

Rh/SiO₂ and Rh/Al₂O₃ Catalysts: Effect of Precursor and H₂ Pretreatment on Chemisorption and Catalytic Activity

INTRODUCTION

In a previous work it was suggested that the nature of the precursor was important in determining the oxidation state of Rh in supported catalysts and therefore in their catalytic activity (1). The initial purpose of the present study was to investigate the influence of the metal precursor (RhCl₃ or Rh(NO₃)₃) used in the preparation, on the catalytic activity of Al₂O₃- and SiO₂-supported Rh catalysts. The reactions chosen for that purpose were the hydrogenolysis of ethane and the hydrogenation of benzene.

The observation that on Al₂O₃-supported catalysts the activity for ethane hydrogenolysis was increasing with time at temperatures slightly higher than the reduction temperature prompted us to determine the effect of rereduction temperature on the catalytic activity. The results of this study are also presented in this note. TPR, TPD, and H₂ chemisorption techniques were used in the characterization of the catalysts.

EXPERIMENTAL

Materials used and catalysts preparation. The catalysts were prepared by impregnating SiO₂ (Cab-O-Sil M5, 200 m²/g) and Al₂O₃ (Aluminium oxide C, 80 m²/g) with aqueous solutions of RhCl₃ · 3H₂O (Fisher Sci. Co.) and Rh(NO₃)₃ · 2H₂O (Alfa Ventron CO.). The Rh loadings measured by atomic absorption were 1 ± 0.05 and 2 ± 0.1% in the Al₂O₃- and SiO₂-supported catalysts, respectively. After impregnation the catalysts were dried for 2 days at room temperature and then 1 h at 393 K in a vacuum

oven. Before reduction the catalysts were further dried *in situ* in an inert gas at 393 K for 1 h. The reduction was carried out in flowing H₂ at 673 K (Rh(NO₃)₃ preparations) for 2 h and at 723 K (RhCl₃ preparations) for 1 h. In order to prevent H₂ adsorption the samples were cooled to room temperature in He (Rh(NO₃)₃ preparations) or under vacuum (RhCl₃ preparations). All the catalysts were stored in contact with air in a desiccator.

The H₂ used was AGA Special grade (99.995%) purified by passage through a palladium diffusion cell. All other gases were high purity or better and were further purified by standard methods. The benzene (UCB p.a.) was used without any additional treatment.

Hydrogen adsorption measurements. The apparatus used and procedures were similar to those described in (2). Before rereduction at the lowest temperatures the samples were oxidized in air at 473 K for 1 h. The samples were rereduced *in situ* for 1 h and then evacuated for 3 h. The procedure was as follows: with the sample in flowing H₂ the temperature was raised at 5 K/min to the desired value and then maintained at that level for 1 h. The evacuation temperature was reached under flowing H₂ when it was lower than the reduction temperature, otherwise the adsorption cell was sealed and the temperature raised to the evacuation temperature under vacuum.

Catalytic activity measurements. The activity measurements were performed in a microcatalytic pulse reactor similar to the one described in (2). The amount of catalyst used in ethane hydrogenolysis was 0.3

TABLE 1

Turnover Frequency ($\times 10\,000$) for Ethane Hydrogenolysis at 503 K^a

Precursor:	Rh/Al ₂ O ₃				Rh/SiO ₂			
	RhCl ₃		Rh(NO ₃) ₃		RhCl ₃		Rh(NO ₃) ₃	
	TOF (s ⁻¹)	E _a (kJ mol ⁻¹)	TOF (s ⁻¹)	E _a (kJ mol ⁻¹)	TOF (s ⁻¹)	E _a (kJ mol ⁻¹)	TOF (s ⁻¹)	E _a (kJ mol ⁻¹)
H ₂ , 473 K, 1 h	28.3 ^b	—	—	—	8.2	—	10.3	—
H ₂ , 573 K, 1 h	41.7	—	28.4	—	7.4	197	9.1	—
H ₂ , 673 K, 1 h	58.2	—	35.1	—	6.2	—	5.2	—
H ₂ , 743 K, 1 h	66.3	172	41.5	180	5.3	—	3.8	205

^a Based on the maximum H/Rh ratio obtained in H₂ chemisorption measurements.^b Taken after 5 min at reaction temperature.

and 0.6 g for SiO₂- and Al₂O₃-supported catalysts respectively. In benzene hydrogenation the catalysts were diluted (4%) in SiO₂ (Cab-O-Sil M5) and the amount of dilution used in each run was between 0.005 and 0.010 g. The ethane (0.05 cm³) and benzene (0.1 μl) pulse injections were accomplished by a Carle 2015 sampling valve and by a Hamilton microsyringe, respectively. Purified H₂ was used as the carrier gas in both cases (30 cm³/min, ethane hydrogenolysis; 50 cm³/min, benzene hydrogenation).

TPR/TPD measurements. The TPR/TPD apparatus is similar to the one described by Robertson *et al.* (3). Prior to TPR measurements the sample (about 0.06 and 0.12 g for SiO₂ and Al₂O₃, respectively) was treated *in situ* under flowing air at the desired temperature (473 or 673 K) for 40 min. The TPR experiments were performed with a mixture of 5% H₂ in Ar at a flow rate of 20 cm³/min. The temperature was raised from 243 to 873 K at 5 K/min.

Before TPD measurements the sample (about 0.5 and 0.9 g for SiO₂ and Al₂O₃, respectively) was treated *in situ* under flowing H₂ at the desired temperature for 1 h after which it was cooled to 243 K. Prior to the H₂ treatment at the lowest temperature the samples were heated in flowing air at 473 K for 1 h. The TPD experiments were performed with Ar at a flow rate of 150 cm³/

min. The temperature was raised from 243 to 873 K at 25 K/min.

RESULTS AND DISCUSSION

The first question we wished to address concerning whether catalysts prepared from different precursors on SiO₂ and Al₂O₃ show different catalytic behavior has been answered. The results obtained using a structure-sensitive reaction (ethane hydrogenolysis, see Table 1) as well as a structure-insensitive reaction (benzene hydrogenation, see Table 2) clearly show no difference in catalytic behavior between samples prepared from different precursors.

What turned out to be interesting and deserving of further investigation was the

TABLE 2

Turnover Frequency (s⁻¹) for Benzene Hydrogenation at 368 K^a

Precursor:	Rh/Al ₂ O ₃		Rh/SiO ₂	
	RhCl ₃ ^b	Rh(NO ₃) ₃ ^b	RhCl ₃ ^b	Rh(NO ₃) ₃ ^b
H ₂ , 473 K, 1 h	100	130	60	70
H ₂ , 573 K, 1 h	80	130	60	—
H ₂ , 673 K, 1 h	80	110	50	60
H ₂ , 743 K, 1 h	20	80	20	30

^a Based on the maximum H/Rh ratio obtained in H₂ chemisorption measurements.^b Precursor.

TABLE 3

H₂ Chemisorption Results, Expressed as H/Rh

Reduction temperature (K)	Evacuation temperature (K)	Rh/Al ₂ O ₃		Rh/SiO ₂	
		RhCl ₃ ^a	Rh(NO ₃) ₃ ^b	RhCl ₃ ^a	Rh(NO ₃) ₃ ^b
473	533	0.86	0.86	0.57	0.68
573	533	0.86	0.84	0.57	0.68
673	533	0.76	0.74	0.51	0.60
743	533	0.74	0.72	0.48	0.52
743	773	—	—	0.61	—
473	693	0.89 ^c	0.86	0.60	0.67
693	533	0.79 ^c	0.75	0.47	0.54
—	693	0.88 ^c	0.85	0.55	0.60
—	773	—	—	—	0.65
743	773	—	—	0.60	—

^a RhCl₃ · 3H₂O as precursor.^b Rh(NO₃)₃ · 2H₂O as precursor.^c New sample of the same batch.

finding that different reduction temperatures lead to pronounced differences in catalytic activity for ethane hydrogenolysis between SiO₂- and Al₂O₃-supported catalysts whereas for benzene hydrogenation the catalytic behavior was the same regardless of the support (and regardless of the oxide used as a diluent, results similar to those of Table 2 were obtained using Al₂O₃-C (Degussa), α-Al₂O₃ (Rhone Poulenc), and SiO₂ Grade 923 (Davison) as diluents). As in the chemisorption measurements these behavior were cyclically reproduced by reoxidizing the used catalysts at 473 K.

Since the active phase for ethane hydrogenolysis is Rh metal, one can in principle, rationalize the results with this reaction attributing the increase in activity with reduction temperature for Al₂O₃-supported Rh to the presence of Rh cations stabilized by this support. Higher reduction temperatures would be then necessary in order to reduce this Rh(+*n*) to Rh(0). Because the existence of Rh(+*n*) stabilized by Al₂O₃ is matter of controversy (1, 4), we conducted TPR measurements on our catalysts. The results obtained (not shown) indicated that Rh(III) is easily reduced to Rh(0) when supported on SiO₂ or on Al₂O₃ in accordance

with (4). These measurements also showed an incomplete oxidation of the SiO₂-supported Rh particles after air treatment at 473 K, in contrast to Al₂O₃-supported Rh which was completely oxidized after the same treatment. This suggests that on Al₂O₃ the Rh particles are mainly bidimensional whereas on SiO₂ tridimensional structures are formed (4).

Having determined that the increase in the activity for ethane hydrogenolysis in Al₂O₃-supported Rh is not due to stabilized Rh ions we now turn our attention to the decreases with reduction temperature observed in the activity (see Tables 1 and 2) and in the chemisorption (see Table 3) measurements. The thermal stability under vacuum or in a H₂ atmosphere of supported Rh catalysts (5) plus the observation that the chemisorption can be recovered by evacuation at higher temperatures precludes tridimensional particle growth or coverage by the support as possible causes for the decreases. We believe that they are due to strongly chemisorbed hydrogen. There is evidence in the literature concerning the presence of strongly chemisorbed hydrogen on supported and unsupported metals after high-temperature treatment in H₂ (6). The

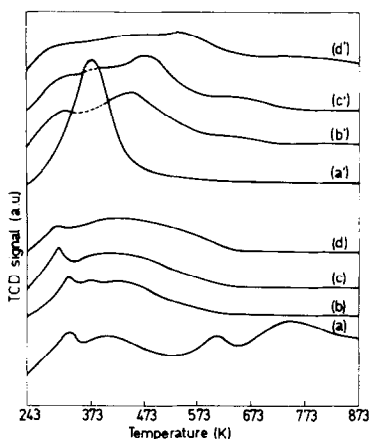


FIG. 1. TPD profiles: Rh/SiO₂ (a,b,c,d) and Rh/Al₂O₃ (a',b',c',d'), oxidized at 473 K, and then subjected to successive reduction treatments at (a,a') 473 K, (b,b') 573 K, (c,c') 673 K, (d,d') 773 K.

metal atoms thus poisoned lose the ability to chemisorb hydrogen and concomitantly the catalytic activity is diminished.

Further support for the existence of strongly chemisorbed hydrogen on Rh after high-temperature treatments in H₂ comes from TPD measurements (see Fig. 1) in which a tendency toward desorption at higher temperatures with an increase in the temperature of the H₂ pretreatment is observed. The high-temperature peaks observed in SiO₂-supported Rh after reduction at 473 K we believe are not related to hydrogen adsorbed on the metal. This is based on the observation that the low-temperature peaks obtained on Rh/SiO₂ after reduction at 473 K are similar to the area under the peaks obtained after higher reduction temperatures. Besides the high H/Rh ratio (1.4) estimated assuming that the area under the high-temperature peaks represents the amount of hydrogen contained in the bulk of the metal suggests that this possibility must be discarded.

It must be mentioned that there are differences in the amount of H₂ poisoning the surface in the adsorption and activity measurements due to the different conditions under which the measurements are done. This prevents a direct comparison between

the effects of this strongly chemisorbed H₂ on benzene hydrogenation and on H₂ adsorption which both require active sites of similar size, and explains the small effect observed in ethane hydrogenolysis which in principle requires a larger active site.

The fact that despite the presence of the strongly chemisorbed hydrogen the catalytic activity for ethane hydrogenolysis increases in Al₂O₃-supported Rh indicates the existence of other predominating phenomenon. As ethane hydrogenolysis is a structure sensitive reaction, the observed behavior must be associated with changes in the structure of the metal particles. There is evidence in the literature showing the structural changes of Rh particles after oxidation–reduction treatments. Wang and Schmidt (7) observed the disruption of Al₂O₃- and SiO₂-supported Rh particles after oxidation at 873 K and reduction at 423 K. Higher reduction temperatures caused the coalescence of the particles.

A surface-sensitive probe like ethane hydrogenolysis could sense the disruption of the particles after oxidation and low-temperature reduction, due to the smaller number of active sites believed to be composed by an ensemble of atoms. An increase in the number of these ensembles by particle coalescence after reduction at higher temperatures overcompensates the poisoning effects of the strongly chemisorbed hydrogen leading to an increase in the catalytic activity for ethane hydrogenolysis. These changes are not “seen” neither by hydrogen chemisorption, since the number of exposed atoms does not change, nor by benzene hydrogenation since it is a structure-insensitive reaction. The fact that we observe the structural changes on Al₂O₃- and not on SiO₂-supported Rh might be attributed to (a) a different Rh₂O₃-substrate interaction at this low-temperature oxidation leading to Rh₂O₃ spreading onto the Al₂O₃ surface and not onto the SiO₂ surface (this has been proposed for Al₂O₃- and SiO₂-supported Pt (8)); (b) a lower degree of contact between Rh₂O₃ and SiO₂ (and con-

sequently a smaller probability of spreading) due to the incomplete oxidation of Rh particles on SiO₂.

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