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Adsorption and Reaction Studies of Aluminophosphate-Supported Ru Catalysts

INTRODUCTION

The characteristics of aluminum phosphate have been the basis of a number of recent studies in the field of catalysis. Aluminum phosphate is isostructural with SiO_2 and can be substituted for silica into crystalline structures such as molecular sieves (*1*). Additionally, it has been shown to exist in amorphous forms and in nonstoichiometric forms with P/Al < 1 (*2*). Because of the excess of aluminum, these nonstoichiometric forms have been dubbed alumina–aluminum phosphate (AAP) and can be envisioned as structural analogs of the common catalyst and catalytic support silica–alumina (*3*).

AAP has been shown capable of modifying the catalytic behavior of such varied metals as nickel (*3, 4*), rhodium (*5*), and palladium (*6*). When used as a support for nickel, AAP can also affect the hydrogen chemisorption ability of the metal (*7*), as well as its behavior for a number of catalytic reactions, including benzene hydrogenation, ethane hydrogenolysis, and CO hydrogenation. The reason for such an interaction is not known. Magnetic measurements of the effect of AAP supports on nickel catalysts have shown a change in the Curie point of the metal, indicating bulk electronic interaction between the nickel metal and the support (*8, 9*).

This paper reports a study of a series of AAP-supported Ru catalysts where the P/Al ratio was varied between 0 and 1. This represents the first systematic effect of the P/Al ratio on the catalytic properties of a supported transition metal catalyst.

EXPERIMENTAL

The preparation of the alumina–aluminum phosphate supports has been described in detail elsewhere (*10, 11*). Following precipitation of the AAPs, they were calcined at 773 K and then used to prepare the AAP-supported ruthenium catalysts by incipient wetness impregnation with an aqueous solution of ruthenium chloride. The dried samples were divided into two batches, one to be reduced at 523 K (LTR) and the other at 723 K (HTR) in flowing hydrogen for 4 h.

The BET surface areas of the AAP supports were determined by nitrogen adsorption at 77 K. Surface acidity measurements were carried out using a Hammet indicator method (*12, 13*). Table 1 gives the composition and surface properties of the supports. As previously observed by Marcelin *et al.* (*11*), the BET surface area decreased with increasing phosphorus content of the AAP. The surface acidity measurements indicated that, although most of the supports exhibit low acid strength, the most acidic support was the AAP with the highest concentration of alumina (9A2AP). The difference in acidity observed was in part due to slight variations in preparation of the AAPs (*14*).

Quantitative analysis of the Ru in the catalyst was carried out using atomic absorption spectrometry. X-ray diffraction (XRD) line broadening using Mo$K\alpha$ radiation was also used to determine the average diameter of the ruthenium crystallites. Hydrogen and carbon monoxide adsorption measurements were carried out at room tempera-

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TABLE 1

AAP-Support Properties

Support	P/Al ratio	BET S.A. (m^2/g)	Acidity H_0
Al_2O_3	0.0	210	+4.0
9A2AP	0.1	220	−3.3
1A2AP	0.5	105	+1.5
$AlPO_4$	1.0	60	−2.0

ture in a conventional gas volumetric system. Prior to chemisorption, the catalysts were reduced *in situ* at the original reduction temperature for 2 h followed by evacuation for 1 h at 10^{-6} Torr at the same temperature. The procedure used to record the H_2 and CO isotherms and to calculate metal particle size and dispersion from the irreversible H_2 chemisorption has been described previously (*15*).

Hydrogen temperature-programmed desorption (TPD) measurements were performed using an automated TPD system (Altamira Instruments) for the HTR samples. Catalyst samples were rereduced in flowing H_2 at 723 K for 2 h. The samples were then cooled in hydrogen to 323 K. After a short flush with argon, the temperature-programmed desorption was carried out by ramping at 15 K/min in flowing argon to 723 K.

CO hydrogenation was carried out in a tubular microreactor where the prereduced catalyst (0.25 g) was first rereduced in a hydrogen stream at either 523 K or 723 K, depending on its original reduction temperature. The reaction was carried out at 1 atm and 473–573 K, except for the low temperature reduction samples for which a maximum reaction temperature of 523 K was used. Carbon monoxide conversion was maintained below 3%. The reaction and product analysis procedures were carried out as reported in Ref. (*15*).

RESULTS AND DISCUSSION

Table 2 summarizes the H_2 and CO chemisorption properties of the AAP-supported Ru catalysts. The Ru crystallite diameter measured by XRD after low temperature reduction of the catalysts is also included. A comparison of these XRD results and the average particle sizes determined from irreversible H_2 chemisorption indicates varying degrees of H_2 and CO chemisorption suppression. Figures 1 and 2 reexhibit these data as the effect of varying phosphorus-to-aluminum ratio and reduction temperature on the chemisorption of hydrogen and carbon monoxide at room temperature. It is apparent from Fig. 1 that, for the samples reduced at low temperature, the H_2 chemisorption, while remaining low regardless of the support composition, was relatively unaffected by varying the P/Al ratio. The irreversible hydrogen uptake varied by only a factor of 2 as the P/Al ratio was varied from 0 to 1. However, when the catalysts were reduced at the higher temperature, the P/Al ratio had a more dramatic effect on hydrogen uptake. The irreversible hydrogen chemisorption was drastically suppressed with increasing P/Al ratios. These results for the catalysts with high phosphorus content are consistent with those obtained for Ni catalysts (*8, 9*).

Marcelin and Lester (*8*) and Ko *et al.* (*9*) found that, for catalysts supported on phosphate-containing materials, increasing reduction temperatures resulted in severe suppression of hydrogen chemisorption and a lowering of the Curie temperature. However, Fig. 1 indicates that, for the ruthenium catalysts, the effect of the P/Al ratio of the support on hydrogen chemisorption is not as straightforward as one would expect from the results on Ni catalysts. At a low phosphorus content of the support, as in the case of the pure alumina- and the 9A2AP-supported catalysts, increasing reduction temperature resulted in an increase in irreversible hydrogen uptake.

This increase in chemisorption upon use of higher reduction temperatures observed for the catalysts with low P/Al ratios can be attributed to a second complicating factor,

TABLE 2

Characteristics of AAP-Supported Ru Catalysts: Effect of Reduction Temperature

Catalyst	Reduction temperature (K)	H_2 uptake (μmol/g)		d_p (Å) from		CO uptake (μmol/g) total
		Tot.	Irrev.	H_2	XRD	
2.6% Ru/Al_2O_3	523	16.8	9.7	112	—	419
	723	46.9	29.2	37		270
3.4% Ru/9A2AP	523	15.1	12.1	116	<30	557
	723	40.2	20.0	70		343
4.0% Ru/1A2AP	523	16.0	12.0	139	<30	213
	723	4.4	3.1	542		36
3.3% $Ru/AlPO_4$	523	5.8	4.8	289	35	16
	723	3.1	0.5	—	—	11

i.e., the effect of chlorine on hydrogen chemisorption. Don *et al.* (*16*) and Narita *et al.* (*17*) have observed that significant amounts of chlorine may be retained on the surface of ruthenium catalysts prepared from $RuCl_3$. The chlorine apparently acts not only by poisoning the hydrogen adsorption sites but also by affecting the hydrogen chemisorption behavior of the surrounding sites (*17, 18*). Lu and Tatarchuk (*18*) reported that, for supported ruthenium catalysts prepared from $RuCl_3$ and reduced in hydrogen at 673 K, hydrogen chemisorption was highly activated and even significantly suppressed at room temperature. This tightly bound chlorine may be removed by hydrogen reduction at very high temperatures in excess of 900 K (*16, 17*).

Thus, by increasing the reduction temperature of the Ru/AAP catalysts, more chlorine was removed resulting in the observed increase in hydrogen uptake for the catalysts with low phosphorus contents. However, at higher P/Al ratios, the competing effect of phosphorus became more pronounced, and a decrease in hydrogen uptake was observed for the catalysts reduced at higher temperatures. Hydrogen adsorption at 373 K, instead of room temperature, on $Ru/AlPO_4$ did not have any effect on the amount of hydrogen chemisorbed. Therefore, the effect of a high phosphorus content of the support is not similar to that of chlorine contamination in terms of the activation of hydrogen chemisorption. Chloride contamination results in activated hy-

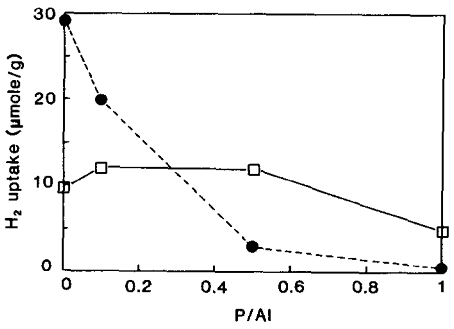

FIG. 1. Effect of P/Al ratio on irreversible H_2 chemisorption. [□], LTR; [●], HTR.

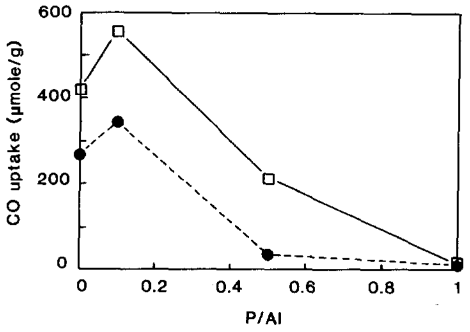

FIG. 2. Effect of P/Al ratio on total CO chemisorption. [□], LTR; [●], HTR.

drogen chemisorption which is attributed to possible electronic perturbation of the metal by adsorbed chlorine. However, close to full coverage of surface Ru sites can be obtained at 373 K (*18*). The hydrogen TPD results (Fig. 3) may be used to substantiate the proposition that hydrogen chemisorption does not become a more activated process with increasing phosphorus content of the support. It is apparent from Fig. 3 that even when adsorption was carried out at temperatures as high as 723 K, hydrogen chemisorption was suppressed with increasing P/Al ratios. At a low P/Al ratio, high temperature peaks appeared to be the only ones significantly suppressed. As the P/Al ratio is further increased, all peaks decrease in intensity.

Reduction temperature had a less drastic effect on CO chemisorption (Fig. 2), although a decrease in total CO uptake was observed for all the catalysts when the reduction temperature was increased. It may be suggested that the presence of adsorbed chlorine on the metal has a less pronounced effect on CO than on hydrogen chemisorption. Narita *et al.* (*17*) have also observed that CO chemisorption is less suppressed than hydrogen adsorption by chlorine, probably due to a dual-site adsorption requirement for the latter. The composition of the support and reduction temperature are the major factors affecting CO adsorption. Carbon monoxide chemisorption was increasingly suppressed as the phosphorus content of the AAP support was increased, whether the catalyst was reduced at a low or high temperature. The suppression of CO chemisorption was more pronounced on the HTR samples.

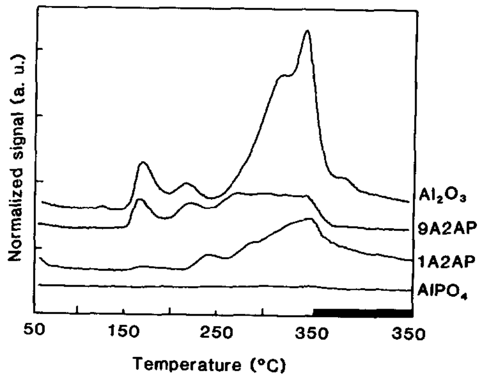

FIG. 3. Effect of P/Al ratio on hydrogen TPD.

Table 3 summarizes the catalytic properties of the AAP-supported Ru catalysts for CO hydrogenation. It is apparent that CO hydrogenation over these catalysts is affected by both the reduction temperature and the P/Al ratio of the support material. However, when the catalysts showed some measurable activity, their apparent activation energy, E_a, remained essentially constant, ranging between 21.1 and 26.2 kcal/mol and was unaffected by the different variables: P/Al ratio, reduction temperature, or reduction time.

Turnover frequencies (TOF) for CO conversion were calculated on the basis of hydrogen chemisorption. However, because of unequal suppression of hydrogen chemisorption on the various catalyst samples, due either to the chlorine poisoning or to a support effect, chemisorption measurements may not provide an adequate measure for reaction site concentrations, and the TOF may not be a good measure of catalyst activity. The specific activity (per gram of catalyst) of catalysts having a high alumina content (the Al_2O_3- and 9A2AP-supported Ru catalysts) remained practically unchanged with increasing reduction temperatures, in agreement with the results reported by Kikuchi *et al.* (*19*). In contrast, those of the catalysts having higher P/Al ratios changes significantly. The data shown in Table 3 and Fig. 4 clearly demonstrate that both specific activity and TOF decline significantly with increasing phosphorus content of the support. For the HTR samples, the activity of the catalysts for CO hydrogenation is completely suppressed at high P/Al ratios. A modest increase in specific activity is observed when the reduction temperature is increased for the samples with low P/Al ratios. Most likely, this

TABLE 3

Catalytic Properties of AAP-Supported Ru Catalysts for CO Hydrogenation

Catalyst:	Ru/Al_2O_3		Ru/9A2AP		Ru/1A2AP			$Ru/AlPO_4$	
Reduction temperature (K):	523	723	523	723	523	523[a]	723	523	723
Activity (mmol/h.g.)	4.2	5.6	4.1	4.4	1.8	0.9	0.0	0.8	0.0
Selectivity (wt%)									
C1	23.6	16.5	32.6	23.0	35.6	28.2	—	28.9	—
C2	9.7	8.6	11.4	9.1	13.1	12.1	—	12.9	—
C3	19.6	21.5	18.0	19.2	22.3	24.1	—	24.8	—
C4	16.8	19.0	15.1	15.7	14.4	15.8	—	15.2	—
C5+	30.2	34.5	22.9	33.1	14.6	19.8	—	18.2	—
Propylene/propane	4.4	8.7	2.3	3.9	3.5	—	—	5.3	—
1-Butene/2-butene	0.8	0.9	0.5	0.6	0.7	—	—	0.8	—
2-Butene *cis/trans*	1.0	1.4	0.8	0.9	0.8	—	—	0.9	—

Note. Reaction conditions: 1 atm, 523 K, $CO/H_2 = 1$, flow rate = 2.4 liter/hr, reaction time = 5 min.

[a] Overnight at 523 K in H_2.

would have been greater except for the fact that Cl is rapidly removed under hydrothermal conditions such as exist during CO hydrogenation. However, there appears to be some memory effect of Cl exposure for Ru catalysts even after the Cl is removed at low reaction temperatures (*20*). Data collected after an overnight reduction of Ru/1A2AP at 523 K (Table 3) indicate that long-term reduction of samples with high phosphorus contents at low temperatures results in the same effect as that obtained with a few hours of reduction at high temperatures. Marcelin and Lester (*8*) have also observed that Ni supported on AAP has an anomalous magnetic behavior after long-term reduction.

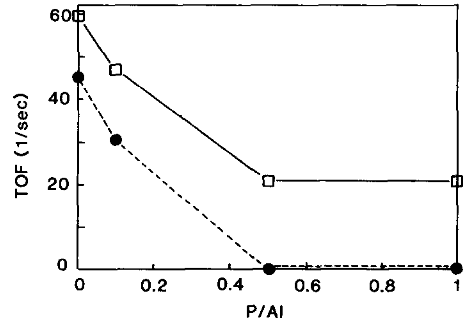

FIG. 4. Effect of P/Al ratio on TOF for CO conversion. [□], LTR; [●], HTR. [Note: ordinate is $\times 10^3$.]

The composition of the support had little effect on the selectivity of the AAP-supported Ru catalysts for methane and higher hydrocarbons. While the availability of adsorbed hydrogen might be considered the major parameter controlling selectivity, no clear correlation exists between these selectivity results and those of hydrogen chemisorption (Fig. 1). Of course, it is really the chemisorption of hydrogen in the presence of CO at reaction conditions which is the most important issue rather than its chemisorption in the absence of CO. A direct correlation with the trends obtained during chemisorption experiments may be misleading, especially since H_2 and CO can be affected differently. Under CO hydrogenation conditions, the presence of Cl had a minimal effect on selectivity since it is rapidly removed under hydrothermal conditions and deposition of electronegative C occurs (*20, 21*).

The propylene-to-propane ratios, shown in Table 3, are indicative of the activity of the catalysts for secondary hydrogenation of the primary olefinic products from CO hydrogenation. It is clear that support composition did not affect the propylene/propane ratio. Although a significant change is observed between the pure alumina–supported catalyst and AAP, all the samples containing phosphorus had relatively similar propylene-to-propane ratios.

The C_4 product distributions as well as the *cis*-2-butene/*trans*-2-butene and 1-butene/2-butene ratios shown in Table 3 for the various catalysts reflect the extent of all the possible secondary reactions of the primary olefinic products of CO hydrogenation. The selectivity trend for *n*-butane follows that of propane since both are formed on metal sites. However, the double bond migration and the *cis–trans* isomerization of the C_4 olefins are generally accepted as being acid catalyzed under these conditions used in CO hydrogenation (*22*, *23*). No isobutane was formed on any of the catalysts, reflecting the absence of any strong acid sites. The lack of any significant difference between the various catalysts for double bond isomerization and the *cis*/*trans* ratio is also indicative of the relative weakness of all of the acid sites on these supports.

In summary, the adsorptive and catalytic properties for CO hydrogenation have been investigated for a series of aluminophosphate (AAP)-supported Ru catalysts. These catalysts, prepared using $RuCl_3$, exhibited hydrogen chemisorption suppression when reduced at 523 K due to the presence of residual Cl. While there was little apparent effect of the P/Al ratio of the support on the hydrogen adsorbed, there was a big effect on CO chemisorption and hydrogenation activity. Reduction at 723 K resulted in a diminished effect of residual Cl but caused a significant effect of the P/Al ratio on hydrogen chemisorption. For catalysts reduced at the higher reduction temperatures, the chemisorption ability for H_2 or CO fell rapidly toward zero as the P/Al ratio increased to 1.0. The catalysts having $P/Al \geq 0.5$ exhibited no detectable CO hydrogenation activity at 523 K.

The suppression of both CO and H_2 chemisorption, as well as the corresponding decrease in activity of the AAP-supported catalysts for CO hydrogenation with the increasing P/Al ratio of the support and reduction temperature may be explained as suggested by Marcelin and Lester (*8*). From the results of their magnetic measurements on AAP-supported Ni catalysts reduced at high temperatures, these authors hypothesized that alloy formation between nickel and phosphorus may explain the observed lowering of Curie temperature on these samples. Similar effects may be present in Ru systems since Ru and P are known to alloy (*24*). Certainly, some such strong interaction is required in order to explain the significant suppression of chemisorption and reaction.

The evidence for secondary reactions of the primary CO hydrogenation products indicates the lack of any strong acid sites on the support. While there are differences in acid site strengths of the various AAP supports, they were sufficiently weak to have a minimal effect on the product selectivity in CO hydrogenation.

Finally, the effect of residual Cl and the effect of reduction temperature on the properties of the AAP-supported Ru catalysts indicates both the need for using lower reduction temperatures and the Ru precursors possessing no Cl or other such electronegative elements which are difficult to remove.

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