Role of Rhenium in Pt-Re-Al_2O_3 Reforming Catalysis—An Integrated Study

The inclusion of Re in Pt-Re-Al_2O_3 reforming catalysts to improve the lifetime is known, but how rhenium functions and how it is disposed in the catalyst remain unclear. These fundamental questions have been attempted in this study by the use of proton-induced X-ray emission and Rutherford backscattering spectrometry (together with electron microscopy and chemisorption studies) to characterize a commercial like catalyst for dehydrogenation of methylcyclohexane.

K. JOTHIMURUGESAN,
A. K. NAYAK, G. K. MEHTA,
K. N. RAI, S. BHATIA AND
R. D. SRIVASTAVA

Indian Institute of Technology
Kanpur-208016, India

SCOPE

Catalysis is one of the most intensely pursued subjects in chemical engineering and related disciplines, primarily because of its economic importance. The development of modern surface science has made possible studies of the catalyst surface at the molecular level, leading to a better understanding of its role in determining catalytic activity. *In situ* measurements by infrared spectroscopy (Eischens and Pliskin, 1958; Blyholder, 1968; Force and Bell, 1975a,b), Mossbauer spectroscopy (Dumesic and Topsoe, 1977), electron spin resonance (Lunsford, 1972) and X-ray diffraction (Srivastava et al., 1982) have enabled chemical engineers to broaden their thinking beyond the semiempirical reaction parameters, and relate them to structural aspects of the catalyst, thus leading to a more comprehensive and integrated modeling of chemical reactors.

In spite of the applications of advanced instrumental techniques in catalysis, there have been great difficulties inherent in studying the structure and composition of surface atoms in dispersed high area systems such as Pt-Re-Al_2O_3, the industrial reforming catalyst. Platinum-rhenium-alumina catalysts contain an amount of rhenium comparable to the amount of platinum present (about 0.3 wt. % of each). The addition of rhenium provides greater stability; however, the reasons for the promotional effect of rhenium are unclear, despite some 25 reported studies. It is important to understand how rhenium functions if alternate and better catalyst systems are to be developed. The impact of the research in this bimetallic catalyst area is likely to increase over the next few years. For example, the MTH (methylcyclohexane-toluene-hydrogen) system using methylcyclohexane as a hydrogen carrier, which requires the catalytic (Pt-Re-Al_2O_3) production of hydrogen from an on-board reactor, is commercially exploited for automotive application (Cresswell et al., 1984).

The application of proton-induced X-ray emission analysis (PIXE) and Rutherford backscattering spectrometry (RBS) can provide a significant insight into the near surface elemental composition. Both these techniques were designed originally for research in nuclear physics, and tended to be temperamental and complicated. Most accelerators are now designed for material analysis; however, the full potential of PIXE and RBS techniques in catalyst research has not yet been exploited.

In this investigation, results are postulated using the techniques of proton-induced X-ray emission and Rutherford backscattering spectrometry with complementary data from electron microscopy and chemisorption studies to characterize and correlate the activity of Pt-Re-Al_2O_3 catalysts in catalytic reforming of methylcyclohexane (MCH) in an interdisciplinary fashion. It is intended here to demonstrate that modern techniques that have been derived from PIXE and RBS offer a much wider prospect of obtaining structural effects in bimetallic-dispersed catalysts.

CONCLUSIONS AND SIGNIFICANCE

This study has provided a comprehensive picture of surface and bulk concentration properties of alumina supported Pt, Re, and Pt-Re catalysts. Activity of Pt catalyst was nearly the same as that of Pt-Re catalyst in the presence of hydrogen. However, in the absence of hydrogen there was a *drastic fall* in activity of Pt with respect to Pt-Re catalyst. PIXE and RBS results indicated the existence of strong chemical disproportionation induced by hydrogen. As a result, Pt tends to migrate deep inside the pores and Re segregates towards the surface. Pt-Re catalyst seems to exist in the form of a small fraction of pure Re and pure Pt particles along with Pt-Re *"alloyed"*

Correspondence concerning this paper should be addressed to R. D. Srivastava at the University of Delaware, Newark, DE 19716

particles. The "alloyed" catalyst behaves similarly to pure Pt. The free Re helps in reducing graphite deposition, whereas selective activation is provided by free Pt and Pt-Re aggregates. Re does not form strong bonds with MCH at the surface during dehydrogenation and therefore contributes no catalytic activity.

The object of the present work was also to bring to the attention of the chemical engineering community the possibilities now emerging in the application of RBS and PIXE to catalytic science. With the increasing availability of suitable ion accelerators, the applications should follow. Studies of this type are expected to lead to a better understanding of the nature of catalysts in relation to the activity.

INTRODUCTION

The field of catalytic science is multidimensional and multidisciplinary. Modern access to research and development in this area requires an integrated approach based on different established practices of science and engineering. Since the working of a practical system is so complex, a reliable and reproducible study on the molecular level must be carried out through the use of model systems. The model system so chosen should be comparable to the real one. In this way the structure, composition, and oxidation state of the catalyst can be correlated with the reaction parameters, leading to a better understanding of its role in determining catalytic activity and in turn the reaction mechanism. To acquire these facts, however, the combined use of several techniques which complement each other is always needed.

During the last three decades, catalytic reforming has become one of the most important industrial applications of catalysis (Sinfelt, 1964; Ciapetta and Wallace, 1971). The use of Pt-Re-Al_2O_3 (0.3 wt. % of each) to replace Pt-Al_2O_3 as a catalyst for reforming was announced 15 years ago. The bimetallic catalyst displays a slower rate of deactivation than the one-component catalyst (Kluksdahl, 1968; Jacobson et al., 1969; Sinfelt, 1981; Carter et al., 1982). The disposition and function of Re in Pt-Re-Al_2O_3 are, however, contradictory despites some 25 reported studies. This is mainly because of inherent limitations of the techniques employed in these investigations. Moreover, systematic studies examining the relationship between catalyst properties and activity of the Pt-Re-Al_2O_3 system have not been attempted.

This paper presents results from the techniques of proton-induced X-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS), together with electron microscopy and chemisorption studies, to characterize commercial catalysts such as Pt-Re-Al_2O_3 in a truly interdisciplinary fashion. The dehydrogenation of methylcyclohexane (MCH), an important industrial operation in catalytic reforming, was employed in the activity studies. It is the subject of the present work to demonstrate that Re's promotion effect in the bimetallic Pt-Re-Al_2O_3 catalyst can be explained by the combined use of PIXE and RBS.

Literature Review

Researchers have sought to establish Re's valence state and whether it is alloyed with Pt in reduced catalyst. The conclusion of Johnson and LeRoy (1974) and Johnson (1975) using chemisorption, IR and X-ray diffraction (XRD) studies indicated that complete reduction of Pt from the +4 oxidation to metal and or Re from +7 to +4 state and the study of XRD data on the metal residue from the leached catalysts showed no evidence for the presence of rhenium metal or Pt-Re alloy. In contrast, chemisorption studies by Webb (1975) on Re-Al_2O_3 catalysts indicated that Re was completely reduced from the +7 state to the metal.

Later experiments using chemisorption and IR (Menon et al., 1973; Freel, 1973; Bolivar et al., 1975, 1976; Betizeau et al., 1976a; Yao and Shelef, 1976; Barbier et al., 1981; Apesteguia and Barbier, 1982) and temperature-programmed reduction (TPR) (Wagstaff and Prins, 1979) were consistent with the results of Webb (1975) in showing a change in oxidation state of rhenium from +7 to 0. These workers also indicated that the properties of Pt-Re-Al_2O_3 catalysts depended on the method of preparation. In the case of catalysts that were simply dried in air at 383 K after impregnation of alumina with H_2PtCl_6 and Re_2O_7, it was concluded that a Pt-Re alloy formed on reduction. However, from the catalysts that were calcined in air at 773 K, prior to reduction in hydrogen, it was concluded that the platinum exhibited much less interaction with rhenium (McNicol, 1977; Betizeau, 1976b; Charcosset et al., 1979; Shiflett and Dumesic, 1982).

Recently, X-ray absorption spectroscopy applied to the Re L_{III} edge showed that the Re is in the +4 state in the reduced catalyst (Short et al., 1981). The valence state problem seems natural for X-ray photoelectron spectroscopy (XPS), since the binding energy shifts for the intense 4f peak the large and well known (Cimino et al., 1980). Characterization of Pt-Re-SiO_2 catalyst using XPS was studied by Biloen et al. (1980). These authors established that a Pt-Re alloy was formed.

More direct evidence of an interaction between Pt and Re on Pt-Re-Al_2O_3 catalyst has been obtained using TPR (Isaacs and Petersen, 1982). This work demonstrates that Pt and Re on this catalyst do not behave as the sum of the individual components but suggests a bimetallic cluster, alloy, or an interaction through a support modification. Recently, an extensive study of the effect of Re addition on reactions related to reforming (Jossens and Petersen, 1982) showed that the rates for production of benzene from methylcyclopentane and of toluene from methylcyclohexane and the rate of self-deactivation by methylcyclohexane (short term) were unaffected. In contrast, the rate for methylcyclopentane ring opening decreased, as did the rates for toluene dealkylation and self-deactivation by methylcyclohexane (long term). The latter reactions are believed to be structure sensitive while the former are not, suggesting that Re directly affects Pt, as would be expected for Pt-Re alloys formed.

As against and conflicting to the above-mentioned prediction of formation of Pt-Re alloy, infrared spectroscopy of carbonaceous residues on Pt, Re, and Pt-Re-Al_2O_3 catalysts showed substantially less carboxylic carbon when Re was present (Ludlum and Eischens, 1976). As with the reaction studies, the IR findings showed that interaction might take place, but did not establish that it was alloying or that it was necessarily associated with Re's catalytic benefit. IR study of Pt, Re, and Pt-Re-Al_2O_3 catalysts (Peri, 1978) indicated no evidence for the formation of Pt-Re alloys. Pt and Re appeared to behave independently on the surface. Also, the catalytic evidence favored separate dispersion: a mixed bed of Pt and Re on separate pellets performed similarly to coimpregnated pellets with no evidence of Re transfer (Bertolacini and Pellet, 1980). Surface analysis by ion-scattering spectroscopy (ISS) and microanalysis by energy-dispersive X-ray spectroscopy in scanning transmission electron microscope studies of Pt-Re-Al_2O_3 catalyst indicate that Re is not significantly associated with Pt, but rather is widely dispersed on the support surface (Kelley et al., 1982).

The small metal particles typical of industrial reforming catalysts give X-ray diffraction features so broad that they are not useful for lattice parameter determination. Large particles are obtained when such catalysts are thermally sintered,and they show the lattice parameter charges expected for alloy formation (Freel, 1973). Efforts to obtain electron diffraction from Pt-Re-Al_2O_3 catalysts have been unsuccessful (Bolivar et al., 1976; Freed and Kelley, 1980).

Proton-Induced X-ray Emission (PIXE) (Ziegler, 1975).

Proton-induced X-ray emission, which represents a highly sensitive elemental method of analysis, has come to be established as an important analytical tool in the study of the near surface elemental composition of supported metal catalysts (Cairns et al., 1975, 1976; Cairns, 1980). A beam of energetic protons is used for the excitation of the inner shell electrons and the resultant characteristic X-rays are used for the identification and quantification of the elements of interest in the sample. In the case of supported metal catalysts, the metal atoms will be distributed over several microns depth. In such cases, PIXE can give the in-depth concentration of the metal.

Rutherford Backscattering Spectrometry (RBS) (Ziegler, 1975; Chu et al. 1978).

Rutherford backscattering spectrometry is one of the most powerful microanalytical techniques available for the study of the absolute surface concentrations as well as the depth distributions. Being based on the elastic backscattering of the ions, the method is truly nondestructive. It is highly sensitive, with surface concentrations of the order of a monoatomic layer being amenable for study when present on a lighter matrix. In the case of supported metal catalyst, at high temperatures, significant redistribution of the metal atoms in the support material can take place due to diffusion. RBS can be very useful in studying this problem. Further, the fact that the support is always a light matrix like Al_2O_3, SiO_2, etc., is an additional attraction. This technique has been recently applied for supported monometallic model systems (Cairns et al., 1983). The samples were prepared by evaporation of thin films of Pt and Rh onto single crystal Al_2O_3 and TiO_2 substrates.

EXPERIMENTAL

Catalyst Preparation

Platinum-rhenium catalyst on alumina support was prepared by the impregnation (incipient wetness) technique. The chemicals used were chloroplatinic acid (Johnson Matthey Chemical Ltd, London), Re_2O_7 (Riedel-De Haen Ag Seelze-Hannover, West Germany) and gamma alumina (1.5 mm dia. × 3 mm long) with an BET surface area of about 220 m^2/g. After impregnation, the catalyst was dried in air at 373 K and calcined in air stream for 5 h at 723 K. The catalyst composition was alumina with 0.3 wt. % Pt and 0.3 wt. %. Re. For comparison, individual metal catalysts of 0.3 wt. % (Pt or Re) on gamma alumina were also prepared under the same conditions except for Re, where the calcination was not performed. Pt-Al_2O_3, Re-Al_2O_3, and Pt-Re-Al_2O_3, hereafter, represent 0.3 wt. % Pt, 0.3 wt. % Re, and 0.3 wt. % Pt-0.3 wt. % Re, respectively, unless otherwise stated.

Description of Catalysts:

1. Pt or Pt-Re (calcined) = Catalyst calcined at 723 K for 5 h.
2. Pt or Pt-Re (reduced) = Catalyst reduced in hydrogen at 698 K for 5 h after calcination.
3. Pt or Re or Pt-Re (used)= Used for 24 h in the reaction (MCH) with-hydrogen.
4. Pt or Pt-Re (spent) = Used for 24 h in the reaction (MCH) without hydrogen.
5. Re (dried) = Catalyst dried at 373 K
6. Re (reduced) = Catalyst reduced in hydrogen at 698 K for 5 h
7. Pt-Re (commercial) = Catalyst reduced in hydrogen at 698 K for 5 h

Physicochemical Characterization

The catalysts were characterized by means of PIXE, RBS, electron microscopy, and gas chemisorption. A brief description of the equipment used in this study is given below.

Proton-Induced X-ray Emission (PIXE)

The proton beam (1.8 MeV) was obtained from a 2 MV Van de Graaff accelerator. The accelerated protons were momentum analyzed by a magnet and focused using a quadrupole doublet onto a 0.4 um thick nickel foil (diffuser). The beam becomes diffused by multiple scattering. The central homogeneous portion of the transmitted beam was selected using a set of collimators and was incident at 45° on the target mounted at the center of the specially designed target chamber using a multiple target holder. The chamber had provisions for coupling an X-ray detector at 90° to the beam direction. The detector was separated from the target by a 10 *m*m thick Mylar window. The target chamber was also provided with an electron gun for spraying electrons onto the target if necessary and an externally operated filter wheel with different filters for the selective absorption of X-rays.

The X-rays were detected using a lithium drifted silicon, Si(Li), detector cooled to liquid nitrogen temperature. The detector has an active area of 13 mm^2, a sensitive depth of 4.26 mm and an energy resolution of 180 eV for 6.4 keV X-rays. The X-ray pulses were amplified and fed to a pulse height analyzer.

The catalysts, prepared, used, or spent, were glued to an aluminized polyester film using Formvar resin. The Formvar resin and the polyester film were analyzed beforehand to insure that they were free from contminants that can interfere with the analysis. The matrix material gamma alumina, on which the catalyst Pt-Re was supported, is an insulator. Thus it was necessary to use the electron gun to neutralize the positive charge buildup on the target. Since interest was restricted to Pt and Re only, the low energy X-rays were absorbed using a 0.0195 mm Mylar filter, thereby enabling a faster data accumulation by increasing the proton flux without causing pulse pileup (Ahlberg et al., 1975; Varier et al., 1980).

Rutherford Backscattering Spectrometry (RBS)

He^+ beam of 1.8 MeV obtained from the 2 MV Van de Graaff accelerator was momentum-analyzed using a magnet and focused using a quadrupole doublet. The foucsed beam was collimated to a 1 mm dia. spot and was incident at 90° on the target. The backscattered He^+ was detected and energy analyzed using a surface barrier detector mounted at a 170° backward angle (Jain et al., 1982).

Electron Microscopy

An International Scientific Instrument model ISI-60 scanning electron microscope (SEM) was employed to study the particle size distribution of the support material. The alumina pellets loaded with platinum or rhenium or both were coated with Pd-Au alloy (film thickness $\simeq$5 nm) for yielding better image contrast and were observed in secondary electron imaging mode.

Transmission electron microscopy (TEM) was similar to that used by Sharma and Srivastava (1980) and Sharma et al., (1980) in the characterization of vanadium-based catalysts. A Phillips E. M. 301 electron microscope excited at 100 kv, at a resolution better than 1 nm was used during this investigation. Electron diffraction patterns from evaporated gold were used as a standard for indexing diffraction patterns from catalysts.

Chemisorption

Chemisorption data on the catalysts were obtained with conventional high-vacuum volumetric system. It consists of a gas dosing device, a pressure measuring device, a specimen chamber, and associated gas handling and vacuum plumbing. The system was capable of being evacuated to a pressure of 1.33×10^{-4} N/M^2. The amount of gas adsorbed was determined volumetrically by taking the difference between the amount of gas dosed into the volume containing the sample, and the amount

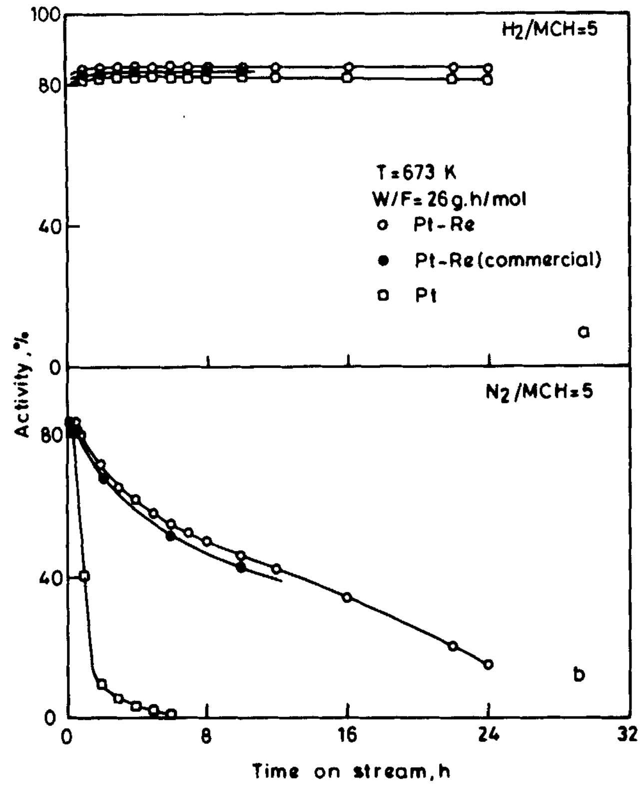

Figure 1. Activity of Pt and Pt-Re catalysts with time on stream: (a) in presence of hydrogen, (b) in absence of hydrogen.

retained in the dead space. The latter was calculated from the measured pressure and the dead space volume, which was measured using helium. Prior to the determination of adsorption isotherms, the catalysts were degassed in the adsorption cell at a temperature of 773 K for 2 h. The samples were subsequently reduced in flowing hydrogen at a temperature of 773 K and finally cooled to room temperature in flowing hydrogen. The system was evacuated prior to obtaining an adsorption isotherm.

Catalytic Activity

The activity of Pt, Re, and Pt-Re catalyst was studied using dehydrogenation of MCH to toluene as the test reaction in the presence of added hydrogen for 24 h. For comparison, runs were also performed for 24 h in the absence of hydrogen. This will be referred to as "without hydrogen." The apparatus is similar to that used by Sharma and Srivastava (1981) in the oxidation of methanol. However, some of the details of the equipment vary between experiments. A brief description of the equipment used in this study is necessary. The MCH was fed by a calibrated metering pump into a preheater where it was mixed with diluent nitrogen or hydrogen gas and vaporized. The vapor was then led to a reactor containing the catalyst bed. Prior to introducing the MCH feed, the catalyst was reduced in flowing hydrogen for 5 h at 698 K. The reactor was stainless steel tubing (2.54 cm dia. × 15.24 cm long) placed into the salt bath. Temperatures at various points in the reactor were measured with the help of chromel-alumel thermocouples. The average temperature was the mean of temperatures measured at a point in the reactor at different time intervals and was controlled to within ±1°C of the value. Pore diffusion limitations were checked in the preliminary experimental runs and no effect of particle size was observed even at the highest reaction temperature. An on-line GLC with a 2 m long, 3.2 mm dia. column of 10% SE-30 on chromosorb W was used to separate the various components in each sample. The experiments were conducted at a temperature of 673 K with a mole ratio of H_2 or N_2/MCH = 5 and W/F = 26 g·h/mol. From the product analysis, it was found that the major products from the dehydrogenation of methylcyclohexane were hydrogen and toluene.

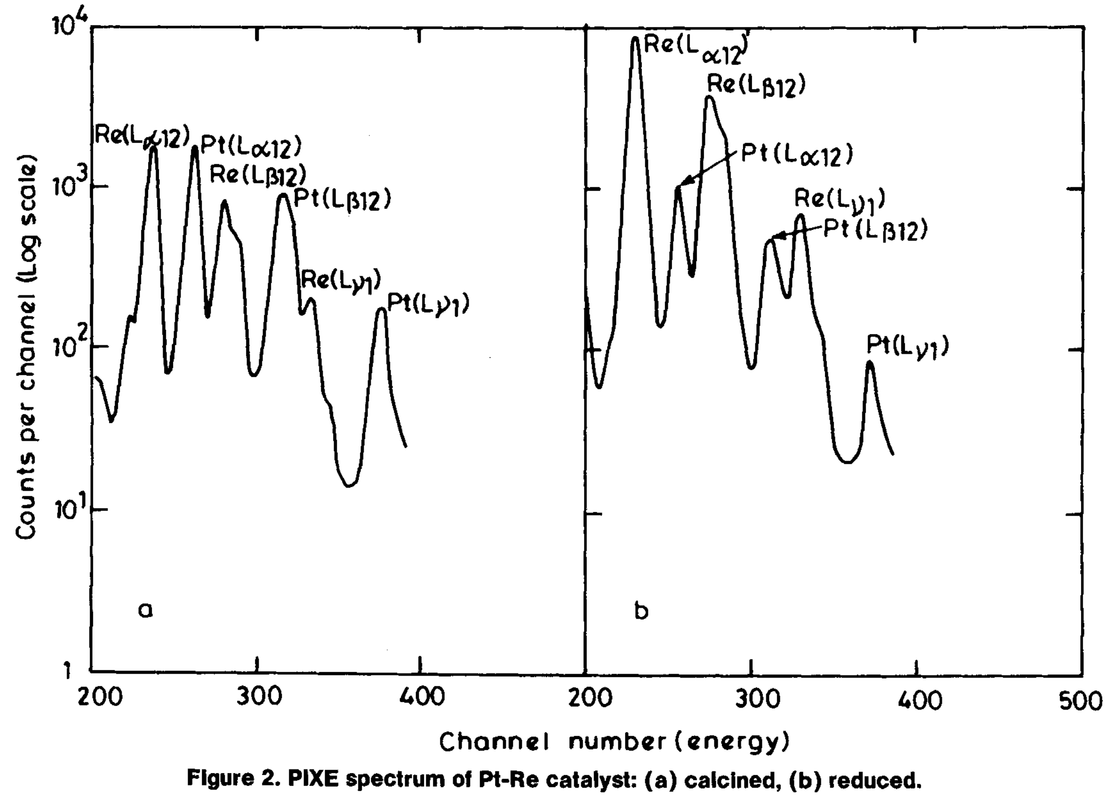

Figure 2. PIXE spectrum of Pt-Re catalyst: (a) calcined, (b) reduced.

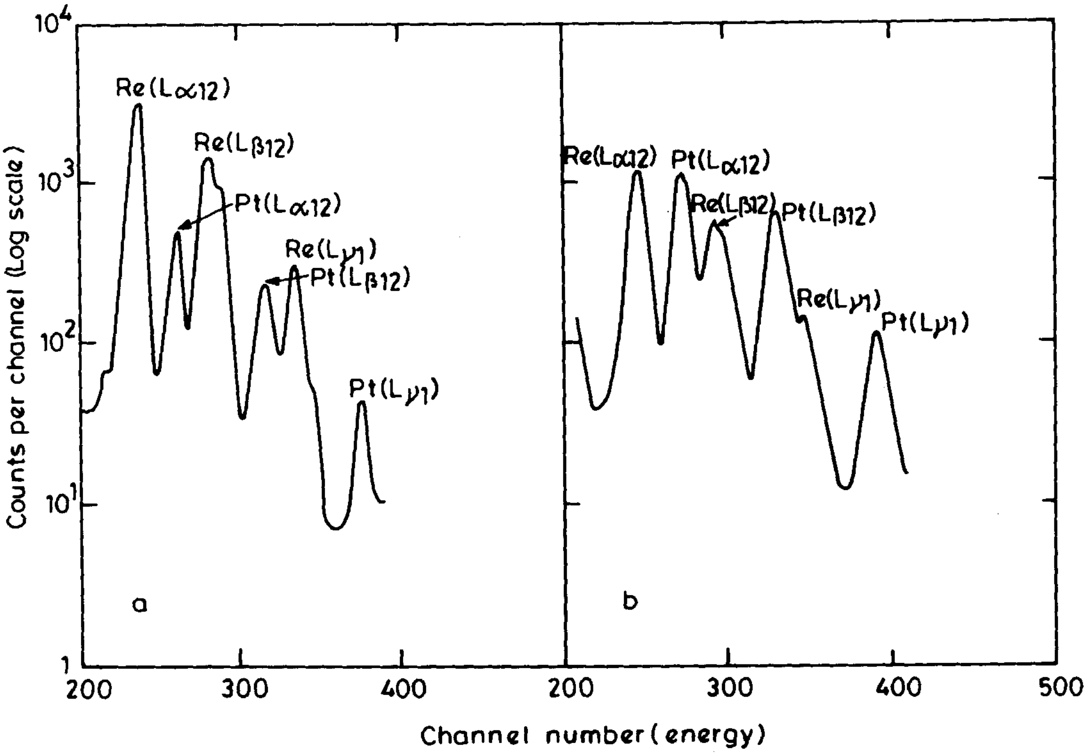

Figure 3. PIXE spectrum of Pt-Re catalyst: (a) used, (b) spent.

RESULTS

Activity Studies

Catalytic activity, expressed in terms of % toluene yield (moles toluene made/mole MCH feed) with and without hydrogen is plotted as a function of time in Figure 1. Runs of 24 h duration were made in hydrogen and nitrogen separately as a carrier gas, primarily to study the catalyst deactivation. A limited number of experiments, in which hydrogen was present in the reactor feed, showed no deactivation (designated as "used" catalyst). From Figure 1a it is clear that the activity of Pt catalyst was nearly the

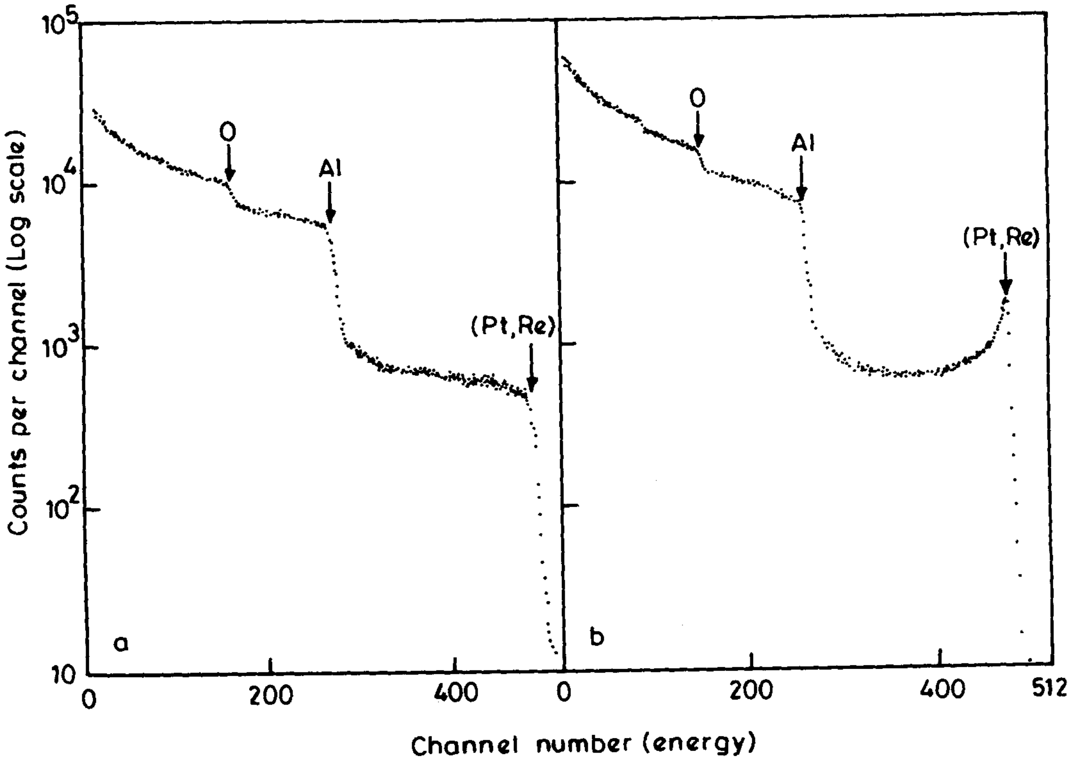

Figure 4. Backscattering spectrum of Pt-Re catalyst: (a) calcined, (b) reduced.

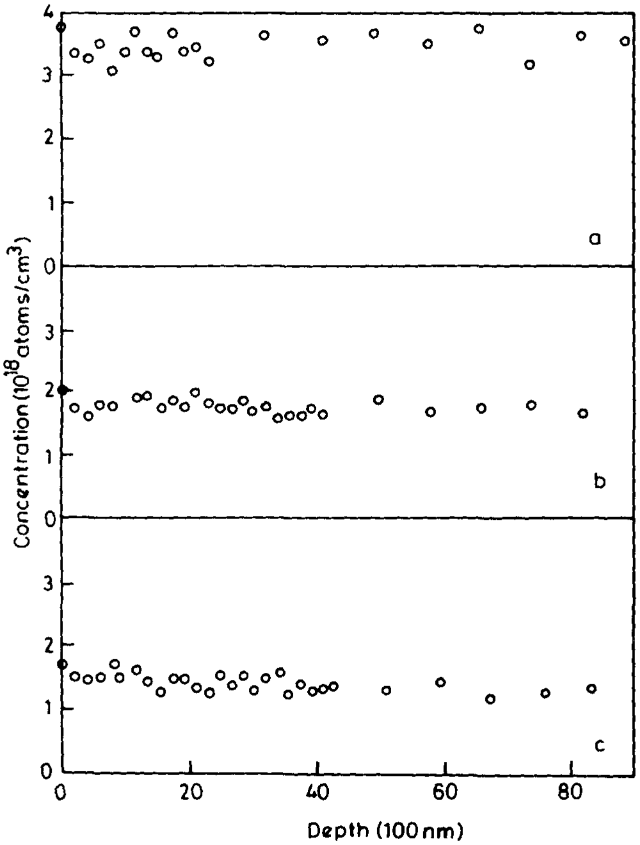

Figure 5. Depth profile for Pt catalyst: (a) calcined, (b) reduced, (c) spent.

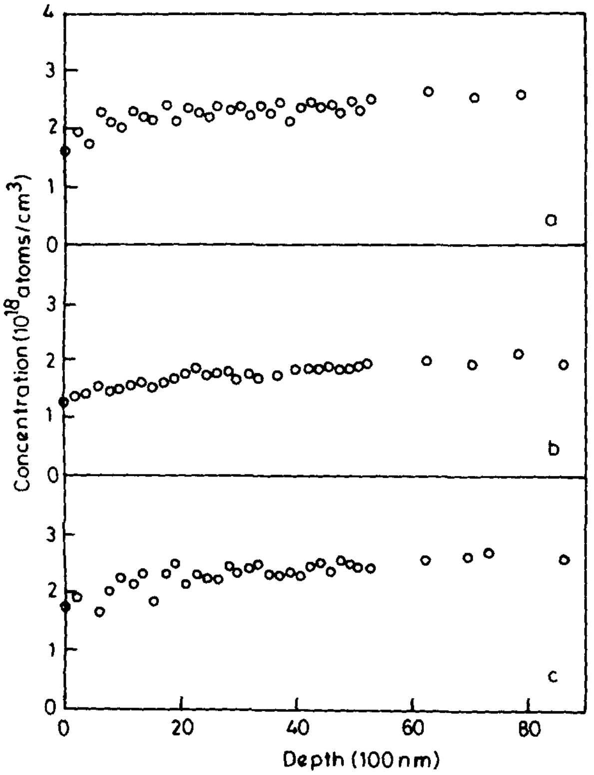

Figure 6. Depth profile for Re catalyst: (a) dried, (b) reduced, (c) used.

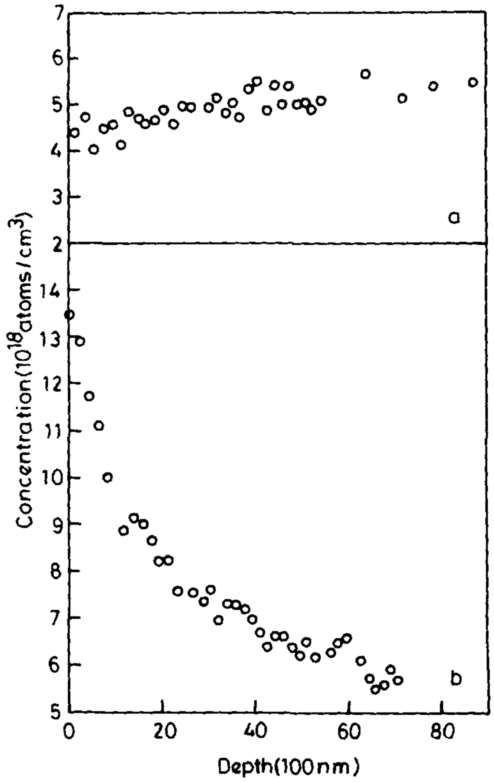

Figure 7. Depth profile for Pt-Re catalyst: (a) calcined, (b) reduced.

same as that of Pt-Re catalyst. Rhenium catalyst showed no activity. Both of the catalysts showed good stability at this hydrogen pressure. It is also clear from Figure 1b that there is a much more drastic fall in activity for Pt catalyst than that for Pt-Re catalyst in the absence of hydrogen (designated as "spent" catalyst). Included in Figure 1 is the performance of a typical Pt-Re commercial catalyst which compares with the prepared Pt-Re catalysts.

Proton Induced X-ray Emission

The results of PIXE analysis are shown in Figures 2 and 3. The X-ray lines have been identified and labeled. The absolute concentration of the elements can be calculated provided the proton energy, the X-ray production cross section, and the detector efficiency as a function of X-ray energy are known. A simpler and more accurate approach would be to calibrate the system for a fixed beam-target-detector geometry using standard thin targets and a given proton energy. A similar approach for thick targets may not always be feasible. But, as long as only the ratio of the elements in near-surface regions (a few microns) and its variation due to changes in experimental conditions is required, one can still use the overall efficiency factor for the thin targets in this case also.

Rutherford Backscattering Spectrometry

Figure 4 shows RBS spectra of the calcined and reduced Pt-Re catalyst. A striking feature is a sharp peak of Pt-Re in the reduced sample. It is, of course, not possible to distinguish Pt and Re separately because of the limitation on the proximity of their mass numbers. The catalyst when used in the test reaction without and with hydrogen again showed a similar behavior, i.e., identical to Figure 4a and b, respectively.

Figures 5 and 6 are the depth profiles of Pt and Re catalyst

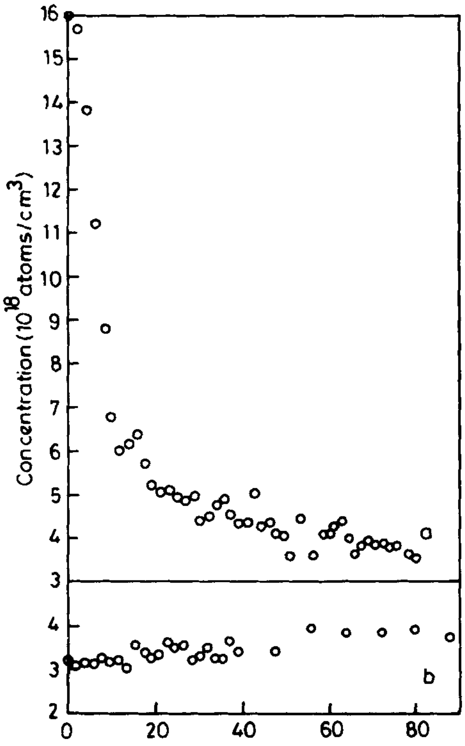

Figure 8. Depth profile for Pt-Re catalyst: (a) used, (b) spent.

respectively, calculated from their respective RBS plots. The procedure to calculate the depth profile from the corresponding RBS plot is given elsewhere (Jothimurugesan, 1984). Figure 7 is a depth profile for Pt-Re catalyst. In the case of reduced catalyst, the surface concentration of Pt (and/or Re) is approximately three times more than the calcined catalyst. This concentration then decreases gradually to the calcined level. The Pt-Re catalyst when used in the test reaction with hydrogen (Figure 8a) shows a profile similar to the reduced catalyst; without hydrogen (Figure 8b) it is identical to the calcined catalyst. These are discussed later.

Electron Microscopy

The effect of impregnation on the support is revealed by scanning electron microscopy. The SEM micrographs of support particle size loaded with Pt, Re, and Pt-Re are shown in Figures 9a, 10a, and 11a, respectively. The corresponding particle size distributions for alumina support particles are shown in Figures 9b–11b. It seems that the presence of Re results in severe fragmentation of the support particles. While in the case of pure

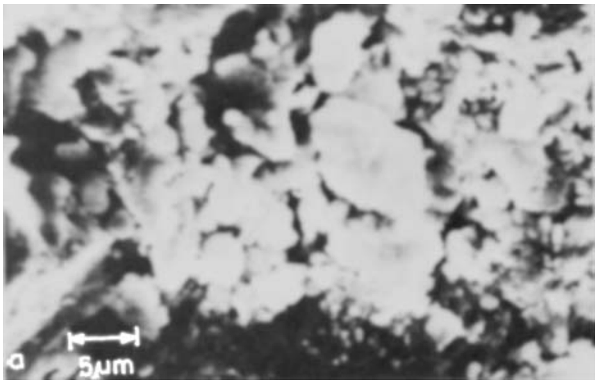

Figure 9a. SEM micrograph of support particles.

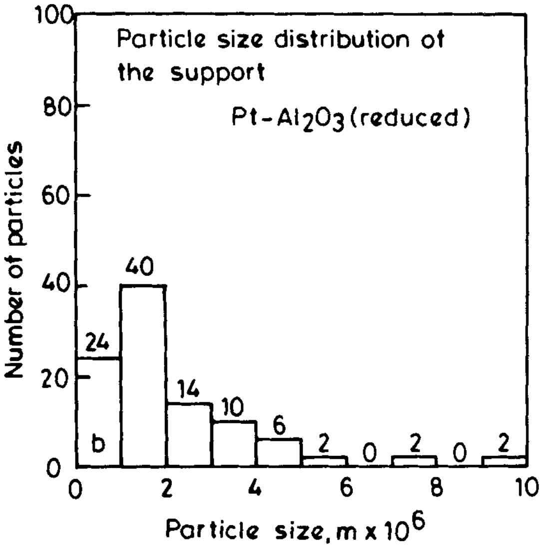

Figure 9b. Particle size distribution of the support (Pt catalyst, reduced.

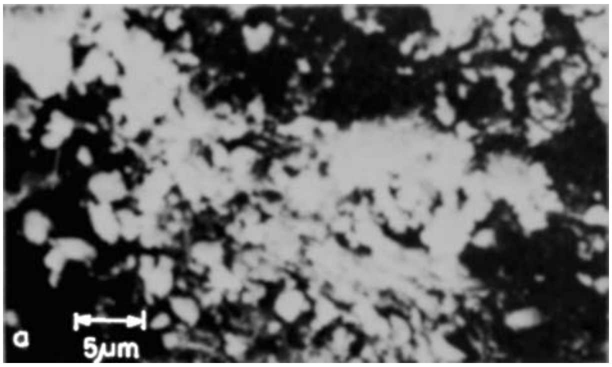

Figure 10. SEM micrograph of support particles.

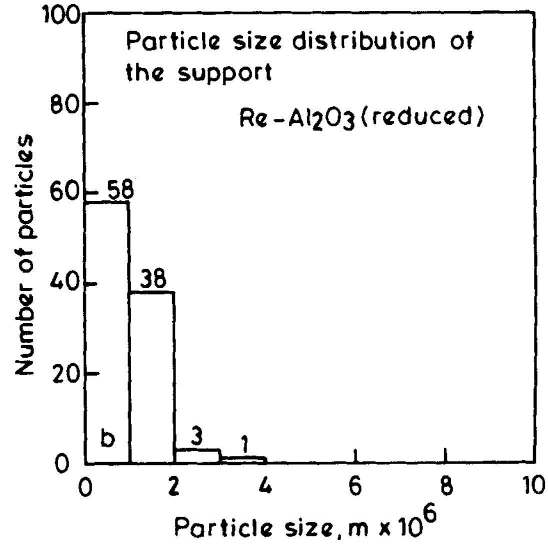

Figure 10b. Particle size distribution of the support (Re catalyst, reduced.

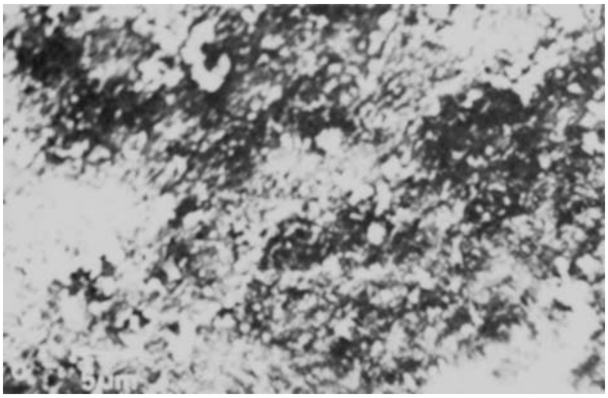

Figure 11a. SEM micrograph of support particles.

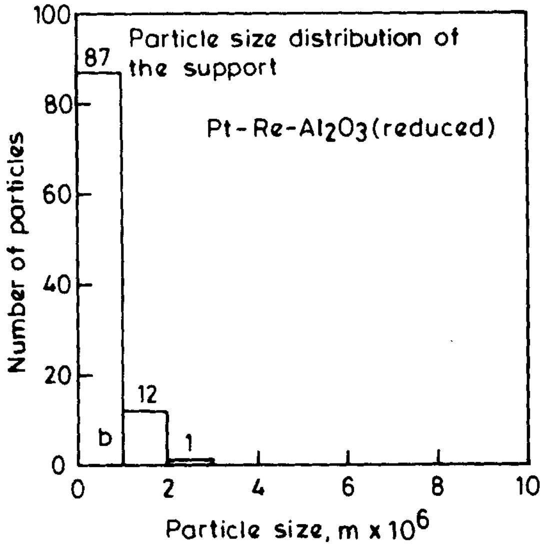

Figure 11b. Particle size distribution of the support (Pt-Re catalyst reduced).

platinum catalyst only about 60% of the total number of particles are below 2 μm, in the case of Re and Pt-Re catalyst more than 96% of the particles are below 2 μm.

Figure 12a shows the transmission electron micrograph of Pt-Al_2O_3 catalyst. The corresponding electron diffraction pattern shown in Figure 12b verified the presence of well-defined Pt particles. In the case of the Re catalyst, neither particle image contrast nor the diffraction lines are observed. Figure 13a shows the TEM of Pt-Re-Al_2O_3 reduced catalyst. Platinum particles are finely dispersed over the support. The electron diffraction from these particles is shown in Figure 13b. The pattern is indexed on the basis of a fluidic catalytic cracking (F.C.C.) structure (a = 0.3923 nm cubic system) which corresponds to platinum. Freed and Kelley (1980) also encountered a similar difficulty when examining Re by electron microscope.

Chemisorption Studies

Data on the chemisorption of oxygen at room temperature were obtained on the platinum, rhenium, and platinum-rhenium catalysts. Typical data on the chemisorption of oxygen on the Pt-Re-Al_2O_3 catalysts are shown in Figure 14. This figure also represents the chemisorption data on Pt-Al_2O_3 and Re-Al_2O_3 catalysts. The extrapolation of the quasilinear part of the oxygen adsorption isotherm to zero pressure gives a value for the amount of oxygen chemisorbed at room temperature. Isotherms A and B show the chemisorption measurements on Pt-Al_2O_3 and Re-Al_2O_3 catalysts, respectively. Two isotherms are shown for Pt-Re-Al_2O_3 catalyst. Isotherm C represents the total oxygen chemisorbed by Pt and Re in Pt-Re-Al_2O_3 catalyst, whereas isotherm D shows the chemisorption of oxygen by Pt in Pt-Re-Al_2O_3 catalyst. Oxygen chemisorption on Pt in a Pt-Re-Al_2O_3 catalyst was calculated from oxygen uptake of Pt-H after reduction of Pt-Re-Al_2O_3 catalyst under hydrogen at room temperature. Reduction of Re-O to Re-H at this room temperature is assumed to be negligible. The difference between oxygen uptake calculated from isotherms C and D is a measure of the amount of oxygen chemisorbed by Re only in Pt-Re-Al_2O_3 catalyst.

Table 1 summarizes the chemisorption data for Pt-Al_2O_3, Re-Al_2O_3, and Pt-Re-Al_2O_3 catalysts. Dispersion of Pt and Re catalysts was calculated from the stoichiometry of gas titration as given by Menon et al. (1973). Metal areas of Pt, Re, and Pt-Re catalysts were then calculated by assuming platinum and rheni-

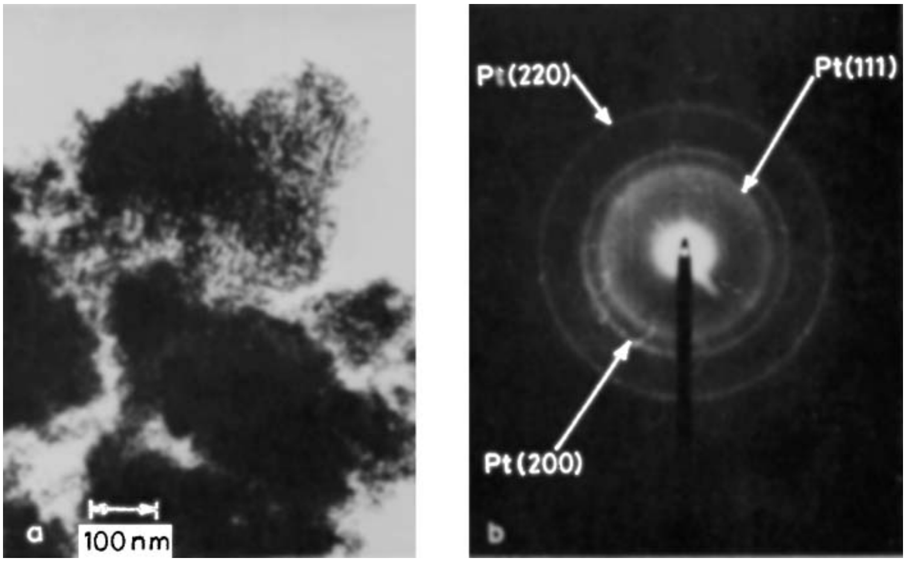

Figure 12. Electron micrograph and diffraction pattern of Pt catalyst (reduced).

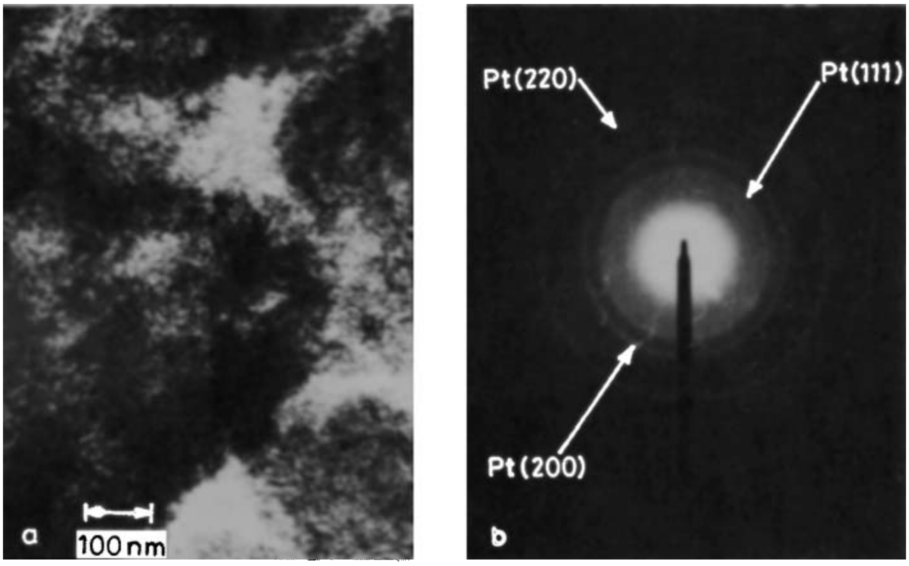

Figure 13. Electron micrograph and diffraction pattern of Pt-Re catalyst (reduced).

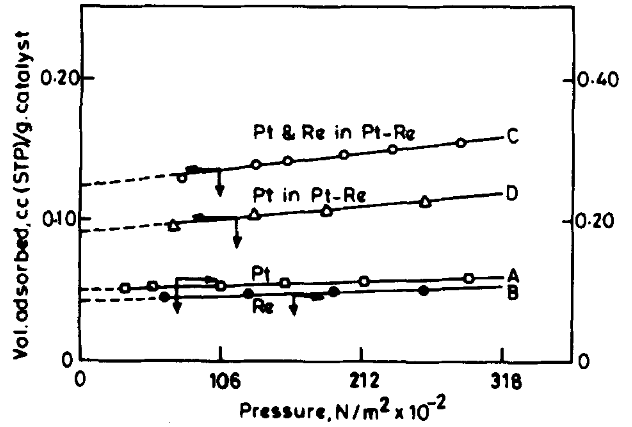

Figure 14. Typical isotherms at room temperature for chemisorption of oxygen on the alumina support Pt, Re, and Pt-Re catalysts. *A*,*B*: chemisorption of oxygen on Pt and Re catalysts, respectively. *C*,*D*: oxygen chemisorbed by Pt and Re, and Pt in Pt-Re catalyst.

um exposed as 12.6×10^{19} and 11.0×10^{19} atoms/m^2, respectively (Kubicka, 1968). Included in Table 1 are the dispersion values of various catalysts reported in the literature. The dispersion values obtained in the present study are comparable with the literature values.

DISCUSSION

The results of transmission electron microscopy studies can be classified in the following three categories:

(i) Pure platinum catalyst on alumina support revealed extremely dispersed particles (Figure 12) showing crystalline F.C.C. type diffraction patterns with a = 0.3923 nm.

(ii) Pure rhenium supported catalyst showed no structural details.

(iii) Pt-Re supported catalyst again exhibited dispersed particulate morphology (Figure 13) with a ring diffraction pattern that had the same crystal structure as pure platinum catalyst.

The observation (iii) that Pt-Re catalyst has a structure similar to pure Pt is expected because Re forms a substitutional solid with Pt, without altering the Pt structure. The solid solubility of Re in Pt up to 41% has been reported (Hansen and Anderko, 1958). However, the evidence that pure Re catalyst did not exhibit any diffraction ring supports the concept of alloy formation with reservation. Thus the following possibilities regarding catalyst configuration seem to exit.

1. Pt-Re are in an alloyed state.
2. Pt and Re disperse separately such that Re remains amorphous.
3. Pt-Re are only partially alloyed.

The question of why platinum is crystalline and Re is not can be explained on the basis of a lower diffusion activation energy of 307 kJ/mol for the former, compared to 520 kJ/mol for the latter.

Table 1. Summary of Chemisorption Data on Pt-Al_2O_3, Re-Al_2O_3, and Pt-Re-Al_2O_3 Catalysts

					% Dispersion (Lit. Value)	
Catalyst†	Calcination Temp. K*	Reduction Temp. K**	% Dispersion	Metal area of Cat., m^2/g	Bolivar et al. (1976)	Apesteguja & Barbier (1982)
0.3% Pt	723	773	39.1	0.29	46	—
0.3% Re	373‡	773	31.3	0.23	40	—
0.3% Pt, 0.3% Re	723	773	48.0	0.35	53	50

† γ = Alumina was the carrier in all the catalysts.
* Calcination conducted in air for a period of 5 h.
** Reductions conducted in flowing hydrogen for 2 h.
‡ Drying temperature.

This favors larger growth of particles by the mechanism of surface migration and coalescence of smaller aggregates of Pt.

The possibility that Pt and Re can distribute on the support differently was investigated using PIXE and RBS techniques. The former technique revealed striking behavior. In the case of calcined and spent Pt-Re catalysts, the distribtuions of these two elements up to a depth of few μm were identical, as shown in Figures 2a and 3b. However, in the case of used and reduced catalysts, Re concentration seemed to predominate over Pt as evidenced by Figures 3a and 2b. The rest of the Pt appeared to migrate deep inside the pores of the catalyst pellets. The platinum mobility on the alumina support has also been observed with electron microscope studies on Pt-Al_2O_3 catalyst by White et al. (1983).

A more revealing concentration depth profile is evident from RBS studies up to a depth of about 10 μm from the pellet surface. In the case of pure Pt as shown in Figure 5 for calcined, reduced, and spent catalyst, the concentration remains constant with depth. A similar plot for the pure Re catalyst is shown in Figure 6. The concentration increases linearly with increase in depth with a rate of about 1% (of its surface value) per μm up to 5 μm and then remains constant in all cases. Thus in the pure state Pt and Re distribute differently within the catalyst pellet. The Re preferentially distributes in increasing amount towards the inside of the support pellet; the Pt distributes equally.

The behavior of Pt-Re catalyst under different conditions is shown in Figures 7 and 8. The calcined catalyst (Figure 7a) behaves similarly to pure Re. However, after reduction (Figure 7b) excessive separation of components (Pt and Re) seems to occur. It appears that more than 50% Re is confined to the surface within 1 μm and concentration decreases rapidly with increase in depth. A similar situation exists for the used Pt-Re catalyst (Figure 8a) also. This behavior is just opposite to pure Re. However, when reduced Pt-Re catalyst is treated in a nitrogen atmosphere, i.e., spent catalyst, the redistribution of Re concentration takes place in an opposite sense (Figure 8b).

The above distinct behavior of changes in Re concentration with reference to Pt indicates the existence of strong chemical disproportionation induced by hydrogen. As a result Pt tends to migrate deep inside the pores, thus Re tends to segregate toward the surface. These interpretations are supported by PIXE results.

The presence of Re then seems to affect the catalyst functioning in at least the following two ways:

(i) Keeping the Pt concentration high towards the interior of catalyst pellets.

(ii) Inhibiting the bond-breaking of hydrocarbons. A third possibility of influencing the catalytic behavior of Pt as a result of change in work function may also be possible.

It seems that the presence of Re, alone or along with Pt, helps in fragmenting the support. As a result the support particle size decreases progressively from pure Pt to Pt-Re and Re catalyst. This is evident from SEM Figures 9–11 and the corresponding distribution curves. It seems that rhenic acid reduces the surface energy more drastically than chloroplatinic acid. As a result, the thermal stress (Tetelman and McEvily, 1967) during calcination reaches the critical fracture stress and fragments these alumina grains that possess sufficiently larger microcracks (Jothimurugesan, 1984).

The result of chemisorption studies on Pt, Re, and Pt-Re supported catalysts shows respective specific areas of 0.29, 0.23, and 0.35 m^2/g with corresponding respective dispersions of 39.1, 31.3, and 48.0%. The presence of Re seems to improve the dispersion of the bimetallic catalyst. It is interesting to note that the Pt-Re catalyst, which has a specific area of 0.35 m^2/g, consists of 0.26 m^2/g from Pt and 0.09 m^2/g from Re. But the sum of the specific surface areas of pure components (0.3% Pt or 0.3% Re) is almost 1.6 times higher than Pt-Re catalyst. Also in the Pt-Re catalyst, Re specific area has decreased (from 0.23 m^2/g) in pure Re (to 0.09 m^2/g) to one-third of its pure-state value. This indicates that almost two-thirds of the Re has possibly "alloyed" with Pt. This is also confirmed from the value of specific surface area contributed by Pt in Pt-Re catalyst (0.26 m^2/g), which is only about 10% smaller than pure catalyst. This small decrease may be attributed to shrinkage in Pt-Re particles due to Pt-Re bonding resulting from their electronegativity differences. This smaller proportion ($\simeq$34 wt. % Re) of Re can easily go into solid solution as expected. The presence of completely unalloyed Pt in small fraction is however not excluded.

Thus Pt-Re catalyst seems to exist in the form of a small fraction of pure Re and pure Pt particles along with Pt-Re "alloyed" particles. The Re may therefore keep the pure Pt and Pt-Re aggregates separated. The work functions of Pt (5.03 eV) and Re (4.95 eV) are quite close, thus their alloys in the composition range 65% Pt-35% Re will not differ significantly from the pure Pt, provided there is not large electronic transfer from Re to Pt. This implies that alloy catalyst will behave somewhat similar to pure Pt.

The increase in lifetime of bimetallic catalyst can now be rationalized in the context of our results. While the selective activation is provided by free Pt and Pt-Re aggregates, the free Re on the surface improves the resistance to poisoning by coke. This is quite understandable, since Re does not form strong bonds with MCH, thereby reducing the chance of adsorbed molecules forming multiple bonds at the surface. A multiple-bond configuration is essentially irreversible, and therefore of no catalytic value. Polymerization of the adsorbed species, which is required for carbonaceous deposits, probably can still occur at exposed Pt metal sites. However, since these sites are isolated and mostly surrounded by Re metal sites, the removal of the carbonaceous deposit by rehydrogenation can be accelerated. A similar explanation for the function of gold has been given by Sachtler et al. (1981), where the catalytic effects of dosing gold onto single crystals of platinum were investigated.

Platinum is unique in its formation of stable, strongly bound polymeric residues because of its very low activity as a hydrogenolysis catalyst (Davis and Somorjai, 1981; Davis et al., 1982). On the contrary, Pt is a better dealkylation catalyst than Re (Jossens and Petersen, 1982). For the dehydrogenation of MCH, dealkylation of toluene is the significant secondary reaction and may occur on the metallic sites of the bifunctional catalysts. However, due to the low dealkylation activity of Re, the presence of Re in Pt-Re catalyst will certainly be less active for dealkylation reaction, despite the fact that Pt and Pt-Re catalysts have the same dehydrogenation activity. Also, because Re is very active for hydrogenolysis, it appears likely that continuous hydrogenolysis may slow down the formation of polymeric carbonaceous deposits.

ACKNOWLEDGMENT

The authors wish to thank D. L. Cresswell, ICI Ltd. (New Science Group), and A. V. Ramaswamy and L. D. Sharma, Indian Institute of Petroleum, Dehradun, for invaluable discussions.

NOTATION

a = unit cell parameter, nm
F = molar feed rate, mol/h
T = temperature, K
W = weight of the catalyst, g

LITERATURE CITED

Ahlberg, M., G. Johansson, and K. Malmquist, "Elimination of Charging in the Proton-Induced X-Ray Emission in Analysis of Insulating Targets," *Nucl. Instr. Meth.*, 131, 377 (1975).

Apesteguia, C. R., and J. Barbier, "The Role of Catalyst Presulfurization in Some Reactions of Catalytic Reforming and Hydrogenolysis," *J. Cat.*, **78**, 352 (1982).

Barbier, J., et al., "Determination of Metallic Surface Areas of Platinum-Rhenium Catalysts," *Appl. Cat.*, **1**, 71 (1981).

Bertolacini, R. J., and R. J. Pellet, "The Function of Rhenium in Bimetallic Reforming Catalysts," *Catalyst Deactivation*, B. Delmon and G. F. Froment, Eds., Elsevier, Amsterdam, 73 (1980).

Betizeau, C., et al., "Platinum-Rhenium-Alumina Catalysts. Variation of Physico-Chemical and Catalytic Properties with the Method of Preparation," *Prep. Cat., Proc. Int. Symp.*, 525 (1976a).

———, "Platinum-Rhenium-Alumina Catalysts. III: Catalytic Properties," *J. Cat.*, **45**, 179 (1976b).

Biloen, P., et al., "The Role of Rhenium and Sulfur in Platinum-Based Hydrocarbon-Conversion Catalysts," *J. Cat.*, **63**, 112 (1980).

Blyholder, G., in *Experimental Methods in Catalytic Research*, R. B. Anderson, Ed., Academic Press, New York (1968).

Bolivar, C., et al., Reduction by Hydrogen," *J. Cat.*, **39**, 249 (1975).

———, "Platinum-Rhenium-Alumina Catalysts. II: Study of the Metallic Phase after Reduction," *J. Cat.*, **45**, 163 (1976).

Cairns, J. A., "The Application of Ions Beams to Catalyst Research," *Characterization of Catalysts*, J. M. Thomas, and R. M. Lambert, Eds., Wiley & Sons, Chichester, U.K. (1980).

Cairns, J. A., et al., "Strong Metal-Support Interactions for Pt and Rh on Al_2O_3 and TiO_2: Application of Nuclear Backscattering Spectrometry," *J. Cat.*, **83**, 301 (1983).

———, in *Ion Beam Surface Layer Analysis*, M. Meyer, G. Linker, and F. Kappeler, Eds., **2**, 773 (1975).

———, "Determination of the Near-Surface Elemental Composition of Catalysts by the Technique of Proton-Induced X-Ray Analysis," *J. Cat.*, **45**, 6 (1976).

Carter, J. L., et al., "Bimetallic Catalysts; Application in Catalytic Reforming," *Appl. Cat.*, **3**, 327 (1982).

Charcosset, H., et al., "The State of Rhenium in Platinum-Rhenium Aluminum Oxide Catalysts," *J. Cat.*, **56**, 468 (1979).

Chu, W. K., J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry*, Academic Press, New York (1978).

Ciapetta, F. G., and D. N. Wallace, "Catalytic Naphtha Reforming," *Cat. Rev.*, **5**, 67 (1971).

Cimino, A., et al., "Photoelectron Spectroscopy (XPS) and Thermogravimetry (TG) of Pure and Supported Rhenium Oxides. 1: Pure Rhenium Compounds," *Z. Anorg. Allg. Chem.*, **460**, 86 (1980).

Cresswell, D. L., et al., "The Catalytic Production of Hydrogen for Use in Road Vehicles," *Frontiers in Chemical Reaction Engineering*, (L. K. Doraiswamy and R. A. Mashelkar, Eds., Wiley Eastern, Delhi (1984).

Davis, S. M., and G. A. Somorjai, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Elsevier, Amsterdam, **4** (1981), and references cited therein.

Davis, S. M., F. Zaera, and G. A. Somorjai, "The Reactivity and Composition of Strongly Adsorbed Carbonaceous Deposits on Platinum. Model for the Working Hydrocarbon Conversion Catalyst," *J. Cat.*, **77**, 439 (1982).

Dumesic, J. A., and H. Topsoe, "Mossbauer Spectroscopy Applications to Heterogeneous Catalysis," *Adv. in Cat.*, **26**, 122 (1977).

Eischens, R. P., and W. A. Pliskin, "The Infrared Spectra of Adsorbed Molecules," *Adv. in Cat.*, **10**, 1 (1958).

Force, E. L., and A. T. Bell, "Infrared Spectra of Adsorbed Species Present During the Oxidation of Ethylene over Silver," *J. Cat.*, **38**, 440 (1975a).

———, "The Relationship of Adsorbed Species Observed by Infrared Spectroscopy to the Mechanism of Ethylene Oxidation Over Silver," *J. Cat.*, **40**, 356 (1975b).

Freed, R. L., and M. J. Kelley, "Elemental Distribution in Platinum-Rhenium-Alumina Naphtha Reforming Catalysts" *Proc. 38th Ann. Meet., Elect. Microsc. Soc. Am.*, 200 (1980).

Freel, J., "Chemisorption on Platinum-Rhenium-Alumina", Preprint, Div. Pet. Chem., Am. Chem. Soc., **18**, 10 (1973).

Hansen, P. M., and R. N. K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958).

Isaacs, B. H., and E. E. Petersen, "The Effect of Drying Temperature on the Temperature-Programmed Reduction Profile of a Platinum-Rhenium-Alumina Catalyst," *J. Cat.*, **77**, 43 (1982).

Jacobson, R. L., et al., "Platinum-Rhenium Catalysts: Major New Catalytic Reforming Development," API, Proc. Div. Refining., **49**, 504 (1969).

Jain, A. K., et al., "Study of Inter-Diffusion in Cu-Al Thin Films by High Resolution Rutherford Backscattering," *Bull. Am. Phys. Soc.*, **27**, 772 (1982).

Johnson, M. F. L., "The State of Rhenium in Pt/Re/Alumina Catalyst," *J. Cat.*, **39**, 487 (1975).

Johnson, M. F. L., and V. M. LeRoy, "The State of Rhenium in Pt/Re/Alumina Catalysts," *J. Cat.*, **35**, 434 (1974).

Jossens, L. W., and E. E. Petersen, "Fouling of a Platinum-Rhenium Reforming Catalyst Using Model Reforming Reactions," *J. Cat.*, **76**, 265 (1982).

Jothimurugesan, K., "Platinum-Rhenium-Alumina Reforming Catalysis—an Integrated Study," Ph.D. Thesis, Indian Inst. of Tech., Kanpur (1984).

Kelley, M. J., R. L., Freed, and D. G. Swartzfager, "Distribution of Pt and Re in Pt-Re:Al_2O_3 Naphtha Reforming Catalyst," *J. Cat.*, **78**, 445 (1982).

Kluksdahl, H. E., "Reforming a Sulfur-free Naphtha with a Platinum Rhenium Catalyst," U.S. Patent 3,415,737 (Dec. 10, 1968).

Kubicka, H., "Specific Activity of Technetium, Rhenium, and Ruthenium, Platinum, and Palladium in Catalytic Reactions of Benzene with Hydrogen", *J. Cat.*, **12**, 223 (1968).

Ludlum, K. H., and R. P. Eischens, "Infrared Study of the Effect of Rhenium for Carbon Deposition on Platinum/Alumina", Preprint., Div. Pet. Chem., Am. chem. Soc., **21**, 375 (1976).

Lunsford, J. H., "Electron Spin Resonance in Catalysis," *Adv. in Cat.*, **22**, 265 (1972).

McNicol, B. D., "The Reducibility of Rhenium in Re on γ-Alumina and Pt-Re on γ-Alumina Catalysts," *J. Cat.*, **46**, 438 (1977).

Menon, P. G., et al., "Separate Determination of Pt and Re in Pt-Re-Al_2O_3 Reforming Catalyst," *J. Cat.*, **29**, 188 (1973).

Peri, J. b., "Infrared studies of Pt and Pt-Re Reforming Catalysts," *J. Cat.*, **52**, 144 (1978).

Sachtler, J. E. A., J. P. Biberian, and G. A. Somorjai, "The Reactivity of Ordered Metal Layers on Single Crystal Surfaces of Other Metals: Gold on Platinum (100) and Platinum on Gold (100)," *Surf. Sci.*, **110**, 43 (1981).

Sharma, R. K., and R. D. Srivastava, "Kinetics of Selective Oxidation of Toluene and Methanol Over Supported V_2O_5-Alkalimetal Sulfates", *AIChE J.*, **27**, 41 (1981).

———, "V_2O_5-K_2SO_4-Silica System: Correlation with Toluene Oxidation Activity," *J. Cat.*, **65**, 481 (1980).

Sharma, R. K., K. N. Rai, and R. D. Srivastava, "V_2O_5-K_2SO_4-Silica System: The Structure and Activity of Silica-Supported V_2O_5-K_2SO_4 Catalysts," *J. Cat.*, **63**, 271 (1980).

Shiflett, W. K., and J. A. Dumesic, "The Use of Ammonia Synthesis as a Probe Reaction for the Study of Supported Re and Re-Pt", *J. Cat.*, **77**, 57 (1982).

Short, D. R., et al., "X-ray Absorption Spectroscopy of Pt-Re/Al_2O_3 Catalysts," *J. Cat.*, **72**, 288 (1981).

Sinfelt, J. H., "Bifunctional Catalysis", *Adv. in Chem. Eng.*, **5**, 37 (1964).

Sinfelt, J. H., "Catalytic Reforming of Hydrocarbons", *Catalysis*, J. R. Anderson and M. Boudart, Eds., Springer-Verlag, New York (1981).

Srivastava, R. D., A. B. Stiles, and G. A. Jones, "Kinetic Measurements and XRD Investigations *in situ* of a V_2O_5-SiO_2 Catalyst for the Vapor-Phase Oxidation of Tetrahydrofuran to γ-Butyrolactone," *J. Cat.*, **77**, 192 (1982).

Tetelman, A. S., and A. J. McEvily, Jr., *Fracture of Structural Materials*, Wiley, New York (1967).

Varier, K. M., G. K. Mehta, and S. Sen, "Proton-Induced X-ray Emission—A Powerful Tool for Trace Element Analysis," *Phys. News.*, **11**, 1 (1980).

Wagstaff, N., and R. Prins, "Alloy Formation and Metal Oxide Segregation in Platinum-Rhenium/γ-Aluminum Oxide Catalysts as Investigated by Temperature-Programmed Reduction," *J. Cat.*, **59**, 434 (1979).

Webb, A. N., "Reducibility of Supported Rhenium," *J. Cat.*, **34**, 485 (1975).

White, D., et al., "Electron Microscope Studies of Platinum/Alumina Reforming Catalysts," *J. Cat.*, **81**, 119 (1983).

Yao, H. C., and M. Shelef, "Surface Interactions in the System Re/γ-Al_2O_3," *J. Cat.*, **44**, 392 (1976).

Ziegler, J. F., Ed., *New Uses of Ion Accelerators*, Plenum, New York (1975).

Manuscript received Feb. 29, 1984, and revision received Feb. 12, 1985.