



Selective Catalytic Reduction of NO_x by CO over Doubly Promoted MeMo/Nb₂O₅ Catalysts (Me = Pt, Ni, or Co)

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Abstract: Doubly promoted MeMo/Nb₂O₅ catalysts, in which Me = Pt, Ni, or Co oxides were prepared for the selective catalytic reduction of NO_x by CO reaction (CO-SCR). Comparable chemical, textural, and structural analyses revealed similarities between NiMo and CoMo impregnated on Nb₂O₅, in contrast to PtMo sites, which were not homogeneously dispersed on the support surface. Both the acid function and metal dispersion gave a synergistic effect for CO-SCR at moderate temperatures. The reactivity of PtMo catalysts towards NO_x and CO chemisorption was at low reaction temperatures, whereas the NO_x conversion over CoMo was greatly improved at relatively high temperatures. Careful XPS, NH₃-TPD, and HRTEM analyses confirmed that the large amounts of strong and moderate acid sites from PtO_x entrapped on MoO₃ sites induced high NO_x conversions. NiMo/Nb₂O₅ showed poor performance in all conditions. Poisoning of the MeMo sites with water vapor or SO_2 (or both) provoked the decline of the NO_x conversions over NiMo and PtMo sites, whereas the structure of CoMo ones remained very active with a maximum NO_x conversion of 70% at 350 °C for 24 h of reaction. This was due to the interaction of the Co³⁺/Co²⁺ and Mo⁶⁺ actives sites and the weak strength Lewis acid Nb⁵⁺ ones, as well.

Keywords: Nb₂O₅; catalyst; synergistic effect; NO_x; CO-SCR

1. Introduction

The future development of the technologies for the abatement of gases from combustion of fossil fuels and diesel engines will require efficient routes for the conversion of these polluting gases into useful chemicals [1–3]. In this respect, selective catalytic reduction of hydrocarbons (SCR) has been recently claimed to be an extremely promising technology to eliminate exhaust gases [1,4]. This approach results in the reduction of the gases' release into the atmosphere, especially nitrogen oxides (NO_x) , carbon oxides (CO_x) , particulate matter (PM), volatile organic compounds (VOC) and sulfur oxides (SO_x) emissions [5-7].

Current SCR processes are conducted worldwide to control both NO_x and hydrocarbons (HC) pollutant emissions including the NH₃-SCR, HC-SCR, and urea-SCR among other SCR technologies [2,8–12]. Alternatively, another reaction employing SCR is the direct denitrification,



in which NO_x can be promptly converted by CO into CO₂ and N₂, the so-called CO-SCR [3,13]. Thus, the need for robust and efficient catalysts for the CO-SCR reaction (Equations (1) and (2)) has increased dramatically over the past decades with the support and active centers of the catalysts playing an important role in achieving good catalytic performances [3,5].

$$NO + CO \rightarrow 1/2 N_2 + CO_2 \tag{1}$$

$$NO_2 + 2 CO \rightarrow 1/2 N_2 + 2CO_2$$
 (2)

Although the NH₃-SCR is the main technology for NO_x removal from mobile and stationary resources, the CO-SCR would be suitable for the reduction of NO_x emitted from low temperature reaction conditions. Regarding the catalyst supports for CO-SCR, we have recently demonstrated that the NO_x denitrification by CO-SCR reaction takes place through bifunctional γ -Al₂O₃ and Al₂O₃-La₂O₃ supported catalysts with appropriate active metal centers, e.g., Pt, Ni, or Co and acid supports [3,5]. Despite the fact that the solids have high activities for the CO-SCR reaction, there are a number of disadvantages in the reaction such as low tolerance to water and SO₂ poisons [5]. Of all the different niobium oxides i.e., NbO₂, NbO, and Nb₂O₅ niobium-pentoxide also known as niobia, is often cited as the most thermodynamic stable form; certainly, it is far and wide used as a carrier and promoter for catalysts [14]. In particular, Nb₂O₅ is perceived as an efficient material with superior physicochemical properties to catalytic reactions due to its characteristic acidity nature having both Br\u00etnsted and Lewis acid sites. Furthermore, niobium pentoxide has a relatively high specific surface area and water tolerant Lewis acid sites, which are desirable features for catalytic reactions [14,15].

Denitrification of NO_x through SCR reactions over Nb_2O_5 -based catalysts has also been reported, owing to its versatile oxidation state i.e., Nb^{5+} , tunable quantity and strength of the acid sites, relatively low cost and a more resistant structure [16–18]. There are still controversial roles for Nb_2O_5 in SCR reactions. If on the one hand, Nb_2O_5 depicts poor tolerance to sulfur poising due to the competition between SO_2 and NO_x for adsorption sites on the Nb-based catalysts; on the other hand, Nb_2O_5 improves sulfur resistance when Nb is added in low amounts to active phases of the catalysts [19–21].

It should be pointed out that surface sulfates species from SO_2 block Nb⁵⁺ active sites for the NO_x-SCR. Consequently, sulfates may hinder the formation of isocyanates e.g., NCO intermediate during the HC-SCR reaction, which implies the inhibitory effect on the aci-nitromethane intermediate formation. The latter entity is responsible for the formation of the NCO species coordinated to the Me sites ([15,19,22] and references herewith).

Both aci-nitromethane and isocyanates are the main HC-SCR reaction active intermediates and, therefore, their low production caused by the sulfation of the solids may decrease the catalytic performance [15]. Thereby, sulfur may also limit the availability of the niobia surface and thus, result in drawbacks to disperse the active metals and consequently, overcome the SO₂ tolerance ability of niobia.

The distinct effects of niobia on the SCR reaction are still under debate. On the basis of the idea of combining the advantages of the acidity of Nb_2O_5 and MoO_3 promoter, herein, modified MeMo/Nb₂O₅-based catalysts were prepared for the CO-SCR reaction. Molybdenum helps to disperse the active metal sites during the HC-SCR reactions [5]. Thus, by adding molybdenum in niobia, it should be possible to determine improvements in the metals' dispersions on the niobia surface. In addition, the complementary investigations on the role of the active metal dispersion e.g., Pt, Co, or Ni in the CO-SCR reaction is also studied under mild reaction conditions.

2. Results and Discussion

2.1. Structure by XRD and Raman Measurements

XRD patterns of the catalysts are depicted in Figure 1. The diffractograms of all catalysts exhibit peaks of high intensity along with broad and weak ones. Some of these diffraction peaks with the (001), (180), (200), (201), (181), (002), (580), and (182) planes can be indexed to the δ -Nb₂O₅ orthorhombic structure (space group *Pbam*, JCPDS: 30-0873).





Figure 1. XRD patterns of the catalysts: (a) CoMo/Nb₂O₅, (b) NiMo/Nb₂O₅ and (c) PtMo/Nb₂O₅.

Other diffraction peaks appearing at 20 values of 23.8, 26.7, 35.2, 43.6, 45.1 and 56.4° are indexed as (001), (100), (101), (002), (110) and (182), respectively. These reflections are associated with the pseudohexagonal γ -Nb₂O₅ structure matching well with the space group (P6/mmm, JCPDS: 28-317).

The niobium pentoxide exists in several structures with the polymorphs mostly being derived from the ReO₃ type structure. The main phase for Nb₂O₅ occurs upon calcination of the amorphous niobium oxide in the 600–800 °C range with predominance of orthorhombic structure e.g., T-Nb₂O₅ while the pseudohexagonal one, e.g., TT-Nb₂O₅ is observed at lower temperatures [23–28].

It is worth mentioning that the coexistence of the mixture of δ -Nb₂O₅ orthorhombic and pseudohexagonal γ -Nb₂O₅ phases arises upon calcination of the solids at 700 °C with the latter phase being predominant. Importantly, the sharp diffraction peaks with narrow widths for δ -Nb₂O₅ phase suggest the high crystallinity of the crystals whereas the weak peaks with broad widths hint that there are relatively small crystal sizes. The poor crystallinity of the δ -Nb₂O₅ structure is observed through their low intensity and broad diffraction peaks. Moreover, it is apparent that some peaks of very low intensity arise with the (110), (140), (130), (111), (160), and (211) planes, which are ascribed to be from α -MoO₃ [5]. Additionally, the average crystallite sizes are estimated to be 24 nm through the (001) plane of the prominent peak at $2\theta = 22.5^{\circ}$ for δ -Nb₂O₅, as estimated using the Scherrer equation. Noteworthy, CoMo/Nb₂O₅ has XRD peaks comparable to those of the support (Figure 1a) besides the α -MoO₃ phase but, a small peak detected at $2\theta = 23.3^{\circ}$ (002) is due to the Co₃O₄ phase. Furthermore, the impregnation of the transition metal oxides on the Nb₂O₅ support does not show characteristic diffraction patterns neither for PtO_x in PtMo/Nb₂O₅ catalyst (Figure 1c) nor NiO as in the case of $NiMo/Nb_2O_5$ one (Figure 1b). This result can be understood taking into account that the amount of metal oxides is extremely low e.g., 1 wt % to generate diffraction peaks in these catalysts. In addition, the Ni and Pt oxides may be well-dispersed on the Nb₂O₅ support due to the action of α -MoO₃ as a promoter to disperse these oxides. Indeed, our previous work reported that Mo oxide helps the dispersion of PtO_x and NiO oxides onto Al_2O_3 -La₂O₃ support [5]. This is also in

accordance with further HRTEM measurements that undergo the dispersion of the nanoparticles onto the Nb_2O_5 support.

Raman spectra depict the structural features of the catalysts (Figure 2). In all the spectra, the strong bands below 150 cm⁻¹ (highlighted in the squares) are attributed to the external modes of the metal–metal vibrations [23]. According to the findings, Nb₂O₅ crystal structure has both NbO₆ octahedra and NbO₄ tetrahedra with the corner and edge shared octahedra vibrations clearly visible by the ν_1 mode of the Nb-O bonds [23,28].



Figure 2. Raman spectra of the catalysts: (a) CoMo/Nb₂O₅, (b) PtMo/Nb₂O₅, and (c) NiMo/Nb₂O₅.

In addition, the pseudohexagonal γ -Nb₂O₅ involves constitutional defects of an oxygen atom per unit cell. Moreover, these defects may interact to give tetra and penta bipyramids with 6 or 7 oxygen atoms shared per niobium atom [24,26]. In the case of the orthorhombic Nb₂O₅, the unit cell can be described as much distorted NbO₆ octahedra and NbO₇ pentagonal bipyramids with 6 or 7 oxygen atoms coordinated per niobium atom [24]. The broad band located at 200–300 cm⁻¹ is assigned to the bending vibrations of the Nb-O-Nb bonds [26,27]. Moreover, the internal modes at 400–750 cm⁻¹ assign the stretching of the Nb-O vibrations, while the band at around 600–650 cm⁻¹ is associated with the v₂ transverse optical mode of Nb-O stretchings [23,24,27]. Besides, it can be noticed that at 930 cm⁻¹, a relatively preeminent mode indicates the high concentration of terminal surface Nb=O groups, whereas the modes at around 906 and 992 cm⁻¹ are associated with the longitudinal optic mode of edge shared O-Nb=O stretchings [23]. Also, the assignment of the vibrational modes of the solids is shown in Table S1 (Supplementary Material).

Hence, Raman spectra are consistent with the XRD results, confirming the existence of both pseudohexagonal and orthorhombic Nb_2O_5 phases in the catalysts.

It is important to note that the terminal oxygen bonds of Mo=O also appear in the range of 900–1000 cm⁻¹ while the translational Raman bands of α -MoO₃ arises below at 130 cm⁻¹ [5,23].

Another observation is that the aforesaid v_2 mode of Nb-O stretching appears in the same region e.g., around 600 cm⁻¹ as those of the triply coordinated oxygen (Mo₃-O) stretching mode arising from the edge-shared oxygen in common with three octahedra [23]. Therefore, the modes of Nb₂O₅ and α -MoO₃ may be overlapped in the Raman spectra. This can be related to the fact that the Mo oxide is dispersed on the Nb₂O₅ support, as suggested by XRD measurements.

Moreover, the Raman spectrum of the CoMo/Nb₂O₅ (Figure 2a) depicts a sharpening of the bands at 199, 483, and 687 cm⁻¹ owing to the ordered structure existing in either δ -Nb₂O₅ or Co₃O₄ phase. More importantly, both PtMo/Nb₂O₅ (Figure 2b) and NiMo/Nb₂O₅ (Figure 2c) have almost the same Raman spectra, in terms of shapes and intensities of the bands. Nevertheless, some shifts in the position of the modes occur in the case of the symmetric stretching Raman bands from 640 to 700 cm⁻¹ due to the band order of the niobia polyhedra. This is consistent with the observations reported in the literature [28]. In addition, no modes of the Ni and Pt metal oxides are observed, confirming their good dispersion on the support.

2.2. Texture and Morphology

The textural properties of the catalysts are examined through nitrogen adsorption–desorption isotherms (Figure 3A).



Figure 3. Cont.



Figure 3. (**A**) Nitrogen physisorption isotherms and (**B**) their corresponding the pore size distribution curves of the catalysts: (**a**) CoMo/Nb₂O₅, (**b**) PtMo/Nb₂O₅, and (**c**) NiMo/Nb₂O₅.

The curves of all samples undergo prominently type-IV isotherm with an H₃ hysteresis loop. According to the IUPAC classification, this type of isotherm is characterized by a sharp capillary condensation step. Additionally, the hysteresis loop is seen at P/P₀ relative pressures close to the saturation pressure e.g., P/P₀ = 0.8–1.0. This is an indication of the presence of slit-shaped pores formed from aggregates of plate-like particles [27]. Moreover, the surface area, total volume, and average pore diameter are listed in Table 1. The Nb₂O₅ support has surface area of about 87 m² g⁻¹ and pore volume of 0.16 cm³ g⁻¹. These values are close to those of the orthorhombic and pseudohexagonal Nb₂O₅ phases obtained at temperature above 600 °C [25].

Compared to Nb₂O₅ support, the textural parameters of the MeMo/Nb₂O₅ supported solids slightly dropped, after loading niobia with CoMo. On the contrary, impregnation of the NiMo and PtMo on niobia gives lower values of the textural parameters, especially for PtMo/Nb₂O₅, which is less than twice that of CoMo/Nb₂O₅ (50 m² g⁻¹ and pore volume of 0.10 cm³ g⁻¹). The various calcination processes to which the MeMo/Nb₂O₅ supported solids are submitted may be responsible for the crystal growth and aggregation of the particles, hence, decreasing the textural parameters of PtMo/Nb₂O₅ and NiMo/Nb₂O₅. These results also illustrate that the good dispersion of the CoMo particles on Nb₂O₅ gives the highest textural parameters, in opposition to the large Pt particles on the support causing the decrease of the textural parameters of the PtMo/Nb₂O₅ solid. Another possibility is that some Pt oxide particles may block the pores of the support, resulting in the reduction of both surface area and pore volume of the catalyst. Also, some agglomeration of Ni oxide particles on the support may cause

the decrease of the textural parameters of the NiMo/Nb₂O_{5.} These observations are further confirmed by SEM-EDS.

Additionally, the pore size distribution curves are broad with the presence of mesopore diameter centered in the range of 21–46 Å (Figure 3B). As it can be seen, PtMo/Nb₂O₅ experiences a remarkable drop in the pore size (Table 1) compared to the other samples due to the pore blockage by Pt particles.

Table 1. Summary of the physicochemical properties of the solids. Total acidity and density of the acid sites are taken by NH₃-TPD whereas the textural properties are obtained from the nitrogen physisorption isotherms.

Catalysts	^a Total Acidity (μmol NH ₃ ·g ⁻¹)	Density of the Acid Sites (µmol _{NH3} ·m ⁻²)	Textural Properties				
			BET Surface Area (m ² ·g ⁻¹)	Pore Volume (cm ³ ·g ⁻¹)	^b Pore Diameter (Å)		
Nb_2O_5	275	3.2	87	0.16	46		
CoMo/Nb ₂ O ₅	88.5	1.8	50	0.10	38		
NiMo/Nb ₂ O ₅	358	8.3	43	0.09	35		
PtMo/Nb2O5	438	17.5	25	0.06	21		

^a NH₃-TPD; ^b From BJH method.

Although the samples are mostly mesoporous, the supported solids also have micropores located within 1 nm that are formed during the calcination processes.

The morphologies of samples are observed by means of SEM-EDS micrographs (Figure 4). As it can be seen, the SEM micrographs indicate that the solids are formed of plates, some of them composed of aggregated nanorods like morphology. These aspects clearly evidence that the catalysts have the same morphology regarding the formation of the platelets with undefined shapes, after the successive calcination processes to which they are submitted. This matches well with the textural properties that suggest the low values of surface area and pore volumes, compared to Nb₂O₅ support, due to the larger sizes of the MeMo/Nb₂O₅ solids. Particularly, NiMo/Nb₂O₅ and PtMo/Nb₂O₅ experience a reduction of their textural properties coming from both the rise in temperature and formation of large particles.



Figure 4. Cont.



(c)

Figure 4. SEM-EDS and HRTEM micrographs of the catalysts: (**a**) PtMo/Nb₂O₅, (**b**) NiMo/Nb₂O₅ and (**c**) CoMo/Nb₂O₅.

Furthermore, the elemental mapping in Figure 4a illustrates the agglomeration of Pt particles, which are surrounded by Mo ones in the PtMo/Nb₂O₅ solid. Accordingly, the contents of Nb, O, Pt, and Mo measured by EDS are 78.1, 10.1, 2.8 and 1.7%, respectively. This means that the Pt/Nb ratio on

the surface is of 0.036, which is considered to be very high as a consequence of the uneven distribution Pt species on the surface of the Nb_2O_5 support.

Moreover, Figure 4b also displays the presence of Ni distributed on the surface of the NiMo/Nb₂O₅ catalyst. Indeed, some of these Ni particles are highly agglomerated and close to those of Mo ones on the Nb₂O₅ support. The contents of Nb, O, Mo, and Ni are 75.4, 21.6, 0.9 and 2.1%, respectively. Accordingly, the Ni/Nb ratio on surface is 0.027, being very high as a consequence of the NiO agglomeration on the solid surface. On the contrary, EDS mapping of CoMo/Nb₂O₅ (Figure 4c) reveals the homogeneous distribution of cobalt particles on the solid surface with Nb, O, Co, and Mo contents of 73.6, 23.0, 1.3 and 2.1%, respectively. Indeed, the Co/Nb is of approximately 0.028, which is indicative of the Co species on solid surface. The Mo helps the dispersion of the of small Co particles, in agreement with the findings [5,29]. This is consistent with the results from textural parameters showing relatively high textural properties for CoMo/Nb₂O₅, most probably due to the small size of the Co particles compared to those of Pt and Ni.

The morphology and structure of the solids are also investigated by TEM. The PtMo/Nb₂O₅ catalyst shows nanoparticles identified as PtO_x with a d spacing of 0.23 nm, corresponding to the Pt (111) plane. These PtO_x particles are surrounded by the large dark MoO₃ particles of various sizes (Figure 4a). In addition, the lattice fringe size of ca. 0.31 nm in the brightest areas confirms the presence of the (180) plane of the orthorhombic γ -Nb₂O₅ phase. The *d* spacings of ca. 0.32 and 0.25 nm correspond to the (100) and (101) planes of the pseudohexagonal δ -Nb₂O₅ [25].

As indicated above, the Raman and XRD assumptions demonstrated the presence of both pseudohexagonal and orthorhombic niobia phases with a long-range order porous structure. The existence of domains of different sizes for PtO_x oxide nanoparticles is clearly visible with particle sizes ranging from 1 to 30 nm (Figure 4a, HRTEM images included). Thus, the Pt particles are enveloped by the Mo ones, the former being not well dispersed on the support, SEM-EDS. Also, this result is corroborated by the textural properties that illustrate low values of surface area and pore volumes due to the formation of large PtO_x particles.

In addition, the Ni particles are randomly attached on the surface of the Nb₂O₅ support (Figure 4b), but they are quite agglomerated on the Mo ones, as marked with an arrow in the high magnification image of Figure 4b. Also, the particle size distribution shows thousands of hundreds of Ni nanoparticles with average sizes of about 5–25 nm. The morphology of CoMo/Nb₂O₅ (Figure 4c) is drastically different from that of PtMo/Nb₂O₅ with a much better uniform cobalt dispersion, which also illustrates that the addition of MoO₃ can improve the dispersion of Co₃O₄ nanoparticles. Some of the smallest particles may be assigned to Co₃O₄, whereas the largest ones come from MoO₃ distributed mainly on the Nb₂O₅ support (Figure 4c inset). The periodic lattice fringe spacings of 0.20 nm (400) and 0.34 nm (201) are found to be from cubic spinel Co₃O₄ and orthorhombic α -MoO₃, respectively. Besides, both pseudohexagonal and orthorhombic Nb₂O₅ phases are still present as support. Compared to PtMo/Nb₂O₅, the diameter of the Co particles lies in the range of 2–14 nm with an average size of about 5 nm.

The differences in the structure and morphology of the samples may come from the better dispersion of Co particles provided by Mo ones while Pt particles are surrounded by Mo having a worse dispersion of these particles. Moreover, the Ni particles are agglomerated on the vicinity of Mo particles, which implies in their low dispersion on the Nb₂O₅ surface.

2.3. Surface Acidity and Oxidation States

To assess the surface acidity of the solids and correlate it with the catalytic performance, NH₃-TPD experiments are performed. The acid strength distribution of the solids is determined in the region of weak e.g., 100–250 °C, medium e.g., 250–350 °C and strong, e.g., 350–450 °C strengths acid sites in the TPD profiles. The Nb₂O₅ support has weak and medium acid sites in the 100–350 °C range (Figure 5) with the acidity of ca. 275 μ mol _{NH3}·g⁻¹ mostly coming from the moderate acidic sites. The corresponding surface acid site density is of ca. 3.2 μ mol_{NH3}·m⁻² (Table 1).



Figure 5. Acid sites amount in function of the desorption temperature of the catalysts: (**a**) Nb₂O₅, (**b**) CoMo/Nb₂O₅, (**c**) PtMo/Nb₂O₅ and (**d**) NiMo/Nb₂O₅.

It is known that the acidity of niobium oxide is known to depend on the degree of hydration with this type of solid having thermal instability at room temperature [30]. Besides, the Brønsted acid sites acidity arises from OH groups bonded to Nb-OH groups [30,31]. Thereby, the acid sites of Nb₂O₅ seem to originate from the coordinative unsaturated Nb atoms due to the calcination of the support at 700 °C, which is in accordance with those observed for Nb₂O₅ prepared by other methods [19,31]. The acidic features of metal supported Nb₂O₅ change with the addition of MeMo. It is important to say that pure MoO₃ exclusively has Lewis acid sites of low to medium strengths, as illustrated by pyridine adsorption [19]. The acidity decreases drastically when CoMo is dispersed on niobia with the acid sites of weak to moderate strengths being responsible for the acidity. The latter is attributed to the highly dispersed Co₃O₄ and MoO₃ oxides on niobia masking the surface acid sites of Nb₂O₅, as previously shown by SEM-EDS and TEM results. Moreover, the results indicate that Mo contributes to decreasing the acidity of Nb₂O₅ [30], which confirms the obtained results for CoMo/Nb₂O₅.

On the contrary, the introduction of PtMo on the surface of niobia enhances the overall acidity as shown for PtMo/Nb₂O₅ catalyst with the acid sites having mostly medium to strong strengths up to 250 °C (Figure 5). Furthermore, the total acidity of PtMo/Nb₂O₅ is of ca. 438 μ mol NH₃·g⁻¹, whereas the acid density is of ca. 17.5 μ mol_{NH3}·m⁻² (Table 1). The latter value is almost six times higher than that of Nb₂O₅ owing to the low surface area of the PtMo/Nb₂O₅. This behavior clearly evidences that the positively charged and acidic PtO_x species are available for ammonia adsorption, even if Pt particles are entrapped by the Mo ones, as previously shown by TEM measurements.

Nonetheless, the acidity increases marginally in the NiMo/Nb₂O₅ catalyst compared to the Nb₂O₅ support. Also, the acid sites of the former are found above 250 °C in the medium to strong regions with a total acidity of ca 358 μ mol NH₃·g⁻¹. This is an indication that Ni increases the acid strength of Nb and thereby forms moderate acid sites, as shown in our previous work for NiMo-dispersed on alumina [5]. Interestingly, the density of the acid sites of NiMo/Nb₂O₅ is half the density of PtMo/Nb₂O₅ due to the relatively higher surface area of NiMo compared to that of PtMo catalyst. Thus, the effect of the textural parameters on the density of the acid sites of NiMo/Nb₂O₅ is very little compared to PtMo/Nb₂O₅.

The total acidity of the solids follows the order, $PtMo/Nb_2O_5 > NiMo/Nb_2O_5 > CoMo/Nb_2O_5 > Nb_2O_5$ but, the density of the acid sites order is as follows: $PtMo/Nb_2O_5 > NiMo/Nb_2O_5 > Nb_2O_5 > CoMo/Nb_2O_5$.

The chemical states of the constituent elements of the catalysts are studied by X-ray photoelectron spectroscopy (XPS). The BE results are summarized in Table 2. XPS spectra of pure Nb₂O₅ and supported catalysts depict binding energies from the Nb 3*d* doublet (Nb $3d_{5/2}$ and Nb $3d_{3/2}$) at 207.3 and 210.0 eV, respectively. This demonstrates the presence of Nb⁵⁺ in all the studied catalysts. Moreover, the high resolution Mo 3*d* region for CoMo/Nb₂O₅ and PtMo/Nb₂O₅ samples (Figure 6a) shows a doublet corresponding to the $3d_{5/2}$ and Mo $3d_{3/2}$ core levels at 232.4 and 235.5 eV, respectively. This assigns the presence of the Mo⁶⁺ species from α -MoO₃ [5], which is in line with Raman and XRD results. For PtMo/Nb₂O₅, the Mo 3*d* spectrum depicts similar doublets having binding energy values of Mo $3d_{5/2}$ contributions at 231.7 eV and 232.9 eV.

Sample	C 1 <i>s</i>	O 1s	Nb 3 <i>d</i> _{5/2}	Mo 3d _{5/2}	Co 2 <i>p</i> _{3/2}	Pt 4f _{7/2}
Nb ₂ O ₅	284.8 (80) 286.2 (12) 288.6 (8)	530.0 (90) 531.6 (10)	207.0	-	-	-
CoMo/Nb ₂ O ₅	284.8 (76) 286.7 (11) 289.0 (13)	530.2 (85) 531.6 (15)	207.2	232.4	780.5	-
PtMo/Nb ₂ O ₅	284.8 (83) 286.2 (13) 288.9 (4)	530.4 (90) 531.8 (10)	207.3	231.7 (29) 232.9 (71)	-	71.6 (16) 73.0 (70) 74.6 (14)
PtMo/ Nb ₂ O ₅ Spent	284.8 (78) 286.4 (18) 288.7 (4)	530.4 (89) 532.0 (11)	207.3	231.7 (19) 232.9 (81)	-	71.4 (80) 72.7 (20)

Table 2. Binding energies (in eV) of the constituent elements for the studied catalysts. The values in parentheses are the area% of each contribution.



Figure 6. Cont.



Figure 6. (a) Mo 3*d* high resolution XPS spectra of fresh CoMo/Nb₂O₅ and PtMo/Nb₂O₅ samples and PtMo/Nb₂O₅ spent catalyst. (b) Pt 4*f* spectra of both fresh and spent PtMo/Nb₂O₅ catalysts.

Importantly, the most intense contribution ca. 71% at 232.9 eV is assigned to be from Mo⁶⁺ species from α -MoO₃ on the surface of niobia, in agreement with the HRTEM results that suggest the existence of the molly species. Also, the minor contribution of ca. 29% at 231.7 eV is attributed to the presence of Mo⁵⁺ species [32].

Additionally, the O 1s core level spectra comprise of a pair of doublets with asymmetric signals at about 530.4 and 531.7 eV (Table 2). The most intense peak at low binding energy value could be related to the lattice oxygen species of the metal oxides mainly that of the Nb₂O₅ support, whereas the low intensity contribution is associated with the OH surface groups [16].

Meanwhile, CoMo/Nb₂O₅ depicts BE at 781.1 eV from Co 2*p* core level. This indicates that Co is mostly in Co²⁺ state [5]. Particularly, the Mo/Nb atomic ratio is of ca. 0.165 (Table 3) suggesting that Co nanoparticles are mostly on the solid surface, in close contact with the Mo ones, as illustrated by the HRTEM images. Regarding the Co/Mo surface atomic ratio of 0.72, it is plausible to have a small amount of Co²⁺ on solid surface.

Table 3. Surface chemical composition in atomic concentration (%) of the studied catalysts determined by XPS.

Sample	С	0	Nb	Мо	Со	Pt	Mo/Nb	Pt/Nb	Co/Nb
Nb ₂ O ₅	-	56.14	21.62	-	-	-	-	-	-
CoMo/Nb ₂ O ₅	-	53.98	16.67	2.75	5.38	-	0.165	-	0.035
PtMo/Nb2O5	-	54.38	17.82	4.53	-	0.78	0.254	0.042	-
PtMo/Nb ₂ O ₅ Spent	20.27	57.03	17.74	4.53	-	0.32	0.255	0.018	-

The Pt 4*f* core level spectra of PtMo/Nb₂O₅ sample is shown in Figure 6b. The deconvolution of the spectra reveals three doublets at low BE for Pt 4*f*_{7/2} peak at 71.4 eV (16%), 73.0 (70%), and 74.7 eV (14%). A peak overlapping with the peak at 74.7 eV along with two peaks at 76.1 and 77.4 eV can be found for Pt 4*f*_{5/2} (Figure 6b). According to the findings, the BE at 73.0 and 74.7 eV are due to Pt²⁺ from PtO_x

species, whereas the contribution at 74.7 and 77.4 eV are assigned to the presence of Pt^{4+} species [33,34]. The minor contribution at 71.4 eV is associated with the Pt° [33], although this specie is not probable in the fresh catalyst. Moreover, the Mo/Nb ratio for $PtMo/Nb_2O_5$ sample is 0.254, being higher than that of CoMo/Nb₂O₅ indicating that Mo particles are mostly exposed on surface of the $PtMo/Nb_2O_5$ catalyst.

After the catalytic test (Figure 6b), the BE for Pt $4f_{7/2}$ core level observed at 71.4 (80%) and 72.7 eV (20%) remain with the former having a major contribution. This indicates that the PtO_x species are reduced from to Pt⁴⁺/Pt²⁺ from PtO_x species to Pt^o. Also, the Pt/Nb ratio decreases from 0.0042 in the fresh sample to 0.0018 as found for spent catalyst suggesting the leaching of the Pt species after the catalytic test. Indeed, the Pt content of ca. 0.32% for the spent solid confirms these assumptions (Table 3). Additionally, the Mo species amount for PtMo/Nb₂O₅ catalyst does not change after the catalytic test.

The C 1*s* core level spectra for CoMo/Nb₂O₅ and PtMo/Nb₂O₅ are deconvoluted into three contributions. The first one at about 288.7 eV can be related to the presence of carboxyl groups, in addition to the other typical peak at 284.8 eV of adventitious carbon. At 286.2 eV, the C-OH groups can be detected. All these contributions could be related to the carbon deposition after the catalytic test, which further will explain the low performance of PtMo/Nb₂O₅. In agreement, the BE for O 1*s* core level reveals peaks at 530.4 and 532.0 eV, which are associated to surface oxygen groups. The peak at 530.4 eV is assigned to be from C-O/C=O and Me-O functional groups while the peak at 532.0 eV can be attributed to the presence of other carboxylic species bonded to the OH functional groups [35]. Moreover, a slight increase in the oxygen content after the catalytic test is observed (Table 3) in comparison to the fresh Pt-containing solid. This might be attributed to the surface oxidation, mainly Mo species in the presence of CO and NO_x species from SCR reaction.

2.4. Catalytic Results

2.4.1. Temperature Effects

The catalysts are screened for the CO-SCR reaction to find out the optimum conditions for maximum NO_x conversions. In all cases, the amounts of the catalysts are 150 mg and the total flow of NO_x, CO, and He is 80 mL·min⁻¹ with the variations in reaction temperatures from 50 to 500 °C (Figure 7).

At temperatures below 200 °C, all solids exhibit negligible NO_x conversion in the CO-SCR reaction. Considering that the SCR is not a fast reaction [36]; thus, NO_x and CO are stable as temperature increases from 50 to 200 °C, requiring more heat to be decomposed. It is noted that for PtMo/Nb₂O₅, the increase of temperature to 200 °C more likely provides the NO_x and CO decomposition by moderated temperatures with NO_x being converted ca. 10%. Eventually, all the available PtO_x nanoparticles on Nb₂O₅ surface act catalyzing the reaction along with the high conversions at higher temperatures. This is probably due to either the adsorption of CO by Pt sites and NO_x decomposition, in line with the literature reports for SCR reactions [14,34].

A further increase in temperature up to 200 °C increases the overall conversion of NO_x for PtMo/Nb₂O₅ reaching 90% at 300 °C. On the contrary, the CoMo/Nb₂O₅, NiMo/Nb₂O₅ and Nb₂O₅ catalysts illustrate that the SCR reaction is limited at temperatures below 350 °C. It is notable that in the case of the Nb₂O₅ support, the NO_x conversion starts at 350 °C and reaches a maximum value of 19% at 500 °C. Thermal conversion of the Brønsted to Lewis acid sites Nb₂O₅ above 350 °C evidences the reduction of NO_x and the oxidation of CO to form N₂ and CO₂, respectively. Based on the NH₃-SCR reaction over niobia catalysts [21], the Brønsted acid sites present on Nb₂O₅ works in the SCR reaction at relatively low temperature ranges and maybe difficult to convert NO_x at temperatures higher than 350 °C due to its low stability. Most probably, the Lewis acid sites of Nb₂O₅ help to convert NO_x at relatively high temperatures, as indicated by acidity measurements (Figure 5).



Figure 7. Influence of the temperature on overall NO_x conversions using the MeMo/ Nb₂O₅ catalysts: (a) Nb₂O₅, (b) CoMo/Nb₂O₅, (c) NiMo/Nb₂O₅, and (d) PtMo/Nb₂O₅. Reaction conditions: 500 ppm of NO, 1000 ppm of CO, and balance with He. Catalyst mass = 150 mg, total flow rate = 80 mL·h⁻¹ and GHSV = 48,000 h⁻¹.

At temperatures above 400 °C, the activity of the MeMo supported catalysts gradually raised with $PtMo/Nb_2O_5$ and $CoMo/Nb_2O_5$ achieving NO_x conversions greater than 90% at 550 °C, while the NiMo/Nb₂O₅ catalyst converts 83% of NO_x at the same temperature. Apparently, the activity is influenced by the physicochemical properties of MeMo with PtMo and CoMo having more pronounced effects to improve the catalytic performance than NiMo counterparts. In agreement, studies on Co-based bimetallic and Ir monometallic catalysts demonstrate a superior catalytic performance at relatively low temperatures as a result of the strong adsorption of the gases on Me active sites [37,38]. Besides, total acidity follows the same order of the activity whereas the acidity of the Lewis acid sites is not the only factor affecting conversion.

Important is to note that the Mo/Nb₂O₅, Ni/Nb₂O₅, and Co/Nb₂O₅ are inactive in the CO-SCR reaction under all the above mentioned conditions whereas Pt/Nb_2O_5 catalysts exhibit a very modest performance up to 400 °C.

2.4.2. Stability of the Catalysts against Poisons

Attempts are also being made to investigate the impact of H_2O and SO_2 (or both) poisons on NO_x conversions and correlate with the stability of the MeMo/Nb₂O₅ samples. These studies are carried out after each run at 350 °C for the samples for 24 h.

Figure 8A depicts the evolution of the reaction after 6 h of operation solely in the presence of 10 wt % water vapor, as poison. For all catalysts, no noticeable variation of NO_x conversions is observed upon time on stream. The CoMo/Nb₂O₅ catalyst, among the tested solids, is the most active towards the CO-SCR reaction, as evidenced by the very high NO_x conversion of 74% in 6 h of reaction, whereas the conversion dropped below 47% as measured for PtMo/Nb₂O₅ and CoMo/Nb₂O₅ catalysts. In agreement, the NH₃-TPD results (Figure 5) illustrate that the Lewis sites are formed on MeMo/Nb₂O₅ catalysts at 350 °C, especially for CoMo/Nb₂O₅ and PtMo/Nb₂O₅ ones.



Figure 8. Cont.



Figure 8. (A) CO-SCR performances of catalysts in the presence of distinct poisons. The catalysts studied are as follows: (a) CoMo/Nb₂O₅, (b) PtMo/Nb₂O₅, and (c) NiMo/Nb₂O₅. Reaction conditions: catalyst mass = 150 mg, total flow rate = 80 mL h⁻¹, GHSV = 48,000 h⁻¹ at 350 °C. (B) Cutting in and cutting off the poison experiments using the following catalysts: (a) CoMo/Nb₂O₅, (b) NiMo/Nb₂O₅, and (c) PtMo/Nb₂O₅. Reactants composition: 500 ppm of NO, 1000 ppm of CO and balance with He. A 10 wt% (v/v) of water vapor or 50 ppm of SO₂ (or both) was used during the poisoning tests for 24 h. GHSV = 48,000 h⁻¹ at 350 °C.

Thus, H₂O vapor is unlikely to poison Lewis acid catalytic active sites possessing medium to stong acidity. Hence, water vapor does not compete with either CO or NO_x for active sites, leading to increased stability of CoMo/Nb₂O₅ and MoMo/Nb₂O₅ catalysts. This result corroborates with the findings that explain the weak interaction between water molecules and Nb_2O_5 acid active sites resulting in low H₂O adsorption energy on these sites; thus, water does not affect the active sites of niobia necessary to maintain the catalytic activity of solids, as found elsewhere [39,40]. Despite considerable efforts to define the role of water as poison during SCR reactions, the debate on this issue still continues in the NO_x, CO, and H₂O adsorption at different sites on the surface of CoMo/Nb₂O₅ and PtMo/Nb₂O₅ catalysts. Even if there is a competitive NO_x , CO, and H_2O adsorption for the active species, the linear, bridged, or germinal CO interaction with the Me and the Me monodentate nitrate or nitrite sites from NO_x may exist [14,40], but the CO-SCR remains unaffected by H_2O vapor addition. On the contrary, Ni and Nb Lewis acid sites of NiMo/Nb₂O₅ catalyst with weak to medium strengths have low water tolerance, presumably because Ni is quite reactive towards H₂O and therefore lead to irreversible adsorption on Ni sites with consequent loss of catalytic performance. Studies on water adsorption on NiO demonstrate that water can be decomposed on NiO surfaces, forming saturated OH groups [41,42], in agreement with our observations.

Further experiments with the addition of 50 ppm of SO_2 are carried out, as shown in Figure 8A. As one can see, the SO_2 inlet declines more the catalytic performance of the solids compared to just the H_2O inlet, especially for NiMo and PtMo catalysts. Sulfur is considered to be a poison for catalytic reactions as it strongly interacts with both acid and metallic active sites of a catalyst that allows the deactivation of the catalysts [43]. The favorable adsorption of the sulfur species bound to the MeMo or Nb surface may lead to a blocking of the catalyst's surface and pores and, thus, the coexistence of SO_2 , CO, and NO_x deactivate the catalyst. Similarly, PtMo sites are deactivated by SO_2 addition due to the sulfur bound to Pt sites giving sulfided phases, which produce a diminution in the availability of active sites, being Pt sites less effective to activate the hydrocarbons during HDS reactions [43,44].

On the literature for NH₃-SCR, dispersed Ni and Mo species on CeO₂ that possess strong Lewis acid depicts low catalytic performance due to the active sites' deactivation by sulfur [45].

Although there is a slight reduction in the catalytic activity of $CoMo/Nb_2O_5$, the NO_x , conversion by 63% in 6 h of time on stream evidences that the well dispersed Co_3O_4 and MoO_3 on Nb_2O_5 gives a more resistant catalyst against sulfur poison than the NiMo and PtMo analogues. Due to the similarity in the structural and acid properties of $CoMo/Nb_2O_5$ and $CoMo/Al_2O_3$ catalyst, the former shows an excellent activity in the SCR reaction due to the availability of its cobalt sites for CO and NO_x adsorption, whereas sulfided $CoMo/Al_2O_3$ shows a modest catalytic performance [43,46].

To verify whether the catalysts are stable against the simultaneous addition of H_2O and SO_2 , the same experiment is performed with all three catalysts, as shown in Figure 8. As before, PtMo/Nb₂O₅ and NiMo/Nb₂O₅ exhibit poor performances reaching NO_x conversions less than 5%. In marked contrast, the catalytic performance of CoMo/Nb₂O₅ is not restrained, when adding both water vapor and SO₂ with NO_x conversion of ca. 63% in 6 h. Such a difference in catalytic activity suggests that the formation of Co and Mo active species on Nb₂O₅ played the crucial role in the CO-SCR owing to Co ability to adsorb CO and NO_x at the Mo and Nb sites. IR spectra of carbon monoxide adsorbed on a series of CoMo/Al₂O₃ and NiMo/Al₂O₃ confirm these assumptions demonstrating that CO can interact either with a Co atom or with a Mo atom adjacent to a Co atom in CoMo/Al₂O₃ while CO adsorption on Ni centers of NiMo/Al₂O₃ results in competitive adsorption of CO for Ni or Mo sites [45,47]. The focus will now be directed towards the stability of the solids by performing long-term stability runs. Thus, the CO-SCR reaction is studied as a function of reaction time using poisons in cutting in and cutting off experiments (Figure 8B).

At the beginning of the reaction, NO_x conversion is high for both CoMo/Nb₂O₅ and PtMo/Nb₂O₅ catalysts, in contrast to the low performance depicted by NiMo/Nb₂O₅. This is expected considering that the dispersion of active PtO_x and Co₂O₄ species on Nb₂O₅ surface is helped by MoO₃ (XPS, TEM, and SEM-EDS). This results in the availability of Co and Mo for CO and NO_x. Also, the acidity of PtMo/Nb₂O₅ greatly enhances the NO_x conversion, as discussed above. In the case of NiMo/Nb₂O₅, the agglomeration of Ni particles may hamper the reactants to be adsorbed by the Lewis Nb sites and Ni redox ones and, thus, both CO and NO_x adsorption decreased slightly compared with their PtMo/Nb₂O₅ and CoMo/Nb₂O₅ corresponding ones (Figure 8B).

As the reaction proceeds, water vapor is introduced into the reaction (step II) and the catalytic activity follows similar trends, as previously shown by short term stability runs (Figure 8A). Interestingly, the NO_x conversion of CoMo is maintained in 64%, while NiMo/Nb₂O₅ activity only increases to 10% in the presence of steam. In contrast to CoMo/Nb₂O₅, the Pt sites of PtMo/Nb₂O₅ experience a remarkable decay from 70 to 60% in NO_x conversion. It is understandable that the density of the acid sites of the solids themselves change much for PtMo/Nb₂O₅ due to the steam poisoning; consequently, a decrease of the strength of the medium to strong Lewis acid sites. On the contrary, NiMo/Nb $_2O_5$ has lower values of the density of the acid sites, which can effectively illustrate the deactivation of Ni active sites by water vapor, as aforesaid. For CoMo/Nb₂O₅, the low density of the acid sites ca. 1.8 µmol_{NH3}.m² seems do not influence its performance. Afterwards, water vapor is cut off from the reaction and SO₂ is added immediately with the consequent decay in CO-SCR activity to values nearly to zero on PtMo/Nb₂O₅ and NiMo/Nb₂O₅. These results are ascribed to the strong chemisorption of SO_2 by Pt and Ni active species, which greatly decrease the effective active sites availability for CO and NO_x. Theoretical studies through DFT calculations corroborate with our results demonstrating the detrimental effect of NO_2 and SO_2 on the Pt sites [48]. Such decrease in NO_x conversion is less pronounced for the CoMo/Nb₂O₅ catalyst, since CO preferentially adsorbs on Co and Mo sites, forming mono and bidentate species, as found elsewhere [49,50]. Also, the Mo and Nb sites may form the nitrate and nitrites species, which are in close proximity of the CO adsorbed on the Co and Mo bound to the previous CO species forming the intermediate isocyanate. This chemical entity is responsible for forming CO_2 and N_2 during the CO-SCR reaction [3,14,16]. Thereby, the activity of CoMo/Nb₂O₅ is not severely affected by low SO_2 concentration such as 50 ppm with the NO_x conversion remaining

nearby 63%. Subsequently, the introduction of SO₂ and H₂O vapor gives similar results for NO_x conversion in 7 h of reaction. The suppression of the poisons restores the NO_x conversion on all the studied solids from 10 to 20 h of reaction. However, there is significantly more deactivation of the PtMo/Nb₂O₅ and NiMo/Nb₂O₅ catalysts by repeating the cycles of cutting in and cutting off again upon using the poisons during the CO-SCR reaction. Especially for PtMo/Nb₂O₅ and NiMo/Nb₂O₅, the NO_x conversion drops continuously for 24 h. Possible reasons for the activity decay could be due to the covering of a part of the Ni and Pt species by coke deposits from CO decomposition, as previously shown for Ni and Pt-based catalysts [34,51]. Although the NO_x conversion decreases in the presence of SO₂ over CoMo/Nb₂O₅, the solid shows excellent tolerance to the poisons, when H₂O is added simultaneously with sulfur during more than 20 h of reaction. This may be due to the surface Co and Mo active sites interaction with CO, while NO_x may be adsorbed on Nb sites of moderate acidity. As the sites are in close proximity, isocyanate species could be formed and react with the NO₃⁻/NO₂ surface complex, which is formed by both oxidation of NO_x and CO. Careful observation of acidity, HRTEM, and XPS results confirm that the surface of Co and Mo as well as the acid nature of the Nb species formed in the catalysts play an important role on the catalytic performance.

3. Materials and Methods

3.1. Nb₂O₅ Supported Transition Metal Catalysts Preparation

Commercial Nb₂O₅ powder was purchased from Sigma-Aldrich (Sigma-Aldrich, Darmstadt, Germany) and calcined at 700 °C for 2 h under air flow. In a typical procedure, 1.0 g of the calcined niobia was mixed with 1.0 wt % of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) precursor (Vetec) and dispersed by rotatory evaporator at 50 °C for 1 h. Then, the pH of the solution was adjusted to 9.0 by adding ammonia aqueous solution. After that, the sample was calcined at 500 °C for 2 h by flowing air producing the Mo/Nb₂O₅ sample. Subsequently, the Mo/Nb₂O₅ catalyst was impregnated with either Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O solution possessing a 1.0 wt % of each metal. The mixture was heated at 70 °C in a rotatory evaporator for 4 h. Finally, the previous sample was washed, dried, and calcined at 350 °C for 2 h under air, yielding the supported transition metal oxides denoted as CoMo/Nb₂O₅ and NiMo/Nb₂O₅.

A Pt-containing sample was obtained by impregnating a 1.0 wt% of hexachloroplatinic acid ($H_2PtCl_6\cdot 6H_2O$) ethanolic solution to the Mo/Nb₂O₅. After calcination of the solid, the catalyst was denoted as PtMo/Nb₂O₅. For simplifications, the catalysts were denoted as MeMo/Nb₂O₅ (in which, Me=Co, Ni, Pt) referring to CoMo/Nb₂O₅, NiMo/Nb₂O₅, and PtMo/Nb₂O₅.

3.2. Characterizations

The crystal structure of the catalysts was determined by the X-ray diffraction (XRD) in a DMAXB Rigaku diffractometer (Rigaku, Tokyo, Japan) using CuK α radiation at 40 kV and 40 mA. The intensities were determined at 2 θ angles in the 20–60° range. The diffractograms were compared with those of the Joint Committee of Powder Diffraction Standard (JCPDS) database files.

Raman spectroscopy measurements were performed using a LabRAM HR Horiba Scientific spectrometer (Horiba—Jobin Yvon, Kyoto, Japan) with a liquid nitrogen cooled detector at a resolution of 2 cm^{-1} and a laser power of 10 mW. The 514.5 nm line of an argon ion laser was used and an objective lens from Olympus was used. The recorded spectra were obtained in the 100–1100 cm⁻¹ range.

The morphology of catalysts was observed by scanning electron microscopy (SEM) in a FEI, Quanta 200 FEG electron microscope (FEI Company, Hillsboro, OR, USA) in SEM mode, which was coupled to an energy dispersive spectroscopy (EDS) system. Previously, the samples were silver sputtered to better conduction.

Transmission electron microscopy (TEM) images were carried out in a field emission FEI Tecnai 20 G2 microscope operating at 200 kV. Previously, the samples were dispersed in ethanol, sonicated, and then drop casted onto a holey-carbon copper TEM grid.

The textural properties of the solids—such as surface areas, and pore volumes and sizes—were obtained by nitrogen adsorption–desorption isotherms at –196 °C in a ASAP 2420 apparatus from Micromeritics (Norcross, GA, USA). Before analyses, the solids were heated at 150 °C under vacuum for 5 h. The surface areas and pore volumes were assessed by the Brunauer–Emmett–Teller (BET) equation whereas the average pore diameters were calculated from the Barrett–Joyner–Halenda (BJH) method to the adsorption curves.

The acidity of the solids was determined by temperature-programmed desorption of ammonia (NH₃-TPD) in a Chembet-3000 model from Quantachrome Instruments equipment (Anton Paar, Ashland, VA, USA). The samples were previously pretreated flowing N₂ at 300 °C. Then, a mixture of 5% NH₃ in N₂ was introduced during NH₃ adsorption at 100 °C for 40 min. After purging with nitrogen to remove the physically adsorbed ammonia from the solid surface, the desorption was performed at 10 °C. min⁻¹ in the 100–470 °C range.

X-ray photoelectron spectroscopy (XPS) spectra were collected to provide information on the surface composition and oxidation states of the constituent elements of the studied catalysts in a Physical Electronics VersaProbe II Scanning XPS Microprobe (Physical Electronics GmbH, Feldkirchen, Germany). The scanning monochromatic X-ray Al K α radiation (100 μ m area analyzed, 52.8 W, 15 kV, 1486.6 eV) and a charge neutralizer were used. The C *1s* electron binding energy corresponding to adventitious carbon was used as a reference at 284.8 eV.

3.3. Catalytic Activity Tests

The selective catalytic reduction of CO (CO-SCR) was carried out using a quartz fixed-bed reactor with an inner diameter of 8 mm at ambient pressure. About 150 mg of catalysts (40–60 mesh) were placed into the reactor and pretreated in 80 mL·min⁻¹ flowing 10% O₂/He at 350 °C for 1 h. Subsequently, the solids were evacuated with helium and cooled to room temperature. Then, the reactants with the composition of 500 ppm of NO_x and 1000 ppm of CO balanced with helium were fed into the reactor.

The total flow rate was kept at 80 mL·min⁻¹ during the catalytic experiments. The reaction temperature was elevated to 50 °C increments and maintained constant to reach the steady-state NO_x conversion. Unless otherwise described, the catalytic reactions were carried out in the 50–500 °C range. The concentrations of NO and NO₂ were obtained by a NO/NO₂/NO_x electrochemical analyzer from Seitron model chemistry 400 flue gas analyzer (Seitron, Mussolente VI, Italy). Evaluation of the catalytic activity was through the NO_x conversions, which was calculated according to previous work [3].

The poisoning experiments were conducted using a composition of 500 ppm of NO_x, 1000 ppm of CO, and balance with He. A 10 wt % (v/v) of steam or 50 ppm of SO₂ (or both) was used as poison during the reaction for 24 h at 350 °C. The space velocity in GHSV was 48,000 h⁻¹.

The catalytic performance is evaluated through the NO_x conversion

$$%X_{NO_x} = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} x \ 100$$

where X_{NOx} is the NO_x conversion. The subscripts *in* and *out* in the equation are the inlet and outlet concentration of NO_x at steady state, respectively.

4. Conclusions

A series of MeMo/Nb₂O₅ catalysts (Me=Co, Ni, or Pt) oxides were prepared and characterized by various physicochemical techniques. Molybdenum had a promoter effect of helping the dispersion of Me oxides on the catalyst surfaces. The strengths of the Lewis acid sites were believed to be correlated to the acid PtO_x and NiO aided by MoO₃ on Nb₂O₅, whereas Co₃O₄ is well dispersed by MoO₃ on niobia having acid sites of moderate to weak strengths.

The influence of the nature and dispersion of the Me oxide active sites on the activity of supported MeMo catalysts in the CO-SCR reaction was considerably greater than that of the acidity of the catalysts.

Little difference with respect to the dispersion of NiMo and PtMo, namely, Ni or Pt sites close to Mo, and on the other hand, the Co sites away from Mo particles determine the performance of the solids in the reaction. Among the MeMo/Nb₂O₅ catalysts, PtMo/Nb₂O₅ had a remarkably low-temperature NO_x conversion due to the PtO_x ability to convert NO_x and CO, whereas Co₃O₄ and NiO active sites of CoMo/Nb₂O₅ and NiMo/Nb₂O₅ worked better above 350 °C. In other words, the PtO_x and MoO₃ and Nb sites with Lewis acid sites of moderate to strong strengths were only active for a short CO-SCR reaction period. For CoMo/Nb₂O₅, Co³⁺/Co²⁺ sites on Nb₂O₅ promoted the oxidation of CO and generated more N₂ through NO_x reduction in 6 h of the title reaction. In similar lines, the synergistic effect between Co³⁺/Co²⁺ and Mo⁶⁺ sites in CoMo/Nb₂O₅ was a key parameter for the performances of the catalyst towards either water vapor or SO₂ (or both) poisons.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/9/1048/s1, Table S1: Raman modes vibrations and their corresponding assignations.

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