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Propane Hydrogenolysis as a Chemical Probe on the Stability of Niobia Surface Oxide Supports

Surface oxides, which consist of one oxide deposited onto another, constitute an important class of catalytic materials. In such a system, the dispersion of the surface, or supported, phase is to a large extent controlled by the oxide–oxide interfacial interactions. Such interactions can stabilize the surface phase as a highly dispersed monolayer and in so doing, significantly change its catalytic properties in relation to the bulk oxide. Thus, there have been numerous studies on the preparation and characterization of surface oxides, with the aim of establishing the interrelationships among interactions, stability, and reactivity (*1–3*).

A complication arises when a surface oxide is used as a support for metal catalysts. Since there are now metal–oxide as well as oxide–oxide interactions, we need to address the fundamental issue of how the interaction of the surface oxide with the support affects its interaction with the metal. In our previous work with Ni supported on Nb_2O_5–SiO_2, we have demonstrated that a monolayer of Nb_2O_5 deposited onto SiO_2 exerts the same mechanism of metal–support interaction as bulk Nb_2O_5 (*4, 5*). The extent of interaction, however, is weaker due to the lower concentration and mobility of Nb_2O_5 which is stabilized by SiO_2. One significant consequence is that under the same reducing conditions, the Ni particles on the Nb_2O_5–SiO_2 support have less of the decorating species and remain relatively active for structure-sensitive reactions such as hydrogenolysis (*6*). In the case of propane hydrogenolysis, the activity of Ni is almost 1000 times lower on Nb_2O_5 than on SiO_2, but only an order of magnitude lower on Nb_2O_5–SiO_2 (*5*).

In this note we describe a method which takes advantage of the vastly different support behavior of Nb_2O_5 and SiO_2 to study the thermal stability of Nb_2O_5 surface oxides. Even though the method is illustrated for propane hydrogenolysis over Ni, the same idea is applicable to any system in which the surface and supporting oxides have very different reactivities with respect to a particular probe.

The Nb_2O_5–SiO_2 supports were prepared by impregnating silica (Davison 952) with a hexane solution of niobium ethoxide to incipient wetness as described previously (*4*). The resulting sample after calcination at 773 K for 2 h was denoted as NS(I) (one monolayer of Nb_2O_5 on SiO_2). NS(II) was a sample with a second layer of Nb_2O_5 deposited onto NS(I) by repeating the same procedure. Different batches of these supports were then subjected to a range of thermal treatments *prior to the introduction of Ni* with the treatment conditions expressed as (temperature in K, time in h).

Nickel catalysts were prepared with the heat-treated supports by the incipient wetness impregnation of $Ni(NO_3)_2 \cdot 6H_2O$. The Ni loading was either 10 or 5 wt%, depending on the surface area of the support. For kinetic studies, all catalysts were reduced *in situ* in flowing hydrogen at 773 K for 1 h. This condition was sufficient for the complete reduction of Ni on all these supports (*5*).

Propane hydrogenolysis was studied over these catalysts in a differential reactor by

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TABLE 1

Kinetic Data of Propane Hydrogenolysis over Supported Nickel Catalysts[a]

Support	Ni loading [wt%]	Ni particle size [nm][b]	Activity × 10^4 [s^{-1}]		E_{a1}	E_{a2} [kcal/mole]	P_{H_2}		$P_{C_3H_8}$	
			r_1	r_2			m_1	m_2	n_1	n_2
SiO_2	18	5.5	14.3	11.9	39	64	−1.6	−3.0	1.0	1.0
Nb_2O_5	10	4.0	0.13	0.03	14	34	−0.1	−0.7	0.9	0.6
NS(I)	10	5.5	2.7	1.8	34	58	−1.3	−2.4	1.0	0.9
NS(I)(873,48)[c]	5	3.0	1.8	1.0	31	48	−1.4	−2.4	1.0	1.0
NS(I)(973,48)	5	3.0	2.7	1.6	30	45	−1.2	−2.2	1.0	1.0
NS(I)(1073,48)	5	3.0	2.8	1.0	36	56	−1.3	−2.1	1.0	1.0
NS(I)(1273, −)[d]	5	3.0	5.5	3.5	36	57	−1.4	−2.5	1.0	1.0
NS(I)(1273,16)	5	3.0	8.9	5.5	36	58	−1.5	−2.6	1.0	1.1
NS(I)(1273,48)	5	14	26	16	39	58	−1.6	−2.9	1.0	1.0
NS(II)	10	6.0	0.3	0.2	20	39	−0.4	−1.0	0.9	0.8
NS(II)(873,16)	10	4.2	1.8	1.1	37	54	−1.4	−2.5	0.9	0.9

[a] Kinetic parameters for the rate law shown as Eq. (1) in text. Subscripts 1 and 2 denote reaction pathway 1 and 2, respectively. Experimental conditions were T = 478 K, P_{H_2} = 152 Torr, and $P_{C_3H_8}$ = 22.8 Torr.

[b] Particle size calculated from X-ray line broadening.

[c] (873,48) refers to calcination at 873 K for 48 h.

[d] (1273, −) refers to calcination with a temperature ramp of 10K/min up to 1273 K without holding at 1273 K.

following a previously described procedure (*5*). Briefly, a rate law of the form

$$r_i = k_i \exp\left[-\frac{E_{ai}}{RT}\right] P_{H_2}^{m_i} P_{C_3H_8}^{n_i} \qquad (1)$$

was established for each of the two reaction pathways (hydrogenolysis into ethane and methane (pathway 1) versus complete hydrogenolysis into methane (pathway 2)). The two pathways could be considered as independent since at the low conversion levels used in this study, the subsequent hydrogenolysis of ethane from pathway 1 into methane was negligible (*7*). The rate, expressed as a turnover frequency, was calculated on the basis of the weight loading and particle size as determined by X-ray diffraction line broadening of Ni in each sample.

Table 1 summarizes the results for propane hydrogenolysis over Ni supported on a series of NS(I) and NS(II) heat treated under different conditions. Data for SiO_2 and Nb_2O_5 (*5*), which are included for comparison, show clearly the interacting effects of Nb_2O_5 as a support in terms of lower activities and different kinetic parameters (activation energy and reaction orders). For NS(I) calcined at 773 K for 2 h, the activities were intermediate between those of SiO_2 and Nb_2O_5, and the kinetic parameters were closer to those of SiO_2. These observations were interpreted as a less interactive surface Nb_2O_5 phase stabilized on SiO_2 (*5*). It is then significant to note that the kinetic parameters did not vary much on NS(I) up to a treatment temperature of 1273 K, above which the activities increased. In fact, one could define a percent Nb_2O_5 surface coverage on a particular sample as

$$\%\ \text{surface coverage} = \frac{a_{SiO_2} - a_{\text{sample}}}{a_{SiO_2} - a_{NS(I)}} \qquad (2)$$

where a_i denotes the sum of activities for Ni on support i.

This definition, which gives theoretical limits of 0 and 100% for the SiO_2 and NS(I) supports, respectively, is based on two assumptions. The first assumption is that the activity due to Ni supported on bulk Nb_2O_5

TABLE 2

Thermal Stability of Nb_2O_5 Surface Oxides

Support	% surface coverage[a]
NS(I)	100
NS(I)(873,48)	108
NS(I)(973,48)	100
NS(I)(1073,48)	103
NS(I)(1273,–)	79
NS(I)(1273,16)	54
NS(I)(1273,48)	0
NS(II)(873,16)	107

[a] See text for explanation.

is negligibly small, which is valid in view of the data in Table 1. The second assumption is that NS(I) indeed represents a stable Nb_2O_5 monolayer over SiO_2. Our previous results (*4, 8*) have shown that the surface phase in this sample is highly dispersed and, even though it may not completely cover 100% of the SiO_2 surface, is a good base case against which the heat-treated samples can be compared.

Table 2 shows the % surface coverage of Nb_2O_5 in the heat-treated NS(I) supports as calculated by Eq. (2). Values larger than 100% are due to uncertainties in kinetic rate measurements; they are sufficiently close to 100% to suggest that the surface Nb_2O_5 phase remained stable up to 1073 K. At the other extreme, the NS(I) (1273,48) support showed higher activities than SiO_2. This observation could be explained by the uncertainty in calculating turnover frequencies for a support which had the lowest surface area from the severe heat treatment and consequently the largest Ni particle size. We believe such high activities reflect a support which is void of surface Nb_2O_5 (hence the entry of 0% in Table 2). The heat treatment could have caused the encapsulation of Nb_2O_5 by SiO_2. Thus, it is encouraging that Eq. (2), which is based on a phenomenological model, gives physically meaningful limiting cases. At intermediate values of Nb_2O_5 surface coverage, Eq. (2) may be less accurate due to the assumptions involved but still useful as a relative gauge. Note in particular that the % surface coverage begins to drop off at 1273 K, a temperature at which SiO_2 becomes mobile (*9*). This deviation from full coverage would be consistent with the exposure of SiO_2 surface as a noninteracting support for Ni.

Propane hydrogenolysis was equally sensitive as a chemical probe on NS(II). As shown in Table 1, the activities decreased when a second layer of Nb_2O_5 was deposited onto NS(I) as there was more Nb_2O_5 to interact with Ni. When NS(II) was heat treated at 873 K for 16 h, the formation of TT–Nb_2O_5 was detected by X-ray diffraction (*4*) and the hydrogenolysis activities resembled those of NS(I) after the subsequent introduction of Ni. In fact, the % surface coverage of Nb_2O_5 in NS(II) (873,16) was calculated to be near 100% (see Table 2). Thus, there is strong evidence that the crystallization of Nb_2O_5 occurs primarily from the second layer and not at the expense of the first. A monolayer of Nb_2O_5 is thus stabilized by its interaction with SiO_2, which is consistent with the results presented earlier for the heat-treated NS(I) supports.

In summary, we have described a chemical means to characterize the thermal stability of supported oxides. As applied to the particular system of Nb_2O_5 on SiO_2, the method confirms an earlier finding (that the first layer of Nb_2O_5 interacts strongly with SiO_2) as well as providing new insight that the crystallization of NS(II) leaves the first layer intact.

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REFERENCES

1. Xie, Y., Gui, L., Liu, Y., Zhang, Y., Zhao, B., Yang, N., Guo, Q., Duan, L., Huang, H., Cai, X., and Tang, Y., *in* "Adsorption and Catalysis on Oxide Surfaces" (M. Che and G. C. Bond, Editors), p. 139. Elsevier, Amsterdam, 1985.
2. Wachs, I. E., Saleh, R. Y., Chan, S. S., and Chersich, C., *Chemtech,* 756–761 (December 1985).
3. Margraf, R., Leyrer, L., Taglauer, E., and Knözinger, H., *React. Kinet. Catal. Lett.* **35,** 261 (1987).

4. Ko, E. I., Bafrali, R., Nuhfer, N. T., and Wagner, N. J., *J. Catal.* **95,** 260 (1985).
5. Burke, P. A. and Ko, E. I., *J. Catal.* **116,** 230 (1989).
6. Ko, E. I., Lester, J. E., and Marcelin, G., *ACS Symp. Ser.* **298,** 123 (1986).
7. Guilleux, M. F., Dalmon, J. A., and Martin, G. A., *J. Catal.* **62,** 235 (1980).
8. Weissman, J. G., Ko, E. I., and Wynblatt, P., *J. Catal.* **108,** 383 (1987).
9. Iler, R. K., "The Chemistry of Silica," Wiley, New York, 1979.

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