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Improved Mechanical Stability of Supported Ru Catalysts: Preparation by the Sol-Gel Method

Supported Ru catalysts are active for a large number of reactions. They are the most active metal catalysts for methanation (*1–3*) and for the Fischer–Tropsch synthesis (*4, 5*). They are exceptionally good CO oxidation catalysts (*6, 7*) and also have a high hydrogenation activity (*8*). The Sachtler–Fahrenfort (*8*) and the Tanaka–Tamaru (*9*) plots place Ru at the top of the corresponding "volcano" plots for the hydrogenation of ethylene, the decomposition of ammonia, and the hydrogenolysis of ethane. The high selectivity towards the formation of nitrogen–nitrogen bonds in the catalytic reduction of NO with either hydrogen or hydrocarbons suggests that they might potentially be used as automotive catalysts for the control of auto emissions (*10*). Unfortunately, it has not been possible to take advantage of these highly desirable catalytic properties due to the poor mechanical stability of supported Ru catalysts. Supported Ru catalysts are unstable in an oxidizing atmosphere (*11*). Not only do they sinter at relatively low temperatures in oxygen, but they also undergo substantial Ru loss due to the formation of volatile Ru oxides (*11*). Although their hydrogenation activity is very high, they undergo deactivation at a very rapid rate due to the formation of carbonaceous residues (*12, 13*). Turnover frequencies for the methanation reaction observed over Ru are also strongly dependent on particle size (*5*). This means that superimposed on a loss in catalytic activity due to volatilization of Ru, there is also a loss in catalytic activity due to particle size effects.

Because of these considerations, methods capable of stabilizing Ru dispersions should be pursued. One method which shows promise is the so-called sol–gel method of preparation (*14*). This technique has been successfully used in the preparation of silica-supported Pt catalysts (*15*). In this method the metal atoms are incorporated directly into the support framework. The technique results in surface areas which sometimes exceed 1100 m^2/g (*16*). Unfortunately, this very large increase in surface area is also accompanied by a loss in catalytic activity due to the loss of surface sites capable of adsorbing reactant molecules. However, Pt/SiO_2 prepared by this method has shown moderate to good activity in hydrogenation reactions. A very high selectivity in the hydrogenation of phenylacetylene to styrene (100%) has also been observed over Pt/SiO_2 prepared by the sol–gel method (*17*). In addition to these properties, catalysts prepared by this method have shown remarkable stability with respect to deactivation (*16, 17*). Because of these considerations a natural trade-off between surface area and metal stability on the one hand, and catalytic activity on the other, will occur. The purpose of this study is to probe the variables which result in the stabilization of the mechanical properties of Ru. In a future study the catalytic properties of these supported Ru catalysts will be considered.

A solution consisting of 0.205 g of anhydrous $RuCl_3$ (Strem Chemicals, Newburyport, MA), 20 ml of deionized water, and 10 ml of ethanol (Pharmco, dehydrated 200 proof) were placed in a flask. In order to dissolve the $RuCl_3$ and to catalyze the gelation, 10 ml of HCl (37% HCl) were added to the solution. The addition of concentrated HCl results in the formation of the octahedral metal complex $[RuCl_5(H_2O)]^{2-}$. The solution was filtered and the $RuCl_3$ which was

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TABLE 1

Comparison of Surface Areas and Pore Sizes of Ru Catalysts Prepared by the Sol–Gel and Ion-Exchange Methods

Sample	Pretreatment	BET surface area (m^2/g)	Pore radius (nm)
Cab-O-Sil	Vacuum dried	200	14
Sol–Gel	Vacuum dried	250	
Ru/SiO_2	H_2 400°C	170	
Ru/SiO_2	O_2 150°C, H_2 400°C	165	
Ru/SiO_2	O_2 250°C, H_2 400°C	165	
Ru/sol–gel	H_2 400°C	672	2
Ru/sol–gel	O_2 200°C, H_2 400°C	701	2
Ru/sol–gel	O_2 300°C, H_2 400°C	704	2
Ru/sol–gel	O_2 450°C, H_2 400°C	706	2

not dissolved was discarded. The pH of the resulting solution was measured and found to be equal to 1.4. The solution was refluxed at 70°C under constant stirring for a period of approximately 4 h. During this time 37 ml of TEOS (tetraethoxysilane) (Johnson Mathey, Ward Hill, MA) was added in a dropwise fashion. Refluxing was continued until a gel was formed. The resulting gel was placed in a vacuum desiccator until it was dry.

The physical properties of the sol–gel preparation were compared to those of a standard Ru/SiO_2 catalyst prepared by ion exchange (*18*). The method of preparation has been published in detail elsewhere (*11*). Briefly, it was prepared by ion exchanging $[Ru(NH_3)_6]Cl_3$ onto a Cab-O-Sil support (grade M-5, 200 m^2/g, 14-nm pore radius) at a pH equal to 9. Reduction of the dried powder was performed in H_2 at 400°C taking care to exclude oxygen from the catalyst prior to the reduction step. Ru/SiO_2 catalysts prepared by this method were observed to be highly dispersed (~70%).

BET surface areas and pore size distributions were obtained using a fully automated Coulter Omnisorp 100CX Sorptometer. The results of these measurements are summarized in Table 1. For comparison purposes we have also included a sol–gel support prepared by the same method as the Ru/SiO_2 sol–gel catalyst except that Ru was not included in the preparation. The BET surface areas for the Ru catalysts prepared by the sol–gel method are in the neighborhood of 670–700 m^2/g, compared to about 170 m^2/g for the standard Ru/SiO_2 catalysts prepared by ion exchange. The average pore radius decreased from 14 nm for the Cab-O-Sil supported materials to about 2 nm for the catalysts prepared by the sol-gel method, suggesting that catalysts prepared by the sol–gel method are highly porous. Heat treatment in flowing oxygen at temperatures up to 450°C did not result in a decrease in BET surface area.

Of fundamental significance is the superior mechanical resistance of the Ru/SiO_2 catalysts prepared by the sol–gel method. This is conclusively shown in Fig. 1. In these experiments the final Ru metal loading was determined by ICP (intercoupled plasma) following heat treatment in O_2 at different temperatures and subsequent reduction in H_2 at 400°C. For the case of the Ru/SiO_2 catalyst prepared by ion exchange (Fig. 1A), a sharp decrease in Ru metal loading was observed following heat treatment in O_2 at 200°C for 1 h. This Ru metal loss in an oxidizing atmosphere has been observed in a previous study and is well documented (*19*). For the Ru/SiO_2 catalyst prepared by the sol–gel method no such loss was observed

(Fig. 1B). The apparent increase in metal content observed above 400°C is due to the dehydroxylation of the support followed by the evolution of water.

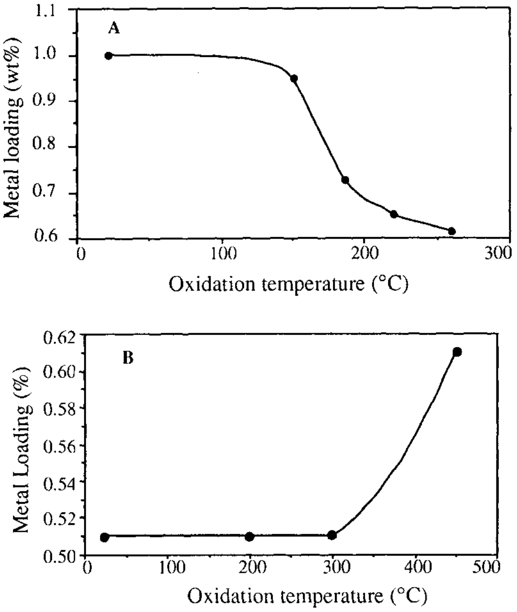

FIG. 1. Metal loading of Ru catalysts as a function of oxidation temperature analyzed by ICP: (A) Ru/SiO_2 prepared by ion exchange; (B) Ru/SiO_2 prepared by the sol–gel method.

Average metal particle sizes obtained by transmission electron microscopy and CO chemisorption are summarized in Table 2. The particle size measurements were obtained using a Phillips EM410 transmission electron microscope equipped with a LaB_6 crystal. It had a maximum magnification of 500k and a maximum accelerating voltage of 100 keV. Two specimens were prepared for each sample and as many as 10 spots from different locations from the grid were imaged and recorded in the bright field mode. The specimens were prepared by suspending a 5-mg sample in ethanol. The beaker containing the ethanol suspension was placed in an ultrasonic cleaner and sonicated for a period of 1 min. A drop of this well-mixed suspension was placed on a carbon coated 300-mesh copper grid. The specimen was placed in the sample holder of the microscope following drying under ambient conditions. About 500 particles were analyzed from each sample. CO chemisorption measurements were performed using the dynamic pulse method as outlined by Sarkany and Gonzalez (*20*).

The results in Table 2 show differences between the two methods of preparation. Rapid particle growth with increasing temperature in flowing O_2 treatment was observed for the catalysts prepared by the ion-exchange method. The average particle size was observed to increase form 1 to 5 nm when the oxidation temperature was increased to 250°C. The particle size growth observed for the Ru/SiO_2 catalysts prepared by the sol–gel method was much more modest. The increase to larger particle sizes was only observed when the O_2 pretreatment temperature was increased to 450°C.

Particle sizes determined by TEM and CO chemisorption measurements complement each other well for the Ru/SiO_2 catalysts prepared by ion exchange. However CO chemisorption is sharply depressed on the catalysts prepared by the sol–gel method. Two possibilities immediately come to mind: (i) either the Ru surface sites are occluded on the sol–gel catalysts and cannot chemisorb CO, or (ii) Ru is incorporated into the framework structure modifying the chemisorption properties of Ru.

The observation that the BET surface area is increased from 250 m^2/g (sol–gel without Ru) to 700 m^2/g (Ru sol–gel) strongly suggests that the Ru has been incorporated into the framework structure. Methods to reactivate the chemisorption of CO on these catalysts without decreasing the large surface areas obtained remains a challenge to be pursued in future studies. The optimization of preparation variables and the aerogel method by using supercritical conditions will be performed. We are encouraged by catalytic studies on the hydrogenation of phenylacetylene over Pt/SiO_2 catalysts prepared by the sol–gel method with BET surface areas in excess of 1100

TABLE 2

Comparison of Dispersions and Particle Sizes of Ru Catalysts Prepared by the Sol–Gel and Ion-Exchange Methods

Sample	Pretreatment	Particle size (nm) by TEM	D_{co} (%)
Ru/SiO_2	H_2 400°C	1–1.5	~70
Ru/SiO_2	O_2 150°C, H_2 400°C	3.0	35
Ru/SiO_2	O_2 250°C, H_2 400°C	5.0	16
Ru/sol–gel	H_2 400°C	1–1.5	13
Ru/sol–gel	O_2 200°C, H_2 400°C	1–1.5	~10
Ru/sol–gel	O_2 300°C, H_2 400°C	~1.5	~10
Ru/sol–gel	O_2 450°C, H_2 400°C	~2.5	~10

m^2/g (*17*). Although reaction rates obtained on the basis of TEM data were substantially lower than those observed over standard ion exchanged Pt/SiO_2 catalysts, TOFs calculated on the basis of Pt atoms exposed (as measured by H_2 chemisorption) were similar. Additionally, the selectivity to styrene was 100% on the sol–gel catalysts as compared to about 60% on the ion-exchanged catalysts. Catalytic activity is therefore not completely lost by incorporating the metal into the framework structure.

Transmission electron micrographs are shown for the Ru/SiO_2 catalysts prepared by the sol–gel method in Fig. 2. Figure 2A shows the very high dispersion obtained following reduction in H_2. Some particle growth is observed following treatment in O_2 at 450°C (Fig. 2B).

The following conclusions emerge from this study:

(1) Very large BET surface areas for supported metal catalysts can be obtained by using the sol–gel method of preparation.

(2) Ru is apparently incorporated into the support framework resulting in the formation of a stable microporous solid with very large BET surface areas.

(3) Ru is stabilized within this framework structure and does not sinter or volatize following treatment in O_2 at temperature up to 450°C.

(4) On the negative side, the metal atoms

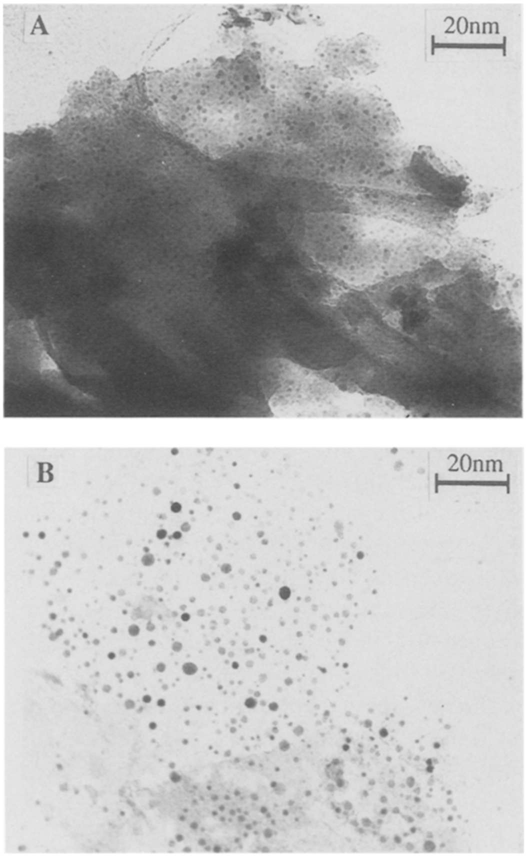

FIG. 2. Transmission electron micrographs of Ru/sol–gel catalysts using different pretreatments: (A) H_2 400°C; (B) sample oxidized in O_2 at 450°C followed by reduction in H_2 at 400°C.

appear to be occluded resulting in the suppression of CO and H_2 chemisorption. Methods to reactivate these "lost" surface sites need to be explored.

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