

Redox properties of niobium oxide catalysts

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Abstract

Niobia catalysts can contain niobium oxide as a two-dimensional niobium oxide overlayer (surface niobia species), an oxide support (niobia supported surface redox sites) or a mixed oxide (solid solution or compound of niobium oxide). The molecular structures and redox properties of these different niobia-containing catalysts are investigated for several different oxidation reactions. These studies reveal that niobia present as surface metal oxide species, an oxide support and mixed oxides can directly as well as indirectly influence the redox properties of oxide catalysts.

Keywords: Niobium oxide catalysts; Redox properties

1. Introduction

Niobium-based materials are effective catalysts in numerous catalytic applications [1,2]: pollution abatement, selective oxidation, hydrocarbon conversion reactions, hydrogenation and dehydrogenation, hydrotreating, carbon monoxide hydrogenation, dehydration and hydration, photochemistry and electrochemistry, and polymerization. The number of niobium catalyst literature references have been steadily increasing over the past two decades, which reflects the growing interest in this area of catalysis [1–4]. A major application of niobium-based catalysts has been in the area of oxidation catalysis and this article will review the fundamental information currently available about the redox properties and molecular structures of niobium oxide catalysts. Niobia catalysts can contain niobium

oxide as a two-dimensional niobium oxide overlayer (surface niobia species), an oxide support (niobia supported surface redox sites) or a mixed oxide (solid solution or compound of niobium oxide), as shown in Fig. 1.

2. Molecular structural determination of niobia catalysts

Fundamental information about the molecular structures of niobia in niobium-based catalytic materials can be obtained with Raman spectroscopy and EXAFS/XANES measurements. Raman spectroscopy provides information about the Nb–O bond length and bond order since these parameters are directly related to the Nb–O vibrational frequencies [5]. Terminal Nb=O bonds typically occur between 850–1000 cm⁻¹ and Nb–O bonds usually occur between 500–700 cm⁻¹. The coordination of niobia can be

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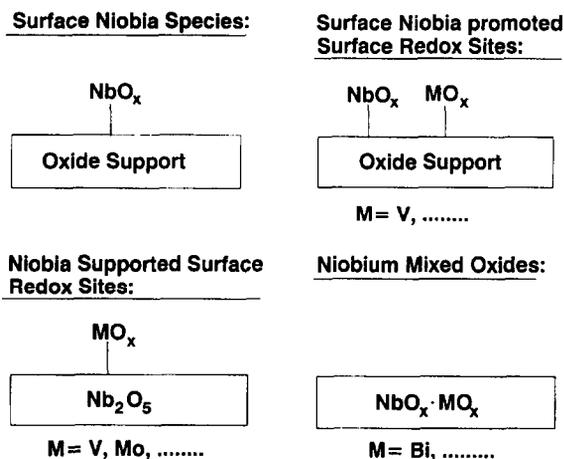


Fig. 1. Structural arrangements of niobium oxide catalysts.

determined with XANES and EXAFS provides additional information about the number and distances of the Nb–O bonds [6]. Raman spectroscopy and EXAFS/XANES have been the primary characterization techniques for surface niobia species and niobia supported surface redox sites (see Fig. 1) because of the amorphous nature of the two-dimensional overlayers that are present in such catalytic materials [5–8]. X-ray diffraction (XRD), high resolution electron microscopy (HREM) as well as Raman and EXAFS/XANES have been the usual techniques employed to characterize niobium mixed oxides (see Fig. 1) [5,6,9,10]. However, only Raman and EXAFS/XANES are capable of providing fundamental molecular structural in-

formation about the niobia sites in powdered niobium mixed oxide catalytic materials.

3. Surface niobia species

Surface niobia species are formed by depositing niobium-containing salts (alkoxides, chlorides, oxalates, allyl, etc.), with the aid of suitable solvents such as water or alcohol, on high surface area oxide supports (e.g., alumina, silica, titania, etc.). These materials are subsequently dried and calcined at elevated temperature to anchor the niobia species to the oxide supports. The surface niobia species primarily anchor to the oxide supports by titrating the surface hydroxyls initially present on the support [11].

Three different surface niobia species on oxide supports have been identified with in situ Raman and XANES studies and are depicted in Fig. 2 [6,8,12]. Four-fold coordinated surface NbO_4 species are only found at very low surface coverages and give rise to Raman bands at $980\text{--}990\text{ cm}^{-1}$. Five-fold coordinated surface NbO_5 species are present at intermediate surface coverages and give rise to Raman bands at $930\text{--}950\text{ cm}^{-1}$. Six-fold coordinated surface NbO_6 species are typically found at high surface coverages and give rise to Raman bands at about $630\text{--}650\text{ cm}^{-1}$. The relative distribution of these surface niobia species is a function of

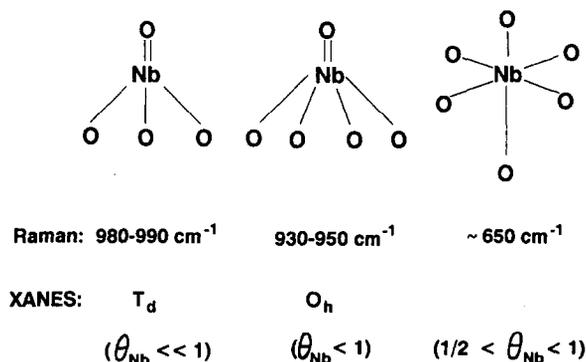


Fig. 2. Structures of surface niobia species determined from Raman and XANES studies.

Table 1
Influence of the specific oxide support on the redox and acid properties of surface niobia species

Catalysts	Redox	Acid	CO + CO ₂
20% Nb ₂ O ₅ / Al ₂ O ₃	0%	100%	0%
7% Nb ₂ O ₅ / TiO ₂	2.5%	96.5%	1%
5% Nb ₂ O ₅ / ZrO ₂	0%	98.0%	2%
2% Nb ₂ O ₅ / SiO ₂	87.2%	5.2%	7.6%

surface coverage and the specific oxide support. For the silica supported niobia species, only the surface NbO₄ species is present because high surface coverages can not be achieved on this support due to the low number and reactivity of the silica surface hydroxyls [13].

The redox and acidic properties of surface niobia species on different oxide supports were chemically probed by the sensitive methanol oxidation reaction and are presented in Table 1 [13,14]. The amount of surface niobia was adjusted to give monolayer coverages on alumina, titania and zirconia, but high coverages of surface niobia species could not be achieved on silica (see above). Only the surface niobia species on silica were found to give rise to redox products (primarily formaldehyde and methylformate) and the surface niobia species on alumina, titania and zirconia primarily gave rise to acidic products (dimethylether). The ability of the surface niobia species on silica to behave as redox sites is not completely understood at present, but may be related to the ease of hydrolysis of the bridging Nb–O–Si bond during methanol oxidation. The surface niobia species on titania also possesses redox activity at elevated temperatures since this catalyst is

active for the selective catalytic reduction of NO_x with NH₃ [15]. The redox activity of this system at elevated temperatures is related to the reducibility of the bridging Nb–O–Ti bond (see discussion in Section 5). Thus, the specific oxide support controls the redox properties of the surface niobia species.

The influence of the preparation method on the molecular structures and reactivity of the surface niobia species on silica was also investigated. The molecular structure of the surface niobia species on silica was found to be independent of the preparation method (oxalate, alkoxide or allyl) and gave rise to a single in situ Raman band at 980–985 cm⁻¹, which is characteristic of surface NbO₄ species (see Fig. 2) [14]. The reactivity and selectivity of the different silica supported niobia catalysts were probed by methanol oxidation and found to yield essentially indistinguishable results as shown in Table 2 (TOF of 7–10 × 10⁻² per s and redox selectivity of 85%–90%). Thus, the synthesis method does not appear to affect the molecular structure and reactivity of the surface niobia species.

4. Surface niobia promoted surface redox sites

Surface niobia species are sometimes present as promoters in catalysts that may positively influence the activity or selectivity of oxidation reactions [1–4]. The influence of surface niobia species on the molecular structure and reactivity of a 1% V₂O₅/TiO₂ catalyst was investigated

Table 2
Influence of the preparation on the molecular structure and reactivity of surface niobia species on silica

Catalysts	Raman band of Nb=O terminal bond (cm ⁻¹)	TOF (s ⁻¹)	Selectivity (%)	
			Redox	Acid
2% Nb ₂ O ₅ /SiO ₂ (Oxalate Prep.)	980	7.1 × 10 ⁻²	87.2	5.2
2% Nb ₂ O ₅ /SiO ₂ (Alkoxide Prep.)	980	8.4 × 10 ⁻²	90.1	3.2
2% Nb ₂ O ₅ /SiO ₂ (Allyl Prep.)	985	10 × 10 ⁻²	84.9	1.9

Redox = HCHO + HCOOCH₃ + CH₂(CH₃O)₂.

Acid = CH₃OCH₃.

CO + CO₂ = 100-Redox-Acid.

with in situ Raman spectroscopy and methanol oxidation. The Raman characterization studies revealed that the presence of the surface niobia species did not change the structure of the surface vanadia species and the methanol oxidation studies demonstrated that the presence of the surface niobia species did not alter the redox properties of the surface vanadia species [16]. The surface niobia species on titania essentially was not active for the oxidation of methanol (especially redox products, see Table 1). However, when the same Nb–V/titania catalyst was used for the selective catalytic reduction of NO_x with NH_3 the presence of the surface niobia species had a dramatic effect on the activity and selectivity (see Table 3). The activity at low temperatures was increased by approximately an order of magnitude and the selectivity towards N_2 formation at complete conversion of NO was essentially 100% [15]. Although the addition of surface tungsten oxide species (the conventional promoter) to the titania supported vanadia catalyst also increased the activity, the presence of the surface tungsten oxide species resulted in a somewhat lower selectivity towards N_2 formation at 100% conversion of NO . The different responses of the methanol oxidation and SCR reaction at low temperatures to the addition of the surface niobia sites is a consequence of the different requirements of these reactions: the unimolecular methanol oxidation reaction requires only one site (a surface redox site such as a surface vanadia species) to proceed and the bimolecular SCR reaction requires two sites (a surface redox site and an

Table 3
Selective catalytic reduction of NO_x with NH_3 over unpromoted and promoted vanadia/titania catalysts

Catalysts	TOF at 473 K (s^{-1})	Selectivity to N_2 at 100% NO conversion (623 K)
1% $\text{V}_2\text{O}_5/\text{TiO}_2$	2.9×10^{-4}	100%
6% $\text{V}_2\text{O}_5/\text{TiO}_2$	1.6×10^{-3}	78%
6% $\text{Nb}_2\text{O}_5/1\% \text{V}_2\text{O}_5/\text{TiO}_2$	2.1×10^{-3}	100%
7% $\text{WO}_3/1\% \text{V}_2\text{O}_5/\text{TiO}_2$	2.1×10^{-3}	91%

Table 4
Butane oxidation over surface niobia promoted V–P–O catalysts

Catalysts	n-Butane Conversion (mol-%)	Selectivity to MAN (mol-%)
Unpromoted Catalyst	22	36
Nb Promoted Catalyst (ca. 0.5 monolayer)	20	51
Nb Promoted Catalyst (ca. 1 monolayer)	22	42

Feed = 1.2% n-Butane, $T = 653 \text{ K}$.

adjacent surface acid site represented by the surface vanadia and niobia species, respectively) to proceed. Thus, nonreducible surface niobia species can promote oxidation reactions that require an adjacent surface acid site, but not oxidation reactions that require only one surface redox site.

The influence of surface niobia species on butane oxidation to maleic anhydride/acid catalysts was also recently investigated [17]. The addition of surface niobia species to titania supported vanadia catalysts did not influence the butane reaction suggesting that butane oxidation requires only one surface redox site (similar to methanol oxidation). However, the addition of surface niobia species to model vanadyl pyrophosphate catalysts has a significant impact on the selectivity towards maleic anhydride during butane oxidation as shown in Table 4. Similar observations were made by Ye et al. [18]. The oxidation of butane to maleic anhydride requires both surface redox and surface acid functionalities and it is not clear from this study which of these surface sites is being influenced by the niobia additive. Additional studies are required to understand how the surface niobia species promotes the vanadyl pyrophosphate catalyst during butane oxidation to maleic anhydride.

5. Niobium oxide support

Surface metal oxide species can be deposited on a high surface area niobia support by reac-

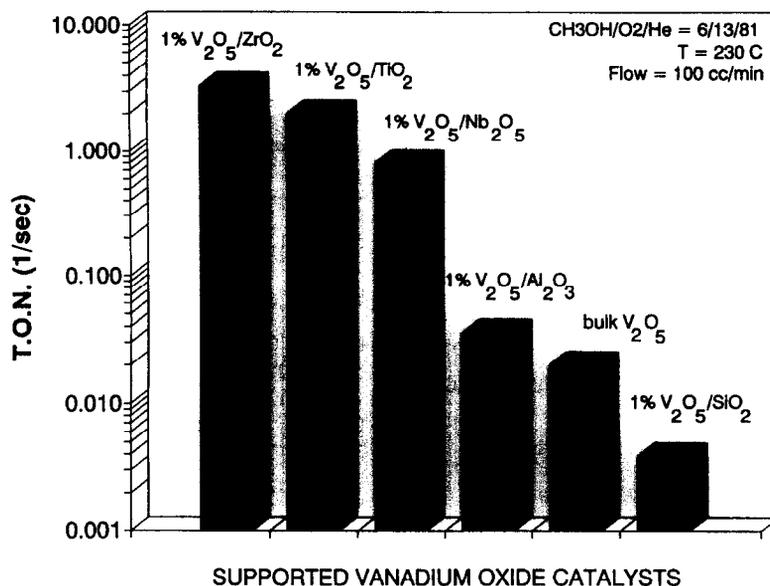


Fig. 3. Redox properties of surface vanadia species on different oxide supports.

tion with the surface hydroxyls of the niobia support. Comparison of the reactivity for surface vanadia species on different oxide supports during methanol oxidation reveals that the niobia supported vanadia species is among the most active catalytic systems (see Fig. 3) [19]. The high reactivity is associated with the ease of reducing the bridging V–O–Nb bond and reflects the redox potential of the niobia support compared to less reducible supports such as silica and alumina (see discussion below). This observation is not unique to the methanol oxida-

tion reaction since similar trends were also observed when other oxidation reactions were investigated over the same series of catalysts: butane [17] and SCR [20]. The influence of the niobia support on the redox properties of several different surface metal oxide species is shown in Table 5 [21]. This table reveals that the redox activity of the surface vanadia > surface chromia > surface molybdena > surface rhenia and that surface phosphate, sulfate and tungstate species do not possess redox activity. The niobia support predominantly possesses Lewis acid

Table 5
The redox and acidity properties of surface modified niobium oxide catalysts

Catalysts	Activity (mmol/g h) [mmol/m ² h]	Selectivity (%)			
		HCHO	CH ₃ OCH ₃	(CH ₃ O) ₂ CH ₂	CO + CO ₂
Nb ₂ O ₅	5.8 [0.145]	5	95	–	–
1% P ₂ O ₅ /Nb ₂ O ₅	36.2 [0.315]	–	100	–	–
1% SO ₄ ²⁻ /Nb ₂ O ₅	32.0 [0.340]	–	100	–	–
1% CrO ₃ /Nb ₂ O ₅	41.0 [0.530]	45.3	46.9	4.5	1.0
1% WO ₃ /Nb ₂ O ₅	10.7 [0.152]	–	98.3	–	1.7
1% Re ₂ O ₇ /Nb ₂ O ₅	8.0 [0.199]	30.4	58.3	5.5	5.8
1% MoO ₃ /Nb ₂ O ₅	15.0 [0.283]	21.8	69.2	7.5	1.5
1% V ₂ O ₅ /Nb ₂ O ₅	74.2 [0.757]	61.4	35.2	–	3.4

HCOOCH₃ = 100 · [HCHO + CH₃OCH₃ + (CH₃O)₂CH₂ + (CO + CO₂)].

All samples were calcined at 773 K.

sites [22] which give rise to dimethylether formation (see Table 5) and the selectivity to dimethylether significantly diminishes as the exposed Nb sites of the support are covered by the surface redox species (V, Cr, Mo and Re) in the two-dimensional overlayer [21]. The ability of the niobia support to produce some formaldehyde during methanol oxidation reveals that it also possesses some redox sites (see Table 5). Thus, the redox properties of surface metal oxide species are enhanced by the intrinsic redox potential of the niobia support.

6. Niobium mixed oxides

Surface niobia species are not stable on basic oxide supports such as magnesia [7,8,13] and bismuth oxide [23] due to incorporation of the acidic Nb^{5+} into these supports as a result of strong acid–base interactions. The influence of calcination temperature on a surface niobia overlayer on bismuth oxide is schematically shown in Fig. 4. The surface niobia overlayer readily reacts with the bismuth oxide support as the calcination temperature is increased. The crystallinity of the Bi–Nb–O phase also increases with calcination temperature. Corresponding XPS surface analysis reveals that the

Table 6

Influence of niobia and calcination temperature on the redox properties of bismuth oxide

Temp (K)	Activity (mol/g h)	Surface area (m^2/g)	Selectivity (%)		
			CO_2	HCHO	CO
Bi_2O_3					
573	128×10^{-3}	3.8	90	9	1
773	25×10^{-3}	1.8	82	18	1
923	3.3×10^{-3}	0.4	36.4	–	63.6
0.6% $\text{Nb}_2\text{O}_5/\text{Bi}_2\text{O}_3$					
573	223×10^{-3}	3.7	98.6	1.4	–
773	132×10^{-3}	1.8	96.6	2.9	0.5
923	58.9×10^{-3}	0.4	53.1	46.9	–

Bi/Nb ratio increases dramatically with increasing calcination temperature and essentially no Nb is detected in the surface region after calcination at 650°C [23]. Raman spectroscopy studies have shown that the Nb^{5+} cations in the Bi–Nb–O mixed oxides consist of NbO_6 units [5,24]. The reactivity and selectivity of bismuth oxide and the niobia–bismuth mixed oxide catalysts were probed with methanol oxidation and are presented in Table 6. For both systems, the surface areas of the catalysts decreased with increasing temperature, but were essentially identical at the same temperature. The niobia–bismuth mixed oxide was always significantly

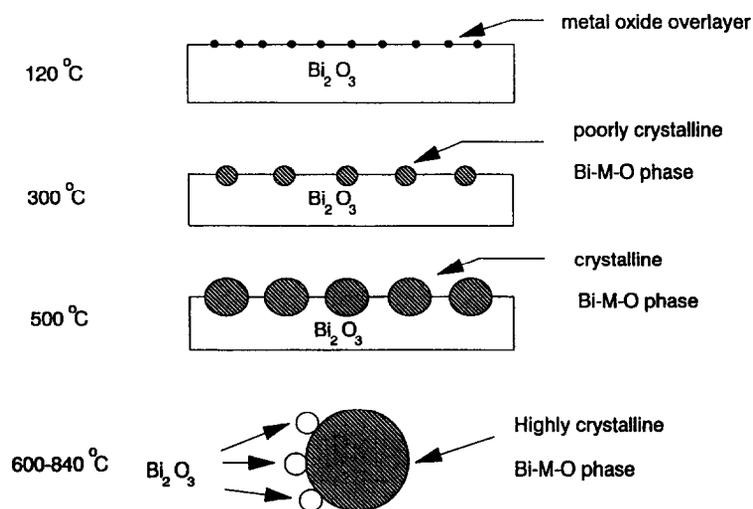


Fig. 4. Evolution of Bi–Nb–O catalyst as a function of calcination temperature.

more active than the unpromoted bismuth oxide catalyst and the difference between the two catalysts increased with calcination temperature. Only the niobia–bismuth mixed oxide catalyst exhibited significant selectivity towards formaldehyde. The higher selectivity to formaldehyde after calcination at elevated temperatures suggests that a highly crystalline niobia–bismuth mixed oxide phase is required for a selective catalyst. Thus, the introduction of niobia to bismuth oxide forms highly crystalline niobia–bismuth mixed oxide phases at elevated temperatures which are significantly more active and selective than the unpromoted bismuth oxide phases.

7. Conclusions

The above review reveals that niobia present as surface metal oxide species, an oxide support and mixed oxides can directly as well as indirectly influence the redox properties of oxide catalysts. At low temperatures, surface niobia redox sites are only present on SiO_2 and surface niobia species on other supports primarily act as surface acid sites. Addition of surface niobia species to vanadia/titania catalysts does not change the molecular structure or redox properties of the surface vanadia species. However, the influence of the surface niobia species depends on the specific requirements of the reaction: reactions requiring only one surface vanadia redox site are not influenced by the surface niobia species (e.g., methanol oxidation) and reactions requiring two adjacent sites, surface redox and acid sites, are enhanced by the surface niobia species (e.g., SCR reaction). The redox potential of the niobia support enhances the redox properties of reducible surface metal oxide species (V, Cr, Mo and Re). Introduction of niobia to mixed metal oxide catalysts can result in enhanced activity and selectivity as shown for the Bi–Nb–O system.

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