



The catalytic activity of $\text{CoO}_x/\text{sulphated-ZrO}_2$ for the NO abatement with C_3H_6 in the presence of O_2 : the dependence of activity and selectivity on the sulphate content

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Cobalt sulphated- ZrO_2 catalysts were prepared by impregnation of ZrO_2 with aqueous solutions of CoSO_4 , or impregnation of sulphated- ZrO_2 with toluene solutions of $\text{Co}(\text{acetylacetonate})_2$. NO reduction with C_3H_6 in the presence of excess O_2 was studied in a flow apparatus fed by a reactant mixture of $\text{NO}:\text{C}_3\text{H}_6:\text{O}_2 = 4000:2000:20,000$ ppm in He.

Diffuse reflectance spectroscopy (DRS) and X-ray photoelectron spectroscopy (XPS) results showed that the presence of sulphates prevented the formation of Co_3O_4 . XPS indicated the presence of Co(II) alone. Irrespective of the preparation method, Fourier transformed infrared (FTIR) showed that catalysts with the same sulphate content had the same covalent sulphates. As the sulphate content in the sample increased, FTIR with CO or NO showed that the Lewis acid-strength of Co(II) increased, whereas the reducibility and heterogeneity of Co(II) decreased.

Sulphated samples with a cobalt content higher than 2 atoms nm^{-2} were far more active and selective than the corresponding unsulphated $\text{CoO}_x/\text{ZrO}_2$. The presence of sulphates had a weaker effect on the catalytic behaviour of samples with lower Co content (<2 atoms nm^{-2}). We conclude that cobalt and sulphate co-operate in determining the catalytic activity and selectivity of cobalt sulphated- ZrO_2 catalysts.

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1. Introduction

In the presence of excess oxygen, isolated Co(II) in ZSM5 [1–5], MOR [5,6], and FER [5,7] is active for the selective catalytic reduction (SCR) of NO with methane. In analogous conditions, Co(II) exchanged in BEA zeolite [8] is active with propane, and CoO_x

supported on SiO_2 [9], Al_2O_3 [10–13], or ZrO_2 [14] is active with propene. The activity of supported catalysts strongly depends on CoO_x loading, preparation method, and calcination temperature, because all these factors affect cobalt dispersion [9–14].

On $\text{CoO}_x/\text{ZrO}_2$, Co dispersion is limited to low-loading samples. Isolated cobalt in $\text{CoO}_x/\text{ZrO}_2$ containing up to about 2 atoms nm^{-2} is active and selective for NO reduction in the presence of excess O_2 [14]. By comparing the turnover frequency number (NO molecules converted per second per site)

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measured on these dilute $\text{CoO}_x/\text{ZrO}_2$ samples with that measured by Yan et al. [11] on Co-ZSM5, we found that isolated cobalt in dilute $\text{CoO}_x/\text{ZrO}_2$ was nearly as active as isolated Co(II) in ZSM5 [14]. In $\text{CoO}_x/\text{ZrO}_2$ containing more than 2 Co-atoms nm^{-2} , small oxide particles, Co_3O_4 , formed. Redox couples Co(III)/Co(II) on the surface of these Co_3O_4 particles were very active for C_3H_6 combustion, thus rendering the corresponding $\text{CoO}_x/\text{ZrO}_2$ non-selective [14].

Like isolated Co(II), isolated Cu(II) in $\text{CuO}_x/\text{ZrO}_2$ is active for NO reduction with propene. As in high-loading $\text{CoO}_x/\text{ZrO}_2$, in $\text{CuO}_x/\text{ZrO}_2$ containing more than 2.5 Cu-atoms nm^{-2} , small oxide particles, CuO, form. Redox couples Cu(II)/Cu(I) on the surface of these CuO particles are highly active for C_3H_6 combustion, thus rendering the corresponding $\text{CuO}_x/\text{ZrO}_2$ non-selective [15]. In a previous study, we found that sulphates prevented CuO formation in high-loading $\text{CuO}_x/\text{sulphated-ZrO}_2$ and $\text{CuSO}_4/\text{ZrO}_2$, and, accordingly, with propene [16] or NH_3 [17] these catalysts were far more selective than the corresponding un-sulphated $\text{CuO}_x/\text{ZrO}_2$ [17,18]. A possible analogous effect of sulphates in preventing Co_3O_4 formation prompted us to investigate $\text{CoO}_x/\text{sulphated-ZrO}_2$ and $\text{CoSO}_4/\text{ZrO}_2$ samples, and to compare their activity with that of $\text{CoO}_x/\text{ZrO}_2$. In this study, to investigate the dependence of activity and selectivity on Co content, we compared samples with Co content from 0.2 to 3.6 atoms nm^{-2} , maintaining the sulphate amount constant (2.4 SO_4 molecules nm^{-2}). To investigate the dependence of activity and selectivity on the SO_4 content, we compared samples with sulphate content from 0 to 4.0 molecules nm^{-2} , maintaining the cobalt amount constant (0.3 or 4 Co-atoms nm^{-2}). Catalytic results are reported here in full. Characterisation data by UV-Vis diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transformed infrared (FTIR) spectroscopy relevant to discussion of the catalytic activity will be given, whereas details on the characterisation will be reported elsewhere [19].

2. Experimental

The ZrO_2 support was prepared by hydrolysis of zirconium oxychloride with ammonia, as already described [20]. Before its use as a support, the material

was dried at 383 K for 24 h and calcined at 823 K for 5 h. After calcination, the BET surface area of the ZrO_2 support (Z) was $53 \text{ m}^2 \text{ g}^{-1}$. XRD spectra showed that Z was in the monoclinic phase.

Sulphated- ZrO_2 was prepared by impregnating Z with an aqueous $(\text{NH}_4)_2\text{SO}_4$ solution and calcining at 823 K (SZ (*b*), with $b = 2.4 \text{ SO}_4$ molecules nm^{-2}).

Cobalt containing catalysts were prepared by two different procedures. In the *first procedure*, $\text{CoSO}_4/\text{ZrO}_2$ were obtained by impregnation of Z with aqueous solutions of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and designated as CoS/Z (*a, b*), where CoS stands for CoSO_4 , *a* specifies the analytical cobalt content and *b* the analytical sulphate content. In the *second procedure*, $\text{CoO}_x/\text{sulphated-ZrO}_2$ were obtained by impregnation of SZ (2.4) with toluene solutions of $\text{Co}(\text{acetylacetonate})_2$, and designated as Co/SZ (*a, b*). After impregnation, CoS/Z, and Co/SZ samples were dried at 383 K and calcined at 823 K. For a comparison, we used portions of $\text{CoO}_x/\text{ZrO}_2$ catalysts previously prepared and characterised [14]. Samples $\text{CoO}_x/\text{ZrO}_2$, prepared by impregnation of Z with aqueous solutions of $\text{Co}(\text{acetate})_2$, are designated as Co/Z (*a*), where *a* specifies the analytical cobalt content. All analytical contents are expressed as molecules nm^{-2} .

Cobalt content was determined by atomic absorption (Varian SpectraAA-30). Sulphate content was determined by ionic chromatography (Dionex 2000i). Specific surface areas were all in the range $50\text{--}55 \text{ m}^2 \text{ g}^{-1}$.

Starting materials for catalyst preparation, catalyst name, analytical cobalt content, and analytical sulphate content are reported in Table 1.

XPS spectra were recorded with a Leybold-Heraeus LHS 10 spectrometer operating in FAT mode and interfaced to a 2113 HP computer, using Al $K\alpha$ radiation (1486.6 eV, 12 kV, 20 mA). Samples were ground in an agate mortar and pressed onto a gold-decorated tantalum plate attached to the sample holder. The analysis chamber was evacuated at pressures lower than 10^{-8} Torr. The computer collected sequentially the kinetic energy region of Co $2p_{1/2}$ and Co $2p_{3/2}$ (665–710 eV), and Zr $3d_{3/2}$ and Zr $3d_{5/2}$ (1290–1310 eV). Binding energy (BE) values (BE = ± 0.2 eV) were referenced to the Zr $3d_{5/2}$ peak, taken as 182.5 eV. Spectra analysis involved the following steps: smoothing, inelastic

Table 1
Catalysts

Starting materials ^a	Catalysts ^b
ZrO ₂	Z
ZrO ₂ + (NH ₄) ₂ SO ₄ (4.0)	SZ (2.4)
ZrO ₂ + Co(ac) ₂ (0.4)	Co/Z (0.4)
ZrO ₂ + Co(ac) ₂ (2.1)	Co/Z (2.1)
ZrO ₂ + Co(ac) ₂ (4.8)	Co/Z (4.8)
ZrO ₂ + CoSO ₄ (0.3)	CoS/Z (0.3, 0.3)
ZrO ₂ + CoSO ₄ (0.7)	CoS/Z (0.7, 0.6)
ZrO ₂ + CoSO ₄ (2.0)	CoS/Z (2.0, 1.9)
ZrO ₂ + CoSO ₄ (4.0)	CoS/Z (4.0, 4.0)
SZ (2.4) + Co(acac) ₂ (0.3)	Co/SZ (0.2, 2.3)
SZ (2.4) + Co(acac) ₂ (2.0)	Co/SZ (2.1, 2.4)
SZ (2.4) + Co(acac) ₂ (4.0)	Co/SZ (3.6, 2.3)

^a The figure in parentheses specifies the nominal content (molecules nm⁻²) of the salt used for impregnation of Z or SZ (2.4).

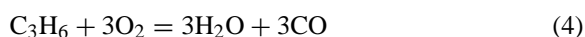
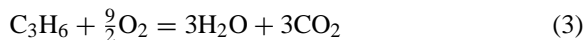
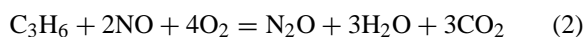
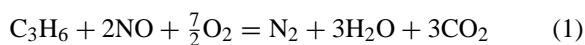
^b For the sulphated-ZrO₂ sample, SZ, the figure in parentheses specifies the analytical SO₄ content. For Co/Z samples, the figure specifies the analytical Co content. For CoS/Z and Co/SZ samples, the two figures after the symbol specify the analytical Co and SO₄ content, *in that order*. All analytical contents are expressed as molecules nm⁻².

background removal by a linear integral profile, curve-fitting by the least-squares method (using a mixed Gaussian–Lorentzian function), and determination of the peak-area by integration.

FTIR spectra were recorded at RT on a Perkin-Elmer 2000 spectrometer equipped with an MCT detector, collecting 4–100 scans at a resolution of 4 cm⁻¹. Powdered materials were pelleted (pressure 1.5 × 10⁴ kg cm⁻²) in self-supporting disks of ca. 15 mg cm⁻² and 0.1–0.2 mm thickness. All samples were placed into an IR quartz cell allowing thermal treatments in vacuo or in a controlled atmosphere. Before experiments, samples were heated in O₂ from RT to 793 K, kept at this temperature for 0.5 h, and evacuated thereafter at the same temperature for 1 h.

The catalytic activity was measured in a flow apparatus at atmospheric pressure. The apparatus included a feeding section where four gas streams (He, 3% NO in He, 1% C₃H₆ in He, and 10% O₂ in He, RIVOIRA) were regulated by means of independent mass flow controller-meters (MKS model 1259). Reactants and products were analysed by gas-chromatography. A thermal conductivity detector (TCD) was used for detecting N₂, N₂O, CO, CO₂, and C₃H₆, and a flame

ionisation detector (FID) for C₃H₆. Peak areas were evaluated by electronic integration. All experiments yielded satisfactory carbon balance. The reaction gas contained NO (4000 ppm), C₃H₆ (2000 ppm), and O₂ (2%), with He as balance. The total flow rate was 50 cm³ STP min⁻¹ and space velocity (GHSV) was 26,400 h⁻¹, based on the apparent ZrO₂ bulk density of 2 g cm⁻³. Before catalytic experiments, a fresh portion of catalyst (0.25 g) was pre-treated in a flow of 2% O₂/He mixture (120 cm³ STP min⁻¹), while heating the reactor from RT to 793 K in about 2 h, then isothermally at 793 K for 1 h and purged with He for about 0.25 h. The percent NO conversion was calculated from the N₂ and N₂O produced and NO inlet, as 100 (2N₂ + 2N₂O)/(NO inlet). The percentage C₃H₆ conversion was calculated from CO₂ and CO produced and C₃H₆ inlet, as 100 (1/3 CO₂ + 1/3 CO)/(C₃H₆ inlet). To compare catalytic activity and selectivity of the various catalysts, we assumed the following set of reactions to take place on all catalysts:



The percentage selectivities, S_{SCR} (NO reduction rather than C₃H₆ combustion), S_{N_2} (N₂ rather than N₂O), and S_{CO_2} (CO₂ rather than CO) were calculated as: $S_{\text{SCR}} = 100 (\text{N}_2 + \text{N}_2\text{O})/(\text{C}_3\text{H}_6 \text{ converted})$, $S_{\text{N}_2} = 100 \text{N}_2/(\text{N}_2 + \text{N}_2\text{O})$, $S_{\text{CO}_2} = 100 \text{CO}_2/(\text{CO}_2 + \text{CO})$.

3. Results and discussion

Compared to DRS spectra of CoO_x/ZrO₂, DRS spectra of all CoS/Z and Co/SZ samples showed that the presence of sulphates prevented the formation of Co₃O₄. The comparison will be reported in details elsewhere [19].

The XRD pattern of SZ, CoS/Z, and Co/SZ samples was that of monoclinic ZrO₂, with a small fraction of tetragonal ZrO₂ (<10%). The absence of XRD peaks from CoSO₄ and Co₃O₄ particles indicated that these particles, if present, were smaller than 5 nm.

The XPS signal of all CoS/Z and Co/SZ samples consisted of two main peaks in the Co 2p region at

about 782.2 eV, Co 2p_{3/2}, and at 797.8 eV, Co 2p_{1/2}, each peak with a satellite at higher BE. The BE of main peaks are consistent with both Co(II) and Co(III), whose relevant band positions differ by 0.9 eV, with Co(II) 2p occurring at higher BE, because of covalency and final state effects [21,22]. Owing to the small BE difference and band broadening caused by “multiplet splitting”, the presence of Co(II) or Co(III), or both, could not be established from the position of the Co 2p band alone. A spectral feature that will distinguish between Co(II) and Co(III) is that the main Co(II) peaks present a satellite, whereas the Co(III) peaks do not.

To determine which cobalt species were present in CoS/Z and Co/SZ, we adopted the same procedure we have previously used for Co/Z samples [14]. We first evaluated by curve fitting the XPS parameters of Co(II) and Co(III) in the mechanical mixture Co₃O₄ + ZrO₂ (2.3 wt.% of Co₃O₄), imposing two components for the main Co 2p_{3/2} and Co 2p_{1/2} peaks and one component for the two corresponding satellites and leaving free band positions and full width at half maximum (FWHM) (Fig. 1, spectrum 1). From the integrated area of the Co(III) peak, we calculated that the percentage Co₃O₄ amount corresponded to 95–103% of total cobalt, as determined from several curve fitting routines. Having shown that this procedure gave reliable results, we used components and FWHM values from the mechanical mixture in the curve fitting of CoS/Z and Co/SZ samples. On the CoS/Z sample (4.0, 4.0), the curve fitting shows that the Co 2p_{3/2} main peak consisted of one component only, with an intense satellite at higher BE (Fig. 1, spectrum 2). The spectrum of the Co/SZ (3.6, 2.3) sample (spectrum not shown) was nearly identical to that of the CoS/Z (4.0, 4.0) sample. On both CoS/Z (4.0, 4.0) and Co/SZ (3.6, 2.3), the intensity ratio of the satellite to the relevant main peak, $I_{\text{sat}}/I_{\text{main}}$, was 1.0, close to the value reported for CoO [21], indicating the presence of Co(II) alone. On Co/Z (2.1) and Co/Z (4.8) the main peak consisted of two components, and the $I_{\text{sat}}/I_{\text{main}}$ ratio was 0.8 in Co/Z (2.1) and 0.6 in Co/Z (4.8) (Fig. 1, spectra 3 and 4), indicating the presence of an increasing amount of Co(III) arising from Co₃O₄, as previously discussed [14].

FTIR spectra of all Co-sulphated samples after evacuation at 793 K, showed bands typical of covalent organic-like sulphates [23–25]. At the same sulphate

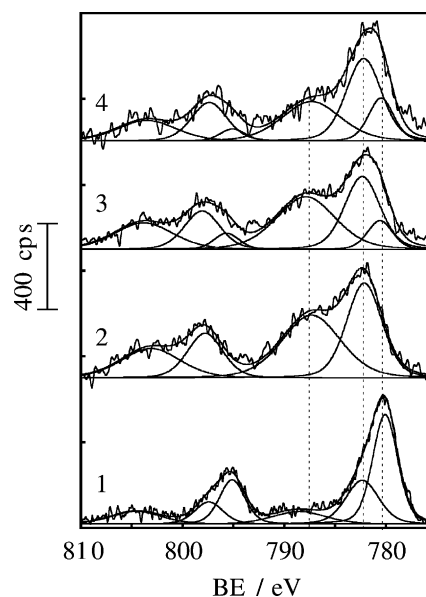


Fig. 1. XPS spectra in the Co 2p region, of the mechanical mixture Co₃O₄ + ZrO₂ (2.3 wt.% of Co₃O₄, corresponding to 5.1 atoms nm⁻², spectrum 1), CoS/Z (4.0, 4.0) (spectrum 2), Co/Z (2.1) (spectrum 3), Co/Z (4.8) (spectrum 4). The XPS parameters of Co(II) and Co(III) in the mechanical mixture were evaluated by imposing two components for the main Co 2p_{3/2} and Co 2p_{1/2} peaks and one component for the two corresponding satellites, leaving band positions and FWHM free. From the curve fitting of the spectrum from the mechanical mixture, the following parameters were determined: Co(II) 2p_{3/2} main peak BE = 782.2 eV, FWHM = 4.1 eV; Co(II) 2p_{1/2} main peak BE = 797.4 eV, FWHM = 4.1 eV; Co(II) 2p satellites FWHM = 6.8 eV; Co(III) 2p_{3/2} BE = 780.2 eV, FWHM = 2.9 eV; Co(III) 2p_{1/2} BE = 795.2 eV, FWHM = 2.9 eV. These parameters were used in the curve fitting of spectra from CoS/Z and Co/Z.

content, CoS/Z and Co/SZ had nearly identical spectra, indicating that the preparation via metal–sulphate and the two-step preparation via Co(acetylacetonate)₂ yielded samples having the same covalent sulphates [19].

The adsorption of NO on Co/Z samples, in addition to the very weak bands observed on pure ZrO₂ [19,26], yielded a band at about 1865 cm⁻¹ and a weak component at 1810 cm⁻¹ (Fig. 2, section a). On increasing NO pressure, the intensity of the band at 1865 cm⁻¹ increased and a new band at 1775 cm⁻¹ appeared, both bands shifting to higher wavenumbers (1875 and 1780 cm⁻¹). The band at 1875–55 cm⁻¹ is assigned to Co(II)–NO species. The band at 1780–75 cm⁻¹ is

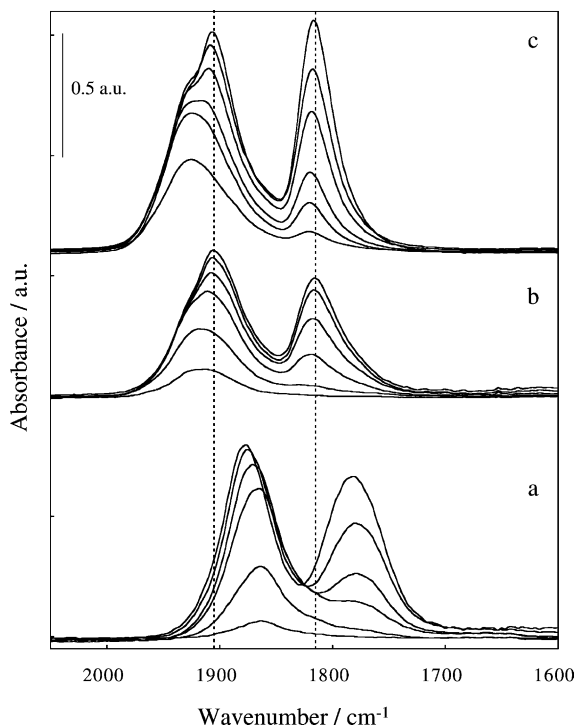


Fig. 2. FTIR spectra at RT of Co/Z (2.1) (section a), CoS/Z (2.0, 1.9) (section b) and Co/SZ (2.1, 2.4) (section c), after exposure to NO at increasing equilibrium pressure from 0.01 to 80 Torr.

possibly the asymmetric stretching of a Co(II)–(NO)₂ species, whose symmetric mode partly overlaps the mono-nitrosyl band at 1875–55 cm⁻¹.

On Co/SZ samples, in addition to the weak bands observed on SZ (2.4), NO adsorption at RT yielded intense bands in the 2000–1700 cm⁻¹ region. On Co/SZ (2.1, 2.4), Co-nitrosyl bands occurred at 1905 cm⁻¹, with a shoulder at 1930 cm⁻¹, and at 1815 cm⁻¹ (Fig. 2, section c). We assign the band at 1930 cm⁻¹ to Co(II)–NO, and the bands at 1905 and 1815 cm⁻¹ to the symmetric and asymmetric stretching modes of Co(II)–(NO)₂ complexes [19].

On Co/Z, CoS/Z and Co/SZ samples, after evacuation at RT all Co-nitrosyl bands decreased by about 30%. In passing from Co/Z (Fig. 2, section a) to CoS/Z (section b) and to Co/SZ samples (section c), Co-nitrosyl bands shifted to higher wavenumbers, sharpened and partially resolved. On the whole, the increased SO₄ content (i) increased the Lewis acid strength of Co(II) sites, owing to the electron with-

drawing effect of sulphates, and (ii) decreased the heterogeneity of Co(II) species. The spectra of all Co/SZ and that of CoS/Z containing a large amount of CoSO₄, CoS/Z (2.0, 1.9), were nearly identical in shape, showing that the preparation via metal–sulphate and the two-step preparation via Co(acetylacetonate)₂ yielded very similar samples. Conversely, the spectra of CoS/Z samples containing a small amount of CoSO₄, CoS/Z (0.3, 0.3) and CoS/Z (0.7, 0.6), resembled those of Co/Z samples. Hence, in samples with low Co content, the presence of sulphates has a weaker effect on the type of Co sites.

On Co/Z, the total integrated intensity of Co-nitrosyl bands was nearly proportional to the cobalt content up to 2 atoms nm⁻², and at higher cobalt content, because of Co₃O₄ formation, remained nearly unchanged. Conversely, on Co/SZ, the total integrated intensity of Co-nitrosyl bands was proportional to the cobalt content up to 3.6 (data not shown). The comparison shows that sulphate maintains cobalt dispersion.

CO adsorption at RT showed that, as the sulphate content in the sample increased, the reducibility and the heterogeneity of cobalt species decreased (data to be reported elsewhere [19]).

3.1. Catalysis

3.1.1. Samples with the same sulphate content

On all Co/SZ samples, containing the same amount of sulphate (about 2.4 molecules nm⁻²) and Co in increasing amount from 0.2 to 3.6 atoms nm⁻², NO conversion reached a maximum as a function of temperature. As the cobalt content increased, the maximum NO conversion value slightly increased, and NO conversion reached the maximum at lower temperature. Propene conversion increased with temperature, reaching 100% at nearly the same temperature of maximum NO conversion (Fig. 3). The selectivity *S*_{SCR} did not depend on Co content, and decreased with temperature, being 100% at about 623 K, and 60% at 750 K. The selectivity *S*_{CO₂} increased with temperature and Co content. In particular, on the sample Co/SZ (0.2, 2.3), the selectivity *S*_{CO₂} increased with temperature from 60% at about 623 K to 100% at about 873 K. On samples Co/SZ (2.1, 2.4), and Co/SZ (3.6, 2.3), the selectivity *S*_{CO₂} was higher than on Co/SZ (0.2, 2.3), and increased with temperature from 80% at about 623 K to 100% at about 823 K. On all samples the

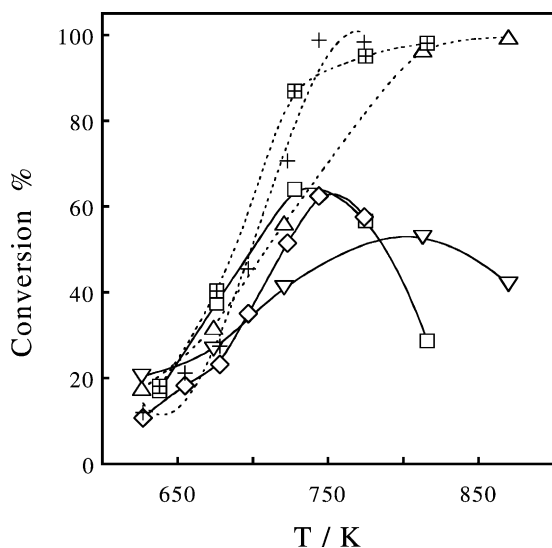


Fig. 3. NO conversion and C₃H₆ conversion on Co/SZ samples as a function of temperature (T, K). Catalysts: Co/SZ (0.3, 2.3) (▽, △), Co/SZ (2.1, 2.4) (□, ⊞), and Co/SZ (3.6, 2.3) (◇, ⋄). Symbols in parentheses refer to NO conversion and propene conversion, in that order.

selectivity S_{N_2} increased with temperature from 80 to 100% and was nearly independent of cobalt content.

3.1.2. Samples with the same cobalt content

In samples with low cobalt content (about 0.3 atoms nm⁻²), the presence of a small amount of sulphate (0.3 molecules nm⁻²) increased the maximum NO conversion. On increasing the sulphate content to 2.3 molecules nm⁻², NO conversion did not increase further, but the temperature required for maximum NO conversion shifted to a value about 100 K higher (Fig. 4). On increasing the sulphate content, NO and C₃H₆ conversion curves shifted in parallel towards higher temperature (Fig. 4). Accordingly, the selectivity S_{SCR} depended little on the sulphate content, and decreased with temperature (80–100% at about 623 K, and 50–70% at about 750 K). In the temperature region 550–800 K, the selectivity S_{CO_2} was 100% on Co/Z (0.4) and CoS/Z (0.3, 0.3), whereas it was somewhat lower on Co/SZ (0.2, 2.3) (70% at 550 K and 90% at 800 K). The selectivity S_{N_2} did not depend on the sulphate content, and increased with temperature (from 70–80% at 550 K to 80–100% at 800 K).

In samples with higher cobalt content (~4 atoms nm⁻²), the presence of sulphate increased the max-

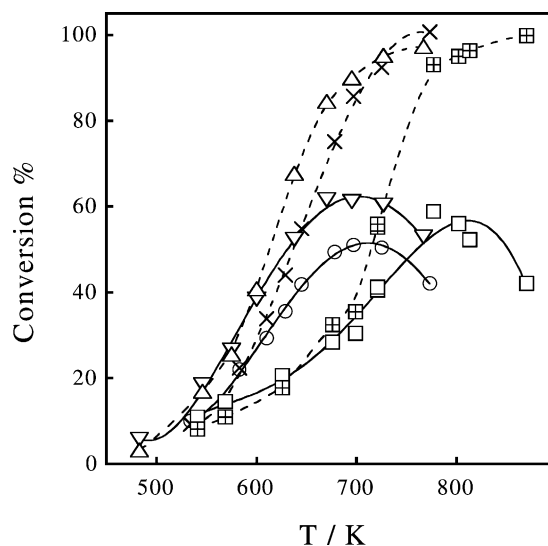


Fig. 4. NO conversion and C₃H₆ conversion as a function of temperature (T, K). Samples with the same cobalt content (about 0.3 atoms nm⁻²) and different sulphate content. Catalysts: Co/Z (0.4) (○, ×), CoS/Z (0.3, 0.3) (▽, △), and Co/SZ (0.2, 2.3) (□, ⊞). Symbols in parentheses refer to NO conversion and propene conversion, in that order.

imum NO conversion, and the temperature required for maximum NO conversion shifted to a value about 200 K higher (Fig. 5). At this high cobalt loading, the selectivity S_{SCR} was much higher on sulphated catalysts than on the unsulphated one. In particular, on Co/SZ (3.6, 2.3), S_{SCR} decreased from 90% at 650 K to 60% at 800 K, whereas on Co/Z (4.8), S_{SCR} decreased from 90% at 500 K to 5% at 600 K. On Co/Z (4.8), the selectivity S_{CO_2} was 100% in the temperature region 500–623 K. On the sulphated samples CoS/Z (4.0, 4.0) and Co/SZ (3.6, 2.3), the selectivity S_{CO_2} was 80–90% at 550 K and increased to 100% at 800 K. On Co/Z (4.8), the selectivity S_{N_2} was 40–60% in the temperature region 500–623 K. On the sulphated samples CoS/Z (4.0, 4.0) and Co/SZ (3.6, 2.3), the selectivity S_{N_2} was 80% at 550 K and increased to 100% at 800 K.

3.1.3. The catalytic activity for C₃H₆ combustion with O₂

On Co/Z catalysts, the C₃H₆ conversion in the combustion reaction markedly increased with cobalt content. On Co/SZ samples, the C₃H₆ conversion was markedly lower than that on Co/Z samples and did not depend on Co content.

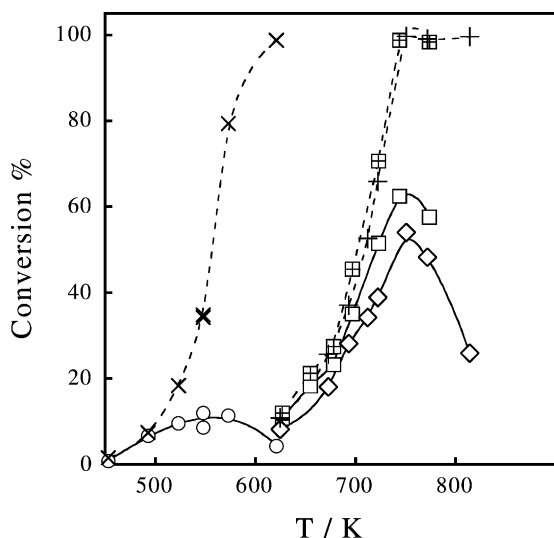


Fig. 5. NO conversion and C_3H_6 conversion as a function of temperature (T, K). Samples with the same cobalt content (about 4 atoms nm^{-2}) and different sulphate content. Catalysts: Co/Z (4.8) (\circ , \times), Co/SZ (3.6, 2.3) (\square , \boxplus), and CoS/Z (4.0, 4.0) (\diamond , $+$). Symbols in parentheses refer to NO conversion and propene conversion, *in that order*.

4. Conclusions

As it is on CoO_x/ZrO_2 [14] and on other Co containing systems [9–13], isolated Co(II) in sulphated- ZrO_2 samples is active for the selective reduction of NO with propene in the presence of oxygen. Sulphated samples with cobalt content higher than 2 atoms nm^{-2} are far more active and selective than the corresponding unsulphated CoO_x/ZrO_2 . The presence of sulphates (i) makes Co(II) less reducible in sulphated samples than in CoO_x/ZrO_2 and (ii) prevents Co_3O_4 formation. Because both effects reduce the catalytic activity for the $C_3H_6 + O_2$ reaction, sulphated samples are more selective than CoO_x/ZrO_2 . The presence of sulphates has a smaller effect on the catalytic behaviour of samples with lower Co content (<2 atoms nm^{-2}). The results show that cobalt and sulphate co-operate in determining the catalytic activity and selectivity of cobalt sulphated catalysts. Whereas cobalt favours NO reduction and maintains S_{CO_2} selectivity high, particularly in samples with higher sulphate content, sulphate maintains S_{SCR} selectivity high, particularly in samples with higher cobalt content.

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References

- [1] Y. Li, J.N. Armor, *Appl. Catal. B: Environ.* 2 (1993) 239.
- [2] A.D. Cowan, R. Dümpelmann, N.W. Cant, *J. Catal.* 151 (1995) 356.
- [3] M.C. Campa, S. De Rossi, G. Ferraris, V. Indovina, *Appl. Catal. B: Environ.* 8 (1996) 315.
- [4] L.J. Lobree, A.W. Aylor, A. Reimer, A.T. Bell, *J. Catal.* 169 (1997) 188.
- [5] D. Kaucky, A. Vondrová, J. Dědeček, B. Wichterlová, *J. Catal.* 194 (2000) 318.
- [6] J.R. Regalbuto, T. Zheng, J.T. Miller, *Catal. Today* 54 (1999) 495.
- [7] Y. Li, J.N. Armor, *J. Catal.* 150 (1994) 376.
- [8] H. Ohtsuka, T. Tabata, O. Okada, L.M.F. Sabatino, G. Bellussi, *Catal. Today* 42 (1998) 45.
- [9] M. Inaba, Y. Kintaichi, M. Haneda, H. Hamada, *Catal. Lett.* 39 (1996) 269.
- [10] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari, H. Tsuchida, *Catal. Today* 29 (1996) 53.
- [11] J.Y. Yan, M.C. Kung, W.M.H. Sachtler, H.H. Kung, *J. Catal.* 172 (1997) 178.
- [12] T. Maunula, J. Ahola, H. Hamada, *Appl. Catal. B: Environ.* 26 (2000) 173.
- [13] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, *Catal. Today* 59 (2000) 287.
- [14] D. Pietrogiaconi, S. Tuti, M.C. Campa, V. Indovina, *Appl. Catal. B: Environ.* 28 (2000) 43.
- [15] D. Pietrogiaconi, D. Sannino, S. Tuti, P. Ciambelli, V. Indovina, M. Occhiuzzi, F. Pepe, *Appl. Catal. B: Environ.* 21 (1999) 141.
- [16] V. Indovina, M.C. Campa, D. Pietrogiaconi, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), 12th International Congress on Catalysis, Studies in Surface Science and Catalysis, vol. 130 B, Elsevier Science B.V., 2000, p. 1439.
- [17] D. Pietrogiaconi, D. Sannino, A. Magliano, P. Ciambelli, S. Tuti, V. Indovina, *Appl. Catal. B: Environ.* 36 (2002) 217.
- [18] V. Indovina, D. Pietrogiaconi, M.C. Campa, *Appl. Catal. B: Environ.* 39 (2002) 115.
- [19] D. Pietrogiaconi, M.C. Campa, S. Tuti, V. Indovina, *Appl. Catal. B: Environ.* 41 (2003) 301.
- [20] A. Cimino, D. Cordischi, S. De Rossi, G. Ferraris, D. Gazzoli, V. Indovina, G. Minelli, M. Occhiuzzi, M. Valigi, *J. Catal.* 127 (1991) 744.
- [21] D. Gazzoli, M. Occhiuzzi, A. Cimino, D. Cordischi, G. Minelli, F. Pinzari, *J. Chem. Soc., Faraday Trans.* 92 (1996) 4567.

- [22] T.J. Chuang, C.R. Brundle, D.W. Rice, Surf. Sci. 59 (1976) 413.
- [23] M. Bensitel, O. Saur, J.-C. Lavallay, B.A. Morrow, Mater. Chem. Phys. 19 (1988) 147.
- [24] F. Haase, J. Sauer, J. Am. Chem. Soc. 120 (1998) 13503.
- [25] C. Morterra, G. Cerrato, V. Bolis, Catal. Today 17 (1993) 505.
- [26] G. Ghiotti, A. Chiorino, Spectrochim. Acta 49A (1993) 1345.