The low-temperature water–gas shift reaction catalyzed by sodium-carbonate-activated ruthenium mono(bipyridine)/SiO_2 complexes

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The effect of a new catalyst activation method on the catalytic activities of several chlorine-containing ruthenium mono(bipyridine) carbonyl complexes in the water–gas shift reaction (WGSR) was studied. The chemical activation of the silica-supported complexes by a sodium carbonate/methanol solution under CO atmosphere produced highly active low-temperature water–gas shift reaction catalysts.

Keywords: ruthenium, bipyridine, catalyst, WGSR

1. Introduction

Ruthenium bipyridine complexes are proven active catalysts or catalyst precursors in homogeneous and heterogeneous water–gas shift reaction (WGSR). Ruthenium bis(bipyridine) complexes catalyze thermal homogeneous WGSR at low temperatures in alkaline reaction conditions or photoinduced reaction under exposure to white light [1].

Chemical modification of supported ruthenium mono (bipyridine) complexes is an effective method to produce active WGSR catalysts. Especially silica-supported, mono- and dinuclear ruthenium mono(bipyridine) carbonyl complexes treated with alkali metal hydroxides (NaOH, KOH) are found to be active catalyst precursors in heterogeneous WGSR [2,3]. The effectivity of alkali metal hydroxide activated treatment is dependent on the catalyst precursor used. The highest activity has been achieved with a NaOH-treated dimer, $[Ru(bpy)(CO)_2Cl]_2$, whereas corresponding mononuclear compounds, such as $[Ru(bpy)(CO)_2Cl_2]$, have turned out to be distinctly less effective [2]. According to the results it seems that the alkali metal hydroxide treatment method is insufficient for effective activation of monomers. Therefore, it was of interest to find an activation method which enables formation of effective catalysts under mild conditions and which activates not only dimeric but also monomeric ruthenium bipyridine carbonyl complexes. There is a wide range of monomeric precursors available [4] and furthermore, monometallic compounds are, unlike dimers, easily soluble in most common solvents. Solubility provides an effective preparation method for highly dispersed supported catalysts by using a simple impregnation technique.

In the new method of catalyst preparation introduced here, sodium carbonate, methanol and carbon monoxide are used as activation agents.

2. Experimental

2.1. Activation procedure

Chemical activation of catalysts is performed prior to WGS reaction and alkaline reaction conditions are not needed after activation. All the catalyst manipulation phases were carried out in nitrogen or CO atmosphere. Catalyst precursors were impregnated onto calcined silica carrier from THF (2 h period) so that the initial ruthenium loading was 1.6%. After the evaporation of the solvent the dried catalyst precursors were activated in methanol under CO atmosphere overnight with Na_2CO_3 present. During the activation period an air sensitive, black catalyst surface was formed. The activated catalysts were washed a few times with methanol and water and dried *in vacuo*. The final ruthenium content of the catalysts was determined by AAS.

2.2. WGSR experiments

The WGSR experiments were carried out in a stainless-steel continuous-flow reactor in the temperature range 100–150 °C. The dried silica-supported catalyst (1–1.4 g) was loaded in a reactor tube (inner diameter 3.4 mm, length 21 cm) in a glove box. Total CO flow rate was controlled during the four days period by adjusting the CO inlet pressure. The gaseous products were analyzed by GC. On the basis of gas analysis the activity of the catalyst was calculated in units of mol H_2/mol Ru per 24 h.

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3. Results and discussion

Alkali metal hydroxides and carbonates under carbon monoxide atmosphere have been reported to act as dechlorinating and reducing agents for the carbonyl-containing ruthenium complexes, and the addition of a base in the solution results in chlorine cleavage from the coordination sphere of ruthenium [5–9]. It has also been suggested that the dechlorination and reduction of ruthenium mono(bipyridine) complexes lead to the formation of Ru–Ru chained polymer, $[Ru(bpy)(CO)_2]_n$. The polymer has been proposed to be the active form of alkali metal hydroxide activated ruthenium mono(bipyridine) carbonyl catalysts and it can also be prepared electrochemically [10–12]. As the effectiveness of the alkali metal hydroxide activation method seems to be dependent on the ruthenium bipyridine complex used it was of interest to find an activation method which results in formation of the same active species and catalytic activity with all activated complexes.

The reaction mechanism of WGSR catalyzed by ruthenium mono(bipyridine) carbonyl complexes is not yet fully characterized. The reaction is, however, suggested to proceed similarly to the known mechanism of the reaction catalyzed by ruthenium bis(bpy) complexes. The catalytic cycle of WGS reaction from $[Ru(bpy)_2(CO)Cl]^+$ is found to involve a nucleophilic attack of –OH to the carbon of the carbonyl group following a thermal decarboxylation of the resulting hydroxycarbonyl complex and finally the evolution of H_2 by the reaction of metal hydride with water [1a].

Catalytic behavior of several silica-supported ruthenium mono(bipyridine) carbonyl complexes, pretreated with sodium carbonate/methanol solution under CO atmosphere was tested in WGSR. The catalytic activity of Na_2CO_3-activated monomers was high throughout the temperature range (100–150 °C), while the highest activities of all complexes were obtained at 150 °C (table 1). To test the effects of the catalyst activation conditions, solvent, base, and a gaseous composition were varied in a few experiments in order to define the effect of reaction conditions on catalytic activities of the tested complexes.

The results shown in table 1 indicate that the activities of all the monomeric complexes were improved considerably with milder reaction conditions. $[Ru(bpy)(CO)_2Cl_2]$ and $[Ru(bpy)(CO)_2ClH]$ activated with Na_2CO_3/MeOH under CO atmosphere were found to be the two most active mononuclear ruthenium complexes. The activities of the Na_2CO_3-activated complexes were distinctly higher than the activities after NaOH treatment [2], and furthermore, the maximum turnover frequencies of the two complexes were of the same order of magnitude, which suggests the formation of similar active species. Monomeric complexes with alkoxy carbonyl groups bonded to ruthenium atom, sodium-carbonate-activated $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ and previously untested $[Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)]$ showed poorer activities in WGSR than their hydride and chloride complexes. It appears, that during the activation chlorine and hydride cleavage occurs more easily than cleavage of alkoxy carbonyls, which may be explained by different reaction mechanisms. Probably complete activation of the alkoxy carbonyl group containing complexes did not take place, although Na_2CO_3 activation is clearly more effective for $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ than NaOH activation.

To test the effects of the catalyst activation conditions, solvent, base, and a gaseous composition were varied in a few experiments in order to define the effect of reaction conditions on catalytic activities of the tested complexes. As can be seen in table 1, modification of the activation conditions of these complexes lowered the catalytic efficiency considerably. The result emphasizes the significance of all activation agents, i.e., Na_2CO_3, MeOH and CO, in the activation process.

The most active catalyst proved to be Na_2CO_3-activated dimeric $[Ru(bpy)(CO)_2Cl]_2$ with a turnover frequency (mol product/mol Ru per 24 h) as high as 17200. The finding is in reasonable good agreement with the activity of the NaOH-activated dimer and it is likely that the same catalytically active species was formed as a result of both base activations. Also, the catalytic activity of the dimer is on

Table 1
Comparison of catalytic activities of silica-supported complexes at 150 °C (as mol product/mol Ru per 24 h).

Catalyst precursor	Na_2CO_3-activated	NaOH-activated [2,3]
$[Ru(bpy)(CO)_2Cl_2]$	15700	4000
$[Ru(bpy)(CO)_2Cl_2]^a$	1200	
$[Ru(bpy)(CO)_2Cl_2]^b$	2600	
$[Ru(bpy)(CO)_2Cl(C(O)OCH_2CH_2OH)]$	7100	
$[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$	7000	4100
$[Ru(bpy)(CO)_2ClH]$	14100	6800
$[Ru(bpy)(CO)_2ClH]^c$	2600	
$[Ru(bpy)(CO)_2Cl]_2$	17200	14500
$[Ru(4,4'\text{-dmbpy})(CO)_2Cl_2]$	3000	2000
$[Ru(4,4'\text{-dmbpy})(CO)_2Cl]_2$	1900	1500

[a] Activated under nitrogen atmosphere.
[b] Activated in a CH_3ONa/MeOH solution without Na_2CO_3.
[c] Activated in a Na_2CO_3/water solution.

the same order of magnitude as the activities of Na_2CO_3-activated monomeric complexes, [Ru(bpy)$(CO)_2$ClH] and [Ru(bpy)$(CO)_2Cl_2$], which may indicate that the active species is similar in all of these three cases.

Catalytic activities have been found to be clearly lower for NaOH-treated ruthenium 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbpy) complexes than for ruthenium 2,2′-bipyridine analogues [3]. The turnover frequencies seen in table 1 indicate that difference in activity was irrespective of the activation method. The least active complexes pretreated with the Na_2CO_3/MeOH/CO system turned out to be ruthenium 4,4′-dmbpy complexes, monometallic [Ru(4,4′-dmbpy)$(CO)_2Cl_2$] and dimeric [Ru(4,4′-dmbpy)$(CO)_2$Cl$]_2$ with an increase of only 1000 and 400, respectively, relative to the NaOH-activated complex. From these results it is evident that an inappropriate activation method was not the reason for the poor activities of the NaOH-activated dmbpy compounds.

4. Conclusions

Pretreating ruthenium mono(bipyridine) carbonyl complexes with sodium carbonate/methanol solution under CO atmosphere affords highly effective catalysts for low-temperature heterogeneous water–gas shift reaction. The best activities are among the highest ever reported for catalysts operating at low temperatures [13]. We found out that the sodium-carbonate-based activation method activates especially monomeric ruthenium mono(bipyridine) carbonyl complexes distinctly more efficiently than dilute NaOH or KOH solutions reported earlier.

Irrespective of the catalyst activation method, the catalytic activities of ruthenium 4,4′-dmbpy complexes remain distinctly lower in comparison with the activities of ruthenium 2,2′-bpy complexes.

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