Catalysis Letters 61 (1999) 121–130

Preparation and reaction mechanistic characterization of sol–gel indium/alumina catalysts developed for NO_x reduction by propene in lean conditions

T. Maunula *, Y. Kintaichi, M. Haneda and H. Hamada

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan
E-mail: teuvo.maunula@kemira.com

Received 29 March 1999; accepted 29 June 1999

The impregnation and sol–gel preparation methods were investigated to develop high activity catalysts and understand the significance of the indium–aluminium interaction on alumina-supported indium catalysts in NO_x reduction with propene. Active In/alumina catalysts with a very high surface area (270 m^2/g) and thermal stability were prepared in controlled conditions by sol–gel processing. When Al isopropoxide and In nitrate in ethyl glycol were used as precursors in aqua media, indium atoms were incorporated evenly distributed as a thermally stable form in the aluminium oxide lattice structure. In wet impregnation it was beneficial to use a certain excess of aqueous In solution (volumes of solution : pores = 2 : 1) to have the highest NO_x reduction activity. The catalyst containing dispersed Al on In oxide (58 wt% In, phase-equilibrium preparation method) showed activity at lower temperatures than any other In–Al oxide catalyst or pure In_2O_3. The adsorption of different reaction intermediates on alumina and stable In_2O_3 sites were detected by FTIR studies. In/alumina catalysts have active sites to oxidize NO to NO_2, partially oxidize HC, form the actual reductant which contains N–H or N–C bonding and react with NO to dinitrogen. The cooperation with indium and aluminium was evident even in the mechanical mixture of sol–gel prepared alumina (301 m^2/g) and In_2O_3 powders (27 m^2/g), where the probability for molecular-scale intimate contact between indium and aluminium sites was very low (particle size 10–250 μm). Short-lived gaseous intermediates and surface migration are the possible reasons for the high catalytic activities on the two physically separated active sites both necessary for the reaction sequence.

Keywords: nitrogen oxides, selective reduction, hydrocarbons, indium, sol–gel, alumina

1. Introduction

The general concept of catalytic NO_x reduction by hydrocarbons in lean conditions was introduced for the first time in the late 1980s [1,2]. After that, several efficient zeolite (Cu, Co, Pt) and oxide (Co, Pt, Ag, Sn, Au, Cu, Ga) based catalysts have been introduced [3–17]. The complicated reaction sequence consists of several competing parallel reactions. NO_2 and partially oxidized hydrocarbons are important intermediates in the presence of oxygen [6]:

$$\mathrm{HC} + \mathrm{NO}_x + \mathrm{O}_2 \rightarrow \text{intermediates} \rightarrow \mathrm{N}_2 + \mathrm{CO}_x + \mathrm{H_2O} \qquad (1)$$

The enhanced activity of sol–gel alumina-based indium, gallium, tin and cobalt catalysts invented in our recent studies [18] motivated us to investigate more closely the performance of alumina-supported indium catalysts. In this study, the preparation methods according to the precursor and the calcination temperature as well as the different reaction conditions and characterization methods, were used to find the reaction mechanism on indium catalysts.

Another object in our studies was to develop new, improved sol–gel preparation methods for deNO_x catalysts based on the polymerization of metal alkoxides. Organic phase in aqueous solution opens new possibilities to control the morphology and reactivity of resulting solids [19]. Sol–gel processing has many advantages compared to conventional methods to prepare raw material and catalysts [20,21]. It has been confirmed in earlier studies that it is possible to prepare active and thermally stable catalysts consisting of promoters for automotive applications by sol–gel methods [22–24].

2. Experimental

2.1. Catalyst preparation

The optimal preparation parameters for sol–gel alumina-based indium catalysts including the composition (Al/In = 650–20, molar ratio) and the calcination temperature (600–900 °C) as variables were investigated in our earlier study [18], where also the preparation of sol–gel alumina-based indium catalysts by wet impregnation as well as the activity experiment procedures, have been described in details. In the present study we have continued the more profound characterization of these In/alumina catalysts and, in addition, prepared new ones by different methods. $In(CH_3COO)_3$ was also used instead of $In(NO_3)_3\cdot 3H_2O$ to ascertain the effects of the precursor salt. In_2O_3 was prepared by precipitation. Sol–gel preparation methods

---

[*] To whom correspondence should be addressed. Present address: Kemira Metalkat Oy, Catalyst Research, PO Box 171, FIN-90101 Oulu, Finland.

Table 1
Composition and surface area after calcination at different temperatures of the catalysts.

Catalyst (Al/In)	In (wt%)	Surface area ($m^2\,g^{-1}$) 600 °C	700 °C	800 °C	900 °C
In/Al-sg(65)	3.3	216	178	161	138
In/Al-sg(65,acet)[a]	3.3	241	na[b]	na	na
In/Al-sg(65,wet2)[c]	3.3	261	206	na	na
In/Al-sg(20)	10.1	180	160	140	na
In–Al-sg1(65)[d]	3.3	271	219	na	na
In–Al-sg2(65)[e]	3.3	199	152	na	na
In/Al-sg(pe)(0.67)	58	85	na	na	na
Al-sg	–	301	243	181	178
InO_x	∼100	27	na	na	na

[a] acet = prepared from indium acetate, other from indium nitrate.
[b] na = not available.
[c] wet2 = wet impregnation method 2.
[d] sg1 = In nitrate added as ethyl glycol solution into Al sol.
[e] sg2 = In nitrate added as water solution into Al sol.

for InAl oxide catalysts were studied. The composition and physical properties of the catalysts investigated are summarized in table 1.

2.1.1. Variation of impregnation methods

The parameters in wet impregnation were investigated: our standard wet method (wet1) contained the volume of solution, which is twice the amount needed for pore filling. The porosity of alumina was estimated to be about 0.80. In the wet2 impregnation method, the Al-sg support was wetted with an amount of water solution almost equal to the volume requirement to fill all the pores. After impregnation, moisture was removed by drying at 110 °C overnight. Other preparation steps (calcination at 600 °C for 3 h, screening to the fraction below 250 μm) were exactly same for each sample.

An In/Al-sg(pe) catalyst was prepared by impregnation of indium on 2 g Al-sg dispersed in 250 ml of 0.04 M indium nitrate solution at 80–90 °C for 12 h in the way usually used in ion exchange. After this treatment denoted as the phase-equilibrium (pe) preparation method, the vessel was cooled down, the sample was filtered, centrifuged, washed, dried and calcined at 600 °C for 3 h. High-indium-concentrated alumina or the mixture of InO_x–Al_2O_3 (82 wt% In_2O_3, molar ratio of Al/In = 0.67) as fine particles was the final product. The large excess of indium present in solution gave the possibility to hydrated indium cations to be attached freely on the support up to the level of equilibrium composition controlled by the forces between cations in solvent and solid alumina surface in treatment conditions.

2.1.2. Sol–gel preparation method for In–Al oxide catalyst

The sol–gel processing was carried out by the following way: aluminum isopropoxide ($Al(OCH(CH_3)_2)_3$ was dissolved in water at 80–90 °C, the solution was mixed for 2 h and an appropriate amount of nitric acid was added by stirring for 30 min to form Al(OOH) sol. Indium nitrate ethyl glycol solution (InAl-sg1) or indium nitrate water solution (InAl-sg2) was added slowly into the aluminium sol by mixing for 1 h. A transparent gel was produced by a rotary vacuum evaporator with a stepwise temperature program (35 → 40 → 50 → 60 → 70 °C). The gel was dried overnight at 110 °C. The primary calcination of the sample to decompose the gel to oxides was carried out in flowing air at 450 °C for 3 h, secondary calcination in static air at 600 °C for 3 h and the samples were screened to a particle size fraction below 250 μm.

2.2. Catalyst characterization

Different characterization methods were used to find the explanation for the detected activities from the solid or surface state properties of these catalysts. The surface area (BET) was measured by the standard method with nitrogen adsorption at −196 °C (Micromeritics Flow Sorb II) after pretreatment in N_2/He flow at 300 °C for 30 min. The chemical composition of catalysts was confirmed by XRF (Seiko Intruments SEA2010) and plasma analysis. Metal and oxide phases after treatments were detected by XRD (Shimadzu XD-D1). Powder samples were analyzed using a Cu Kα target and a 0.6 mm received slit with a rotation speed of $2^\circ\,min^{-1}$.

XPS analysis was carried out by using Mg Kα radiation with a Rikagaku Denkikogyo XPS-7000 (5 kV, 5 mA, 25 W). The states of In species were primarily detected by the binding energy of In $3d_{5/2}$ and the peak of C 1s (285 eV) was used as a chemical shift correction reference. The In phases were also evaluated by calculating the combined binding and kinetic energies of the corresponding peaks. The baseline and the pretreatment pressure was 3×10^{-3} Pa at 25 °C. Pure In metal and In_2O_3 were used as references and the data matched the available literature data.

TG analysis of indium samples (20 mg) was performed in static air with a Shimadzu DTG-50 analyzer (α-alumina as a reference, platinum sample holder) with a heating rate of $10\,°C\,min^{-1}$ to find out possible changes in oxidation states.

2.3. Activity testing

The steady-state activity of the catalysts was evaluated with a simulated exhaust gas mixture ($W/F = 0.05\ g\,h\,dm^{-3}$) which contained 1000 ppm NO, 1000 ppm propene, 0/10% oxygen and 0/10% water in helium in a temperature range of 200–600 °C. In addition, 1000 ppm NO_2 or 500 ppm N_2O in the same mixture was also used instead of NO to evaluate the reaction mechanism. The concentrations of N_2, N_2O, NO, NO_2, CO_2, CO, C_3H_6, C_2H_4, CH_4 were measured quantitatively by two gas chromatographs and a chemiluminescence NO_x analyzer.

2.4. FTIR measurements

The FTIR adsorption bands on In/Al-sg and Al-sg catalysts were measured at 50 and 150 °C in the wavenumber range of 4000–1000 cm^{-1} and a resolution of 4 cm^{-1} with a Shimadzu FTIR-8600PC equipped with a liquid-nitrogen-cooled detector. The powder samples (0.1 g) were pressed to thin, infrared transparent discs, which were installed at a right angle to the beam in the middle of a quartz reactor equipped with NaCl end windows and a thermocouple in a pocket inside the reaction chamber. Before adsorption the sample was outgassed at 480 °C for 30 min for purification and then cooled to the set-point temperature, where a background spectrum was measured at the pressure below 2×10^{-3} Torr. Pure NO (>99%), propene (>99.8%) and oxygen (>99.9%) were introduced into the chamber separately using two different gas sequences (NO $\rightarrow C_3H_6 \rightarrow O_2$ and $C_3H_6 \rightarrow$ NO $\rightarrow O_2$). FTIR spectra during each step were measured both in the presence of 20 Torr gas and in vacuum after 2 and 10 min from the change in conditions. The adsorption of single reactants (NO, C_3H_6, N_2O, CO, CO_2) on these samples was used as internal reference data.

The dynamic *in situ* FTIR experiments in continuous gas flow were performed with the same pretreatment and parameters as the static experiments. The background spectra were measured at 200 °C in He flow. The gas composition and flow rate were approximately the same as in the activity experiments: 920 ppm NO, 910 ppm C_3H_6 and 9.3% O_2 in He (total flow rate 66 ml/min). FTIR spectra were measured on In/Al-sg in gas flow at about 200, 240, 280, 320, 360, 400, 440 and 450 °C in a temperature ramp using the heating rate 10 °C/min. The measurement of each spectrum took about 2 min, corresponding to the average IR data of the temperature range within 20 °C. The main gas compounds (4 (He), 18 (H_2O), 28 (N_2, CO), 30 (NO), 42 (C_3H_6) and 44 (CO_2) amu) in outlet were monitored by a mass spectrometer (Anelva AQA-200), but it was not possible to detect by-products (N_2O, NO_2) because of their low concentrations.

3. Results and discussion

3.1. Catalytic activities for NO reduction

The interaction of indium and alumina surface was examined by adding the same amount of indium on aluminium oxides by several different preparation methods. Our earlier activity results showed that Al-sg made by the sol–gel method was better than the usual commercial γ-alumina as a support for indium impregnation, because it is free from inorganic impurities and has high initial surface area.

The indium/alumina catalyst prepared by impregnation with indium nitrate solution (initial pH = 3) was slightly more active than the one prepared from indium acetate (figure 1). The NO_x reduction activity of the catalyst prepared by the wet2 method was decreased because of the decreased HC oxidation activity at low temperatures. The lower activity of In/Al-sg(65, wet2) compared to In/Al-sg(65, wet1) was not sensitive to the calcination temperature, because the same difference detected with the samples calcined at 600 °C still existed after calcination at 700 °C. Therefore, the activity differences formed during catalyst preparation are relatively permanent in normal use and mild thermal ageing conditions (figure 2).

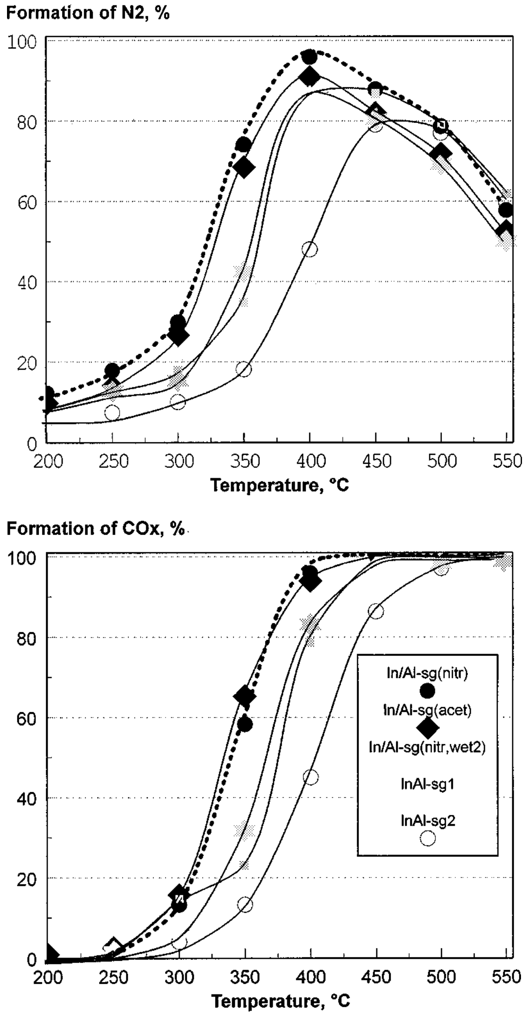


Figure 1. The effect of the preparation method and the alumina type on the activity of NO reduction by propene in dry conditions.

Different type properties were detected with the sample In/Al-sg(pe), which was produced by the phase-equilibrium method (figure 3). The propene oxidation activity of this catalyst containing indium as the main compound, was much higher than that of In/Al-sg, Al-sg or In_2O_3 and it had NO conversion to nitrogen at the low temperature (maximum nitrogen formation 37% at 300 °C). Because of the high indium content and the dealumination (more than 70% of original Al-sg was lost into solution) during the preparation, it is better to denote this catalyst as Al/InO_x instead of In/Al_2O_3, describing that aluminum is dispersed on indium oxide. This method showed a possible way to prepare a catalyst with a high In content and the low-temperature operation abilities.

The In/alumina catalysts, where the indium–alumina interaction was accomplished by the sol–gel method (InAl-sg1, indium from ethyl glycol solution) had about the same

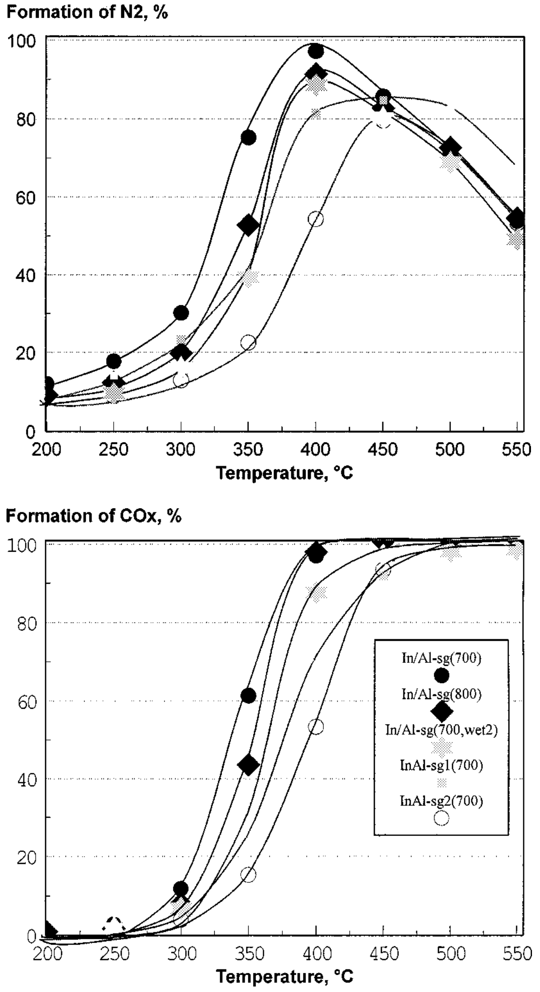


Figure 2. The dependence of the preparation method and alumina on the calcination temperature in the activity of NO reduction by propene in dry conditions.

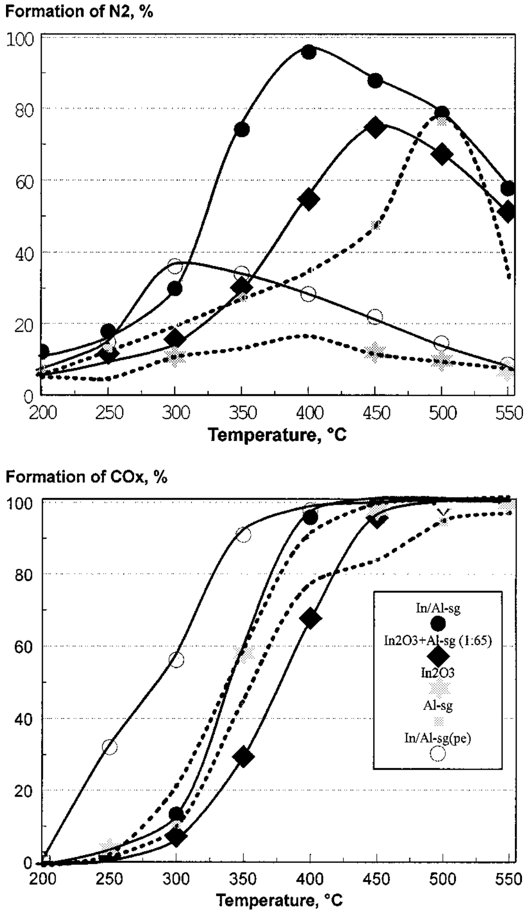


Figure 3. The effect of the In–Al interaction on the activity to reduce NO with propene to nitrogen in dry conditions.

activity as In/Al-sg(wet2). In particular, both of the sol–gel prepared In/alumina catalysts had high activities at high-temperature range (450–550 °C). InAl-sg2 had poor HC oxidation activity compared to the best indium catalysts, with the result that it had a poor ability to catalyze NO$_x$ reduction in the low-temperature range. Sol–gel In–Al oxide catalysts had the same activities when calcined at 600 or 700 °C. This was evidence that the catalysts prepared completely by the sol–gel method are thermally more stable than In/Al-sg. Therefore, we succeeded to prepare more efficient indium catalysts compared to indium on conventional γ-alumina [18] both by using the complete sol–gel method for the catalyst preparation and impregnation of indium on sol–gel prepared alumina.

3.2. Effect of preparation method

3.2.1. Effect of impregnation method

The specific surface area of Al-sg-supported catalysts was higher than that of conventional γ-alumina-based catalysts because of the higher initial surface area and the good thermal stability. The surface area (BET) measured after preparation depended almost linearly on the calcination temperature in the range of 600–900 °C. When the loading was as high as 10.1 wt% (Al/M = 20), the surface area decreased clearly, but in the range of lower loadings, the surface area had a low dependency on the In loading [18]. It was not possible to find a direct correlation between surface areas and activities. The surface area of the indium catalyst impregnated by the wet2 method was higher than by the wet1 method. We expect that the catalyst by the wet2 method had kept as high surface area because of the lower hydrothermal sintering rate of the alumina surface because of the lower amount of water during impregnation. The free water phase outside the interaction of Al_2O_3 is solvent and intermediate for the diffusion of electrolytes, which interact with the solid surface.

The higher surface area with indium acetate precursor (by wet1) showed that acetate modifies the alumina surface less than nitrate as an anion in aqueous solution. However, a total surface area more than 200 m^2/g for these catalysts is not a necessary and permanent property for the activity, but the state and the location of In_2O_3 on alumina is a more significant factor.

XRD analysis of In/alumina samples indicates that indium was as In_2O_3 on Al-sg (figure 4). The detected peaks on In/Al-sg matched the reference peaks of pure In_2O_3.

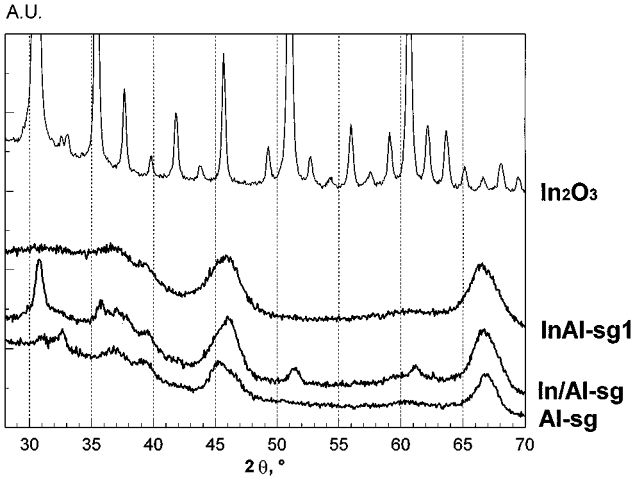


Figure 4. The XRD characterizations of indium/alumina catalysts.

Table 2
The XPS binding, kinetic and calculated combined energies for indium samples (eV).

Sample (Al/In, T_{calc} (°C))	In $3d_{5/2}$	InA (MNN)	In 3d + InA KE	O 1s	Al 2p
Fresh sample					
In/Al-sg(65, 600)	444.2	848.5	849.3	531.0	74.2
In/Al-sg(65, 600)	444.4	848.2	849.7	531.1	74.2
After activity experiment					
In/Al-sg(65, 800)	444.5	848.7	849.4	531.1	74.3
In/Al-sg(20, 600)	444.4	848.5	849.5	531.3	74.4
In/Al-sg(20, 800)	444.2	848.6	849.2	531.1	74.3
References[a]					
In_2O_3	444.3	846.7	851.2	529.9	
In metal	443.6	842.8	854.4		

[a] C 1s = 285.0 eV chemical shift reference.

A metallic indium sample was not measured as a reference, but the XRD parameters should be clearly different for In than for In_2O_3 by reference data [25]. Indium impregnated on Al-sg appeared as such large particles (>10 nm), which can be detected by XRD analysis. Analysis of the samples calcined between 600 and 900 °C proved that In_2O_3 is very stable on Al-sg and the increased In loading was observed by the higher peak intensities. The purpose of TGA was to confirm the stability of phases detected by XRD on indium catalysts. In_2O_3 on Al-sg as well as pure In_2O_3 used as a reference were stable up to 1000 °C in static air as assumed also by thermodynamic equilibrium in the same conditions.

The active form of indium on alumina was traced by XPS analysis. The In loading, support type and calcination temperature were used as variables. Even if the binding energy is not always a direct indication of chemical state, according to these results indium was as In_2O_3 on alumina (table 2). The defects between the sample and the reference spectra of In_2O_3 were caused by the interaction of alumina and indium oxide. The details of this interaction causing the shifts are not clear. Higher calcination temperature or loading did not change the indium state.

3.2.2. Formation of Al–In interactions

The InAl sample prepared by sol–gel method 1 had as high surface area as 271 m^2/g, which proved that it is possible to prevent the hydrothermal collapse of the alumina surface during the preparation almost totally by mixing In nitrate dissolved in ethylene glycol into aluminium sol. When In and Al precursors were surrounded by organic hydrophobic ligands in aqueous media, the controlled gelation can happen between Al and In compounds without the negative effects of water. In contrast, the addition of In nitrate as water solution into Al sol (In–Al-sg2) resulted in a lower surface area (199 m^2/g). Elaloui et al. [26] got also high surface area pure alumina by controlling the low-temperature germination of aluminium oxide crystals in solution containing organic compounds.

The indium oxide in InAl-sg1 could be described as amorphous and particle size less than about 10 nm, because according to XRD only alumina peaks were detectable in this sample (figure 4). The alumina detected by XRD in InAl-sg1 resembles fresh Al-sg where the main form is γ-alumina. Lower temperature operation can be generated by larger isolated active phase particles, which are formed in the case of higher In loadings In/Al-sg(pe).

In general, the same principal interactions and phase formations important for the final activity are occurring when preparing the catalysts by impregnation, precipitation or sol–gel methods. The catalysts where indium has an atom size distribution in the Al_2O_3 structure, have HC oxidation ability changed in the direction of pure alumina. The preparation of In/Al-sg(pe) by the phase-equilibrium method showed that aluminium oxide is not only in the solid state during impregnations but it can be dissolved, too.

3.3. Active sites and reaction mechanism

3.3.1. Cooperation of In and Al

The cooperation between alumina and indium active sites in the reaction mechanism of NO reduction was investigated in more detail to interpret the measured performance (figure 3). In_2O_3 powder had approximately the same activity for propene oxidation as the In/Al-sg catalyst. The detected conversions on the mechanical mixture containing In_2O_3 and Al-sg particles (Al/In = 65, 194 mg Al_2O_3 and 6 mg In_2O_3), confirmed that the NO_x reduction can proceed effectively when we have macro-scale contact between separate indium and aluminium oxide particles (diameter range about 10–250 μm) in the catalyst bed. This scale is still more than 10^5 times larger compared to molecule dimensions, whose scale is in the range of nanometers. In the mechanical mixture with such high particle size the possibilities to spillover of surface intermediates is low. The higher activities detected is evidence for the existence of surface migration or gas-phase intermediates in the reaction sequence [27]. The concentration and stability of gas-phase intermediates other than NO_2 and C_2H_4 is low, because they are not detected in the reactor outlet. Virtual cooperation

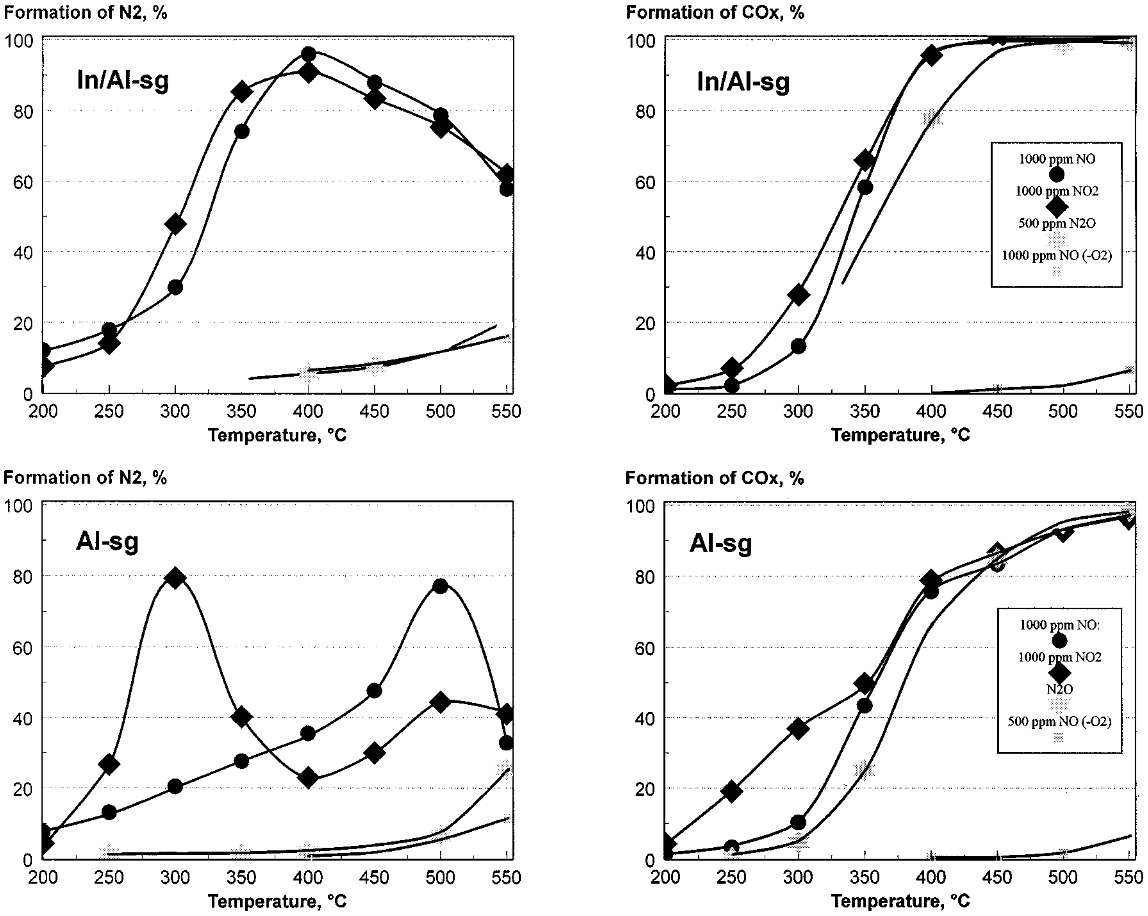


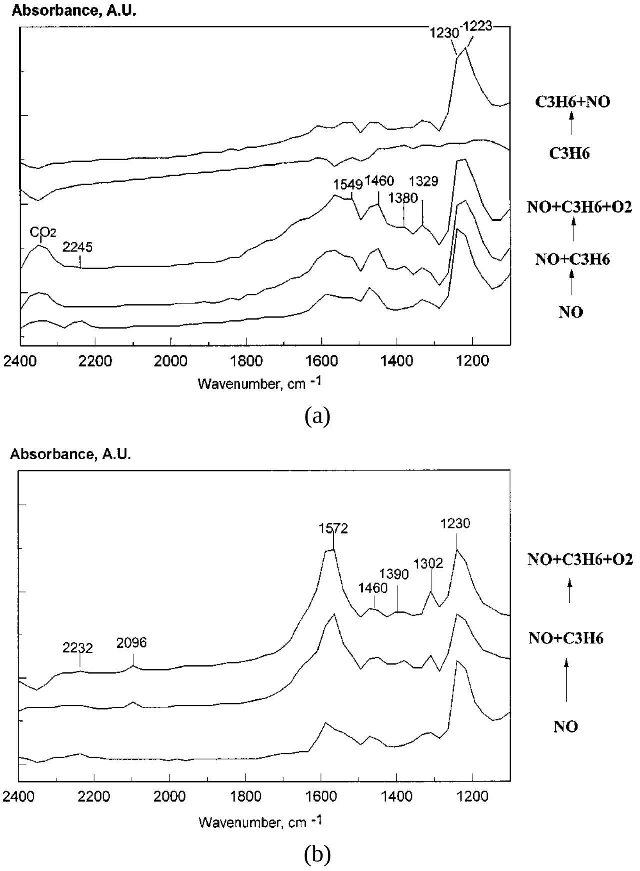
Figure 5. The reduction of NO, NO_2 and N_2O by propene in dry conditions in the presence and absence of oxygen with In/Al-sg and Al-sg catalysts.

phenomena by solid-state reactions between In and Al oxides is not plausible in the range of experimental conditions used, although the thermal stability of In_2O_3 is not very good. The physical mixture of In_2O_3 and Al-sg showed a lower temperature maximum for NO_x reduction than Al-sg, even if its HC oxidation light-off temperature (T_{50}) was higher. The shape of the HC conversion curve suggests that the HC oxidation to CO_x on Al-sg is inhibited, probably by reaction products like water, and indium on alumina promotes instead of the HC oxidation other reactions like the NO oxidation to NO_2 and dinitrogen formation in the reaction sequences. These experiments with physical mixtures were done in the absence of water and according to our other experiments the molecular-scale dispersion and higher concentration of active metal on alumina are more important to keep a higher activity in the presence of water.

3.3.2. *Reactivities of N_2O and NO_2*

The behavior of NO–C_3H_6–O_2, NO_2–C_3H_6–O_2, NO–C_3H_6, N_2O–C_3H_6–O_2 and N_2O–O_2 reactions on In/Al-sg and Al-sg was also investigated more deeply (figure 5). In the absence of oxygen, the NO reduction activity of In/Al-sg and Al-sg was very low and the reactions were initiated at temperatures clearly over 500 °C. According to the blank experiment in an empty quartz reactor, only 2–3% of NO or NO_2 in the presence of oxygen and 1–2% NO in the absence of oxygen were converted to nitrogen at higher temperatures (500–550 °C).

The decomposition and reduction of nitrous oxide over these catalysts were investigated using 500 ppm N_2O, 1000 ppm C_3H_6 and 10% oxygen. These and our other results proved that nitrogen is formed mainly by catalytic N_2O decomposition but C_3H_6 does not markedly reduce N_2O on In/Al-sg and Al-sg catalysts. According to these results N_2O has no effect on propene oxidation. Therefore, NO dissociation or N_2O formation are not the important reaction pathways [28] in NO_x reduction by hydrocarbons on these catalysts. The presence of oxygen is necessary to enhance the NO reduction by hydrocarbons at 300–600 °C. The propene oxidation was enhanced in the presence of NO_2 and $NO+O_2$ compared to the experiments where N_2O was present. Nitrogen is formed from NO_2 with higher conversion on Al-sg than on In/Al-sg at the temperatures below 350 °C. This can be understood by the explanation that alumina has a high capacity to adsorb NO_2 as nitrates, whose surface species activate propene for NO reduction. The low activity with NO is caused by the fact that alumina has a poor ability to form NO_2 at lower temperatures. However, the alumina-only catalyst has lost the high activity in NO_x reduction by propene in the presence of water. The oxidation of NO to NO_2 has a thermodynamical restriction at temperatures above 400 °C [29].



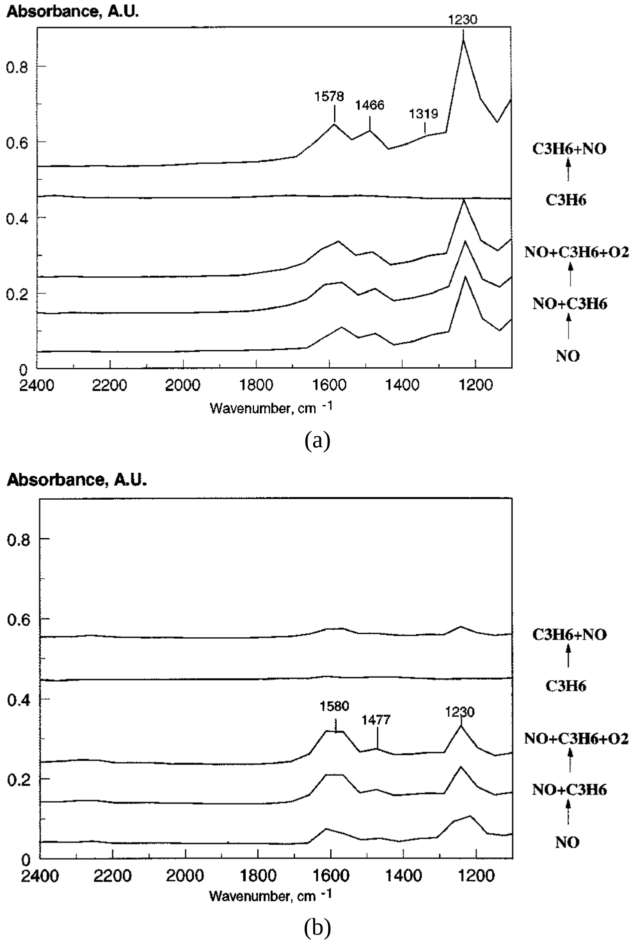
(a)

(b)

Figure 6. The adsorption peaks by static FTIR measurements with NO, propene and oxygen over an evacuated In/Al-sg catalyst at 50 (a) and 150 °C (b).

3.3.3. Reaction intermediates

Detections by static FTIR measurements. The FTIR responses on In/Al-sg at 50 and 150 °C are shown in figure 6. Acidic nitrogen oxides modify clearly the alumina surface producing adsorbed nitrates on the aluminium oxide surface (1220–1230 cm^{-1}) at low temperatures. Several partially oxidized carbon and nitrogen compounds are detected on In/Al-sg around the broad wavelength belt of 1700–1300 cm^{-1} [30], which is partly similar to the data recorded on Al-sg (figure 7). Detectable peaks in this range on In/Al-sg appeared at the wavenumbers of 1549, 1460, 1380 and 1329 cm^{-1} at 50 °C and 1572, 1460, 1390 and 1302 cm^{-1} at 150 °C. The peaks at the wavenumbers of 1230, 1319, 1466 and 1578 cm^{-1} were detected on Al-sg. The appearance of the peaks for organic nitro and nitrite compounds at 1655 (R-ONO) and 1570 ($R\text{-}NO_2$) could be the first evidence about the reaction sequence, where nitrogen atoms are, to a greater extent, attached to hydrogen or carbon atoms in the next steps. Traces of propene adsorption as CH_3O on alumina were detected around 2964 cm^{-1}, probably isocyanates around 2250 cm^{-1} and assumed linear CO on indium at 2096 cm^{-1}. The last peak appeared when propene was introduced into the NO-treated surface at 150 °C, which temperature could favour the partial oxidation of HC leaving a detectable amount linearly bonded CO on the surface. No adsorbed CO, nitrogen or nitrous oxide was detected on Al-sg at 50 °C in the reference experiment. CO_2 adsorbed on Al-sg mainly as compounds detected by the wavenumbers of 1435, 1520 and 1651 cm^{-1} at 50 °C.



(a)

(b)

Figure 7. The adsorption peaks by static FTIR measurements with NO, propene and oxygen over the evacuated Al-sg catalyst at 50 (a) and 150 °C (b).

Possible formate groups on γ-alumina should have simultaneous 1600, 1390 and 1375 cm^{-1} absorption bands [31]. At the temperatures below the initiation of propene oxidation, adsorption of C_3H_6O is detected in other studies [32]. The rupture of C–H bonds is proposed to be a limiting step in partial oxidation of olefins on metal oxides. Surface CN and NCO species detected in rich conditions on Cu/ZSM-5 have been proposed to be important reaction intermediates [33], but we do not propose them as the only final intermediate in lean NO_x reactions on In/alumina catalysts, although they have been found on our sample in oxygen-deficient conditions. When alcohols were used as NO_x reductants with Ag/Al_2O_3 catalysts in lean conditions, high production of surface isocyanates was detected [34]. Changes in hydroxyl groups in alumina are seen in the range of 3600–3900 cm^{-1} [35], especially when NO was introduced before propene on In/Al-sg calcined at 600 °C.

Detections by dynamic FTIR measurements. Because the composition and flow rate of the NO–propene–oxygen mixture in dynamic FTIR experiments is exactly the same as

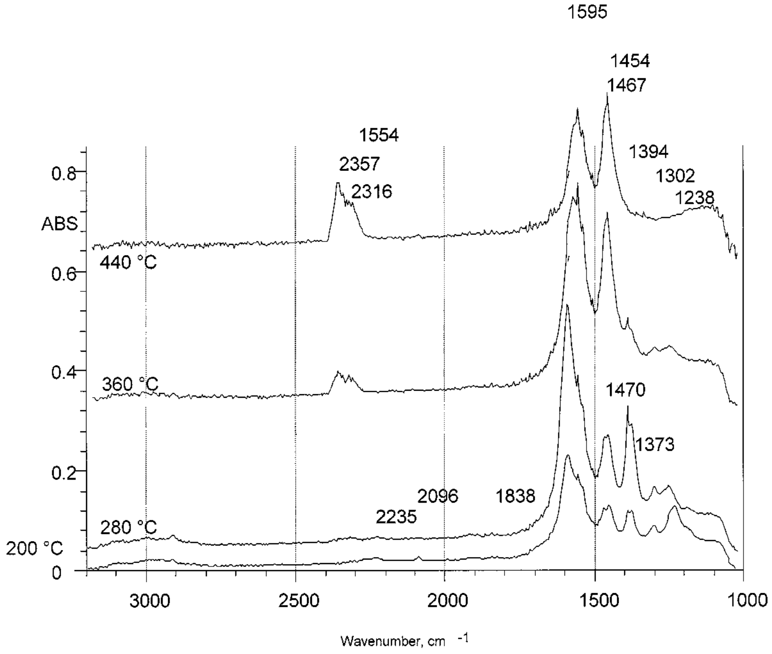


Figure 8. The difference spectra (NO–C_3H_6–O_2 − He) by dynamic FTIR measurements on In/Al-sg(65, 600) in the range of 200–450 °C.

in activity experiments, it is possible to link these surface detections directly to activity experiments. The experiment with He flow was used to evaluate desorption rates caused by heating in inert gas flow. The difference spectra are calculated by subtracting He flow spectra from the NO–C_3H_6–O_2 flow spectra (figure 8). The qualitative mass spectrometer responses of NO, N_2, C_3H_6 and CO_2 match to the FTIR results.

According to the original and difference spectra the main peaks appeared in the range of gaseous CO_2 (2370–2310 cm^{-1}) above 300 °C, adsorbed CO (2096 cm^{-1}) at 200 °C, 2235 cm^{-1} (cyanates) at 200 °C, 1595 (carbonates, nitrates), 1554, 1470–68, 1454 (carbonates), 1394 (formate), 1371 (formate), 1302 and 1238 (nitrates) cm^{-1}. The intensity of the peaks proposed for HCO_3 (1450 cm^{-1}) increased and that of HCO_2 (1596 cm^{-1}) decreased when temperature and propene oxidation rates increased. The peaks of nitrogen- and carbon-containing species were overlapped by these several carbonates in these experiments at normal pressure. The appearance of adsorbed NO_3^- and NO_2^- species was negligible in the temperature range of 360–440 °C when the NO conversion to nitrogen was the highest on In/Al-sg.

When the background was taken at 300 °C and a dynamic FTIR experiment was made between 300 and 450 °C, the result on In/Al-sg was similar to the case when the background was measured at 200 °C.

Reaction mechanism. The adsorption ability of single reactants is a limiting step at lower temperatures, where various molecules are competing for few free surface vacancies. Because the residence time of intermediates on the catalyst surface is typically very short and surface coverage is low during the reactions at the higher temperatures (>300 °C), it is difficult to detect them by FTIR. Based on the experiments described in the previous sections, the reactions are proposed to proceed on two kinds of active sites, which are located on the aluminium and indium oxide surfaces (figure 9), where the actual reductant, NX, contains functional groups like NH_i, NCO, HNO. We propose that it is necessary for this final reductant to contain N–H or N–C bonding, which property creates in the intermediate the ability to react eagerly with the adjacently adsorbed NO to form N–N bonding. The key point to interpret the NO reduction is to understand the reaction mechanism in the nitrogen–nitrogen bond formation. In some earlier papers, the reaction mechanism has also been proposed for rhodium and platinum catalysts, where two adjacently adsorbed NO molecules form

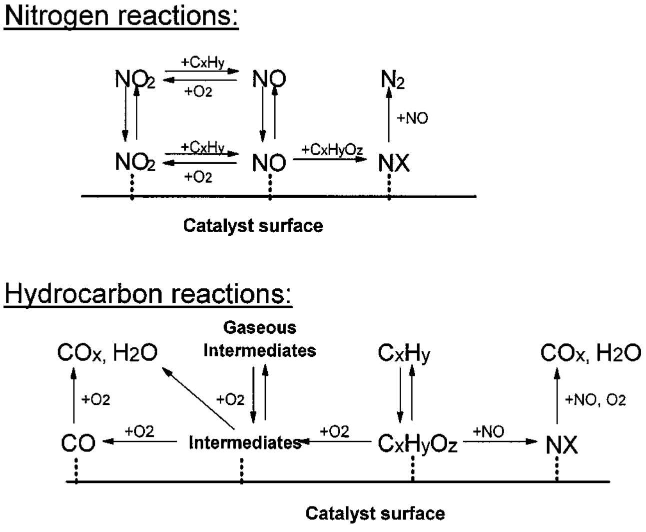


Figure 9. The reaction mechanism proposed for NO_x reduction and HC oxidation.

a nitrogen–nitrogen bond when NO is adsorbed by an oxygen atom on the catalyst surface [29,36]. Our mechanistic investigations with an $In/TiO_2–ZrO_2$ catalyst showed the importance of a high concentration of nitrates on acid sites, which enhance the nitrogen formation rate on In sites [37]. Haneda et al. [38] proposed the formation of isocyanate species to be a rate-determining step on $In/TiO_2–ZrO_2$ and based on the observations with different catalysts on that study, we conclude that the rate-determining step is often changed depending on the catalyst composition. Therefore, in the present study, the active sites are not fixed in single reaction steps, because both indium and aluminium sites are capable to operate in the same reaction steps and depending on the temperature and concentrations the indium or aluminium site is more controlling on a single reaction step. In the presence of water, indium sites have a more important role than aluminium sites to control reaction rates.

In general, the deNO_x catalysts active in the temperature range of 350–600 °C need to have active sites to oxidize NO to NO_2, to oxidize partially HC, to form actual reductant NX and to form nitrogen by the reaction between NO and the actual reductant (figure 9). The experiments on pure aluminium and indium oxides showed that both of these oxides in dry conditions have all the active sites necessary to complete NO reduction by propene to nitrogen. In the presence of water, alumina has lost most of the total NO reduction activity. In general, hydrocarbons can be oxidized to partially oxidized HC by molecular oxygen, but the activation temperature for the reaction is then higher than in the presence of NO_2. At higher temperatures (>500 °C), the total oxidation of HC to CO_x and water is too fast and the concentration of actual reductant on the surface is too low to have a higher rate for nitrogen formation.

4. Conclusions

The method in which indium was originally attached on the aluminium oxide surface during preparation was proved to determine to a great extent the activity of In/alumina catalysts. It is beneficial to the activity that indium precursor ions have a possibility to diffuse rather freely during the impregnation to settle down on the energetically optimal sites on the support and the formation of larger clusters is still possible. The active form of indium was proved to be In_2O_3. In_2O_3 and alumina seemed to be able to operate as catalysts also as a mechanical mixture with no molecular-scale distribution of In_2O_3 on the alumina. The active In/alumina catalyst with very small In_2O_3 particles, very high surface area and high stability was created by sol–gel processing. It was advantageous to dissolve indium nitrate into ethylene glycol instead of water before mixing it into Al sol. An InAl catalyst with as high indium concentration as 58 wt% and low NO_x reduction window was achieved with the phase-equilibrium preparation method. In spite of our results, the best preparation method in each case depends on the active sites which are efficient and selective for the desired reaction.

The reaction and surface studies showed that the key point in NO_x reduction is the mechanism in dinitrogen formation. We propose that nitrogen is formed when the nitrogen-containing actual reductant and NO are reacting on the catalyst surface. NO_2 and partially oxidized hydrocarbons are important intermediates in earlier steps in the reaction mechanism for oxide-based catalysts like indium/alumina. These catalysts have very poor activity in NO_x reduction in rich or stoichiometric conditions. N_2O formation was low and it is not an important intermediate in the reaction mechanism on indium/alumina.

Acknowledgement

This study was carried out in a visiting researcher program funded by a fellowship from AIST and STA. In addition, we are grateful to Cosmo Oil R&D Center for accomplishing XPS and plasma analysis.

References

[1] W. Held and A. Koenig, German Offen. DE 3,642,018 (1987).

[2] Y. Fujitani, H. Muraki, A. Nagoya, S. Kondoh, M. Fukui and A. Toyoake, German Offen. DE 3,735,151 (1988).

[3] M. Iwamoto, S. Yokoo, S. Sakai and S. Kagawa, J. Chem. Soc. Faraday Trans. I (1981) 1629.

[4] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u and N. Mizuno, Appl. Catal. 69 (1991) L15.

[5] W. Held, A. Konig, T. Richter and L. Puppe, SAE paper 900496 (1990).

[6] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and T. Tabata, Appl. Catal. 64 (1990) L1.

[7] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 239.

[8] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett. 15 (1992) 297.

[9] R. Burch, P.J. Millington and A.P. Walker, Appl. Catal. B 4 (1994) 65.

[10] T. Miyadera and K. Yoshida, Jpn. Chem. Lett. (1993) 1483.

[11] T. Miyadera, Appl. Catal. 2 (1993) 199.

[12] Y. Teraoka, T. Harada, T. Iwasaki, T. Ikeda and S. Kagawa, Jpn. Chem. Lett. 5 (1993) 773.

[13] M. Tabata, H. Hamada, F. Suganuma, T. Yoshinari, H. Tsuchida, Y. Kintaichi, M. Sasaki and T. Ito, Catal. Lett. 25 (1994) 55.

[14] A. Ueda, T. Oshima and M. Haruta, in: *Proc. World Congress Environ. Catal.*, Pisa, 1995, p. 343.

[15] G. Centi and S. Peranthoner, Appl. Catal. A 132 (1995) 179.

[16] Y. Ukisu, S. Sato, G. Muramatsu and K. Yoshida, Catal. Lett. 16 (1992) 11.

[17] M. Haneda, Y. Kintaichi, H. Shimida and H. Hamada, Jpn. Chem. Lett. (1998) 181.

[18] T. Maunula, Y. Kintaichi, M. Inaba, M. Haneda, K. Sato and H. Hamada, Appl. Catal. B 15 (1998) 291.

[19] A.J. Lecloux and J.P. Pirard, J. Non-Cryst. Solids 225 (1998) 146.

[20] G. Ji, Sol–gel processing of PZT films, Dissertation, Queen's Univ. Kingston, Canada (1993).

[21] R.D. Gonzalez, T. Lopez and R. Lopez, Catal. Today 35 (1997) 293.

[22] K. Masuda, T. Sano, F. Mizukami and M. Miyazaki, Catal. Lett. 32 (1995) 139.

[23] K. Masuda, T. Sano, F. Mizukami and M. Miyazaki, Catal. Lett. 33 (1995) 229.

[24] S. Fuentes, N.E. Bogdanchikova, G. Diaz, M. Peraaza and G.C. Sandoval, Catal. Lett. 47 (1997) 27.

[25] Joint Commitee on Powder Diffraction Standards, Powder Diffraction File, Sets 1–32 (1974–1988).
[26] E. Elaloui, A.C. Pierre and G.M. Pajonk, J. Catal. 166 (1997) 340.
[27] H. Hamada, Catal. Surveys Jpn. 1 (1997) 53.
[28] T. Maunula, J. Ahola, T. Salmi, H. Haario, M. Härkönen, M. Luoma and V.J. Pohjola, Appl. Catal. B 12 (1997) 287.
[29] G.R. Bamwenda, A. Obuchi, A. Ogata, J. Oi, S. Kushiyama and K. Mizuno, J. Mol. Catal. A 126 (1997) 151.
[30] J.L. Robbins and M.-E.J. Soos, J. Phys. Chem. 93 (1989) 2885.
[31] A.A. Davydov, O.V. Tyunina and A.V. Kravtsov, Russ. J. Phys. Chem. 57 (1983) 1269.
[32] A.A. Davydov, Kinet. Catal. 35 (1994) 608.
[33] C. Li, K.A. Bethke, H.H. Kung and M.C. Kung, J. Chem. Soc. Chem. Commun. (1995) 813.
[34] Y. Ukisu, T. Miyadera, A. Abe and K. Yoshida, Catal. Lett. 39 (1996) 265.
[35] C. Li, W. Yan and Q. Xin, Catal. Lett. 24 (1994) 249.
[36] T.R. Ward, R. Hoffmann and M. Shelef, Surf. Sci. 289 (1993) 85.
[37] Y. Kintaichi, M. Haneda, M. Inaba and H. Hamada, Catal. Lett. 48 (1997) 121.
[38] M. Haneda, Y. Kintaichi, M. Inaba and H. Hamada, Appl. Surf. Sci. 121/122 (1997) 391.