

## Effect of Palladium and Nickel on the Temperature Programmed Reduction of Metal Oxides and Metal Oxide Layers

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**Abstract**—A new binary oxide support was suggested as being useful in many commercial reactions. Our study was focused on the reduction effect of metal oxide layer on alumina during reaction. Hence temperature programmed reduction of both bulk metal oxide and metal oxide layer on alumina was studied first and the effect of palladium and nickel on the reduction of the oxide support was also investigated. Vanadium oxide was mainly studied and niobium oxide, tantalum oxide, titanium oxide and zirconium oxide were also compared. Some metal oxides were reduced in a hydrogen stream at elevated temperature. In these cases both the bulk metal oxide and metal oxide layer were reduced. A tiny amount of palladium or nickel affected the reduction by decreasing the reduction temperature. The decrease of the reduction temperature was explained by means of increased adsorption of hydrogen on the transition metal and ability of the metal to spillover of the hydrogen to the oxides.

Key words: Reduction of Oxides, Transition Metal Effect, Hydrogen Spillover, Bulk Metal Oxide, Binary Oxide Support

### INTRODUCTION

A new binary or ternary oxide support was suggested that consists of deposition of transition metal oxides on the surface of commercial alumina or silica of desired porosity and surface area [Kuen-ski et al., 1986; Glinski and Kijenski, 1992; Choi et al., 2001]. Transition metal oxides containing vanadium, niobium, tantalum, titanium and zirconium are currently under study. The binary oxide was synthesized by the reaction of transition metal alkoxides with surface OH sites of alumina. And then exhaustive hydrolysis to remove alkoxide group, thermal treating to eliminate water and calcination to form metal oxide layer on alumina followed. When new binary oxide support was prepared, another transition metal as catalytically active material could be impregnated on the new support, and hence this type of catalyst system could be applicable in many reactions [Beutel et al., 1992; Reddy et al., 1996; Tieman et al., 1999]. Palladium and nickel were employed as active material in this study, and this type of catalyst system could be useful in many reactions.

However, from this type of catalyst system, we believe that it is very interesting to recognize the role of transition metal oxide layer during the reaction. The oxide layer might interact with the impregnated palladium or nickel [Miller et al., 1993; Santiesteban et al., 1999; Roland et al., 1997]. It may also be possible that the metal oxide layer could be reduced in order to be involved in the reaction and that palladium or nickel may affect the reduction of the oxide layer, possibly as hydrogen supplier. Hence our study focused on the reduction of metal oxide layer and on the effect of added palladium or nickel on the reduction. In addition, we also compared the reduction of metal oxide layer with the reduction of bulk phase oxide and studied the effect of palladium and nickel during the reduction of the bulk phase oxide.

### EXPERIMENTAL

Alumina (Norton Chemical Co) was crushed and sieved to 40/60 mesh. Vanadium isopropoxide (99+%), niobium ethoxide (99%), tantalum ethoxide (99%), titanium isopropoxide (99%) and zirconium isopropoxide (99%) were purchased from Aldrich or Strem, and they were used to prepare binary oxide support. Transition metal oxides of  $V_2O_5$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ,  $TiO_2$  and  $ZrO_2$  were also purchased from Aldrich or Strem and used for the study of temperature programmed reduction. Palladium acetylacetonate and nickel nitrate were used for the addition of palladium and nickel on the surface of the new supports or bulk metal oxide powders. Pure THF as a solvent was further purified by distillation.

The 2 g of alumina (40/60 mesh) was dried at 110 °C to remove any physisorbed water, leaving the surface fully hydroxylated. In a typical preparation of  $VAIO_x$  support, which represents the vanadium oxide layer on alumina, 7.3 ml of vanadium isopropoxide which was required to react with all surface hydroxyl groups was dissolved in 15 ml of dry THF. The alkoxide solution was heated to boiling under nitrogen and kept under reflux for 1 hour. Then the alumina was impregnated with the hot alkoxide solution and heating was continued for 24 hours. The excess solvent along with small amounts of unreacted alkoxide was removed. The remaining solid residue was washed with THF and slowly hydrolyzed by passing water vapor in a nitrogen carrier for 24 hours. At the end of the hydrolysis the material was calcined at 500 °C to yield the final support which contains a monolayer coating of vanadium oxide on alumina.

Then palladium or nickel as an active material was added on the supports or metal oxides. All samples were prepared by the incipient wetness technique, and after the impregnation of palladium acetylacetonate or nickel nitrate the samples were carefully dried. Every sample was prepared so as to contain 1 wt% of palladium or nickel on the total mass basis just to see the effect of palladium or nickel.

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**Table 1. Reduction temperature peaks during reduction process of samples containing vanadium pentoxide**

Sample	Bulk V <sub>2</sub> O <sub>5</sub>		V <sub>2</sub> O <sub>5</sub> layer
	Peak temperature in DTG spectrum	Stoichiometry after reduction	Peak temperature in DTG spectrum
V <sub>2</sub> O <sub>5</sub>	578 °C	V <sub>2</sub> O <sub>3.4</sub>	
Ni/V <sub>2</sub> O <sub>5</sub>	292, 323, 432, 519 °C	V <sub>2</sub> O <sub>3.2</sub>	
Pd/V <sub>2</sub> O <sub>5</sub>	171, 201, 308, 428 °C	V <sub>2</sub> O <sub>3</sub>	
V <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>			488 °C
Ni/V <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>			358 °C
Pd/V <sub>2</sub> O <sub>5</sub> /Al <sub>2</sub> O <sub>3</sub>			220 °C

After the catalyst samples were prepared, a temperature programmed reduction (TPR) experiment was performed to study the reduction behavior by using a Shimadzu TGA-50 connected to a computer. Usually about 20 mg of sample was placed in a quartz sample cell and pure hydrogen flowed into the TGA chamber at room temperature until the entire interior was replaced with pure hydrogen. After hydrogen flow was confirmed, the sample began to be heated at the rate of 10 °C/min up to almost 1,000 °C to obtain TGA spectrum. For more careful analysis, DTG spectrum (differential of thermal gravity spectrum) was obtained by the software operation and each weight loss peak was measured.

## RESULTS AND DISCUSSION

### 1. Reduction of Bulk Phase Metal Oxide Powder

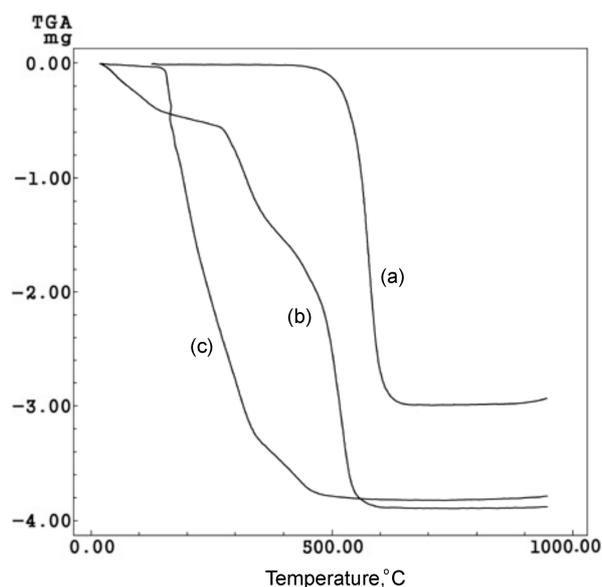
Temperature programmed reduction experiments of several bulk phase metal oxides were carried out as a guide for the reduction of metal oxide layers formed on alumina. The experiment was performed by measuring the sample weight loss using TGA equipment with heating rate of 10 °C/min and with hydrogen flow rate of 10 cc/min. The reduction was performed up to 950 °C because of the limitation of TGA equipment. After TGA data were collected, a DTG spectrum, which is the differential of the TG spectrum, was obtained. Every peak temperature corresponding to the weight loss was carefully measured and compared. The weight loss of TG and integrated area of DTG were also carefully measured and used to compare calculations because they are expected to be the same. The metal oxide powders employed for the reduction study were vanadium oxide (V<sub>2</sub>O<sub>5</sub>), niobium oxide (Nb<sub>2</sub>O<sub>5</sub>), tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>), titanium oxide (TiO<sub>2</sub>) and zirconium oxide (ZrO<sub>2</sub>). In addition to the study on the reduction of the bulk oxide powders, the same experimental procedure was followed to see the effect of added palladium and nickel on the reduction of the bulk oxide powders. The amount of palladium and nickel was fixed as one weight percent based on total weight of bulk oxide powder just to see the effect obviously.

Because palladium and nickel was impregnated on the surface of bulk metal oxide powder as palladium acetylacetonate and nickel nitrate, respectively, a decomposition study for palladium acetylacetonate and nickel nitrate on the surface was performed first. When pure palladium acetylacetonate was studied while hydrogen was flowing, the temperature programmed reduction experiment indicated that almost all of palladium acetylacetonate was decomposed and reduced to palladium metal easily at 62 °C and even decomposed at room temperature. This means that palladium stays as met-

al on the bulk metal oxide powder during the reduction experiments. In case of nickel nitrate, when temperature programmed reduction was performed with nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) while hydrogen was flowing, almost 72% of nickel nitrate was reduced to nickel metal at around 300 °C. This means that although most of nickel stays as metal on the surface, part of the nickel nitrate may still stay as compound during the reduction study.

The temperature programmed reduction experiment for vanadium oxide (V<sub>2</sub>O<sub>5</sub>) was performed and the effect of added palladium or nickel on the reduction was also studied. The results are summarized in Table 1. Fig. 1 presents a comparison of TG spectra of pure vanadium oxide and vanadium oxide containing 1 wt% palladium or nickel.

As seen in Fig. 2, V<sub>2</sub>O<sub>5</sub> powder was mainly reduced at 578 °C, showing one significant reduction peak in DTG spectrum and the V<sub>2</sub>O<sub>5</sub> was reduced to V<sub>2</sub>O<sub>3.4</sub> if stoichiometry is applied according to the calculated weight loss. The expression of V<sub>2</sub>O<sub>3.4</sub> may possibly represent a mixture of several vanadium oxides or oxygen-rich V<sub>2</sub>O<sub>3</sub>. However, it was confirmed that vanadium oxide was reduced. Moreover, one single peak at 578 °C in Fig. 2 meant that the reduction was occurred in a single stage showing one reduction path. During the reduction experiment the color of vanadium oxide was changed



**Fig. 1. TGA spectrum during reduction in hydrogen stream for the samples of (a) vanadium pentoxide (b) nickel on vanadium pentoxide and (c) palladium on vanadium pentoxide.**

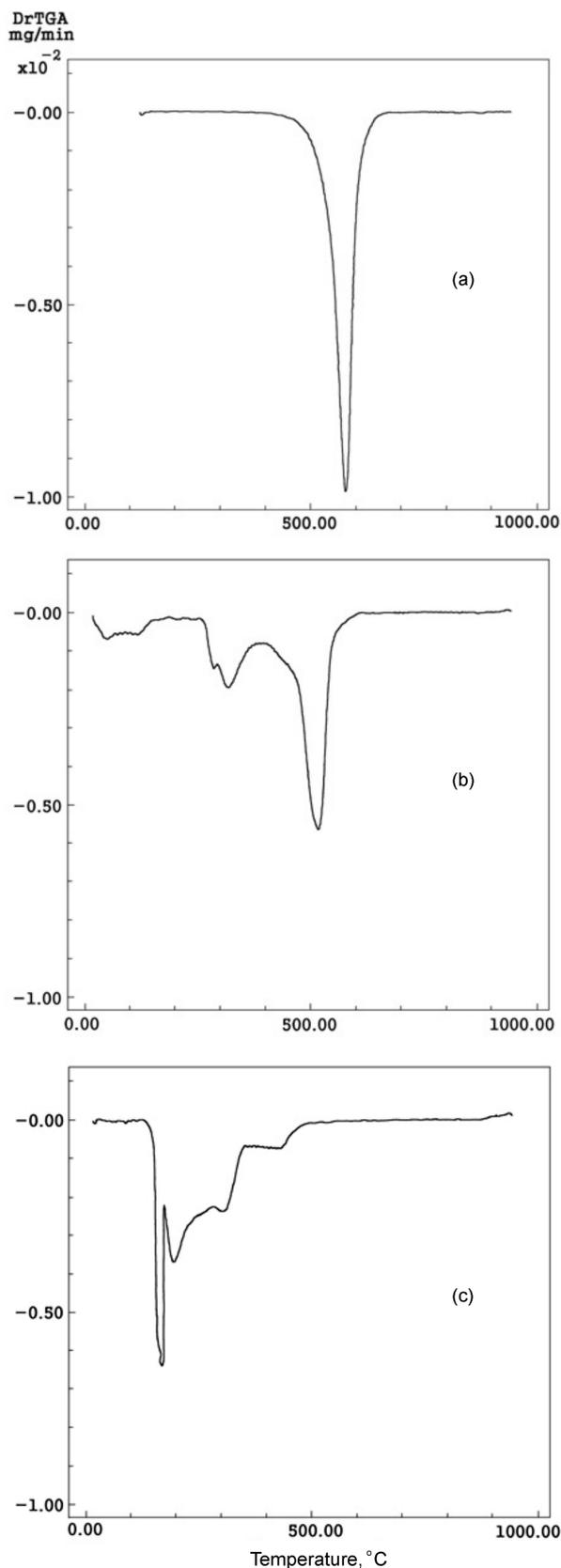


Fig. 2. Differential of TGA spectrum during reduction in hydrogen stream for the samples containing vanadium pentoxide. (a) bulk vanadium pentoxide (b) nickel on vanadium pentoxide and (c) palladium on vanadium pentoxide.

from brown to black. Color change also matched the reduction of vanadium pentoxide ( $V_2O_5$ ) to vanadium trioxide ( $V_2O_3$ ).

When 1 wt% nickel was added on the surface of  $V_2O_5$  powder, the temperature programmed reduction of  $V_2O_5$  showed different behavior, showing four reduction steps in the temperature range of 290 and 520 °C (Table 1, Fig. 2). When a tiny amount of nickel was added on the surface, reduction of bulk metal oxide occurred at lower temperatures. If the stoichiometry is applied according to the calculated weight loss,  $V_2O_{3.2}$  is obtained in this case. This means that nickel addition showed the effect of more reduction at lower temperatures. However, reduction path was observed different, although it is difficult to predict the reduction path.

When 1 wt% palladium was added on the surface of  $V_2O_5$  powder, another different reduction pattern was observed to show four reduction steps in the temperature range of 170 and 428 °C (Table 1, Fig. 2). Reduction temperature peak was clearly shifted to lower temperature than the case in nickel addition. The stoichiometry based on weight loss was also decreased to exact  $V_2O_3$ , which means that palladium played a better role to obtain complete reduction of  $V_2O_5$  to  $V_2O_3$ .

From the series of experiments of  $V_2O_5$  reduction (Table 1), it is clear that vanadium pentoxide was definitely reduced in hydrogen, and this may be the catalytic role of  $V_2O_5$  on binary oxide systems in many reactions. Moreover, catalytically active metal accelerated the reduction of  $V_2O_5$ . This may be explained by the increased hydrogen supply by means of increased hydrogen adsorption on the metal and the hydrogen spillover to  $V_2O_5$ .

The temperature programmed reduction experiment with niobium oxide powder ( $Nb_2O_5$ ) was also studied. When the same experimental condition was applied, niobium pentoxide began to be reduced in the hydrogen stream at 880 °C. However, because the heating was stopped at 950 °C due to limitations of the TGA furnace, weight loss peak and total weight loss could not be obtained. However, it was clear that niobium pentoxide was reduced, but it is hard to say that niobium pentoxide ( $Nb_2O_5$ ) was reduced to niobium trioxide ( $Nb_2O_3$ ) or oxygen-rich niobium trioxide. When 1 wt% nickel and 1 wt% palladium was added on the surface of bulk phase niobium pentoxide powder, the reduction was observed to begin at 850 °C and 860 °C, respectively. The observation of temperature difference may also support the role of nickel or palladium to accelerate hydrogen supply to the niobium oxide powder by means of increased adsorption and spillover of hydrogen. After the reduction experiment the color of the niobium oxide powder was changed to black that represented the  $Nb_2O_3$ .

In addition to vanadium and niobium, tantalum pentoxide ( $Ta_2O_5$ ) was also tested for temperature programmed reduction. However, tantalum was not reduced below 950 °C, which is the experimental limitation. Even when 1 wt% nickel or palladium was added on the tantalum oxide powder, the reduction was not observed below 950 °C. It may be expected that the reaction may occur above the temperature. In the case of both titanium oxide and zirconium oxide, they were also not reduced below 950 °C. This may be easily understandable because the titania and zirconia are the materials which are very hard to reduce.

## 2. Reduction of Metal Oxide Layer on $\gamma$ -Alumina

After the reduction study of bulk phase metal oxide, reduction experiments for metal oxide layer on alumina followed. Since the

binary oxide support was prepared by the surface reaction, vanadium pentoxide in case of  $\text{VAIO}_x$  is expected to exist as an oxide monolayer on alumina. And then in case of  $\text{NbAlO}_x$ ,  $\text{TaAlO}_x$ ,  $\text{TiAlO}_x$  and  $\text{ZrAlO}_x$ , niobium pentoxide, tantalum pentoxide, titanium dioxide and zirconium dioxide may form layers on alumina, respectively.

When vanadium pentoxide on alumina was employed for the temperature programmed reduction experiment, weight loss peak was observed at 488 °C; this weight loss may be regarded as corresponding to the reduction of vanadium pentoxide. Because the exact amount of vanadium pentoxide after preparation of binary oxide support was not measured, it was hard to correlate the amount of weight loss with amount of removed oxygen. However, the reduction temperature peak was decreased from 578 to 488 °C when compared with the bulk case. This means vanadium oxide layer on alumina is more easily reduced. But it is hard to express the stoichiometry of the reduced state; however, it could be  $\text{V}_2\text{O}_{3.4}$  or  $\text{V}_2\text{O}_3$  because  $\text{V}_2\text{O}_{3.4}$  was obtained from the experiment with the bulk vanadium pentoxide.

When 1 wt% nickel and palladium based on total sample weight was added on  $\text{VAIO}_x$ , reduction of vanadium pentoxide layer was observed even at lower temperature, that is, at 358 °C and 220 °C, respectively (Table 1). This observation clearly states that active material such as nickel or palladium played a role of accelerating the reduction of vanadium oxide layer. Although the extent of reduction is not still clear, it can be predicted that  $\text{V}_2\text{O}_3$  phase might be obtained when comparing with the result of the reduction study of bulk vanadium pentoxide. Here, since  $\text{V}_2\text{O}_3$  layer on alumina is very reactive, this  $\text{V}_2\text{O}_3$  together with palladium or nickel could be involved as a catalyst in many reactions.

Similar results were obtained from the temperature programmed reduction experiment with  $\text{NbAlO}_x$  and  $\text{TaAlO}_x$ . In the sample of  $\text{NbAlO}_x$ , reduction peak of niobium pentoxide layer on alumina was observed at 560 °C, while the reduction peak was above 950 °C in the case of bulk niobium oxide. It was also hard to express the oxidative state of niobium from the weight loss measurement because initial amount of niobium pentoxide as a layer was hard to know. When 1 wt% palladium was added on the  $\text{NbAlO}_x$ , the reduction temperature peak was more decreased to 453 °C. This again confirmed the effect of active material to accelerate the reduction of metal oxide. In case of tantalum oxide layer on alumina, a tiny weight loss peak was observed at 480 °C although bulk tantalum pentoxide was not reduced below 950 °C. When 1 wt% palladium was added, the weight loss peak was further decreased to 383 °C. However, the amount of weight loss was so small and the peak temperatures were so low that it might be hard to consider these peaks as the reduction of tantalum oxide layer. In cases of titania and zirconia on alumina, both oxide layers were not reduced and this could be assumed to be due to their own properties of titania and zirconia.

## CONCLUSIONS

A series of reduction experiments for vanadium pentoxide and

niobium pentoxide suggested that these bulk phase oxides were reduced in a hydrogen stream. And when active material such as nickel and palladium was added on the surface of the oxide powder, the reduction occurred more easily at lower temperature. In case of binary oxide support, the metal oxide layer on the alumina was more easily reduced than bulk phase oxide. When nickel or palladium was added on the binary support, it further accelerated the reduction of oxide layer. This result was explained by the increased hydrogen supply to the metal oxide by means of the role of palladium and nickel to increase hydrogen adsorption and to spillover the hydrogen to oxide phase.

## REFERENCES

- Beutel, T., Knozinger, H., Siborov, A. V. and Zalkovskii, V. I., "Metal-Promoter Interaction in Vanadium Oxide Promoted Rh/SiO<sub>2</sub> Catalyst," *J. Chem. Soc. Faraday Trans.*, **88**(18), 2775 (1992).
- Choi, J. H., Kim, S. K. and Ha, S. J., "The Preparation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> Catalyst Supported on a Ceramic Filter Candle for Selective Reduction of NO," *Korean J. Chem. Eng.*, **18**, 456 (2001).
- Choi, J. H., Kim, S. K. and Bak, Y. C., "The Reactivity of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> Catalyst Supported on a Ceramic Filter Candle for Selective Reduction of NO," *Korean J. Chem. Eng.*, **18**, 719 (2001).
- Glinski, M. and Kijenski, J., "Monolayer Vanadia on Titania Systems from Alkoxide Precursors. Part I. Physicochemical Properties," *React. Kinet. Catal. Lett.*, **46**(2), 379 (1992).
- Kuenski, J., Baiker, A., Glinski, M., Dollenmeier, P. and Wokaun, A., "Monolayer and Double Layers of Vanadium Pentoxide on Different Carrier: Preparation, Characterization, and Catalytic Activities," *J. Catal.*, **101**, 1 (1986).
- Miller, J. T., Meyers, B. L., Modica, F. S., Lane, G. S., Vaarkamp, M. and Koningsberger, D. C., "Hydrogen Temperature-Programmed Desorption of Supported Platinum Catalysts," *J. Catal.*, **143**, 395 (1993).
- Reddy, B. M., Kumar, M. V., Reddy, E. O. and Mehdi, S., "Dispersion and Thermal Stability of Vanadium Oxide Catalyst Supported on Titania-Alumina Binary Oxide," *Catal. Letter*, **36**, 187 (1996).
- Roland, V., Salzer, R. and Summchen, L., "Electronic Effect of Hydrogen Spillover on Titania," *Spillover and Migration of Surface Species on Catalysts*, Elsevier Science (1997).
- Santesteban, J. G., Calabro, D. C., Borghard, W. S., Chang, C. D., Vartuli, J. C., Tsao, Y. P., Natal-Santiago, M. A. and Bastian, R. D., "H-Spillover and SMSI Effect in Paraffin Hydroisomerization over Pt/WO<sub>3</sub>/ZrO<sub>2</sub> Bifunctional Catalysts," *J. Catal.*, **183**, 314 (1999).
- Tiernan, M. J., Barnes, P. A. and Parkes, G. B., "New Approach to the Investigation of Mechanism and Apparent Activation Energy for the Reduction of Metal Oxide using Constant Reaction Rate Temperature-Programmed Reduction," *J. Phys. Chem. B*, **103**, 338 (1999).