca. $17\,000 \text{ mol mol}^{-1} (24 \text{ h})^{-1}$. However, turnover frequencies for the alumina-supported metal catalysts have been calculated per metal sites, while our results have been calculated per total amount of metal. For example, the fraction of surface metal atoms in $10\% \text{ Cu}/\text{Al}_2\text{O}_3$ is reported to be only 0.03 [21], indicating very low dispersion. If the activity were calculated per total amount of supported metal, the activity would be considerably lower.

Most of the molecular-based WGS catalysts found in literature are homogeneous [4,5,22,6,7,23,24] [25–31]. These catalysts have been studied in both thermal and photochemical water–gas shift reactions using batch-type reactors. As compared to the homogeneous ruthenium carbonyl catalysts [4–7,9], chemically activated heterogeneous ruthenium mono(bipyridines) are clearly more effective. In alkaline conditions at 150°C , a turnover frequency of about $500 \text{ mol H}_2 (\text{mol complex})^{-1} (20 \text{ h})^{-1}$ has been reported for homogeneous ruthenium bis(bipyridine) catalyst $[\text{Ru}(\text{bpy})_2(\text{CO})\text{Cl}](\text{PF}_6)$ [9]. Somewhat higher activities have been reported for homogeneous ruthenium amine systems for example $\text{Ru}_3(\text{CO})_{12}/\text{trimethylamine}$ [5]. Supported molecular based catalysts are less commonly studied especially in continuous flow reactions. One of the most efficient supported ruthenium carbonyl-based catalyst is the thermally activated $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 . The catalytic behavior of the $\text{Ru}_3(\text{CO})_{12}/2,2'$ -bipyridine/ SiO_2 depends strongly on the

Table 2
Arrhenius parameters of silica supported catalysts

Catalysts	E_a^a	A^b
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2^c$	104.2 ± 10	$3.02 \cdot 10^{10}$
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2]/\text{SiO}_2$	77.9 ± 5	$2.36 \cdot 10^8$
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{ClH}]/\text{SiO}_2$	88.2 ± 3	$5.95 \cdot 10^9$
$[\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}(\text{C}(\text{O})\text{OCH}_3)]/\text{SiO}_2$	68.1 ± 1	$1.21 \cdot 10^7$
$[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]^c$	141.2 ± 14	$9.38 \cdot 10^{14}$
$[\{\text{Ru}(\text{bpy})(\text{CO})_2\text{Cl}\}_2]$	74.2 ± 5	$2.76 \cdot 10^8$

^aApparent activation energy, kJ/mol.

^bPreexponential factor in the equation $r = A \exp(-E_a/RT)$.

^cNon-activated catalyst.

catalyst preparation method. The highest activities have been obtained with the catalysts prepared by CVD-based method (t.o.f. ca. 6500 mol H₂ (mol Ru)⁻¹ (24 h)⁻¹, at 150 °C) [11], while simple impregnated catalysts are significantly less active (t.o.f. ca. 2500 mol H₂ (mol Ru)⁻¹ (24 h)⁻¹, at 150°C) [10]. The highest reported activities for Ru₃(CO)₁₂/2,2'-bipyridine/SiO₂ catalysts at 150°C are comparable with the activity of hydroxide-treated [Ru(bpy)(CO)₂ClH]/SiO₂ and [Ru(bpy)(CO)₂Cl(C(O)OCH₃)]/SiO₂, but clearly less active than the NaOH-activated {[Ru(bpy)(CO)₂Cl]₂}/SiO₂.

4. Summary

Chemical activation of ruthenium mono(bipyridines) with NaOH- or KOH-solution offer an effective route for preparing highly active heterogeneous water–gas shift catalysts directly onto support. Hydroxide-activated ruthenium mono(bipyridines) were active in a temperature range of 100–170°C. The optimum reaction temperature was typically 150°C. At higher temperatures, the catalysts were no longer stable, and the catalytic activity was irreversibly reduced. Effectiveness of the activation process depended somewhat on the used ruthenium mono(bipyridine) compound. The activity of the hydroxide-treated monomers [Ru(bpy)(CO)₂Cl(C(O)OCH₃)]/SiO₂, [Ru(bpy)(CO)₂ClH]/SiO₂ and [Ru(bpy)(CO)₂Cl]₂ showed similar activity in the temperature range of 100–140°C. At higher temperatures, the activity of [Ru(bpy)(CO)₂Cl]₂/SiO₂ was lower than the activity of other monomers. The highest activities in the temperature range of 100–150°C were obtained with the activated dimer {[Ru(bpy)(CO)₂Cl]₂}/SiO₂. The activity of all tested ruthenium mono(bipyridine) carbonyl/SiO₂ catalysts was superior compared to supported metallic ruthenium catalyst. Compared to homogeneous molecular-based ruthenium catalyst such as [Ru(bpy)₂(CO)Cl](PF₆) or Ru₃(CO)₁₂/amine

activated silica supported ruthenium mono(bipyridines) gave also considerably higher activities.

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