Cobalt–iridium impregnated zirconium-doped mesoporous silica as catalysts for the selective catalytic reduction of NO with ammonia

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Abstract

Catalysts based on cobalt–iridium supported on zirconium-doped mesoporous silica, with a Si/Zr molar ratio of 5, a cobalt loading of 16 wt.% and Co/Ir molar ratios of 10, 20, 30 and 60 were prepared by impregnation, characterised and then tested in the selective catalytic reduction of NO with ammonia in an excess of oxygen. These catalysts are active in the targeted catalytic reaction showing high conversions of NO at low reaction temperatures with a low yield of N_2O. The incorporation of iridium increases the dispersion of cobalt, thus improving the catalytic performance. These catalysts maintain their activities when water is added to the feed on stream, but are less active with the addition of 100 ppm of SO_2.
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1. Introduction

One of the main environmental problems that concerns the scientific community today is related to nitrogen oxides (NO_x) emitted into the atmosphere. NO_x is one of the most harmful pollutants involved in acid rain as well as playing a major role in the formation of trophospheric ozone with volatile organic compounds, etc. N_2O is responsible for global warming and the destruction of stratospheric ozone. Restrictive legislation has led to the control of these emissions around the world [1].

NO is produced during combustion processes by the oxidation of atmospheric nitrogen at very high temperatures. Some NO is also formed by oxidation of nitrogen compounds present in fuel [2]. Thus, NO formation may be controlled either by improving the combustion process or by reducing its concentration in the flue-gases. The latter can be achieved with catalytic technology such as the selective catalytic reduction (SCR), where a reductant such as ammonia [3,4], CO [5,6] or hydrocarbons [7,8] are necessary to convert NO into N_2. Nowadays, for stationary sources of emission, the only available method to reduce the NO concentration in waste gases on an industrial scale is the SCR of NO with ammonia. Recently, much effort has been devoted to replacing ammonia with hydrocarbons [9–11],

but an active catalyst for industrial applications has not yet been obtained. The most commonly used catalysts are based on mixed oxides: V_2O_5–WO_3–TiO_2 for the SCR of NO with ammonia. However, these catalysts suffer from some disadvantages: their activity is highest at temperatures above 250 °C, the toxicity of vanadium, etc. For these reasons, over recent decades, many research groups have been studying other systems for supports and active phases which are effective in the SCR of NO with ammonia. Research has been carried out on catalysts based on zeolites [12,13], SiO_2 [14], Al_2O_3 [15,16], etc., and on others loaded with different metals such as Fe [13,14], Cu [12,17], Cr [18,19] or Mn [15,20].

Since Li and Armor [21] reported that Co-catalysts could reduce the NO to nitrogen with methane in the presence of oxygen, the use of cobalt as an active phase has been limited mainly to the presence of methane as a reductant. Other catalysts are also active in the catalytic reduction of NO with methane such as Ga [22], Ir [23] or Pd [24]. However, the Co-catalysts are not stable in the presence of water vapour or SO_2 [25,26]. To overcome these undesired effects, bimetallic catalysts have been synthesised and tested in the SCR of NO with hydrocarbons. Supported bimetallic catalysts are of great interest because one metal can tune or modify the catalytic properties of another as a result of both electronic and structural influences. Normally, the second metal added to the Co-catalyst is a noble metal such as Pd [27] or Pt [28]. The presence of Pt or Pd appears to produce an increase in the amount of NO adsorbed, and may also

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be responsible for NO oxidation to NO_2 (an important reaction intermediate for HC-SCR) and water tolerance. Nevertheless, the Co-catalysts have not been tested in depth in the SCR of NO with ammonia. There are only a few reports based on co-catalysts [29–31] giving worse results than those reported when methane is used as a reductant. Chmielarz et al. [32] found that a titania-pillared montmorillonite exchanged with cobalt achieved a NO conversion close to 100% at temperatures higher than 400 °C, whilst displaying high selectivities towards nitrogen. Co-ZSM-5 catalysts prepared with different methods have been assayed with *iso*-butane as reductant showing high yield of nitrogen at low temperature for catalysts containing Co^{2+} oxo-ions or Co_3O_4 clusters [33].

Recently, catalysts based on iridium have received much more attention since they exhibit high activity in the reduction of NO in excess oxygen [34,35] with different reductant agents. Ogura et al. [36] reported that Ir-silicate exhibits high activity for the NO–CO reaction. Wang et al. [37] have reported that Ir-ZSM-5 monoliths could efficiently reduce NO with CO under lean conditions. Yoshinari et al. [38] reported that Ir–SiO_2 showed excellent activity for NO reduction with hydrogen in the presence of O_2 and SO_2. Moreover, several authors have emphasised the promotional effect of SO_2 present in the feed stream [38,39].

Our previous work related to Co-catalysts [40] used in the SCR of NO with ammonia showed that cobalt could be an excellent active phase with high activities and selectivity towards nitrogen. In order to improve its catalytic activity in the presence of water vapour and SO_2 in the feed stream, iridium has been selected as the promoter because the presence of iridium may improve the catalytic activity of the cobalt catalyst by increasing the dispersion of cobalt oxides and therefore the number of active sites. Thus, a family of Co/Ir catalysts supported on a zirconium doped-mesoporous silica with a Si/Zr molar ratio of 5 was prepared with a view to testing its catalytic activity in the SCR of NO with ammonia in the presence of water vapour and SO_2.

2. Experimental

2.1. Preparation of catalysts

A zirconium-doped mesoporous silica, with a Si/Zr molar ratio of 5, was prepared by following the method described in previous papers [41,42]. The material was calcined at 550 °C (1 °C min⁻¹ heating rate) for 6 h and was denoted as SiZr5. This material was used as a support with a cobalt loading of 16 wt.% and Co/Ir atomic ratios of 10, 20, 30 and 60 which were prepared by the incipient wetness method. Both metals were added simultaneously to the support. After impregnation, the samples were calcined at 550 °C for 4 h (1 °C min⁻¹ heating rate). For comparison, two monometallic catalysts with a cobalt loading of 16 wt.% and a iridium loading of 2 wt.% were prepared, following the same method. The monometallic catalysts were named as Co-16 and Ir-2 and the bimetallic catalysts as CoIr10, CoIr30, CoIr20 and CoIr60, depending on the Co/Ir atomic ratios.

2.2. Characterisation methods

Powder XRD patterns were obtained with a Siemens D500 diffractometer, equipped with a graphite monochromator and using Cu-K$_\alpha$ radiation. X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non–monochromatic Mg Kα radiation (300 W, 15 kV, 1253.6 eV) for the analysis of the photoelectronic signals of Si 2p, Zr 3d, O 1s, Co 2p and Ir 4f, and equipped with a multi-channel detector. The Co 2p photoelectronic signal was collected by using a non-monochromatic Al Kα radiation (300 W, 15 kV, 1486.6 eV) as an excitation source to avoid the overlapping of the O KLL Auger line with the photoelectronic Co 2p signal. Spectra of powdered samples were recorded with the constant pass energy values at 29.35 eV, using a 720 μm diameter analysis area. During the data processing of the XPS spectra, binding energy values were referenced to the C 1s peak (248.8 eV) from the adventitious contamination layer. The PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves in order to determine the binding energy of the different element core levels more accurately. The error in BE was estimated to be ca. 0.1 eV.

Textural parameters were obtained from N_2 adsorption–desorption isotherms (BET method) as determined with a Micromeritics ASAP 2020. Temperature-programmed reduction of H_2 (H_2-TPR) was performed between room temperature and 800 °C using a flow of Ar/H_2 (40 cm³ min⁻¹, 10 vol.% of H_2) and a heating rate of 10 °C min⁻¹. Water produced in the reduction was eliminated by passing the gas flow through a cold finger (−80 °C). The consumption of H_2 was monitored by an on-line gas chromatograph (Shimadzu GC-14) provided with a TCD.

Temperature-programmed desorption of NO (NO-TPD) was performed by adsorbing NO onto the catalysts at room temperature (150 cm³ min⁻¹ flow rate and 0.05 vol.% NO balanced with He) for 1 h, and performing desorption between 40 and 550 °C, using a heating rate of 10 °C min⁻¹. Before the adsorption of NO, the catalysts were heated at 550 °C under a He flow for 1 h. During desorption, helium was flushed through and the eluted gas phase was carefully monitored and quantified using a Balzers GSB 300 02 on-line quadrupole mass spectrometer.

2.3. Catalysis

Catalysts were tested in the SCR of NO by using a Pyrex glass tube microreactor (6.85 mm o.d.) working at atmospheric pressure in a steady-state flow mode and with a catalytic charge of 150 mg of pelletised solids, sieved to 0.3–0.4 mm, in all cases without dilution. Samples were pretreated at 350 °C in situ for 2 h under a He flow (30 cm³ min⁻¹). The gas reaction mixture was composed of 1000 ppm NO, 1000 ppm NH_3 and 2.5 vol.% O_2 (balanced with helium). In some tests, 10 vol.% H_2O, passing helium through a saturator with deionized water and 100 ppm of SO_2, was added to the feed stream. The flows were independently controlled by channel mass flowmeters (Brooks) and a total flow rate of 42 cm³ min⁻¹ was used in the feed. The space