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Catalytic Probe for Alloy Formation in Supported PtRe Catalysts

Isotope Exchange and Hydrogenolysis of Cyclopentane

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The H/D isotope exchange and the hydrogenolysis of cyclopentane (CP) as catalyzed by alumina- or silica-supported Pt, Re, their alloys, and physical mixtures have been studied. The number of surface-exposed metal atoms is determined by chemisorbing deuterium and exchanging it with hydrogen. The CP exchange reaction is found to be nonspecific for the composition of the catalyzing ensembles: PtRe alloys exhibit the same rate and exchange pattern as a physical mixture of these metals with the same number of metal atoms exposed. The exchange rate can therefore be used to "count" exposed metal atoms. The exchange patterns over Pt and PtRe show partial maxima for d_5 and d_{10}; over PtRe all products are formed in quantities intermediate to those obtained over Pt and Re respectively. CP hydrogenolysis is highly ensemble-specific. The TOF for methane formation over PtRe exceeds that over the separate metals by a factor of 40. This finding is used to estimate the extent of alloy formation in supported bimetallic PtRe catalysts. Even in physical mixtures of Pt and Re, initially supported on separated support particles, some alloy formation can be detected.

1. INTRODUCTION

Bimetallic catalysts are widely used in modern chemical and petroleum industries. They usually contain two reducible metals on an oxidic support of high surface area. After preparation and reduction of the catalyst, part or all of the metal ions are converted to the zerovalent state. These atoms can either combine with others of the same element to make "pure metal" particles, or atoms of different elements may combine with each other to form "bimetallic clusters" or "alloy particles." In this paper we shall use the term "alloy" for the latter case, irrespective of the particle size, even if the particles do not fulfill some of the criteria characterizing macroscopic alloys. This terminology is used to avoid confusion with certain organometallic complexes such as carbonyls which contain metal atoms of different elements and for which expressions such as bimetallic clusters are often used.

The catalytic metal function of such catalysts depends largely on three criteria:

(1) the extent of reduction to the zero oxidation state,

(2) the dispersion, i.e., the fraction of the atoms of the reducible element capable of chemisorbing certain molecules such as carbon monoxide.

(3) the extent of alloy formation of the reduced atoms.

While the first two criteria are, of course, common to mono- and bimetallic catalysts, the extent of alloying is obviously specific for catalysts with two or more reducible elements.

It is conceivable that for certain catalytic processes the degree of alloying is not essential; alloying might even be undesirable. However, for the vast majority of catalysts, for which some understanding of the reaction mechanism has been achieved, it is certain that alloying is decisive for their

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performance. A large body of research in recent years has clearly proven that alloy catalysts often possess specific characteristics which distinguish them from the pure metals and any physical mixture of separate metal particles. This is not the place to dwell on the precise causes of this specific behavior, which were discussed in previous publications and review articles (*1–5*). We just mention that electronic interactions and a geometric principle, the so-called "ensemble effect" (*6*), have been discussed. The latter has actually been identified as the main cause of the peculiar selectivity and activity effects in many alloy catalysts.

In brief, this approach accepts that an active site often consists of a group of contiguous surface atoms. For instance, the stable position of a sulfur atom adsorbed on the (100) face of a transition metal is above the center of four surface atoms which thus form the adsorbing M_4 ensemble (*7*). If the adsorbing material is a binary alloy, containing A and B atoms, five possibilities exist for the composition of a M_4 ensemble. It depends on the chemical nature of the constituent elements and the reaction to be catalyzed, which of these ensembles will be most active. Experimental evidence shows, e.g., that for hydrogenolysis large ensembles of Group VIII metal atoms are beneficial; undesired hydrogenolysis can thus be suppressed by diluting this metal with inert "spacer" atoms (*8, 9*). A different situation exists when two active metals, which form chemisorption bonds of different strength, are alloyed. This results in an enhancement of catalytic reactions for which the rate is highest on sites where the surface intermediate is adsorbed neither too strongly nor held too weakly, i.e., some mixed ensemble. For alloys of two transition metals it depends therefore on the nature of the rate-limiting step whether "pure" or "mixed" ensembles are most efficient as catalyst sites.

In the preparation of a bimetallic catalyst of optimum performance it is, therefore, essential to know what compositions of surface ensembles are best for the desired process. A second, often much more difficult, problem is to find ways to maximize the formation of alloy particles of such composition on a surface.

To assess whether the optimum ensemble composition has been achieved is not trivial. In principle, a number of physical techniques are available for the detection of alloy formation. Unfortunately, most of these have some severe limitations. X-ray diffraction is probably best suited to detect the formation of alloys from a mixture of pure metals, but this technique fails for very small particles, i.e., high dispersion. EXAFS is another powerful technique which also has been used in this laboratory (*10*). Unfortunately, it is not applicable to all pairs of metal elements. Highly diluted Pt–Re catalysts, e.g., cannot be analyzed. Similar limitations apply to electron microscopic atom probe methods (*11*). Another technique is based on Mössbauer spectroscopy and was recently applied in elegant work by Guzci *et al.* (*12*) for the identification of bimetal cluster formation in FeRu catalysts. Yet it is obvious that this technique is limited to nuclei which can produce Mössbauer signals. All physical techniques mentioned, with the exception of electron microscopy, tend to give information on the average composition of supported particles; but for catalysts it is more important to know how large a fraction of the particles possesses the desired unique catalytic properties.

In this paper we describe a chemical method, based on the combination of two catalytic probe reactions, to monitor the formation of alloy particles on silica or alumina supports.

We have chosen the PtRe system for a number of reasons. First its application in industrial practice is important (*13*), but usually very low metal loads below 1% are used (*14, 15*), where most physical methods become highly problematic. It thus appeared a challenging task to determine the extent of alloying in such catalysts. Second, our previous research using argon arc melted PtRe alloys showed that they exhibit a hydrogenolysis activity distinctly superior to the separated metals (*16*). Also results by Haining *et al.* (*17, 18*) on supported PtRe catalysts strongly suggest that mixed ensembles display a much higher hydrogenolysis activity than either of the pure elements.

2. EXPERIMENTAL

2.1. *Catalysts*

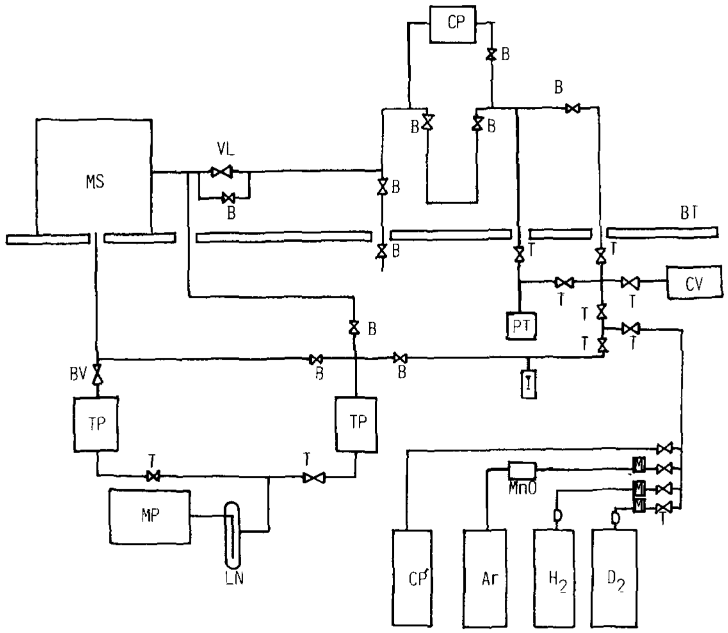
All supported catalysts were prepared by the incipient wetness impregnation method. Davison 62 SiO_2 whose surface area had been reduced by a hydrothermal treatment at 200°C (BET surface area: 205 m^2/g; pore volume 1.1 cm^3/g, mesh size 60–80) and Cyanamid PHF γ-Al_2O_3 (surface area 180 m^2/g, pore volume 0.5 cm^3/g; mesh size 60–80) were used as catalyst supports. The procedure for crushing the alumina extrudate and subsequent treatment followed that of Kobayashi *et al.* (*19*). Cleaning the silica was done as recommended by Uchijima *et al.* (*20*). Solutions of $Pt(NH_3)_4(NO_3)_2$ (Alfa 88960) and NH_4ReO_4 (Aldrich 20416-1) in doubly distilled water were used for impregnation. In the case of the alumina-supported bimetallic catalyst co-impregnation made use of a solution containing both the Pt and the Re compound. After impregnation, the alumina-supported catalysts were dried at 120°C in an oven overnight, calcined at 500°C in flowing dry air for 3 hr, then stored in bottles before use. These catalysts were subsequently dried for 1 hr in Ar and reduced for 2 hr in H_2(or D_2) at 500°C (flow rates of 60 ml/min). In the case of the silica-supported bimetallic catalyst a different procedure was used to achieve a much higher metal load. The support was first impregnated with platinum as described. After calcination the Re was supported on the Pt/SiO_2 through several impregnations of NH_4ReO_4 to incipient wetness; after each impregnation the catalyst was dried at 120°C. These catalysts were slowly reduced by heating to 400°C in flowing hydrogen with a heating rate of 8°C per minute. They were then oxidized in flowing O_2 at 300°C, and this cycle was repeated after which the catalysts were reduced again at 500°C in H_2(or D_2). Temperature-programmed reduction results showed that all the metal in these catalysts was reduced under these conditions. The Re/SiO_2 catalyst could not be calcined due to the volatility of Re_2O_7 and required a more severe reduction treatment for 6 hr at 500°C, as stated by Sinfelt (*21*). Catalysts prepared as such included 0.35 wt% Pt/Al_2O_3, 0.2 wt% Re/Al_2O_3, 0.33 wt% Pt–0.22 wt% Re/Al_2O_3, 2.9 wt% Pt/SiO_2, 4.7 wt% Re/SiO_2, and 2.9 wt% Pt–4.7 wt% Re/SiO_2.

2.2. *Reagents*

Cyclopentane was purchased from Fluka and exceeded 99% purity. It was dried prior to use by exposure to a 4-Å molecular sieve in a static vacuum for 3 days. All gases were purchased from Matheson and were classified as ultrahigh purity. They were further purified by passing them through reduced, SiO_2-supported manganese oxide traps and molecular sieve traps at −78° or −195°C. In addition to this, the hydrogen and deuterium were also passed through Deoxo catalyst traps prior to the other traps. The D content of the deuterium gas was determined by mass spectrometry to be 97%.

2.3. *H/D Isotopic Exchange of Cyclopentane*

These reactions were done at low pressure in a batch reactor which is schematically represented in Fig. 1. It consists of a reaction loop (156 ml total volume) in which the gaseous components are mixed by a magnetically driven circulation pump. The gas mixture is continuously bled through a Granville–Phillips variable leak valve at a rate such that the pressure inside the reaction vessel decreased less than 3% per



B	Bakeable Valve	M	Molecular Sieves
BT	Bakeable Table	MP	Mechanical Pump
BV	Butterfly Valve	MS	Mass Spectrometer
CP	Circulation Pump	MnO	Oxygen Trap
CP'	Cyclopentane	PT	Pressure Transducer
CV	Calibrated Volume	T	Teflon Valves
I	Ionization Gauge	TP	Turbomolecular Pump
LN	Liquid Nitrogen Trap	VL	Variable Leak Valve

FIGURE 1

hour. The products are analyzed by a Dycor M100 mass spectrometer which is interfaced to a Zenith 158 personal computer for data retrieval and processing. The system is differentially pumped by two Balzers turbomolecular pumps. Due to the temperature limitations of the variable leak valve and the mass spectrometer the system cannot be baked at high temperature, but it is periodically pumped at a temperature of 150°C overnight to remove adsorbed molecules from the walls and achieve a vacuum of 10^{-6} Torr.

Prior to each experiment cyclopentane and deuterium were mixed in a control volume, where their pressures were monitored by a Datametrics diaphragm manometer, and allowed into the reaction volume. The catalyst had been preheated to 100°C, the hydrogen–cyclopentane ratio was 25, and the total pressure was 26 Torr. The exchange pattern was recorded at 15% conversion according to the method of van Broekhoven *et al.* (*22*) and corrected for the natural abundance of heavy isotopes and for the fragmentation that occurs from ionization in the mass spectrometer.

2.4. *Hydrogenolysis of Cyclopentane*

Two types of hydrogenolysis experiments have been carried out. Runs at low pressure including a kinetic study of the rate dependence on hydrogen pressure were done in the reactor mentioned above. Conditions were 240°C, an overall pressure of 20 Torr, and a hydrogen–cyclopentane ratio of 9. For the kinetic study, the temperature was the same, the hydrogen pressure was varied from 27 to 96 Torr, and the cyclopentane pressure was 3 Torr. In these experiments reaction rates were measured by the change in peak intensity at masses 16 and 70. Calibrations were done to convert these intensities to molar quantities.

Another series of hydrogenolysis reactions was carried out at atmospheric pressure. A flow type reactor was used for this work. The reaction temperature was also 240°C, and the saturator temperature was held at −7°C to obtain a hydrogen–cyclopentane ratio of 9. The products from this reaction were analyzed by a Hewlett–Packard 5790 gas chromatograph with a crosslinked methyl-silicone capillary column and a 3390A integrator. The conversion for these reactions were generally kept well within the differential kinetic regime.

2.5. *Dispersion Measurements*

It has been reported that supported Re (*23*) or Re powder (*24*) adsorbs very little hydrogen at room temperature. Presumably this adsorption is a kinetically limited process. Therefore we used a different method to measure metal surface area, viz., the room temperature exchange of preadsorbed deuterium with gaseous protium after saturating the catalyst with adsorbed deuterium (*25*). This was done by reducing the catalyst at 500°C in deuterium and then cooling it. The reactor was then purged at 20°C for 0.5 hr in Ar and evacuated for at least 3 hr at 10^{-5} Torr. A quantity of hydrogen which was at least 20 times greater than the expected amount of adsorbed deuterium was then introduced into the reactor system. Metal catalyzed exchange of hydrogen with adsorbed deuterium atoms reaches equilibrium almost instantaneously at room temperature, while exchange of the surface hydroxyl groups is a much slower process. Therefore, the percentage of hydrogen exchanged as a function of time was extrapolated to zero time to determine the amount of hydrogen adsorbed on the metal.

2.6. *X-ray Diffraction Measurements*

These measurements were done with a Rigaku diffractometer with CuKα radiation. Only the high loading PtRe/SiO_2 catalyst was analyzed to determine the amount of metal alloyed. The diffraction pattern showed that two alloy phases were formed. No peaks for pure Pt or Re clusters were detected, though this does not rule out the possibility of very small, X-ray amorphous Pt or Re particles being present. An estimate for the upper limit of this undetectable, unalloyed Pt was obtained from separate measurements with sintered Pt/SiO_2 samples of various metal loads. The maximum amount of Pt undetectable corresponds to about 10% of the total amount in the PtRe/SiO_2 samples. From a Végard's law analysis of the peak position it was determined that the two phases contained 58 mole percent Pt (lattice spacing = 2.32 Å, FCC structure) and 16 mole percent Pt (lattice spacing = 2.37 Å, HCP structure). The widths of the peaks were fairly narrow indicating an average particle size of the order of 100 nm.

3. RESULTS

3.1. *Deuterium Exchange of Cyclopentane*

The rate of disappearance of light cyclopentane versus time followed apparent first-order kinetics (Fig. 2). The measured rates along with dispersion measurements are presented in Table 1 for the Al_2O_3-supported catalysts. The exchange turnover frequency (TOF) for Pt/Al_2O_3 was compared with some earlier work done by Wong *et al.* (*26*), who studied a similar catalyst under different conditions. When their TOF was corrected for the experimental differences there is fairly good agree-

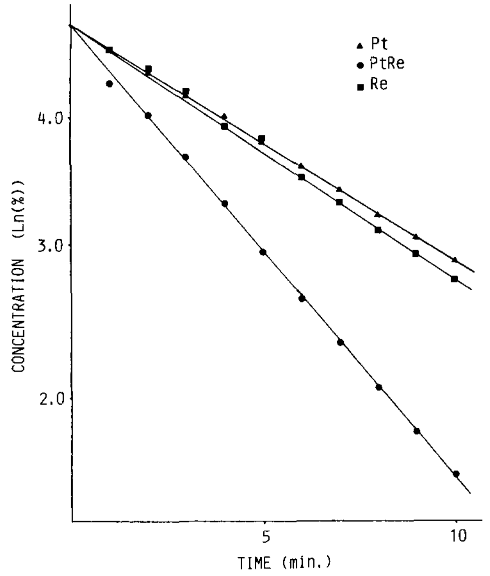


FIGURE 2

ment of their data with this study. The exchange rate per surface atom was higher for Re than for Pt, which was also observed by Haining *et al.* (*18*). The rate over the physical mixture (Pt + Re/Al_2O_3) is between these values, as might be expected. The last entry in this table is a calculated value (PtRe/Al_2O_3(c)). It was determined by taking the measured deuterium exchange turnover frequencies for the Pt and Re monometallic catalysts, weighting them for the relative, total amount of each metal in the bimetallic sample, and multiplying them by the number of surface metal atoms in this catalyst. If the rate of this reaction is insensitive to whether the metals are physically mixed or alloyed, then the rate calculated in this way should equal the experimental rate. Within experimental error this is indeed the case.

The selectivity for this reaction, which is taken at 15% light cyclopentane exchanged, is presented in Fig. 3. It shows the expected combination of stepwise and multiple exchange, as observed earlier by Burwell (*27*), Kemball (*28*), and Dessing *et al.* (*29*) for several metal catalysts. Other well-known features characteristic for supported-Pt catalysts are the two local maxima at 5 and 10 hydrogens exchanged, which are significant of a high probability for complete exchange on one side of the C_5 ring. These were also apparent for the bimetallic catalyst. The exchange over Re at 15% total exchange was limited to four hydrogen atoms per molecule. A point which should be highlighted from this figure is that the relative amounts of each deuterated product over the PtRe catalyst are always intermediate between those over the monometallic catalysts. This is another strong indication for the absence of a major selectivity change due to alloying.

The correlation of the reaction rates with the measured dispersion makes it quite clear that the rate of this reaction is proportional to the number of exposed surface metal atoms. Consequently there are now two methods at our disposal that "count" active metal atoms. We prefer to use the rate of isotopic exchange of cyclopentane to normalize for different percentages of active surface metal exposed, so the hydrogenolysis data can be expressed in terms of turnover frequencies. This preference exists because we wish to probe only those surface sites which are active for hydrocarbon conversion and eliminate differences which are not relevant to the catalytic activity. Since it is difficult to determine the relative surface concentrations of Pt and Re atoms in such a highly dispersed catalyst, the measured rates of isotope exchange of any sample are expressed as the equivalent

TABLE 1

Rates of Deuterium Exchange of Cyclopentane (26 Torr; 100°C)

Catalyst	Metal loading Pt/Re (wt%)	Metal dispersion (H/M)	Disappearance of light cyclopentane (%/min–25 mg cat)
Pt/Al_2O_3	.35/0	.91	15.4 ± 5.2
Re/Al_2O_3	0/.20	.68	16.9 ± 3.3
Pt + Re/Al_2O_3	.18/.10	.79	16.6 ± 1.7
PtRe/Al_2O_3	.33/.22	.70	29.4 ± 1.1
PtRe/Al_2O_3(c)	.33/.22	.70	28.1(calculated)

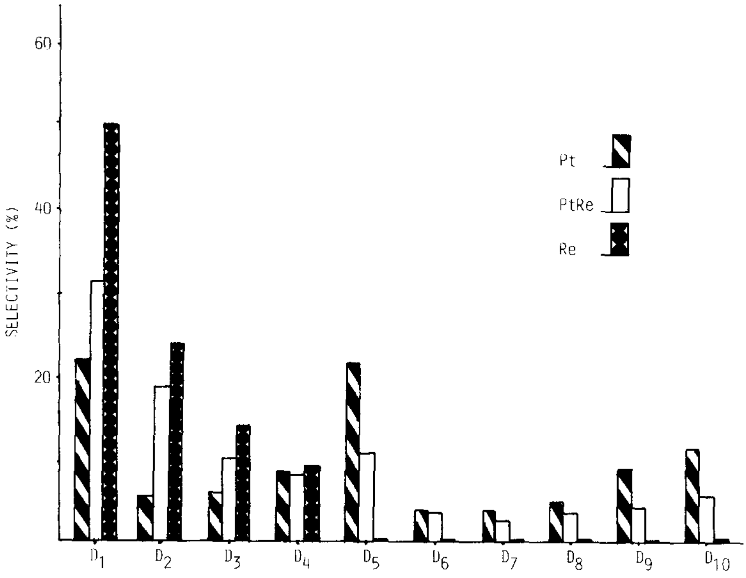


FIGURE 3

number of Pt surface atoms that would give the same exchange rate under these conditions (Pt_{eq}). This number is defined by:

$$Pt_{eq} = \frac{\text{Rate/g of sample}}{\text{Rate/g of Pt-cat}} N_{Pt,s}$$

where $N_{Pt,s}$ is the number of exposed Pt atoms per gram of the Pt catalyst. The values are reported in Table 2 as Pt_{eq} in μmol/gram of catalyst.

TABLE 2

Deuterium Exchange (26 Torr; 100°C)

Catalyst	Metal loading Pt/Re (wt%)	Disappearance of light cyclopentane (%/min.–25 mg cat)	Pt_{eq}[a] (μmole/g)
Pt/Al_2O_3	.35/0	15.4 ± 5.2	16.3
Re/Al_2O_3	0/.20	16.9 ± 3.3	17.9
$Pt + Re/Al_2O_3$	.18/.10	16.6 ± 1.7	17.6
$PtRe/Al_2O_3$	.33/.22	29.4 ± 1.1	31.2
$PtRe/SiO_2$	2.9/4.7	8.89 ± .62	9.42
$Pt + Re/SiO_2$	1.5/2.4	3.34 ± .60	3.54
Pt/SiO_2	2.9/0	2.55	2.70
Re/SiO_2	0/4.7	4.13	4.38

[a] These values have been calculated by dividing the measured rate of deuterium exchange in column 3 by the TOF for the exchange of cyclopentane over the Pt/Al_2O_3 catalyst.

3.2. *Hydrogenolysis of Cyclopentane*

The hydrogenolysis reactions at 1 atm provide useful data for comparing the catalyst samples. The product selectivities are presented in Table 3. The products are predominantly normal alkanes, with *n*-pentane being the major product in most cases. Methane yield was highest with the bimetallic SiO_2-supported catalyst.

The reaction rates decreased with time on stream for most catalysts, so the turnover frequencies which were observed after 10 min time on stream are reported in

TABLE 3

Hydrogenolysis of Cyclopentane Product Selectivities after 10 min Time on Stream

Catalyst	nC_5	iC_5	nC_4	C_3	C_2	C_1
Pt/Al_2O_3	100					
Pt/SiO_2	100					
Re/Al_2O_3	60.9	—	11.4	8.9	7.5	11.3
Re/SiO_2	24.8	1.3	11.1	10.1	11.0	41.8
$PtRe/Al_2O_3$	87.1	0.5	3.7	2.4	1.8	4.7
$PtRe/SiO_2$	50.8	0.6	13.2	8.1	7.3	20.0
$Pt + Re/Al_2O_3$	94.9	—	1.6	1.2	1.2	1.0
$Pt + Re/SiO_2$	70.4	0.9	8.1	4.5	4.3	11.9

Note. Moles converted to product/all moles converted; %.

TABLE 4

Atmospheric Pressure Hydrogenolysis of Cyclopentane (1 atm; 240°C)

Catalyst	Cyclopentane consumption	Methane production
Pt/Al_2O_3	6.09 ± 1.71	0
Re/Al_2O_3	0.78 ± 0.08	0.40 ± 0.01
$Pt + Re/Al_2O_3$	7.04 ± 0.87	0.34 ± 0.01
$PtRe/Al_2O_3$	13.5 ± 3.8	3.16 ± 1.06
$PtRe/SiO_2$	832. ± 45.	774. ± 37.
$Pt + Re/SiO_2$	33.2 ± 2.0	18.9 ± 0.2
Pt/SiO_2	34.1	0
Re/SiO_2	25.2	42.1

Note. TOF for cyclopentane conversion and methane production (10^{-3} molecule/Pt_{eq} s).

TABLE 5

Low Pressure Hydrogenolysis of Cyclopentane (20 Torr; 240°C)

Catalyst	Cyclopentane consumption	Methane production
Pt/Al_2O_3	6.79 ± 0.28	0.055 ± 0.004
Re/Al_2O_3	NM	0.054
$Pt + Re/Al_2O_3$	3.01 ± 0.27	0.052 ± 0.002
$PtRe/Al_2O_3$	1.93 ± 0.22	0.201 ± 0.011

Note. TOF for cyclopentane conversion and methane production (10^{-3} molecule/Pt_{eq} s).

Table 4. They clearly show maxima for the bimetallic catalysts prepared by co-impregnation. The conversion rate of cyclopentane is highest for the silica-supported high metal load catalysts, exceeding that of the physical mixture by a factor of 25. For the alumina-supported samples the difference in conversion rates is also marked, though in this case the TOF for the bimetal catalyst exceeds the sum of that for the physical mixture of the monometallics only by a factor of 2. The effect of alloying is much more pronounced for the rates of methane formation. For the silica-supported samples the bimetallic samples again surpass the diluted physical mixture for methane production by a large factor of 40; for the alumina-supported samples the catalyst prepared by co-impregnation exceeds the physical mixture by a ninefold higher TOF. The value for this physical mixture (0.34) is still significantly higher than the calculated average of the pure components (0.2). It is obvious that methane formation is an indicator for the proximity of the metal atoms to each other.

Table 5 presents initial TOF data for hydrogenolysis at 20 Torr. Only alumina-supported samples were tested under these conditions. The TOF for all Re-containing samples is lower under these conditions, reflecting the higher degree of catalyst deactivation at the lower hydrogen pressure. Still, although the TOF for cyclopentane conversion is highest on Pt/Al_2O_3, the TOF for methane production is highest for the bimetal catalyst, illustrating, once again, the high selectivity of PtRe combinations for methane production.

The dependence of the total cyclopentane conversion on hydrogen pressure is illustrated graphically in Fig. 4. The dependence on hydrogen is much stronger for the bimetallic catalysts than for Pt alone. The familiar model that hydrogen is required to remove coke precursors from active sites is in agreement with this finding, if one

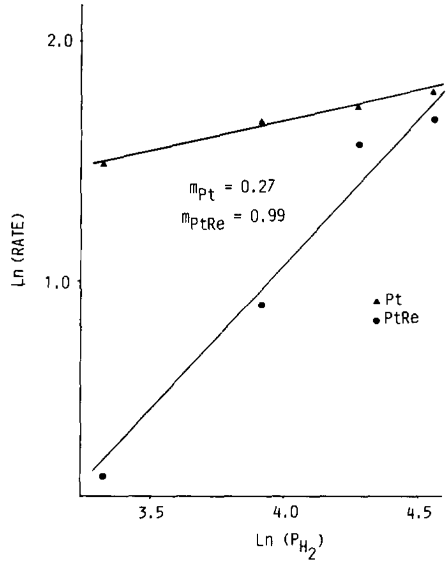


FIGURE 4

accepts that PtRe ensembles form stronger bonds to coke precursors than do pure Pt ensembles. Indeed, the kinetic studies show that the reaction order in hydrogen is approaching unity for hydrogenolysis over the bimetallic and is only 0.23 for Pt (Fig. 3), indicating that product desorption is becoming the rate-limiting step for the bimetal catalysts.

4. DISCUSSION

The first result of relevance is the high specificity of PtRe catalysts, prepared by co-impregnation and co-reduction, for methane formation. This matches the earlier observations on macroscopic, unsupported PtRe alloys, prepared by melting (*16*). We, therefore, assume that this methane selectivity is characteristic for PtRe alloy particles on the support. As to the mechanistic causes of this high selectivity we agree with Haining *et al.* (*17, 18*), who found a similar specificity for methane production in butane hydrogenolysis over PtRe/Al_2O_3 catalysts. They assume that on pure Pt the rate-limiting step for hydrogenolysis is C–C bond scission, but on Re the carbon-to-metal bonds are so strong that removal of carbon from the surface limits the reaction. This concept agrees well with the model based on adsorbing ensembles.

It is known that the ensemble requirement for hydrogenolysis is large (*2, 5, 8*). The heat of adsorption of the precursor to hydrogenolysis on such an ensemble would then be the parameter decisive for the probability of forming the adsorption complex leading to C–C bond rupture. An ensemble consisting of Pt atoms only would have the lowest heat of adsorption, while this parameter would be highest for pure Re ensembles, and have intermediate values for mixed PtRe ensembles. Accepting that the extremes of too weak adsorption and too strond bonds with the primary fission products represent unfavorable limits, it follows that some mixed ensemble, containing Pt *and* Re atoms has the highest activity for methane formation. The TOF for methane formation, in other words, when plotted versus the ensemble composition must be a curve of the "volcano-shaped" type (*17*).

The position of the maximum should depend on the reaction conditions. Using the simple concept, that hydrogen is needed to remove coke precursors from the active sites, while the formation of such precursors is due to the hydrocarbon, one expects an effect of the partial pressures. The results from Tables 4 and 5 are for reaction mixtures of the same composition but different total pressures. Consequently, they show that the reaction order in hydrogen for removal of carbonaceous residues is higher than that in hydrocarbon for their formation. There should be a shift in maximum activity with lower pressure away from the ensembles which form stronger adsorption bonds. This is confirmed by the data at 20 Torr, which show a higher initial activity for Pt than for PtRe.

For the application of the methane selectivity as an experimental criterion for the formation of alloy particles it is useful that this reaction is little disturbed by acid sites in bifunctional reforming catalysts. The known chemistry of the carbenium ions on acid sites implies that methane is formed only in negligible quantities.

Having an experimental method to estimate the extent of alloy formation on supported-PtRe catalysts might provide the possibility to answer some pertinent questions which have often been asked, including the following:

Is alloy formation complete on PtRe/Al_2O_3 or is only a certain fraction of the two metals interacting?

Is alloy formation limited to co-impregnated catalysts or can it also occur in physical mixtures of the pure metals, supported on separate carrier particles?

How does alloy formation for co-impregnated catalysts or physical mixtures depend on the nature of the support?

To each of these questions a tentative answer can be given on the basis of published data by other authors or from work in this laboratory. In our previous work we stressed that alloy formation of Pt and Re on alumina need not be complete, though there are strong indications that the alloyed fraction is responsible for some of the typical characteristics of this catalyst system (*15*). More recently we have identified the nonreduced fraction of Re by ESR and we have shown that these Re ions contribute to the Brönsted acidity of alumina (*30*). Their concentration in PtRe catalysts is, however, small after thorough reduction, and the additional acidity is negligible in comparison to that caused by the chlorine content of technical reforming catalysts. The present XRD data for silica-supported samples of high metal load show that alloy formation is fairly complete.

The observation that the methane TOF on this highly alloyed catalyst exceeds that of the physical mixture by a factor of 40, while in the case of the alumina-supported catalysts the gain of the co-impregnated sample over the physical mixture is only a factor of 9, suggests that alloy formation is incomplete for the alumina-supported catalyst. There is, however, an important *caveat* attached to this conclusion: the size of the metal particles is different on the two supports, and methane yield increases with increasing particle size (*31*). We have tried to minimize this complication by comparing catalysts of the same overall metal load for each support, but we cannot exclude that also the "gain factor" of enhanced methane production over the alloyed versus the separated metals of equal size may to some extent be particle size dependent.

In the limit, where these particle size effects can be ignored, the following simple calculation can be made: Call the contribution to the TOF by the alloy x and the contribution due to the presence of the metals in the unalloyed form y, and α will be the extent of alloying. The TOF for methane production can then be expressed as

$$\alpha x + (1 - \alpha)y = \mathrm{TOF}.$$

A correction must then be inserted to the contribution of the alloy term for the surface enrichment of Re, which is called β, and the mole fraction of Re in the physical mixture and the co-supported catalyst. However, in the quotient E,

$$E = \mathrm{TOF}\ \text{of sample/TOF of separated metals},$$

the mole fraction will cancel if a co-impregnated sample is compared with a physical mixture of two separated metals in the same molar ratio. E is then given by

$$\frac{\alpha x/\beta + (1 - \alpha)y}{y} = E.$$

If we assume that β is equal to 1, the boundary conditions for E, which may be thought of as the enhancement in the TOF due to alloying, will be 1 for $\alpha = 0$ and 40 for $\alpha = 1$, assuming that the high load silica-supported bimetal catalyst was indeed completely alloyed.

Applying this to the data in Table 4 yields a value of 21% as the calculated extent of alloying of the metals present in the bimetallic Al_2O_3-supported catalyst.

It should be stressed again that this number is a very rough approximation, and further refinement requires much more work in this area. What appears certain is that the combination of the two probe reactions of deuterium exchange and hydrogenolysis of cyclopentane gives evidence of alloy formation in a low load, highly dispersed, Al_2O_3-supported, PtRe catalyst, where conventional physical methods fall short.

Within these limitations the results indicate that alloy formation on alumina might be less complete than on silica, which agrees with the more severe preparation techniques for the latter catalyst and observations that metal sintering is often found more pronounced on silica than on alumina supports, the rationale being a better anchoring of metals on alumina.

The data in Table 4 show that the methane production over the physically mixed Al_2O_3 is 30% higher than the average of the monometallic catalysts, indicating some alloy formation. Since this effect is not seen in the SiO_2 physical mixture, it is assumed that migration of Re took place via gas phase transport of volatile Re_2O_7 during the one hour drying step. This step was not included in the pretreatment procedure for the SiO_2 catalysts. Re migration has also been reported by Bolivar *et al.* (*32*) between particles of α-alumina.

One conclusion from the present work is that the degree of alloying in a bimetallic catalyst can be estimated by catalytic probes which are sensitive to the composition of the catalyzing ensembles.

Further work will be needed to provide more reliable quantitative data. This should also include the preparation of catalysts with mixed ensembles of known composition, preferentially by the deposition and decomposition of mixed metal carbonyl clusters. In this way it might be possible to identify the composition of the most active ensembles and detect their presence in real world catalysts. Also it would be interesting to study, in more detail, the inter-support-particle migration that was observed in this work.

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