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Infrared study of the influence of surface hydrophobicity of the support of Rh/SiO_2 catalysts

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The characteristics of the superficial structure of a hydrophobic silica subjected to treatment at various temperatures and heating times, and of the Rh catalysts supported on the silica, are studied by FTIR. The catalysts obtained have different dispersions that depend on the superficial methoxyl fraction of the support, and are independent of the superficial OH groups. This procedure for changing the metal dispersion is different from the pretreatment of the catalyst reported previously.

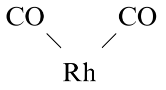
KEY WORDS: catalysis; dispersion; support catalysts; rhodium; methylated silica.

1. Introduction

Catalysts of the noble metals Pt, Pd and especially Rh supported on silica and alumina have been studied extensively over the past 20 years because of their efficiency in the reactions of CO with O_2 (CO–O_2 reaction) or with NO (CO–NO reaction), which are an important part of the catalytic control of motor vehicle exhaust emissions [1].

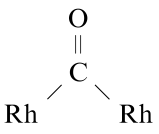
An aspect that probably deserves greater attention than it has had so far is the study of the influence of the surface characteristics of the support on the conformation and operation of the catalyst. Some interesting background is provided by the work of Oh *et al.* [2] on the influence of the metal's particle size and the type of support on the above-mentioned reactions. Oh found that under certain conditions, in the case of catalysis on Rh the CO–O_2 reaction kinetics is independent of Rh particle size, but is moderately sensitive to the nature of the support. In the CO–NO reaction, on the other hand, there was a substantial increase in reaction rate with Rh particle size, and yet the type of support had only a small effect on Rh activity and selectivity for this reaction.

The first research of CO adsorbed on Rh supported on alumina was reported by Yang and Garland [3], who identified three different types of Rh sites supported on alumina:



I

II



III

Later work [4] confirmed the existence of the same types of sites on silica and added spectroscopic evidence, assigning the infrared bands at 2090 and 2033 cm^{-1} to symmetric and antisymmetric stretching modes for adsorbed species I, the gem-dicarbonyl $Rh^I(CO)_2$, a band at 2060 cm^{-1} associated with species II of linearly adsorbed CO, while a band at 1860 cm^{-1} would correspond to bridge-CO species III.

An interesting phenomenon related to the structure of the support, observed by different researchers [5], is that which causes the adsorption of CO on these catalysts, disturbing the local coordination of superficial Rh_x^- clusters and achieving the formation of atomically disperse Rh^I sites (disruption of the Rh crystallites). Yates *et al.* [6], who have been studying for many years the chemisorption of CO on Rh supported on the surface of acidic solids such as silica and alumina, have proposed a mechanism that involves the OH groups existing on the surface of the support to interpret the phenomenon of the oxidation of Rh ($Rh^0 \rightarrow Rh^I$), explaining the formation of gem-dicarbonyl $Rh^I(CO)_2$ on the isolated Rh sites produced by the process [7]. In the case of alumina for, example, isolated surface AlOH groups acted as oxidizing agents in the presence of CO causing the following reaction:

$$Rh_x^0 + OH \xrightarrow{CO} Rh^I(CO)_2 + \tfrac{1}{2}H_2.$$

This reaction can be reversed by exposure to $H_2(g)$.

These superficial species would be in contrast with the CO adsorbed linearly or as a bridge on particles made of large Rh_x^0 clusters. In later studies, Yates and co-workers [8] showed that the removal of the superficial OH groups of alumina by silation of Rh/Al_2O_3 avoids the tendency for the CO to destroy the Rh_x^0 by forming gem species, thereby retaining the chemisorption capacity of the Rh_x^0 sites for CO.

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Usually, hydrophilic silicas are used as catalyst supports, and as far as the present authors can tell there have been no studies done on hydrophobic silicas. Recent advances show evidence of the constant interest over the last several decades in the study of structural changes in the surface of the silicas [9]. In this paper, a spectroscopic study is made of the surface characteristics of a hydrophobic silica and of the Rh catalysts supported on it when the support or the catalyst are subjected to various temperature and heating-time treatments. As will be seen, this makes it possible to obtain catalysts having different metal particle size as calculated from dispersion determinations.

2. Experimental

For this work, a methoxylated hydrophobic silica, Aerosil R972 (Degussa) (BET area 130 m^2/g) [10], was subjected to various temperatures and heating times under atmospheric conditions. As a comparative reference, a hydrophilic silica with the same specific area, Aerosil 130 (Degussa), was also used. These silicas were then used as support for Rh/SiO$_2$ catalysts with 1% (w/w) Rh prepared by impregnation using as a precursor the organic salt rhodium dicarbonyl acetylacetonate ($C_7H_7O_4Rh$). The catalysts were calcined in a 2 cm^2/min oxygen stream at temperatures of 300 and 500 °C, respectively, for 2 h, and were then reduced at 400 °C for 3 h under a stream of a mixture of 5% H_2 in argon flowing at 15 cm^3/min. The dispersions of the catalysts were determined by chemisorption of H_2 at 298 K using a dynamic pulse method, and the results were confirmed for some of the samples by using a JEOL model 1200 EX II transmission electron microscope at 120 kV and 3 A resolution.

2.1. IR experiments

IR analysis of the different samples was carried out in an IR-reactor cell (ISRI Research & Development, Indiana, USA) placed in the chamber of a model Vector 22 Bruker IR spectrometer. The IR-reactor cell had a gas inlet and outlet and temperature control, allowing the conditions to be changed while the *in-situ* analyses of the different IR-active species were being performed. The IR spectra were obtained at a resolution of 2 cm^{-1} and at 20 scans per spectrum. The procedure used for the IR studies was the following: once the sample (support disc compressed at 13.000 psi) was in place, the reactor was heated to 200 °C for 30 min under a 70 cm^3/min flow of He with the purpose of eliminating the physisorbed water. The temperature was then reduced to 150 °C, and the IR spectrum of the sample was obtained, using air as background. In this way all the IR-active species are detected in the 4.000–1.000 cm^{-1} range.

2.2. Kinetics experiments in the piston flow reactor

The kinetics studies were made in a 1 cm diameter and 50 cm long tubular quartz reactor, with a flow regime of the piston flow type. The reactor has temperature control and mass flow gauges that allow control of the reaction conditions. Once the reactor has been loaded with the catalyst (approximately 0.2 g), it is heated to 200 °C under a 15 cm^3/min flow of 5%H_2/Ar, and that temperature is kept for 1 h to re-reduce the catalyst *in situ*. The H_2 is then desorbed for 1 h under an 80 cm^3/min flow of pure He. The reactor is then taken to the desired reaction temperature and the reactive gases are fed in order to obtain the reaction conditions specified below.

The effluent from the reactor was analyzed by gas chromatography in a Perkin-Elmer Autosystem equipped with a TCD detector. The products of the reduction reaction of NO with CO, CO_2 and N_2O, and of CO_2 in the case of the oxidation of CO with O_2, were analyzed in a Hayasep D column (180 cm × 3.2 mm i.d.).

3. Results and discussion

The experiments described above showed various interesting characteristics and phenomena concerning the structure of the support and of the catalyst and their relation with some characteristics of catalytic interest, which will be discussed below.

3.1. Treatment of the support

Figures 1 and 2 show the FTIR spectra of hydrophobic Aerosil R972 (Degussa, 130 m^2/g) subjected to different temperatures and heating times. As the temperature and heating time are increased, there is a decrease of the superficial methoxy groups in the silica corresponding to the decrease in the 2900 cm^{-1} absorption band, with the simultaneous appearance of isolated superficial OH groups characterized by the 3745 cm^{-1} absorption band. Figure 1 shows this phenomenon clearly through a series of difference spectra corresponding to 500 °C and various heating times, calculated by subtracting the background spectrum of untreated Aerosil R972 which appears in figure 2. As shown in figure 2 also, it was necessary to treat Aerosil R972 at 600 °C to eliminate completely the methyl groups, giving a spectrum that is almost identical to that of untreated hydrophilic Aerosil (Degussa, 130 m^2/g).

3.2. Catalyst treatment

Figure 3 shows the FTIR spectra of a series of Rh/SiO$_2$ catalysts (1% w/w) prepared with untreated Aerosil R972 as support. These catalysts were subjected for 2 h to calcination temperatures of 300 °C and 500 °C in a controlled 2 cm^3/min oxygen stream, and were then

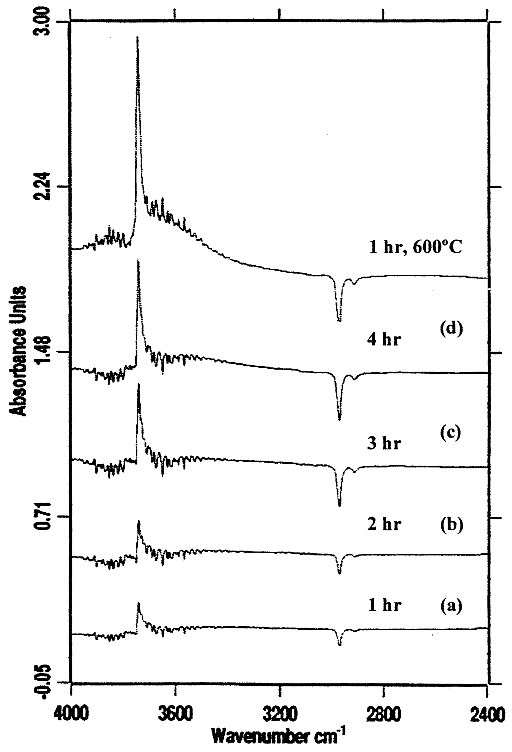

Figure 1. Evolution of surface groups in hydrophobic silica with calcination time. Difference IR spectra with respect to the original untreated solid hydrophobic Aerosil R972 calcined at 500 °C and subjected to different heating times: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, The catalyst calcined at 600 °C for 1 h is included as reference.

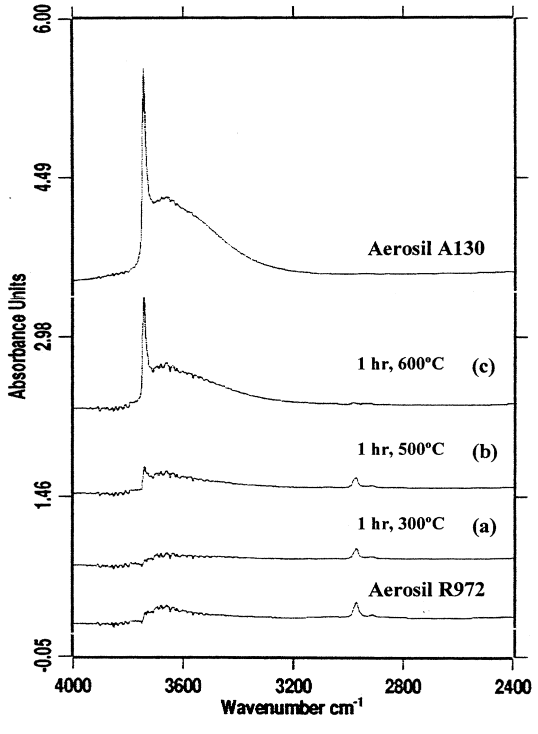

Figure 2. Evolution of superficial groups in hydrophobic silica with calcination temperature. IR spectra of hydrophobic Aerosil R972 calcined for 1 h at different temperatures (a) 300 °C, (b) 500 °C, (c) 600 °C. The IR spectra of original untreated hydrophobic Aerosil R972 and Aerosil A130 are included as references.

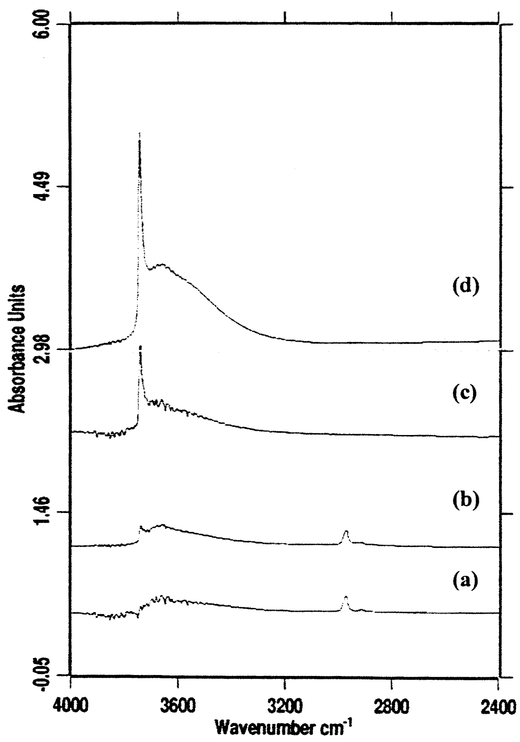

Figure 3. IR spectra of 1% Rh/Aerosil R972 catalysts. (a) Calcined at 300 °C for 2 h without reduction. (b) The same as (a) but reduced at 400 °C for 2 h. (c) Calcined at 500 °C for 2 h without reduction. (d) The same as (c) but reduced at 400 °C for 2 h.

reduced at 400 °C for 3 h in a stream of 5% H_2 in argon. In general, no important differences were seen between the spectra of the reduced and unreduced samples. If these results are compared with those of figure 2, it is seen that the disappearance of the methyl groups and the simultaneous appearance of the hydroxyl groups does not yet occur at 300 °C, but is complete at 500 °C, a temperature lower than that needed in the case of the support alone, as seen in figure 2. This shows an interesting catalytic action of the Rh particles in the process, which should therefore occupy topological positions near the methoxy groups on the surface of the catalyst.

3.3. Catalyst dispersion

The above treatments allow Rh/SiO$_2$ catalysts to be obtained on sets of supports having different degrees of hydrophobicity defined by the decrease of the methoxy groups and the consequent appearance of superficial hydroxyl groups. Figure 4 shows how the hydrophobicity affects the catalyst dispersion. Two series of catalysts are seen for which the treatment conditions of the support lead to a decrease of the superficial methoxy groups as determined by integration of the peak areas using the OPUS 2.0 software of the FTIR equipment. Series I corresponds to the previously-described calcination of the catalyst at 500 °C followed by reduction at 400 °C, and series II corresponds to calcination at 300 °C. It has been reported [13] that a decrease in the

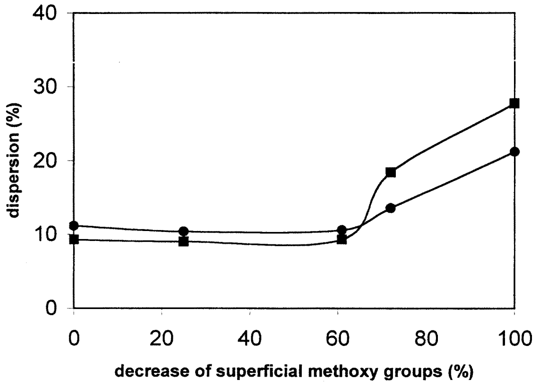

Figure 4. Dispersion of 1% (w/w) Rh/Aerosil R972 catalysts *versus* the percentage decrease of superficial methoxy groups by treatment of the support (figure 1) with respect to the original untreated solid for series I (catalyst calcined at 500 °C for 2 h) (●) and series II (catalyst calcined at 300 °C for 2 h) (■).

calcination temperature of a Rh/SiO_2 catalyst causes an increase in the dispersion.

Figure 4 shows that hydrophobicity has no influence on dispersion at values lower than approximately 50% of methoxy group decrease, both series keeping a constant dispersion value, regardless of the calcination temperature. A decrease greater than 50%, however, leads to increasing dispersion, although in general higher values are obtained in the second series calcined at a lower temperature, similarly to what has been found with Rh catalyst on hydrophilic silica. This is an interesting phenomenon that makes it possible, in addition to contributing to the knowledge of the influence of the characteristics of the support on the catalyst obtained, to produce catalysts having different dispersions in a different way from that reported so far, which consists of pretreating the catalysts supported on hydrophilic silicas and aluminas [13].

To specify the effect of the methoxy and hydroxy groups, whose variation has been related to the catalyst dispersion, we have made comparative studies with silicas whose hydrophobicity is obtained by eliminating the superficial OH groups by heating instead of methoxylating them. To that end, hydrophilic Aerosil 130 was heated at various temperatures. It is known that the OH groups of this silica are completely removed at 1000 °C if the treatment is *in vacuo* [9]. In our case, in the presence of air under atmospheric conditions, the OH groups were eliminated completely only by heating at 1240 °C for 2 h. Under these conditions, however, sintering occurs, decreasing the specific area to less than $10\,m^2/g$, which makes impractical the use of this silica as a support at that temperature.

With the purpose of studying the effect of hydrophobicity due to the decrease in superficial OH groups without altering significantly the specific area of the solid, a Rh/SiO_2 catalyst with 1% w/w Rh was prepared as described, using as support hydrophilic Aerosil 130 heated at 900 °C for 2 h, giving a specific area of $101.7\,m^2/g$. As is well known from the literature, calcination at 900 °C produces an irreversible loss of a considerable number of OH groups from the surface of silica, in spite of which the dispersion of the catalyst prepared with this support is 23.8%, of the same order as the 24.6% dispersion obtained when using completely hydroxylated Aerosil 130. This shows that the number of OH groups on the surface of the silica does not affect substantially the catalyst dispersion. Even more, if the dispersion value of 23.8% obtained using the Aerosil 130 calcined sample is compared with those of figure 4, it may be concluded that what causes the effect on the dispersion is not the change in the OH groups, but the methoxy groups that prevent the process of decreasing the size of the Rh particles on the surface of the support, a decrease greater than 60–70% of the methoxy groups being required for an increase in the value of the dispersion in the catalyst.

Table 1
Comparison of activities for the $CO–O_2$ and CO–NO reactions of catalysts having similar dispersion, obtained by the methods described in the text

Dispersion (%)	T.O.N.	
	$CO–O_2$	CO–NO
8.1[a] (6.9)[b]	0.099[a] (0.113)[b]	1.267[a] (1.333)[b]
20.2[a] (21.4)[b]	0.123[a] (0.148)[b]	0.476[a] (0.406)[b]

[a] By changing the hydrophobicity of the support.
[b] By changing the calcination temperature. Hydrophilic support.

An interesting aspect is to compare the activities on the reactions $CO–O_2$ and CO–NO of the catalysts prepared in this work with those of catalysts having the same dispersion prepared on hydrophilic silicas, whose dispersion is essentially determined by the calcination temperature. Table 1 shows the activities of two catalysts of series II (calcined at 500 °C) with extreme dispersions of 8.1 and 20.2%, prepared on Aerosil R972 and in parentheses the dispersion and activity of two catalysts having dispersions similar to the above, but prepared on Aerosil A130. The latter were obtained by dry impregnation of $RhCl_3$ on silica and calcined for 3 h at 650 °C (6.9%) and 550 °C (21.4%), and then reduced for 3 h at 450 °C in a stream of 5% H_2 in argon [14]. As can be seen in table 1, the activity of the catalysts having similar dispersion is practically the same, regardless of the method used to obtain the catalyst. In other words, the activity depends only on the final dispersion of the Rh and is not affected by the way in which a given particle size is achieved. Because of the lower calcination temperature required for obtaining low dispersion catalysts by the method introduced in this paper (500 °C), substantial structural differences might be expected between both catalysts. Wong and McCabe [15] have shown that at high calcination temperatures there is a higher degree of arrangement of the Rh oxide particles.

Although the arrangement of the Rh atoms in the particles seems to have no importance in these reactions, it may be important in other catalytic systems. This aspect falls within the scope of a line of work that is currently being investigated in our laboratory. In the above example, however, since the difference between the calcination temperatures is not sufficiently significant, it is not yet possible to arrive at any conclusions in that relation.

4. Conclusions

It is shown spectroscopically that silica hydrophobized by surface methoxylation and subjected to heat treatment up to 600 °C for different times decreases its methoxy groups, with a consequent increase in the number of isolated hydroxyl groups on the surface. Rhodium catalysts prepared with these silicas as support show an increasing dispersion with the corresponding decrease in the size of the metal particles if the superficial methoxy groups undergo a decrease greater than 50%. Comparative studies using a hydrophilic silica as support show that the change in the percentage of isolated superficial hydroxy groups has no influence on the value of the catalyst's dispersion, pointing to the methoxy groups as causing the effect. This way of changing the metal particle size, and therefore the catalyst's dispersion, is different from that reported in the literature, which consists in changing the pretreatment time and temperature of catalysts supported on hydrophilic silicas and aluminas. This is also different from the work of the Yates group, where the isolated –OH groups on Al_2O_3 or SiO_2 were only effective if CO was also present to coordinate with the isolated Rh^I ions, driving the reaction to the ultimate dispersion into a single atom of Rh as Rh^I.

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