Recent Catalytic Applications of Niobium-Based Materials

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ABSTRACT

The literature review of niobium oxide catalysts reveals that niobium-based materials are effective catalysts for many catalytic reactions: pollution abatement, selective oxidation, hydrocarbon conversion, dehydrogenation, carbon monoxide hydrogenation for synthetic fuels and chemicals, hydration/dehydration, and photochemistry. The niobium oxide catalytic materials are present as bulk layered niobium oxides, surface niobium oxide phases, hydrated niobium oxide, oxide support, or mixed oxide. Recent research activities are focusing on the development of new niobium-based catalysts such as surface niobium oxide phases and layered niobium oxide compounds.

1. INTRODUCTION

In the past two decades, niobium-based materials have been found to be effective catalysts for many catalytic reactions: pollution abatement, selective oxidation, hydrocarbon conversion, hydrotreating, hydrogenation/dehydrogenation, carbon monoxide hydrog enation for synthetic fuels and chemicals, polymerization, hydration/dehydration and photochemistry/ electrochemistry /1/. In the 1970's niobium-based catalysts were primarily investigated for their performance in the area of selective oxidation reactions (partial oxidation, ammoxidation, and oxidative dehydrogenation). In the 1980's, the use of niobium-based catalysts became more versatile, and their catalytic applications received

more attention in the areas of hydrocarbon conversion reactions (cracking, alkylation, metathesis, isomerization, and reforming) and carbon monoxide hydrogenation to synthetic fuels and chemicals. In the latter part of 1980's, niobium-based catalysts were further developed and utilized for the catalytic reactions of dehydration/hydration, esterification, and photocatalysis. The previous studies have pointed out that the development of new niobium oxide materials is essential to advancing the catalytic applications of niobium oxide.

One of the most interesting developments in niobium-based catalytic materials is that niobium oxide can form bulk layered structures /2-4/ as well as two-dimensional surface niobium oxide phases on high surface area oxide supports such as Al_2O_3, TiO_2, and SiO_2 /5-12/. The layered niobium oxide materials doped with 0.1 wt% Pt or Ni exhibit an unusually high and stable activity for photocatalysis of H_2O into H_2 and O_2 /2,3/. The two-dimensional surface niobium oxide phases have a pronounced effect on the physical and chemical properties of the oxide supports. The thermal stability of the Al_2O_3 and TiO_2 supports is increased by the presence of the surface niobium oxide overlayers /12/. Furthermore, the surface niobium oxide phase on the Al_2O_3 support was also found to possess strong Brønsted acidity which results in a high hydrocarbon cracking activity at elevated temperatures /5/. The Nb_2O_5/TiO_2 catalysts were reported to possess considerable activity for the reduction of NO with NH_3 from stationary emissions /13/. Silica supported niobium oxide catalysts were found to be active and selective for ethanol dehydrogenation /9/, propene metathesis /6/, and

propene photocatalysis /14/. In addition, the synthesis of methyl methacrylate from methyl propionate and formaldehyde was also catalyzed by the Nb_2O_5/SiO_2 system /15-16/. Thus, bulk layered structures and two-dimensional niobium oxide phases, on different oxide supports, have shown extensive catalytic applications.

The present review is limited to niobium oxide materials because most of the recent studies have concentrated on the catalytic properties of niobium oxide, and is classified into 1) bulk layered niobium oxides, 2) surface niobium oxide phases, 3) hydrated niobium oxide, 4) niobium oxide support, and 5) niobium mixed oxides.

2. BULK LAYERED NIOBIUM OXIDES

Layered niobium oxides, $M[Ca_2Nb_nO_{3n+1})]$ (M = K, Rb, and Cs; n = 3 or 4), can undergo an alkali exchange reactions with the protons present in aqueous acidic solutions due to their high ionic conductivity. The ion-exchanged layered niobium oxides, $H[Ca_2Nb_nO_{3n+1}]$ (n = 3 and 4), were found to exhibit an unusually high activity for the photo-catalysis of aqueous methanol solutions to H_2 and O_2 /2,3/. The H_2 evolution rates over the layered niobium oxides in aqueous methanol solutions (with or without ion-exchange) are shown in Table 1, and the H^+-exchanged $KCa_2Nb_3O_{10}$ doped with 0.1 wt% Pt possesses the highest H_2 evolution rate. The H_2 evolution rates in the aqueous solutions was also found to decrease with increasing size of the alcohol molecule due to the limited intercalation space as shown in Table 2. Thus, the layered niobium oxides possess interesting catalytic properties.

3. SURFACE NIOBIUM OXIDE PHASE

In the past few years, supported niobium oxide catalysts, on oxide supports such as Al_2O_3, TiO_2, and PVG (Porous Vycor Galss), have received much attention as the potential new niobium-based catalytic materials /5-12, 17, 18/. Deposition of niobium oxide on high surface area oxide supports yields high surface niobium oxide catalysts that possess important physical and chemical properties. The molecular states of the dispersed surface niobium oxide phases contrast sharply to bulk Nb_2O_5, and are reflected in the unique molecular structures and catalytic properties of the surface niobium oxide phases.

The catalytic properties for ethanol dehydro-genation over the supported niobium oxide on Al_2O_3 and SiO_2, as well as bulk Nb_2O_5, are shown in Table 3 /7/ . The surface niobium oxide phases exhibit very high activity and selectivity for ethanol dehydrogenation compared to bulk Nb_2O_5, and the specific oxide support has a pronounced effect on the catalytic properties of the supported niobium oxide catalysts. The surface niobium oxide phases also impart thermal stability to oxide supports, Al_2O_3 and TiO_2, at elevated temperatures by retarding the loss of surface area and phase transformations as shown in Table 4. This stabilizing effect extends the useful temperature range of catalytic materials and decreases catalyst deactivation. The surface niobium oxide phase also forms strong Brønsted acid sites on these oxide supports as shown in Table 5 /13, 19-21/. The Brønsted acidity is necessary for many catalytic reactions such as hydrocarbon conversion and pollution abatement. Thus, the thermal stability, Brønsted acidity and high surface area of the surface niobium oxide phases have led to many catalytic applications for

TABLE 1

Photocatalysis of aqueous methanol solutions over layered niobium oxides

Catalyst	H_2 evolution rate ($\mu mol \cdot h^{-1}$)		
	Original	H^*-exchanged	H^*-exchanged + 0.1 wt% Pt
$K_4Nb_6O_{17}$*	130	750	740
$KCa_2Nb_3O_{10}$	14	5900	19000
$RbCa_2Nb_3O_{10}$	3	3100	17000
$CsCa_2Nb_3O_{10}$	2	970	8300
$KCa_2NaNb_4O_{13}$	5	790	18000

* not layered structure

Catalyst: 1g, Hg lamp (450W)
Aqueous methanol solution: 50ml CH_3OH and 300ml H_2O

TABLE 2

The molecular size of alcohols effects on the H_2 evolution rate over layered niobium oxide

Alcohol	H_2 evolution rate ($\mu mol \cdot h^{-1}$)		
	$KCa_2Nb_3O_{10}$	H^*-exchanged	H^*-exchanged + 0.1 wt% Pt
Methanol	6.9	920	4700
Ethanol	7.0	73	380
2-propanol	3.7	48	220
1-propanol	2.5	27	43
1-butanol	2.5	19	30

TABLE 3

Ethanol dehydrogenation depends on the nature of oxide supports

Catalyst	Reaction Temp.	Initial rate	% Selectivity		
			Acetaldehyde	Ethene	Diethyl ether
5.5% Nb_2O_5/SiO_2	523K	1.25	96.1	2.8	1.1
	548K	1.66	93.2	6.1	0.7
	573K	3.17	84.4	13.7	1.9
6.3% Nb_2O_5/Al_2O_3	523K	4.03	4.6	5.7	89.7
	548K	5.33	4.1	19.6	76.3
	573K	11.78	3.4	26.9	69.7
Nb_2O_5	523K	2.05E-5	68.3	16.2	15.5
	573K	8.43E-5	32.2	40.7	27.2

Initial rate unit: mol min^{-1} g_{Nb}^{-1}

* M. Nishimura, K. Asakura, and Y. Iwasawa, J. Chem. Soc. Chem. Commun., 1986

TABLE 4

Surface niobium oxide phase stabilizes oxide supports at elevated temperatures

Treatment	TiO_2* (Degussa P-25)	8% Nb_2O_5/TiO_2* (Degussa P-25)
500°C-2 hrs. in Air	56 m²/g (Anatase/Rutile)	56 m²/g (Anatase/Rutile)
700°C-2 hrs. in Air	31 m²/g (Anatase/Rutile)	46 m²/g (Anatase/Rutile)
850°C-2 hrs. in Air	12 m²/g (Rutile)	20 m²/g (Anatase/Rutile)
Treatment	Al_2O_3** (Degussa γ-Aluminum Oxide C)	2.9% Nb_2O_5/Al_2O_3** (Degussa γ-Aluminum Oxide C)
500°C-16 hrs. in Air	99 m²/g	97 m²/g
1100°C-16 hrs. in He/O_2/H_2O	7 m²/g	71 m²/g

* J. M. Jehng, F. D. Hardcastle, and I. E. Wachs, Solid State Ionics 32/33, 904, 1989

** L. L. Murrell and D. C. Grenoble, U. S. Patent 4,415,480, 1983

TABLE 5

Surface niobium oxide phase forms strong Brønsted acid sites on oxide supports

Method of Bronsted Acidity Determination	Oxide Materials	
	TiO_2-	10% Nb_2O_5/TiO_2-
Isomerization of Cyclo-propane to Propene	5% Coversion	20% Coversion
	Al_2O_3 (Degussa γ-Alumina Oxide C)	2.9% Nb_2O_5/Al_2O_3
Modified Benesi Method	3 μMoles/g (S.A.C.--)	50 μMoles/g (S.A.C--)
Light Gas Oil Cracking (Relative Activity)	1---	76---

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these novel catalytic materials.

A new application of supported niobium oxide catalysts is the redox properties found for Nb_2O_5/SiO_2 and Nb_2O_5/PVG catalysts during photocatalytic oxidative dehydrogenation of alcohols (2-propanol) and olefins (ethylene and propylene) /14,17/. The surface niobium oxide phases on silica and PVG are catalytically active only when the surface niobium oxide phases are irradiated with ultraviolet light in the presence of alcohols and olefins. The UV-VIS absorption measurements showed that the surface niobium oxide phases were reduced by the alcohols and olefins during irradiation to form Nb^{+4}, and were reoxidized by gaseous oxygen. Thus, the surface niobium oxide phases on silica and PVG possess redox properties for photocatalysis.

Another significant new application of supported niobium oxide catalysts is the promotional effect of niobium oxide upon V_2O_5/TiO_2 catalysts for selective reduction of NO_x with NH_3 /22/. The addition of niobium oxide to V_2O_5/TiO_2 catalysts significantly increases the catalytic activity and allows the reaction to be performed at lower temperatures. The low reaction temperatures are important for emission control of stationary sources which usually operate at temperatures less than 300°C. The surface niobium oxide phases also suppress the oxidation of SO_2 to SO_3, a highly undesirable side reaction, over the V_2O_5/TiO_2 catalysts. In addition, the surface niobium oxide phases on titania stabilize these catalysts during high temperature treatments to reactivate the catalyst.

The catalytic applications of supported niobium oxide catalysts are summarized in Tables 6-8.

4. HYDRATED NIOBIUM OXIDE

Hydrated niobium oxide, $Nb_2O_5 \cdot nH_2O$, is a new type of strong solid acid exhibiting high catalytic activity and selectivity for hydration of olefins, dehydration of alcohols, esterification of carboxylic acids with alcohols, and condensation of bultylaldehyde /23-27/. Hydrated niobium oxide catalyzes the hydration of ethylene to ethanol with 97% selectivity, high activity and long catalyst life. The esterification of ethyl alcohol with acetic acid occurs over hydrated niobium oxide with 100% selectivity. The dehydration of butylaldehyde to 2-ethylhexenal over hydrated niobium oxide is achieved with 92.5% conversions and 95.5% selectivity without the catalyst contaminating the product and effluent, as usually occurs.

Acidity measurements have shown that considerable strong Brønsted acid sites are presented on hydrated niobium oxide when it is

TABLE 6

Catalytic applications of niobium oxide supported on silica

- Olefin metathesis

- Olefin Dimerization

- Olefin Isomerization

- Alcohol dehydrogenation

- Acetylene trimerization to benzene

- Methyl methacrylate from condensation of HCHO and methyl propionate

- Photocatalysis of alcohol and olefin

TABLE 7

Catalytic applications of niobium oxide supported on alumina

- Light gas oil cracking

- Hydrocarbon isomerization

- Alcohol dehydration

- Acetylene trimerization to benzene

TABLE 8

Catalytic applications of niobium oxide supported on titania

- H_2S and CO to CH_3SH and CH_3SCH_3
- Selective reduction of NO_x to N_2 and H_2O
- Alcohol dehydrogenation

treated at 120-300°C. The acidity and catalytic activity decreases dramatically at high temperature treatments (>400°C) due to loss in surface area, removal of water, and crystallization of the hydrated niobium oxide structure. However, the addition of phosphoric acid to the hydrated niobium oxide surface retards the loss in surface area during high temperature treatments (400-600°C) and enhances the surface acidity. The H_3PO_4-treated niobium oxide catalysts exhibit high activity for the alkylation of benzene with methanol as shown in Table 9 /28/. The catalytic activity depends on the H_3PO_4 concentration, and 1 mol/dm^3 H_3PO_4 on the hydrated niobium oxide surface possesses the highest activity for alkylation of C_6H_6 to $C_6H_5CH_3$.

Recently, hydrated niobium oxide, $Nb_2O_5 \cdot nH_2O$, was also found to be an effective catalyst for the hydrolysis, isomerization, and solvolysis of phenyloxirane in liquid solutions /30/. The hydrolysis of phenyloxirane in liquid solutions over some solid acid catalysts is presented in Table 10, and $Nb_2O_5 \cdot nH_2O$ exhibits a higher activity and selectivity towards 1-phenyl-1, 2-ethanediol than the other solid acid catalysts due to its high surface hydrophilicity /29/.

5. NIOBIUM OXIDE SUPPORT

Recent catalytic studies have revealed that niobium oxide is a highly effective oxide support material for supported metallic catalysts used in

TABLE 9

Alkylation of benzene with methanol over H_3PO_4-treated niobium oxides

Catalyst	Conversion of C_6H_6 to $C_6H_5CH_3$ for 50mg catalyst (mol%·m^{-2})
Nb_2O_5	0.3
0.5M H_3PO_4/Nb_2O_5	2.3
1.0M H_3PO_4/Nb_2O_5	2.5
2.0M H_3PO_4/Nb_2O_5	2.1
5.0M H_3PO_4/Nb_2O_5	0.35

TABLE 10

Hydrolysis of phenyloxiran over $Nb_2O_5 \cdot nH_2O$ in liquid solution

Catalyst	Conversion (%)	Selectivity (%)	
		PA	PE
$Nb_2O_5 \cdot nH_2O$	100	11.4	88.6
$SiO_2-Al_2O_3$ (Al₂O₃·13.5 wt%)	96.1	34.8	61.2
$SiO_2-Al_2O_3$ (Al₂O₃·28.5 wt%)	92.0	36.4	55.7
Zeolite (SiO₂/Al₂O₃·2100)	36.3	33.8	2.5

PA: Phenylacetaldehyde
PE: 1-Phenyl-1,2-ethanediol

carbon monoxide hydrogenation to synthetic fuels and chemicals /30/. Niobium oxide has been recently used as support for metals such as Ru, Rh, and Ni /30-32/ and exhibit higher olefin selectivity during carbon monoxide hydrogenation compared to conventional oxide supports such as alumina and silica. The influence of the oxide support upon supported ruthenium catalysts during the hydrogenation of carbon monoxide to synthetic fuels is presented in Table 11 /31/. Supported ruthenium on niobia decreases the formation of methane and by-products, and increases the yield of olefins. The influence of the oxide support on the supported rhodium catalysts during the hydrogenation of carbon monoxide to synthetic fuels is also presented in Table 12 /30/. The

TABLE 11

Hydrogenation of carbon monoxide to synthetic fuels over supported ruthenium catalysts

Catalyst	Temp. (°C)	CO Conversion (%)	Selectivity (%)	
			CH_4	$> C_2$
Ru	226	3.5	96	4
1% Ru/SiO_2	223	4.1	87	13
1% Ru/Al_2O_3	228	8.8	66	34
1% Ru/Nb_2O_5	244	5.7	41	59

TABLE 12

Hydrogenation of carbon monoxide to synthetic fuels over supported rhodium catalysts

Catalyst	Temp. (°C)	CO Conversion (%)	Selectivity (%)			
			C_1	C_2	C_3-C_5	CO_2
2.3% Rh/Nb_2O_5	220	75.9	71.8	6.8	19.7	1.7
2.3% Rh/Al_2O_3	220	1.4	89.2	7.6	-	3.2

niobia supported rhodium catalysts exhibit very high activity and selectivity towards olefin production compared to the analogous alumina supported systems.

Metal oxides can also be supported on niobium oxide. The niobium oxide support promotes the catalytic properties of the supported vanadium and molybdenum oxide catalysts during the dehydration of isopropanol to propene (see Table 13 and 14). The niobia supported molybdenum oxide catalysts exhibit higher isopropanol dehydration activity and propene selectivity than bulk MoO_3 /33/. Similarly, the niobia supported vanadium oxide catalysts exhibit a 60-230 increase in activity relative to bulk V_2O_5 for the dehydration of isopropanol to propene /34/.

6. NIOBIUM MIXED OXIDES

Niobium oxide reacts with most metal oxides to form new niobium mixed oxide phases. The molecular structures of these niobium mixed oxide phases depend on the relative composition of the

TABLE 13

Dehydration of isopropanol to propene over supported MoO_3/Nb_2O_5 catalysts

Catalyst	Conversion (%)	Selectivity (%)	
		Acetone	Propene
MoO_3	0.5	46	54
3 wt% Mo/Nb_2O_5	4	49	51
5 wt% Mo/Nb_2O_5	10	30	70
8 wt% Mo/Nb_2O_5	9	21	79
Nb_2O_5	very low	nondetectable	

TABLE 14

Dehydration of isopropanol to propene over supported V_2O_5/Nb_2O_5 catalysts

Catalyst	Activity molecules·mg$(V_2O_5)^{-1}$·s^{-1}
V_2O_5	1×10^{17}
0.14 wt% V_2O_5/Nb_2O_5	2.3×10^{19}
0.59 wt% V_2O_5/Nb_2O_5	8×10^{18}
0.95 wt% V_2O_5/Nb_2O_5	6×10^{18}

mixed oxides and the calcination temperature. Niobium mixed oxides have a pronounced impact on the resulting niobium oxide catalytic properties especially in the area of selective oxidation reactions. The presence of niobium oxide as a catalyst component usually shows an improvement in both the catalytic activity and selectivity. Some of the most widely used niobium mixed oxide catalysts are found in selective oxidation and pollution abatement reactions, and are presented as follows:

Nb_2O_5-MoO_3 mixed oxides with a niobium to molybdenum atomic ratio between 0.5 and 2 exhibit high selectivities to acrylic and methacrylic acids for acrolein oxidation /35/. The selective oxidation of isobutylene to methacrolein over the mixed oxides $Mo_{12}Bi_9O_x$, $Mo_{12}Nb_3O_x$, and $Mo_{12}Bi_9Nb_3O_x$ are shown in Table 15 /36/. Catalysis studies indicate that the bismuth molybdate-niobate systems result in much higher isobutylene conversion (96%) and methacrolein selectivity (74%). Similar improvements for these niobium mixed oxide catalysts were also found for the selective

TABLE 15

The conversion of isobutylene to methacrolein over niobium mixed oxide catalysts

Mixed oxide catalyst	Isobutylene conversion	Methacrolein selectivity	CO and CO_2 selectivity
$Mo_{12}Bi_9O_x$	71.5	69.9	24.8
$Mo_{12}Nb_3O_x$	82.6	65.8	29.1
$Mo_{12}Bi_9Nb_3O_x$	96.1	74.4	22.7

oxidation of propylene to acrolein, propylene ammoxidation to acrylonitrile, and butene oxidative dehydrogenation to 1,3-butadiene.

The oxidation dehydrogenation of ethane to ethylene is also improved by adding niobium oxide to mixed molybdenum and vanadium oxide materials as shown in Table 16 /37/.

The addition of niobium oxide to the MoO_3-V_2O_5 mixed oxides enhances the selectivity for the oxidation of ethane to ethylene to 100% and significantly lowers the reaction temperature (286°C) required to achieve 10% conversion.

Niobium oxide was also found to promote

TABLE 16

Oxidative dehydrogenation of ethane to ethylene over niobium mixed oxide catalysts

Mixed oxide catalyst	Temperature(°C) for 10% conversion	Ethylene selectivity
$Mo_{1.0}$	500	88
$Mo_{0.92}V_{0.08}$	562	59
$Mo_{0.8}V_{0.2}$	540	100
$Mo_{0.8}Nb_{0.2}$	634	74
$Mo_{0.73}V_{0.18}Nb_{0.09}$	286	100

vanadium pentoxide catalysts for the oxidation of o-xylene to phthalic anhydride as shown in Table 17 /38/, and the catalytic activity was found to depend on the Nb_2O_5

concentration. A 3:2 ratio of the Nb_2O_5/V_2O_5 mixed oxide catalyst exhibits the highest activity for the oxidation of o-xylene to phthalic anhydride.

TABLE 17

Oxidation of o-xylene to phthalic anhydride over over niobium mixed oxide catalysts

Mixed oxide catalyst	Activity $(mol \cdot g^{-1} \cdot min^{-1} \times 10^5)$
V_2O_5	2.2
$20\ Nb_2O_5$-$80\ V_2O_5$	5.7
$40\ Nb_2O_5$-$60\ V_2O_5$	8.2
$60\ Nb_2O_5$-$40\ V_2O_5$	11.8
$80\ Nb_2O_5$-$20\ V_2O_5$	7.0

Niobium oxide has recently been found to be an effective promoter for the reduction of NO_x with NH_3 to N_2 and H_2O over iron oxide catalysts /39/. The presence of niobium oxide in the FeO_x catalyst remarkably enhanced the catalytic activity for NO_x reduction from 40% conversion to 90%

conversion at reaction temperatures between 300 and 400°C as shown in Table 18. The catalytic activity for the reduction of NO_x with NH_3 to N_2 and H_2O over a TiO_2 catalyst is also considerably enhanced by adding Nb_2O_5 /22/.

TABLE 18

NOx reduction with NH_3 to N_2 over niobium mixed oxide catalysts

Mixed oxide catalyst	NO_x conversion at 300°C (%)	NO_x conversion at 400°C (%)
FeO_x	40	15
5 Nb_2O_5-95 FeO_x	87	78
20 Nb_2O_5-80 FeO_x	90	95
50 Nb_2O_5-50 FeO_x	85	92
80 Nb_2O_5-20 FeO_x	62	90
95 Nb_2O_5-5 FeO_x	45	78
Nb_2O_5	12	42

7. CONCLUSIONS

The literature review of niobium oxide catalysts reveals that niobium-based materials are effective catalysts for many catalytic reactions: pollution abatement, selective oxidation, hydrocarbon conversion, dehydrogenation, carbon monoxide hydrogenation for synthetic fuels and chemicals, hydration/dehydration, and photochemistry. The niobium oxide catalytic materials are present as bulk layered niobium oxides, surface niobium

oxide phases, hydrated niobium oxide, oxide support, or mixed oxide. Recent research activities are focusing on the development of new niobium-based catalysts such as surface niobium oxide phases and layered niobium oxide compounds. The surface niobium oxide phase has a pronounced effect on the physical and chemical properties of oxide supports (i.e., acidity and thermal stability), and these important characteristics are being utilized in many catalytic applications. However, the molecular states of the surface niobium oxide phases on oxide supports

as well as the relationships between the molecular structures of the surface niobium oxide phases and the corresponding catalytic properties are not presently understood and are essential for the molecular design of improved niobium-based catalysts.

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