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The Use of Ammonia Synthesis as a Probe Reaction for the Study of Supported Re and RePt

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Ammonia synthesis has been used as a probe reaction selective for the rhenium component in supported Re and RePt catalysts. The kinetic parameters of the reaction over Re/SiO_2 and RePt/SiO_2 were similar indicating a minor degree of interaction between Re and Pt. Re/Al_2O_3 and RePt/Al_2O_3 catalysts exhibited kinetic behavior sensitive to pretreatment conditions, and in all cases, the RePt/Al_2O_3 catalysts differed markedly from the Re/Al_2O_3 catalysts. In particular RePt/Al_2O_3 catalysts which were reduced without prior calcination showed apparent activation energies for ammonia synthesis which were smaller than those for Re/Al_2O_3 catalysts; however, calcined RePt/Al_2O_3 catalysts showed the opposite behavior with respect to Re/Al_2O_3. This can be explained in the former case by the presence of RePt alloy, or bimetallic, particles following direct reduction, and by the separation of the Pt and Re components during calcination in the latter case. Yet even after this phase separation, the presence of Pt alters the catalytic properties of Re for ammonia synthesis, presumably due to hydrogen spillover. Finally, the influence on the ammonia synthesis kinetics of chlorine as a catalyst component was also investigated. The incorporation of chloride ions onto the surface of alumina increased the apparent activation energy for ammonia synthesis over Re/Al_2O_3. This suggests that the presence of Cl on the support decreases the electron density of the supported Re.

INTRODUCTION

The industrial use of supported RePt catalysts has prompted a number of fundamental studies in the past decade (*1–7*). Due to the importance of Pt-based catalysts as reforming catalysts for petroleum feedstocks, such studies have been directed primarily toward determination of the influence of the Re component on the Pt component. The present study, however, has taken the complementary point of view by centering upon the influence of Pt upon the Re component. This has been accomplished through the use of ammonia synthesis as a probe reaction selective to the Re component. Prior work using supported, potassium-promoted Re and Pt catalysts (*8*) has revealed an ammonia synthesis activity for the Re-based catalyst (at ca. 0.1 MPa) nearly two orders of magnitude greater than that of the respective Pt catalyst. Hence, the ammonia synthesis rate at similar conditions for RePt catalysts should reflect primarily the activity of the Re component.

The utility and significance of kinetic parameters obtained through the use of ammonia synthesis as a catalytic probe have been discussed previously, and sensitivity of the probe reaction for supported Ru catalysts has been demonstrated (*9*). The current work represents an extension of the earlier work to supported Re and RePt catalysts.

EXPERIMENTAL

The catalysts used in this study were prepared by impregnation of silica and alumina supports to incipient wetness with aqueous solutions of the appropriate metals. In the

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case of RePt catalysts, the two metals were impregnated sequentially, and studies showed that the order of impregnation was unimportant. The supports used were silica gel (Davison grade 952, 300 m^2/g) and γ-alumina (Davison SMR-7, 260 m^2/g). $HReO_4$, $Pt(NH_3)_4(NO_3)_2$, and $H_2PtCl_6 \cdot 6H_2O$ (all Alfa Division, Ventron) were used as the precursor compounds. In one case, aqueous HCl was used to chlorinate the alumina prior to metal impregnation. The impregnated catalysts were dried in air at 380 K, but were not calcined. However, certain specified alumina-supported catalysts were subjected to a standardized, high-temperature oxygen treatment, similar to that used by Yao and Shelef (*10*). This treatment was comprised of the following steps: heating to 770 K in flowing helium for 3.6 ks, oxidation in a stream of 20 mol% O_2 in helium at 770 K for 1.8 ks, and cooling to the subsequent reduction temperature in helium saturated with H_2O at 273 K. Reduction and kinetic studies were conducted in a packed-bed microreactor, operated at a nominal pressure of 0.1 MPa and temperatures ranging from 630 to 770 K. The partial pressures of both hydrogen and nitrogen remained constant during such operation due to the small overall extent of reaction. Ammonia partial pressures at the reactor outlet fell in the range from 3 to 30 Pa. Additional details can be found elsewhere (*9, 11*). The results of H_2 and CO chemisorption studies on a number of the chlorine-free, alumina-supported samples investigated in the present study have been presented elsewhere (*12*). All metal loadings of the supported catalysts reported in this paper are expressed as weight percent.

RESULTS AND DISCUSSION

Silica-Supported Catalysts

The ammonia synthesis kinetic parameters for the silica-supported Re, Pt, and RePt catalysts are presented in Table 1. The turnover frequencies are based on total Re content. These parameters are derived from the convenient, power-law expression for the overall rate of ammonia production r,

$$r = \frac{A \exp(-E_A/RT)}{P_{NH_3}{}^{2m}} \tag{1}$$

where A and E_A are the preexponential factor and apparent activation energy, P_{NH_3} is the partial pressure of NH_3 in the reactor effluent, and $2m$ is the corresponding reaction order. The significance of using such a rate expression for the reactor configuration used here has been discussed elsewhere (*11*), and a detailed account of the possible relationships between such a model expression and mechanistic rate expressions has been compiled (*12*).

The activity of the Pt-based catalyst is negligible under reaction conditions, as expected in view of previous studies (*8*). The activities of the Re and RePt catalysts are essentially the same. In proceeding from a Re/SiO_2 catalyst to a $RePt/SiO_2$ catalyst, only modest increases in the values of m and E_A are observed, suggesting minimal

TABLE 1

Ammonia Synthesis Kinetic Parameters for Silica-Supported Catalysts[a]

Catalyst	Composition (wt%)	E_A (kJ/mole)	m	Apparent turnover frequency[b]
Re/SiO_2	1.1% Re	150	0.70	1.1×10^{-4}
Pt/SiO_2	0.98% Pt	—	—	No measurable activity
$RePt/SiO_2$	1.1% Re 0.98% Pt	170	0.76	1.2×10^{-4}

[a] Reduction temperature, 705 K.

[b] Reaction conditions, $P_{H_2} : P_{N_2} = 3:1$, $P_{NH_3} = 20$ Pa; $T = 700$ K.

interactions between the metals. These results are consistent with an earlier finding that only 15% of the Re might be expected to alloy with Pt in such a catalyst (*7*).

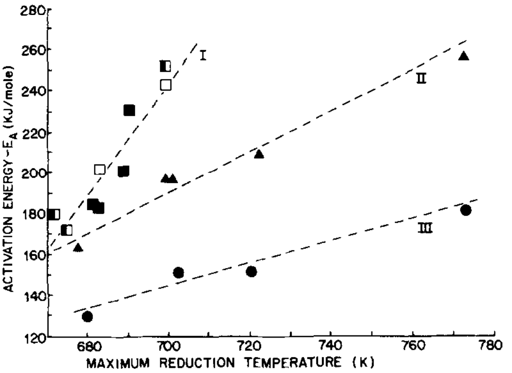

FIG. 1. Ammonia synthesis activation energy dependence on reduction temperature for chlorine-free, alumina-supported Re and RePt catalysts. Class I: □, 1.2% Re/Al_2O_3 + 0.8% Pt/Al_2O_3, physical mixture; ◧, (1.2% Re + 0.008% $Pt)/Al_2O_3$; ■, O_2-treated (1.2% Re + 0.8% $Pt)/Al_2O_3$. Class II: ▲, 1.2% Re/Al_2O_3. Class III: ●, (1.2% Re + 0.8% $Pt)/Al_2O_3$.

Chlorine-Free, Alumina-Supported Catalysts

As will be shown below, it is convenient to divide the catalysts investigated into three classes:

I. (a) 1.2% Re/Al_2O_3 + 0.8% Pt/Al_2O_3, physical mixture
   (b) (1.2% Re + 0.008% $Pt)/Al_2O_3$, sequential impregnation
   (c) O_2-treated (1.2% Re + 0.8% Pt)/ Al_2O_3, sequential impregnation
II. 1.2% Re/Al_2O_3
III. (1.2% Re + 0.8% $Pt)/Al_2O_3$, sequential impregnation.

The Class III catalysts are similar to those studied for which alloy, or bimetallic, particle formation has been proposed to explain their catalytic properties (*1–4*).

The kinetic parameter most sensitive to changes in catalyst structure for these samples was the apparent activation energy, E_A. In all cases, the value of E_A was found to depend on the highest temperature to which the catalyst was subjected in a reducing gas atmosphere. That is, following reduction (in either H_2 or $H_2:N_2$) at a given temperature, E_A was determined by collecting kinetic data at lower temperatures. The results of this procedure are shown graphically in Fig. 1. It is clear that each type of catalyst (I, II, or III) exhibits a characteristic increase in E_A with increasing reduction temperature. For lower reduction temperatures (ca. 670 K), the E_A values for Class I and II catalysts appear to converge to a common value. Oxygen treatment of a Class II catalyst has no effect on the relation shown in Fig. 1, while such a treatment converts a Class III catalyst into a Class I catalyst.

Initially, it might be expected that the dependence of the activation energy on the maximum reduction temperature could be related to the difficulty of reducing Re on alumina (*1, 6, 10, 13*). If attention is paid to the substantial past experience in the catalysis of ammonia synthesis (*14*), it is clear that the reaction is catalyzed by metals or interstitial compounds such as nitrides and carbides (*15*). Hence, partially reduced, oxidic Re species would be expected to be significantly less active (and to display a higher activation energy) than metallic Re for ammonia synthesis. In addition, temperature-programmed reduction studies (*6, 10, 13*) show that increased reduction temperature favors Re metal formation. The observed trend of increase in activation energy with increasing reduction temperature, therefore, cannot be rationalized by reducibility arguments (according to which increased reduction temperature should lower the activation energy). It might be further argued that different classes of Re-containing catalysts could arise from different oxidation states of Re in each. This cannot consistently explain the experimental data. The addition of Pt to Re/Al_2O_3 would be expected to facilitate the reduction of Re (*1, 6*), and this should be manifested by a decrease in the apparent activation energy for ammonia synthesis. While this behavior is observed in comparing Class II and Class III catalysts, the addition of Pt to Re/Al_2O_3 in forming a Class I catalyst is accompanied by an increase in activation energy. In addition, X-ray photoelectron spectroscopy studies were carried out on two samples analogous to Class II and III catalysts (*12*), prepared by impregnating Re and RePt onto Alon-C (a nonporous, high surface area Al_2O_3). The binding energy of the Re ($4f_{7/2}$) peak was measured to be 41.3 eV (±0.5 eV) for these samples, in agreement with other determinations of this peak position for Re/Al_2O_3 samples (*16*). This is indicative of Re in an oxidation state lower than Re^{4+} (for which a binding energy in the range from 43.2 to 44.8 eV has been reported (*16, 17*)). In contrast, the Re in RePt/Al_2O_3 catalysts following calcination and then H_2 reduction at 758 K has been reported to be present as Re^{4+} (*18*). If the oxidation state of Re in catalysts which had been calcined prior to reduction were higher than that in directly reduced catalysts, then one could explain the higher activation energy for RePt/Al_2O_3 catalysts following O_2 treatment (i.e., conversion of a Class III catalyst into a Class I catalyst); however, O_2 treatment does not alter the activation energy for Re/Al_2O_3 (Class II catalysts) and a physical mixture of Re/Al_2O_3 and Pt/Al_2O_3 forms a Class I catalyst without the need of an O_2 treatment. Thus in summary, it can be said that variations in the oxidation state of Re cannot consistently explain all of the observations of the present study.

The increase in the activation energy with maximum reduction temperature for the Re/Al_2O_3 catalysts (Class II) can be explained in terms of support dehydroxylation with increased reduction temperature. Removal of a hydroxyl group on Al_2O_3 produces a Lewis acid site (*19*). Hence, the observed increase in E_A with increased treatment temperature may be a manifestation of increased support acidity (electron-withdrawing capability) exerted through a metal–support interaction with Re. The fact that an O_2 treatment did not influence E_A is a direct consequence of that portion of the treatment involving cool-down from the high oxidation temperature in helium saturated with water. As a result, the hydroxyl content of the support is determined by the highest reduction temperature and not by the oxidation temperature. The lower activation energy for the Class III catalysts in comparison to the Class II catalysts is indicative of a less electron-deficient Re species (*9*). This is not inconsistent with alloy, or bimetallic, particle formation in Class III. The fact that these Class III catalysts exhibit a trend in activation energies similar to that of the Class II catalysts suggests that the bimetallic species on the former are influenced by the nature of the support surface to an extent comparable to that experienced by the monometallic Re species in the Class II catalysts.

The behavior exhibited by the Class I catalysts in Fig. 1 apparently represents a different activated process from that of Class II or III catalysts. These catalysts have E_A values comparable to Re/Al_2O_3 at ca. 675 K while such values exceed those of the Re/Al_2O_3 catalysts by more than 50 kJ/mole for reduction temperatures near 700 K. The observation that a physical mixture of Re/Al_2O_3 and Pt/Al_2O_3 forms a Class I catalyst implies that Pt has an indirect effect on Re: such as hydrogen spillover from Pt to Re. The results of infrared spectroscopy are consistent with this belief. Infrared spectra were obtained for wafers made from a Class II and a Class I catalyst [the latter being (1.2% Re + 0.008% Pt)/Al_2O_3] using an FTIR spectrometer (Nicolet Instruments, MX-1). For the Class II, single-component Re, catalyst the hydroxyl band intensity at 3733 cm^{-1} decreased significantly in proceeding from H_2 treatment at 470 K to treatment at 670 K. This is in accord with predicted dehydroxylation of the support (*19*). On the other hand, for the same H_2 treatments, the above Class I catalyst exhibited a substantial increase in the same OH band upon increasing the reduction temperature. An analogous occurrence in the Pt/Al_2O_3 +

SiO_2 system has been attributed to hydrogen spillover (*20*).

Recent work by Kramer and Andre (*21*) provides information concerning the nature of hydrogen spillover in Pt/Al_2O_3 systems. These workers found that the rate of spillover increases with temperature and becomes appreciable at ca. 670 K. Their results were consistent with a model in which the surface diffusion of atomic hydrogen across the alumina was taken to be rate-determining. The Pt content was found not to influence the spillover rate. In addition, their data suggested that the coverage of alumina by spilled-over hydrogen increased with temperature, an effect observed earlier by Bianchi *et al.* (*22*) for Ni/Al_2O_3 systems. Hence, the greater importance of hydrogen spillover with increasing temperature observed by earlier workers is paralleled by the effects ascribed to spillover in the present study. However, the spillover effect noted here appears to be irreversible in that it is the maximum temperature of exposure to hydrogen that dictates catalytic behavior. This irreversibility may not be surprising in view of the fact that the thermal desorption peak for spilled-over hydrogen obtained by Kramer and Andre (*21*) occurred at ca. 730 K, a temperature higher than that used for H_2 treatments of the Class I catalysts. In addition, Teichner *et al.* (*23*) has also observed an irreversible effect of hydrogen spillover in the activation of several aluminas (by admixed Pt/Al_2O_3) for hydrogenation of ethylene, butenes, and benzene as well as methylcyclopropane isomerization. Finally, precedence for the importance in ammonia synthesis of hydrogen from the support can be found in the work of Altenburg *et al.* (*24*). These authors proposed the following mechanism for ammonia synthesis over singly promoted iron catalysts:

$$-OH + (N)_a \rightarrow -OH \cdots (N)_a \rightarrow -O \cdots (NH)_a \tag{2}$$

$$-O \cdots (NH)_a + H_2 \rightarrow -O + NH_3 \tag{3}$$

$$-O + \tfrac{1}{2} H_2 \rightarrow -OH \tag{4}$$

where –O and –OH represent oxygen and hydroxyl ions associated with Al_2O_3 and the subscript a denotes an adsorbed species.

TABLE 2

A Comparison of Kinetic Parameters for (1.2% Re + x% Pt)/Al_2O_3 Catalysts[a]

Sample	Pretreatment	x (wt%)	E_A (kJ/mole)	m
1	Direct reduction	0.008	184	0.7
2	Direct reduction	0.08	172	0.6
3	Direct reduction	0.8	130	0.5
4	O_2-treated	0.8	184	0.6

[a] Reduction temperature, 680 K.

The conversion of a Class III catalyst into a Class I catalyst by high-temperature oxidation is consistent with metal component separation induced by oxidation of the individual metals. This is in agreement with previous investigations (e.g., *4, 6, 25–28*) of the effects of oxygen treatments for silica- and alumina-supported Pt alloys (e.g., PtRe, PtIr, PtRh, PtPd). The extent of metal component separation for the present study can be estimated by comparison of the kinetic parameters for an oxidized sample to those obtained for directly reduced $RePt/Al_2O_3$ samples of varying Pt content. This has been done in Table 2. The comparison suggests that on the order of 1% of the total Pt remains associated with the Re after oxidation and subsequent reduction.

Chlorine-Containing, Alumina-Supported Catalysts

Since chlorine is a typical component of RePt reforming catalysts, the probe reaction concept was used to investigate the possible effects that chlorine may have in altering the catalytic properties of Re. As a control catalyst, 1.2% Re on alumina previously chlorided by impregnation with aqueous HCl was investigated, and this sample is denoted as Re/Al_2O_3–Cl. Subsequent catalysts studied incorporated chlorine from the Pt precursor compound H_2PtCl_6. The

TABLE 3

Kinetic Parameters for Chlorine-Containing Catalysts 1.2% Re/Al_2O_3 and (1.2% Re + 0.8% Pt)/Al_2O_3

Catalyst	Number of O_2 treatments	Wt% Cl[a]	Cl source	Reduction temperature (K)	E_A (kJ/mole)	m
A. Re/Al_2O_3	None	0.7	HCl	770	340	1.0
B. RePt/Al_2O_3	None	0.9	H_2PtCl_6	770	No measurable activity	
C. RePt/Al_2O_3	1	—	H_2PtCl_6	690	172	0.5
	2	0.5[b]	H_2PtCl_6	690	300	1.0
D. RePt/Al_2O_3	1	—	H_2PtCl_6	730	184	0.5
E. RePt/Al_2O_3	None	0.9	H_2PtCl_6	690	138	0.6

[a] Cl content measured after kinetic studies.

[b] Acid vapor (i.e., HCl) detected in reactor effluent during second O_2 treatment.

results of these kinetic studies are presented in Table 3. The behavior of Re/Al_2O_3–Cl is analogous to that observed for Ru/Al_2O_3–Cl catalysts (9), where increased support acidity due to chlorination results in a high activation energy for ammonia synthesis. The behavior of the directly reduced RePt catalysts is intriguing. High-temperature reduction produces an inactive catalyst, B in Table 3, while low-temperature reduction produces a catalyst (E) having the characteristics of a chlorine-free alloy catalyst (Class III). Repeated oxygen treatments apparently result in chlorine loss from the sample, but also to a more intimate interaction between Re and the chlorinated support (due for example to the migration of Cl and/or Re over the support surface). This is suggested by the resemblance of catalyst C, after a second O_2 treatment, to catalyst A. However, singly treated catalysts exhibit unique parameters unlike those of the chlorine-free Class I catalysts (see Fig. 1). Instead, catalyst C, after a single O_2 treatment, is quite similar to catalyst sample 2 in Table 2, the chlorine-free PtRe catalyst containing 0.08% Pt. This result suggests that one possible role of chlorine may be to partially inhibit component separation during oxygen treatments. This could be due to decreased mobility of Re over chlorided alumina under oxidizing conditions.

CONCLUSIONS

The use of ammonia synthesis as a catalytic probe reaction has permitted interactions in the supported Re and RePt systems to be qualified in terms of their effects on the Re component. Bimetallic interactions in the silica-supported system were found to have a minimal effect on the catalytic properties of Re. On the other hand, alumina-supported Re was found to be sensitive to the surface state of the support; and bimetallic catalysts using an alumina support were found to exhibit two types of behavior, dependent on the pretreatment, that differed from the Re/Al_2O_3 catalysts. While it is not possible from kinetic measurements alone to determine the nature of the interactions between Re, Pt, and the Al_2O_3, it is possible to formulate a description which is consistent with the results of the present study and previous investigations of RePt/Al_2O_3. Specifically, catalysts which were reduced without previous calcination contain RePt alloy or bimetallic particles, while high-temperature oxidation leads to separation of the two metal components. In spite of this phase separation, the presence of Pt alters the catalytic properties of Re in these latter samples, presumably due to effects of hydrogen spillover.

Finally, the presence of chlorine in RePt/Al_2O_3 catalysts was found to significantly alter the surface chemistry of Re as probed by ammonia synthesis.

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