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Support effect in a WGSR catalyzed by Na_2CO_3 activated $[Ru(bpy)(CO)_2Cl_2]$ catalyst

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The support effects on the water gas shift reaction activity of $[Ru(bpy)(CO)_2Cl_2]$ based catalyst were investigated. A series of oxide supports, Al_2O_3, TiO_2, SiO_2, Zeolites, ZrO_2 and $ZrSiO_4$, was studied. The catalytic activity was significantly improved when the catalyst was supported on weakly acidic alumina.

KEY WORDS: ruthenium catalyst; WGSR; support effect.

1. Introduction

The water gas shift reaction (WGSR) is an important method for producing hydrogen for many industrial purposes: Fischer-Tropsch type syntheses, ammonia syntheses, and organic chemicals [1]

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad (1)$$

Hydrogen production *via* WGSR is exothermic and reaches maximum conversions at low temperatures. However, for reasons connected with kinetics most of the commercial WGSR catalysts are metal oxides, which are active only at relatively high-reaction temperatures (315–485 °C) [2,3].

The catalytic performance and durability of various molecular metal compounds have been improved by using supports [4–6]. The effects of the support have been studied principally in the case of highly dispersed metallic catalysts operating at high temperatures. Less attention has been paid to the actual effects induced by the metal oxide supports on the molecular organometallic catalyst. Theoretical methods have been used to study the role played by the surface in the WGSR over porous catalysts [7]. The surface phenomena investigated by molecular modelling have shed some light on the nature and strength of the metal-support interactions [8,9], but the well-known complexity of these systems imposes limitations on the computational approach. Materials such as silica and alumina are included in the category of "active" supports because they can actively interact with the impregnated metal complexes [10]. Such interactions may then have either a positive or a negative impact on the catalytic process.

The structure and catalytic performance of the $[Ru(bpy)(CO)_2Cl_2]$ has been well documented. Typically, $[Ru(bpy)(CO)_2Cl_2]$ itself is not a highly active catalyst. The active form is obtained by means of appropriate chemical or electrochemical reduction. In consequence, previous studies have focused mainly on modifications of these "activation" methods or on modifications of the $[Ru(bpy)(CO)_2Cl_2]$ precursor, while the support effects on the catalytic activity have been studied only briefly [11–14]. In the present study we examine further the effect of different supports on the WGSR activity of the $[Ru(bpy)(CO)_2Cl_2]$ derived catalyst, employing batch reactors.

2. Experimental

2.1. Catalyst preparation

The catalyst precursor, $[Ru(bpy)(CO)_2Cl_2]$, was prepared according to the literature method [18,19] and supported by an impregnation from methanol solution. All of the supports were ≥999% pure (ZrO_2 from Alfa, $ZrSiO_2$, TiO_2 anatase, TiO_2 rutile, Al_2O_3 weakly acidic, Al_2O_3 strongly acidic, Al_2O_3 neutral, Al_2O_3 basic obtained from Aldrich, Zeolite ZSM-5, and Zeolite Mordenite, from Alsi-Penta zeolites, and SiO_2 obtained from Merck) and were dried for 2 h at 300 °C under vacuum prior to use. Impregnation was performed by introducing 1.3 mmol of $[Ru(bpy)(CO)_2Cl_2]$, 5 g of support and freshly distilled THF into a round-bottom flask, where the mixture was stirred overnight. After evaporation of the solvent, the catalyst was "activated" by adding 30 mL of CH_3OH solution, which contained 0.722 mmol of anhydrous Na_2CO_3 (99% Aldrich) to the reaction vessel. The solution was then heated under reflux and under CO (99%) atmosphere overnight. The catalyst was removed from reflux and cooled to room temperature and the product was filtrated and washed with water and ethanol to remove excess of Na_2CO_3.

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This activation procedure gives an almost black air-sensitive carbonyl containing molecular catalyst. In each experiment the calculated Ru content of the supported catalyst was set at 2%. This value was also used for all activity calculations, where activity was calculated as moles of product per mole of Ru.

2.2. Properties of the support

The BET surface area of the supports and the supported catalysts were measured in a Micrometrics ASAP 2010 and the average particle size was measured in a Sympatec helos laser diffraction system after the oxides had been dried in a vacuum (See table 1).

NH_3 TPD of the aluminas were carried out in a Micromeritics AutoChem 2910 instrumet equipped with a thermal conductivity detector. The sample (200 mg) was treated at 300 °C in Helium flow for 30 min. It was saturated at 120 °C with 10% NH_3/He mixture and then purged 120 min with He. Desorption of ammonia was measured by heating to 600 °C at a rate of 20 °C/min in helium flow of 20 mL/min. A water trap (KOH on quarz wool) was located before detector.

2.3. Catalytic activity

The catalytic reactions were performed in 100 mL Berghoff autoclaves equipped with a teflon liner. A sample of 0.500 g of the supported catalyst, 0.5 mL of H_2O and 8 bar of CO were introduced into the autoclave. The autoclave was first heated to 60 °C and maintained in this temperature overnight to stabilize the system and to achieve reproducible results, no conversion was observed then. Temperature was raised to 120 °C and gas samples were taken after 2 h of reaction and analyzed using a Hewlett-Packard 6890 series GC with a multicolumn system. The TOF were calculated based on the amount of ruthenium.

Table 1
Support surface properties

Support	BET surface area (m^2/g)	Average particle size microns
Al_2O_3 wa	157	100
Al_2O_3 sa	154	100
Al_2O_3 b	150	100
Al_2O_3 n	166	100
SiO_2	501	100
TiO_2 rutile	2	<10
TiO_2 anatase	9	<10
ZrO_2	5	1<10
$ZrSiO_4$	2	1<10<100
ZSM-5	700	100
Mordenite	800	100

wa = weakly acidic, sa = strongly acidic, b = basic, n = neutral. Surface areas were measured by nitrogen adsorption after supports were heated under vacuum at 300 °C for 2 h.

Table 2
Support effect on the WGS activity of the $[Ru(bpy)(CO)_2Cl_2]$ catalyst

Support	$TOF(H_2) \times 24^{-1}$	Catalyst BET surface area (m^2/g)
Al_2O_3 strongly acidic	130	164
Al_2O_3 neutral	138	176
Unsupported	421	–
Al_2O_3 basic	682	176
ZrO_2	700	7
ZSM-5	725	777
$ZrSiO_4$	828	3
SiO_2	920	525
Mordenite	955	821
TiO_2(anatase)	1038	13
TiO_2(rutile)	1068	4
Al_2O_3 weakly acidic	2660	176

Conditions: H_2O = 0.5 mL; g Cat = 0.5; PCO = 8 bar. Catalyst BET surface areas were measured at 120 °C and dried at same temperature under vacuum before measuring. All samples were taken after 2 h of reaction at 120 °C in a batch autoclave reactor with a volume of 76 mL.

3. Results and discussions

The support effect on the activities of the ruthenium catalysts is summarized in table 2.

The most striking feature is the behavior of the aluminum oxides. The weakest activities were obtained by using acidic or neutral Al_2O_3. In contrast, the best activity was again achieved with Al_2O_3, but this time using weakly acidic alumina. Between these extremes there existed a set of oxides for which the support effect was less pronounced. A relatively small but steady increase in the activity could be found from basic alumina to TiO_2 (table 1).

The relation between surface area and activity (table 2) shows that a low surface area support may even lead to a better catalytic performance than a high surface area support.

Bare supports have a finite number of adsorption sites. When the porous molecular catalyst is formed on the support, it brings its own adsorption sites, increasing the surface area of the supported catalyst compare to the bare supports (see Tables 1 and 2). According to equation (1), the ratio of the products, CO_2 and H_2, should be 1:1. However, in our experiments the ratio varied. The amount of H_2 was typically slightly higher than the amount of CO_2. The difference between the amount of products has its origin in the adsorption of CO_2 by the support. A chemisorption experiment revealed also that part of CO_2 was dissolved in water under the reaction conditions. In the case of catalyst the water is highly dispersed over the catalyst/support surface, which could further enhance the dissolution. Because of these effects the amount of CO_2 analyzed was underestimated compared to the H_2. The produced H_2 was neither dissolved nor adsorbed. An estimated amount of 0.5 mmol CO_2 was lost due to dissolution in water and adsorption on the surface after 2 h of reaction.

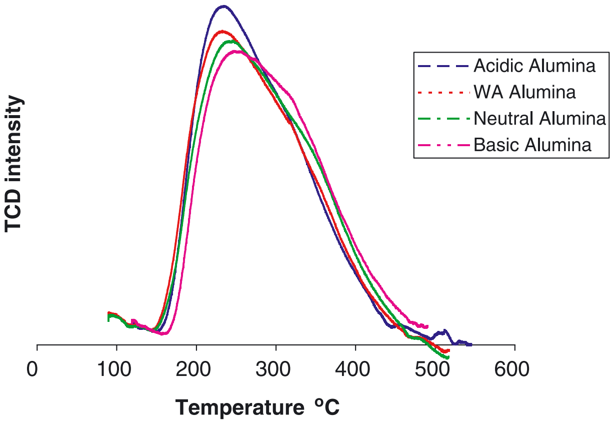

Figure 1. TPD of NH_3 curves for Al_2O_3 acidic, neutral and basic.

The supports studied can be categorized in three groups according in terms of activity. Group 1 contains the low-activity systems with strongly acidic and neutral alumina. In this group the support effect is negative compared with the unsupported catalyst. Group 2 includes the moderate activity supports: basic alumina, zirconium dioxide, zirconium silicate, zeolites, titanium oxides and silica, while group 3 contains only weakly acidic alumina. This classification is in good agreement with that proposed by Basset *et al.* [15], where surfaces are classified according to basicity and acidity.

It is important to remember that the catalyst is a true carbonyl containing molecular catalyst and not a metal dispersed on a support, our catalyst is a molecular species which contains also organic ligands. FTIR experimets showed that the catalyst does not decompose during reaction. The same set of stretching bands appeared before and after the reaction. A thin film of $[Ru(bpy)(CO)_2Cl_2]_n$ obtained electrochemically showed three carbonyl bands [16]. In the oxide supported catalyst the signals are broaden but they still overlayable with the ones found in the electrochemically prepared film. Also the reaction temperatures employed during catalysis are below the decomposition limit ca. 150–170 °C for this particular ruthenium compound [17]. The majority of the supports (groups 1 and 2) seems to act merely as carriers, by providing a suitable surface area but exerting no obvious influence on the chemical nature of the active sites. Changes in the behavior of different samples of Al_2O_3 show that the acidic character of the support plays a role in determining the activity. A similar pH effect has been observed in several chemical processes, and the influence of the acidity of surface sites in catalysis is well known [18]. The acidity of the aluminas employed was measured by ammonia TPD showing a clear difference in acidic properties (see figure 1).

In our case, a positive acidity effect has a certain pH limit, and the strongly acidic environment again reduces the turnover numbers.

4. Conclusions

The WGSR activity of the $[Ru(bpy)(CO)_2Cl_2]$ derived catalyst increases in the order: Al_2O_3 strongly acidic < Al_2O_3 neutral < Unsupported < Al_2O_3 basic < ZrO_2 < ZSM-5 < $ZrSiO_4$ < SiO_2 < Mordenite < TiO_2 (anatase) < TiO_2 (rutile) < Al_2O_3 weakly acidic. The surface area of the support alone is not sufficient to explain such differences in activity.

The influence of chemical properties such as acidity seems to play an important role in the catalytic performance. When a weakly acidic alumina support is employed, the activity increases 2.5 times compared with the result obtained with the second-best support, rutile. However, use of the strongly acidic alumina leads to the lowest activity among the systems examined. A clear reduction in activity also occurs with the basic Al_2O_3. In other words, the extreme pH properties of the supports produce a reduction in the turnover frequencies.

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