JOURNAL OF CATALYSIS **136**, 423–431 (1992)

Reactions of Propane on Modified Metal Oxides

ZHENTAO FENG, LUJIA LIU,[1] AND RAYFORD G. ANTHONY[2]

Department of Chemical Engineering, Kinetics, Catalysis and Reaction Engineering Laboratory,
Texas A&M University, College Station, Texas 77843

Received July 8, 1991; revised March 23, 1992

Transformation of propane over Mo-, Ni-, Pd-, and Zr-incorporated silica titania and zirconia was studied. The reaction of propane on these catalysts was significantly different from that on ZSM-5. Dehydrogenation was the main reaction of propane on metal-incorporated silica titania and zirconia catalysts. Comparison of the performance of different dispersed metals showed that Pd-exchanged catalysts had the highest activity. Relations between catalyst acidity and reaction mechanisms were also studied. © 1992 Academic Press, Inc.

INTRODUCTION

There are strong economical incentives today to develop catalysts for the selective conversion of light alkanes, especially propane. There are several routes to transform light alkanes to higher value hydrocarbons:

$$\text{light alkanes} \rightarrow \begin{cases} \text{gasoline} & (1) \\ \text{aromatics} & (2) \\ \text{alkenes.} & (3) \end{cases}$$

One of the examples of the first route is alkylation reaction, which is currently focused on zeolites (*1, 2*). But alkylation of hydrocarbons of less than four carbons is unfavorable. The second route is to convert propane and other saturated light hydrocarbons to aromatics. There has been much work in this field, and many promising catalysts have been developed, mostly ZSM-5 series (*3–5*). In fact, ZSM-5 has been used in pilot plant scale production of aromatics from propane and butane (*6*).

However, compared to the first and second route, the third route, dehydrogenation of propane to propylene, has received little interest, possibly because of the thermodynamic barrier. The most common dehydrogenation catalysts, different types of chromia–alumina, are not effective enough to make the process economical at 600°C (*7*). Presently, propylene is produced from thermal cracking or catalytic cracking of other petroleum fractions. Searching for potential catalysts for dehydrogenation of propane to propylene is economically attractive, especially considering the relatively important use of propylene in industry as the raw material in the mass production of polypropylene, acetone, isopropylbenzene, isopropyl halides, etc., as compared to the limited use of propane as a fuel.

One of the materials that drew wide attention in catalysis research in the past decade is hydrous metal oxides. Hydrous metal oxides were first used for waste water treatment and direct coal liquefaction (*8*). Other applications include the selective catalytic reduction of NO with NH_4 (*9*). These investigations identified several properties of hydrous metal oxides, including high surface area, large ion exchange capacity, dual ion exchange properties for cation and anion, and strong thermal stability (*8, 10*). These properties make hydrous metal oxides promising materials as catalyst supports.

In this study, hydrous metal oxides were

---

[1] Present address: Department of Chemical Engineering, Daqing Petroleum Institute, Daqing, China.

[2] To whom the correspondence should be addressed.

0021-9517/92 $5.00

employed as support materials to synthesize catalysts for dehydrogenation of propane to propylene.

EXPERIMENTAL

CATALYST PREPARATION AND ANALYSIS

1. HZSM-5

In order to compare the reaction of propane on metal oxide supported catalysts with that on zeolites, a batch of HZSM-5 was prepared by slurring NaZSM-5 in 1 *M* NH_4Cl solution. Four washes were sufficient to change NaZSM-5 to NH_4ZSM-5. Calcine NH_4ZSM-5 in air at 540°C and obtain HZSM-5.

2. Hydrous Metal Oxides

Preparation of the two hydrous metal oxides, hydrous silicon titanium oxide and hydrous zirconium oxide, followed the procedure in the patent by Dosch *et al.* (*11*):

Hydrous silicon titanium oxide. Tetraisopropyl orthotitanate was mixed with tetraorthoethyl silicate to get a clear solution. Then slowly add the alkoxide mixture into a 10 wt% methanol solution of sodium hydroxide to get a very thick soluble intermediate. The intermediate was rapidly added to a solution of 1 : 10 water and acetone. The slurry was continuously stirred until it was homogenized, then filtered and rinsed with acetone. The precipitate was collected and dried in a vacuum oven at 80°C overnight. This procedure was used to prepare the hydrous silicon titanium oxide with a ratio of sodium, titanium and silicon of 0.3 : 0.8 : 0.2.

Hydrous zirconium oxide. Preparation of hydrous zirconium oxide followed a similar procedure as that of hydrous silica titanium oxide except tetraisopropyl orthotitanate and tetraorthoethyl silicate were replaced with zirconium isopropoxide, and sodium hydroxide with potassium hydroxide. The ratio of potassium to zirconium was 0.5 : 1.

The yield of hydrous metal oxide was 20 to 30 g for each batch. Surface areas and pore size distributions of these materials were determined by a Micromeritic Digisorb 2600 surface area and pore size analyzer. The diameters of the pores are in the range of 38 to 100 Å with surface areas of 390 m^2/g and 260 m^2/g for hydrous silicon titanium oxide and hydrous zirconium oxide, respectively. X-ray diffractions of hydrous metal oxides showed amorphous structures. Hydrous metal oxides as prepared contained 30 to 35 wt% volatiles.

3. Incorporation of Metals

Active metals, Mo, Ni, Pd and Zr, were incorporated via ion exchange. Before loading the metals, hydrous metal oxides were changed to their proton forms by 0.1 *M* sulfuric acid treatment at pH = 3. Two washes with filtering and rinsing with acetone between each batch were usually necessary. The first batch removed about 89% of the alkali metal and the second about 99%. Then ion exchange the hydrogen form of hydrous metal oxides with 0.1 *M* $(NH_4)Mo_7O_{24} \cdot 4H_2O$ at pH = 3, 0.1 *M* $NiNO_3 \cdot 6H_2O$ at pH = 6, or 0.1 *M* $ZrOCl_2 \cdot 8H_2O$ at pH = 3 to load Mo, Ni, or Zr on the materials. Pd was incorporated by ion exchanging hydrous metal oxides with $PdCl_2$ solution. The pH of the final slurry was about 10. Then acidify the resulting material with sulfuric acid to a pH of 3.5 to 4. During the ion exchange process, sulfuric acid and ammonium hydroxide were used to adjust pH. Usually, it took 2 h for each ion exchange.

The catalysts after ion exchange were calcined in air at 300°C after the incorporation of metals. Then they were acidified with sulfuric acid to a pH of 3 followed by filtering and rinsing. Finally, the catalysts were calcined in air at 540°C in a muffle furnace. During calcination, the catalysts were converted to their oxidized forms, except for palladium, which was in the elemental metallic state. For convenience, the catalysts were referred to as (Mo, Zr)/$Si_{0.2}Ti_{0.8}O_2$ (molybdenum oxide and zirconium oxide on silica titania, 14.3% Mo and 13.6% Zr), (Pd)/$Si_{0.2}Ti_{0.8}O_2$ (palladium on silica titania, 0.659% Pd), (Mo)/ZrO_2 (molybdenum oxide

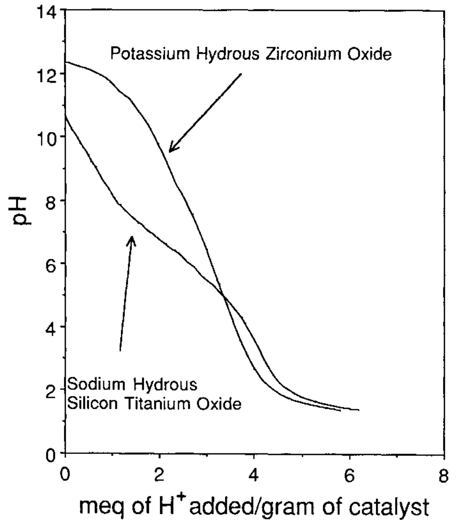

FIG. 1. Titration of hydrous metal oxides with HCl.

on zirconia, 16.2% Mo), (Ni)/ZrO_2 (nickel oxide on zirconia, 1.41% Ni), (Pd)/ZrO_2 (palladium on zirconia, 0.523% Pd). The compositions were based on dry weight.

4. *Acidity of Catalysts*

Characterization of catalysts with NaOH titration and temperature programmed desorption (TPD) of ammonia showed weak acidity of the catalysts. Figure 1 is the titration curves of the starting materials—sodium hydrous silicon titanium oxide and potassium hydrous zirconium oxide. During the experiment, 0.5 *N* HCl was titrated into the slurry of sodium hydrous silicon titanium oxide or potassium hydrous zirconium oxide. The change of pH in the slurry was monitored and plotted versus the amount (milli-equivalent) of acid added. Each data point was taken with a 10-min interval to ensure chemical equilibrium. From the titration curves, it can be concluded that sodium hydrous silicon titanium oxide has two basic sites (indicated by the two inflection points in the curve), while potassium hydrous zirconium oxide has only one basic site. After the acid treatment, both hydrous metal oxides were changed to their proton forms, and back titration with 0.5 *N* NaOH (Fig. 2) showed that hydrogen form of hydrous silicon titanium oxide has two weak acid sites, while hydrous zirconium oxide has only one. The ion exchange capacity was estimated to be 4.4 to 4.8 meq/gram, which is in the same range as reported by Dosch *et al.* (*10*). Titration experiments show that while both materials are weak acids, hydrous zirconium oxide has stronger acidity than hydrous silicon titanium oxide.

Temperature programmed desorption of ammonia also demonstrated the weak acidity of hydrous metal oxides. Figure 3 presents the results of ammonia TPD for the HZSM-5, (Pd)/ZrO_2 and (Pd)/$Si_{0.2}Ti_{0.8}O_2$. Based on the amount of ammonia desorbed from the catalysts, acidity was in the order of HZSM-5 $\gg$ (Pd)/ZrO_2 > (Pd)/$Si_{0.2}Ti_{0.8}O_2$.

APPARATUS AND PROCEDURE

The activity of the catalysts was studied in a microreactor system. The 1-in. i.d. reactor was made of Pyrex. The products were analyzed by an on-line HP 5830A and an off-line Carle 196 gas chromatographs, with flame ionization and thermal conductivity detectors, respectively. The reactions were carried out under atmospheric pressure and 600°C. Two grams of catalyst were charged

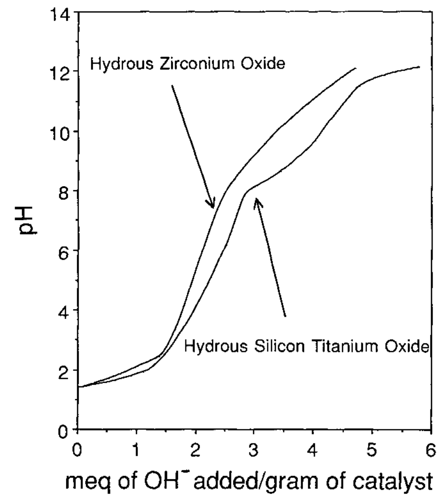

FIG. 2. Back titration of proton form of hydrous metal oxides with NaOH.

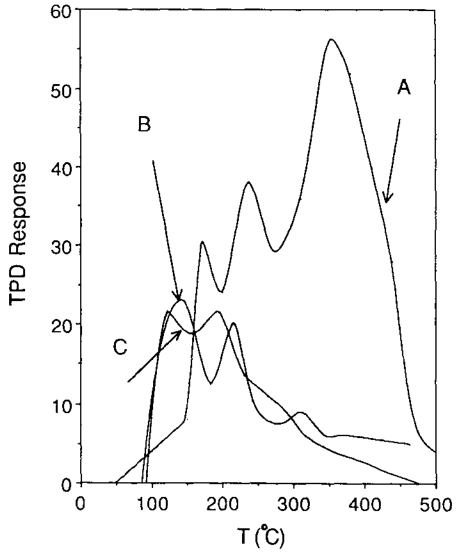

FIG. 3. Temperature programmed desorption of ammonia, 50 to 500°C at 10°C/min: (A) HZSM-5, (B) (Pd)/ZrO_2, and (C) (Pd)/$Si_{0.2}Ti_{0.8}O_2$.

to the reactor. During reaction, propane was mixed with nitrogen, and the flowrates of gases were controlled by mass flow meters to give a feed stream of 20 mole% propane and 80% nitrogen. Propane weight hour space velocity was 1.8 h^{-1}. The reactant was continuously fed into the reactor system. The experimental procedure has been described in greater detail by Feng (*12*).

The conversion and selectivity were calculated on the carbon mole basis, if not described otherwise, as follows:

Conversion was the moles of propane reacted per mole of propane fed. Selectivity was defined as the total moles of carbon in a product over the total moles of carbon reacted. Yield was defined as total moles of carbon in a product over moles of propane fed. Propane weight hour space velocity was defined as grams of propane fed per hour per gram of catalyst.

RESULTS AND DISCUSSION

PROPANE REACTION ON HZSM-5

Figure 4 is the plot of percentages of product selectivity versus conversion of propane. Propane conversion is larger than 80%, and the main products are aromatics (about 55% benzene, 35% toluene, and 10% A_9 and A_{10}) and methane. Only a very small amount of propylene was produced, leading to a conclusion that propylene undergoes further reactions on HZSM-5. The performance of HZSM-5 coincided with that reported in the literature (*3, 4*).

Similar work on metal modified ZSM-5 (*3, 4, 6*) showed a similar reaction pattern, with propane undergoing a series of reactions, such as cracking and aromatization, to produce mainly C_1, C_2, and aromatic hydrocarbons. As in the case of HZSM-5, the yield of propylene in the product was very low.

PROPANE REACTION ON ZIRCONIA AND SILICA TITANIA

Propane conversion and propylene selectivity were plotted as a function of propane WHSV in Fig. 5. To minimize the effect of deactivation, all the data points were taken at the time on stream of 5 min. At high WHSV, or short contact time, conversion of propane decreased while selectivity to propylene increased.

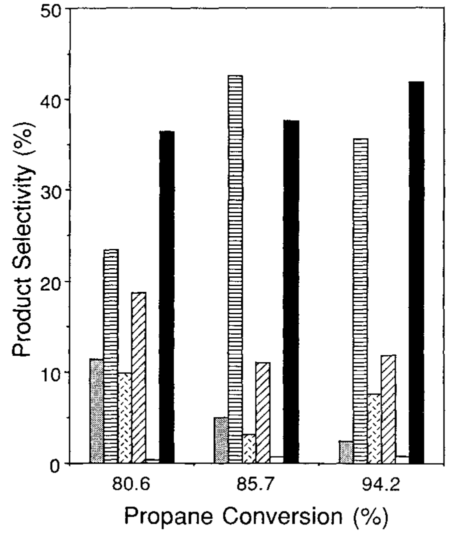

FIG. 4. Propane reaction on HZSM-5. Propane WHSV = 1.8 h^{-1}: ▦, propylene; ▤, methane; ▧, ethylene; ▨, ethane; ☐, C4–C6 aliphatics; ■, aromatics.

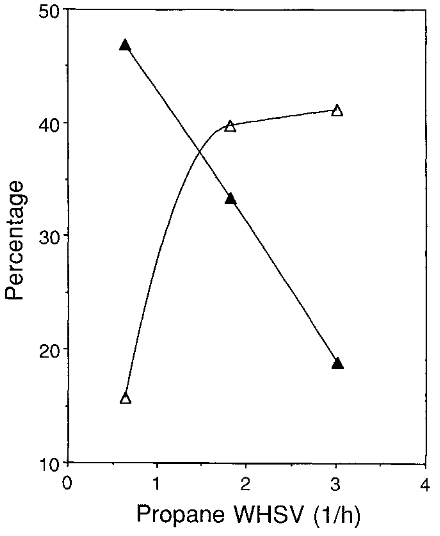

FIG. 5. Effects of propane WHSV on propane conversion and propylene selectivity for Mo/ZrO_2: ▲, propane conversion; △, propylene selectivity.

Figures 6a–e show the activity tests on $(Pd)/Si_{0.2}Ti_{0.8}O_2$, $(Mo, Zr)/Si_{0.2}Ti_{0.8}O_2$, $(Pd)/ZrO_2$, $(Mo)/ZrO_2$, $(Ni)/ZrO_2$, respectively. The selectivities to hydrocarbon products were plotted with propane conversion. Under the reaction conditions, propylene was the largest portion of the products and hence dehydrogenation was the main reaction. Selectivity to propylene exceeds 55% on most catalysts. The rest of the product consists of methane, ethane, ethylene, and small amounts of aromatics (mostly benzene) and C_4 to C_6 aliphatics. Selectivity to methane, ethane or ethylene is 5 to 15 mole%. The figures also shows that propane conversion on zirconia-type catalysts is usually higher than that on silica titania catalysts. For example, initial conversion of propane on $(Pd)/ZrO_2$ exceeds 45%, while on $(Pd)/Si_{0.2}Ti_{0.8}O_2$, the propane conversion is below 20%. The activities of catalysts are compared in Table 1.

The fact of high selectivity to propylene on the catalysts in this work can be seen by the comparison with commercial catalysts, predominantly various types of chromia-alumina. Reaction temperature usually falls in the range of 570 to 650°C to achieve significant levels of conversion. The yields of propylene on $(Pd)/ZrO_2$ and $(Mo)/ZrO_2$ in this study are comparable to the 18 to 25% reported for commercial alumina or chromia alumina at 575°C (*13, 14*) and 18 to 20% for platinum promoted alumina at 580°C (*14*). However, the relatively low conversion of propane and consequently low yield of propylene for the silica titania catalysts in this work are apparent.

Figure 7 is a comparison of the catalytic activity of different dispersed metals. Conversion of propane is plotted versus time on stream. The figure shows that palladium is the most active metal in this study in that conversion of propane on palladium catalyst retains higher value than either molybdenum or nickel catalyst. The activity is in the order of Pd > Mo > Ni.

Deposition of coke on the catalyst deactivated the catalyst. Activity could be recovered by regenerating the catalyst in 1% oxygen in nitrogen at 450°C. Sintering of the catalysts was observed from the decrease of surface area and pore volume. As an example, $(Pd)/ZrO_2$ has a surface area of 120 m^2/g and pore volume of 0.40 cc/g before the activity test, whereas after the reaction at 600°C for 12 h the surface area and pore volume decreased to 90 m^2/g and 0.33 cc/g, respectively. The permanent loss of activity after 20 deactivation–regeneration cycles was 8 to 13% depending on the catalysts.

CATALYST STRUCTURE AFTER REACTION

High temperature treatment (600°C reaction temperature) of zirconia and silica titania catalysts in this work increased the crystallinity. Figure 8 shows the X-ray diffraction patterns of the catalysts after reactions. Because of the differences in relative intensity, and in order to obtain a clear picture for those with low intensity, the highest peaks of $(Ni)/ZrO_2$ and $(Mo)/ZrO_2$ are shown about half the height. The catalysts prepared from hydrous silicon titanium oxide had the structure of anatase titania after reactions, while those for hydrous zir-

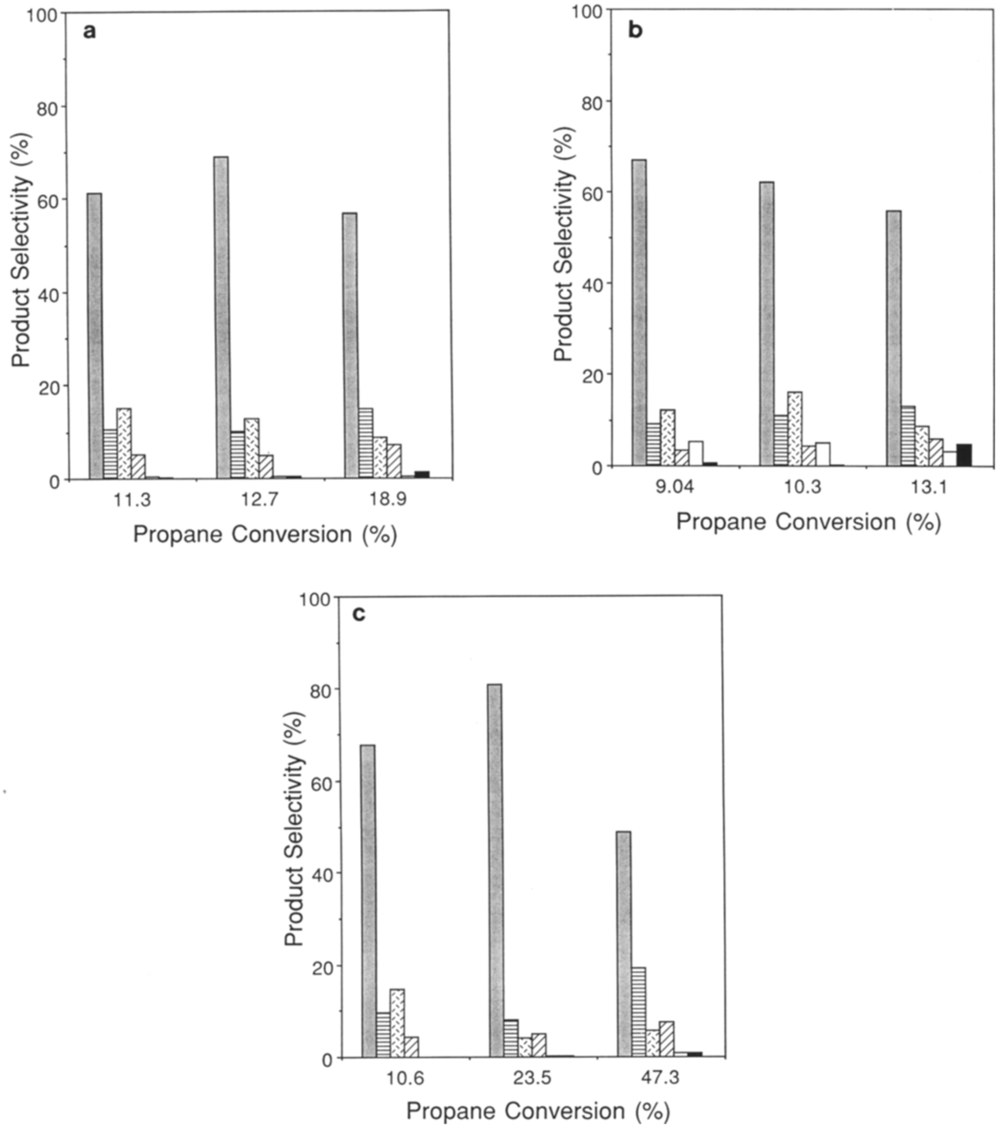

FIG. 6. Reactions of propane on metal modified zirconia and silica titania. Propane WHSV = 1.8 h^{-1}: ▒, propylene; ▤, methane; ▦, ethylene; ▨, ethane; □, C4–C6 aliphatics; ■, aromatics. (a) Product distribution on (Pd)/$Si_{0.2}Ti_{0.8}O_2$; (b) product distribution on (Mo, Zr)/$Si_{0.2}Ti_{0.8}O_2$; (c) product distribution on (Pd)/ZrO_2; (d) product distribution on (Mo)/ZrO_2; (e) product distribution on (Ni)/ZrO_2.

conium oxide were the cubic or tetragonal phases.

THERMODYNAMIC ANALYSIS

Dehydrogenation of propane is carried out at high temperature in order to overcome the thermodynamic barrier. The equilibrium constants of propane dehydrogenation are 0.0323, 0.326 and 2.04 at 500, 600, 700°C, respectively. Therefore, the reaction conditions have to be severe enough to achieve a significant level of conversion. The equilibrium conversion to propylene from propane is 49% at a tem-

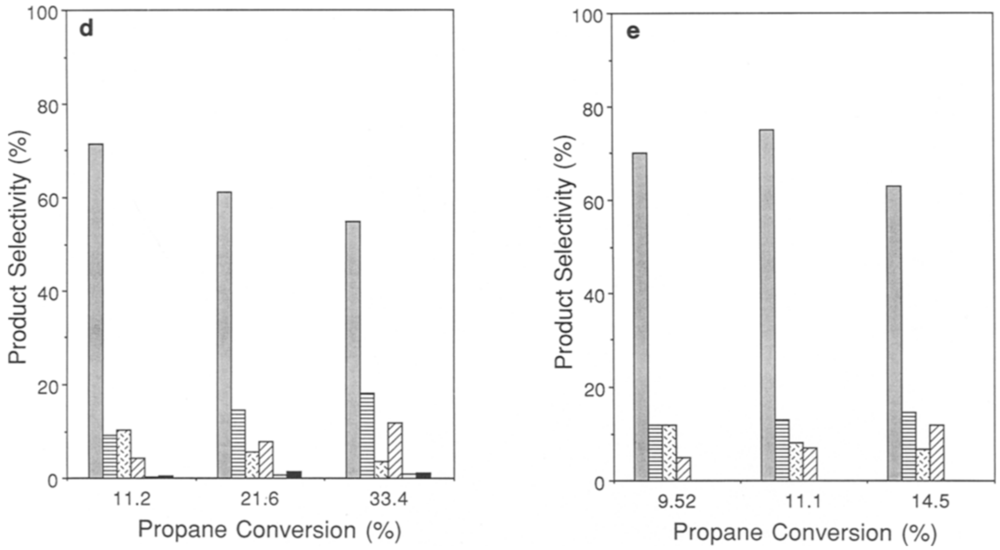

FIG. 6—*Continued*

perature of 600°C. However, thermodynamically, the formations of some other hydrocarbons such as methane and aromatics are far more favorable than the dehydrogenation to propylene. The followings are several routes of propane transformation and their Gibbs free energies at 600°C:

$C_3H_8 \rightarrow C_3H_6 + H_2$ 1.94 kcal/mole

$C_3H_8 \rightarrow \frac{2}{3}C_3H_6 + CH_4$ −9.41 kcal/mole

$C_3H_8 \rightarrow \frac{1}{2}C_6H_6 + \frac{5}{2}H_2$ −7.94 kcal/mole

$C_3H_8 \rightarrow \frac{2}{9}C_6H_6 + \frac{5}{3}CH_4$ −21.4 kcal/mole.

The first reaction is dehydrogenation, the least favorable route. However, formations of other products significantly decrease the Gibbs free energy, which explains the difficulties in achieving high selectivity to propylene from propane dehydrogenation.

TABLE 1

Initial Activities of Different Catalysts

Catalyst	Conversion (%)	Yield (%)
(Pd)/ZrO_2	47.3	23.1
(Mo)/ZrO_2	33.4	18.4
(Ni)/ZrO_2	14.5	9.08
(Pd)/$Si_{0.2}Ti_{0.8}O_2$	18.9	10.7
(Mo, Zr)/$Si_{0.2}Ti_{0.8}O_2$	13.1	7.31

REACTION MECHANISMS

1. ZSM-5

Transformation of propane over HZSM-5 is believed to be carbonium ion reactions (*3*). Carbonium ions were formed on the strong acid sites in the channels of the catalysts. The high selectivity to methane and aromatics in this work confirms the following carbonium reaction path: formation of $C_3H_9^+$ on the acid sites from the reaction of propane with H^+; reactions of $C_3H_9^+$ with alkanes to form higher carbon number hydrocarbons, including aromatics; decomposition of carbonium ions on the acid sites to form light hydrocarbons, mainly methane.

The reaction of propane over metal-modified ZSM-5 is also believed to follow similar carbonium ion mechanism and differs only in the type of intermediate formed. A study of alkane reactions on Ni-, Zn-ZSM-5, and H-ZSM-5 by Riley and Anthony (*15*) showed that on metal promoted ZSM-5, the active metals catalyzed the dehydrogenation of an alkane to an alkene. The alkene

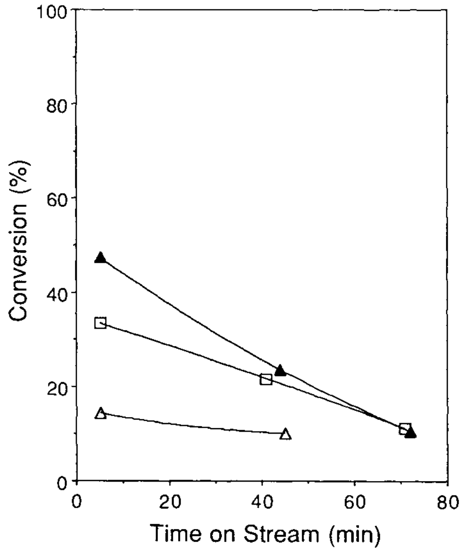

FIG. 7. Comparison of the activities of different dispersed metals: ▲, (Pd)/ZrO2; □, (Mo)/ZrO2; △, (Ni)/ZrO2.

further reacted with a Bronstead acid site on the zeolite to give a carbenium ion, whereas on HZSM-5, a carbonium ion could be formed by the direct reaction of an alkane with an acid site. Gnep *et al.* (*4*) and Inui *et al.* (*16*) studied the transformation of propane over Ga- and Pt-ZSM-5, and proposed a similar mechanism. Their results showed that C_1, C_2, and aromatic hydrocarbons accounted for most of the products, while the yield of propylene was relatively low.

In conclusion, on ZSM-5, regardless of the presence of metals, the main products of propane reaction are aromatics and light alkanes (methane and ethane) with very small amounts of propylene due to the strong acidity of the catalysts. Carbonium ion formation and reaction on acid sites are the overall reaction mechanism.

2. *Zirconia and Silica Titania*

There were several major differences in the reaction of propane on HZSM-5 and that on zirconia and silica titania supported catalysts: on zirconia and silica titania catalysts, propylene was the main product of the reaction, the selectivity to methane or ethane was below 20% for most catalysts, and active metals showed significant effects of the activity of a catalyst. On the other hand, on HZSM-5, aromatics and methane were the major products, and the selectivity to methane usually fell in the range of 25 to 40 mole% based on the values from this work and the literature (*4, 16*).

The differences in the product distributions on zirconia and silica titania catalysts

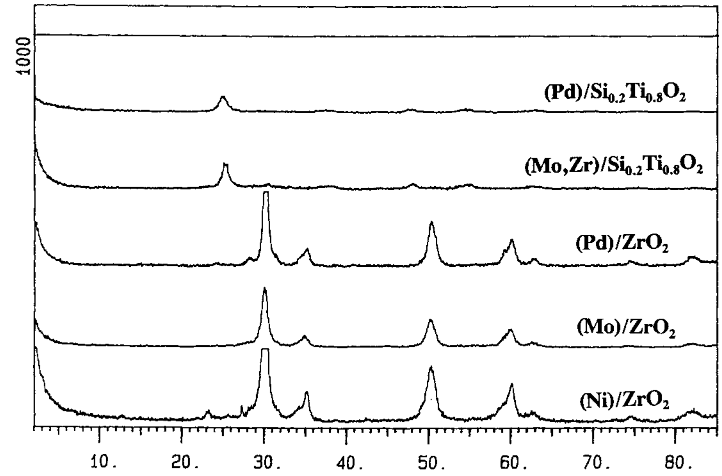

FIG. 8. X-Ray diffraction patterns of zirconia and silica titania catalysts.

with those on ZSM-5, as well as the weak acidity of the catalysts which is unfavorable for the formation of carbonium ions, suggests a mechanism other than carbonium ion reaction to explain the propane reaction on these metal oxide catalysts. The significant effects of active metals lead to the assumption of hydrogen abstraction from adsorbed propane on metals as the main route of propylene formation,

$$(C_3H_8)_s \rightleftharpoons (C_3H_7)_s + H_s \rightleftharpoons (C_3H_6)_s + 2H_s$$

(s denotes surface reaction).

The order of Pd > Mo > Ni on activity of C–H bond scission in this study was comparable to those reported by Riley and Anthony (*15*) and Yan (*17*), where they presented data on the hydrocracking of napthas on different active metals, such as Ni, Pd, and Zn.

Though hydrogen abstraction plays a dominant role in the reaction mechanism, carbonium ions can still be formed from the reaction of propylene with the weak acid sites, which results in the formation of methane and aromatics. However, compared to the case in ZSM-5, carbonium ion mechanism is far less important for the weak acid materials such as zirconia and silica titania.

CONCLUSIONS

The study of propane reaction over metal modified zirconia and silica titania showed that in absence of strong acidity, propylene was the main product. Hence, the materials were promising dehydrogenation catalysts.

Comparison of propane transformation over strong and weak acidic materials showed that the mechanisms of propane reaction strongly depended on the properties of the catalysts. On strong acid materials, such as ZSM-5, acidity was a major factor to affect the reaction path, and carbonium ion formation and reaction mechanisms satisfactorily explained the performance of the catalysts. On the other hand, on weak acid materials, such as metal modified silica titania and zirconia, the effects of active metals become more significant, and hydrogen abstraction on the active metals was the dominating mechanism. Consequently, dehydrogenation was the overall reaction of propane on weak acid catalysts.

ACKNOWLEDGMENTS

This material is based in part upon work supported by the Texas Advanced Technology Program under Grant 999903-323, TEES 32131-70560. The synthesis of the palladium catalysts by Dr. R. G. Dosch of Sandia National Laboratories is very much appreciated. The financial support of Texaco, Inc., for the Texas A&M Research Foundation Project 6448 is also gratefully acknowledged.

REFERENCES

1. Chen, Y. F., and Chester, A. W., *Zeolites* **6,** 195 (1986).

2. Chkheidze, G. S., Zen'Kovskii, S. M., and Mortikov, Ye. S., *Neftekhimiya* **21,** 515 (1981).

3. Kitagawa, H., Sendoda, Y., and Ono, Y., *J. Catal.* **101,** 12 (1986).

4. Gnep, N. S., Doyemet, J. Y., Seco, A. M., Ribeiro, F. R., and Guisnet, M., *Appl. Catal.* **35,** 93 (1987).

5. Bragin, O. V., *Russ. Chem. Rev. (Engl. Transl.)* **50,** 1045 (1981).

6. Doolan, P. C., and Pujado, P. R., *Hydrocarbon Process.* **72** (Sept. 1989).

7. Thomas, C. L., "Catalytic Processes and Proven Catalysts," Chap. 6. Academic Press, New York, 1970.

8. Stephens, H. P., Dosch, R. G., and Stohl, F. V., *Ind. Eng. Chem. Prod. Res. Dev.* **24,** 15 (1985).

9. Gruber, K. A., M.S. Thesis, Department of Chemical Engineering, Texas A&M University, 1989.

10. Dosch, R. G., Stephens, H. P., Stohl, F. V., Bunker, B. C., and Peden, C. H. F., *in* "Hydrous Metal Oxide-Supported Catalysts: Part I. A Review of Preparation Chemistry and Physical and Chemical Properties," DOE Report Sand89-2399. Department of Energy, Washington, DC, 1989.

11. Dosch, R. G., Stephens, H. P., and Stohl, F. V., U.S. Patent 4,511,455 (1985).

12. Feng, Z., M.S. Thesis, Department of Chemical Engineering, Texas A&M University, 1991.

13. Burgin, E. C., and Groll, H., U.S. Patent 2,270,165 (1942).

14. Imai, T., and Schmidt, R. J., U.S. Patent 4,886,928 (1989).

15. Riley, M. G., and Anthony, R. G., *J. Catal.* **100,** 322 (1986).

16. Inui, T., Makino, Y., Okazumi, F., Nagano, S., and Miyamoto, A., *Ind. Eng. Chem. Res.* **26,** 647 (1987).

17. Yan, T. Y., *Chem. Eng. Commun.* **21,** 123 (1983).