


Provided by the author(s) and University College Dublin Library in accordance with publisher policies. Please cite the published version when available.

<b>Title</b>	The influence of SO <sub>2</sub> -/4 on the catalytic combustion of soot using O-2 and NO/O-2 mixtures over Na-promoted Al <sub>2</sub> O <sub>3</sub> catalysts
<b>Author(s)</b>	Sullivan, James A.; Keane, Orla; Maguire, Linda
<b>Publication date</b>	2005-07
<b>Publication information</b>	Catalysis Communications, 6 (7): 472-475
<b>Publisher</b>	Elsevier
<b>Item record/more information</b>	<a href="http://hdl.handle.net/10197/4002">http://hdl.handle.net/10197/4002</a>
<b>Publisher's statement</b>	This is the author's version of a work that was accepted for publication in Catalysis Communications. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Catalysis Communications, 6 (7) 2005-05, pp.472-475. DOI: 10.1016/j.catcom.2005.04.008
<b>Publisher's version (DOI)</b>	<a href="http://dx.doi.org/10.1016/j.catcom.2005.04.008">http://dx.doi.org/10.1016/j.catcom.2005.04.008</a>

Downloaded 2018-05-25T15:25:32Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd\_oa) 

Some rights reserved. For more information, please see the item record link above.



**The influence of  $\text{SO}_4^{2-}$  on the catalytic combustion of soot using  $\text{O}_2$  and  $\text{NO/O}_2$  mixtures over Na-promoted  $\text{Al}_2\text{O}_3$  catalysts.**

James A. Sullivan, Orla Keane and Linda Maguire  
Department of Chemistry,  
UCD,  
Belfield,  
Dublin 4  
Ireland.

**Abstract.**

Na/ $\text{Al}_2\text{O}_3$  catalysts are tested in the soot oxidation reaction using  $\text{O}_2$  and  $\text{NO/O}_2$  as oxidising agents. The activity of the catalysts varies with oxidising agent and the presence of surface  $\text{SO}_4^{2-}$ .

$\text{NO}_{(\text{g})}$  increases conversion of soot to  $\text{CO}_x$ . Surface  $\text{SO}_4^{2-}$  has no effect on activity for the  $\text{C}_{(\text{s})}+\text{O}_2$  reaction but shows decreased activity in the Carbon+ $\text{NO/O}_2$  oxidation. This is interpreted in terms of  $\text{SO}_4^{2-}$  blocking  $\text{NO}$  adsorption sites, thus poisoning the  $\text{NO}+\text{O}_2 \rightarrow \text{NO}_2$  reaction, which is essential for the  $\text{NO}_x$  promoted oxidation.

*Keywords:* Soot Combustion, Sulphate,  $\text{NO}_x$ .

**1. Introduction**

One of the major pollutants formed during the combustion of fossil fuels are carbonaceous particles<sup>1</sup>. These particles range in size between  $< 10 \mu\text{m}$  in diameter up to visible soot and have several detrimental consequences for the environment. These range from (in the case of larger particles) the defacing of urban buildings and contributing significantly to global warming (particulates which land on arctic ice decrease the albedo of the ice leading to increased UV absorbance and subsequent increased rates of melting of ice)<sup>2</sup> to, in the case of smaller particles, serious human

health implications as these can penetrate and lodge within the alveoli of the lung<sup>3</sup>. It is thought that the particles are primarily carbonaceous in nature although it is reported also that they form using sulphate species as nucleation sites<sup>4</sup>.

One proposed technique for the destruction of these species involves their trapping and subsequent oxidation to CO<sub>2</sub> using O<sub>2</sub> or NO/O<sub>2</sub> mixtures<sup>5</sup>. In the latter case the NO is thought to act as an O-atom carrier between O<sub>2</sub> and the carbonaceous species through the formation and reduction of NO<sub>2</sub>. NO<sub>2</sub> is a more oxidising material than O<sub>2</sub> and the presence of NO increases the conversion of soot to CO and CO<sub>2</sub>.

If this cycle were to take place on the surface of a catalyst rather than both at the surface and in the gas phase then it could be envisaged as being similar to a nitrite / nitrate-type redox cycle (where nitrite corresponds to adsorbed NO and nitrate to adsorbed NO<sub>2</sub>). Alkali metals form stable nitrite and nitrate type species on Al<sub>2</sub>O<sub>3</sub> and for this reason they have been studied as possible catalysts for the combustion of carbonaceous particles<sup>6</sup>.

Generally SO<sub>4</sub><sup>2-</sup> has been regarded as a poison for catalysts and catalytic processes<sup>7</sup> although recently it has been found to promote such reactions as propane combustion<sup>8</sup> and NO<sub>x</sub> reduction using NH<sub>3</sub> as a reducing agent<sup>9</sup>. Previous work<sup>10</sup> has shown that SO<sub>4</sub><sup>2-</sup> remains anchored to an Al<sub>2</sub>O<sub>3</sub> surface when sulphate salts are used as catalyst precursors while related work has demonstrated that SO<sub>4</sub><sup>2-</sup><sub>ads</sub> blocks adsorption sites for NO and NO<sub>2</sub><sup>11-13</sup>. With respect to sulphation Ciambelli<sup>14</sup> *et al.* have noted that combustion activity (of a V/Cu/C/Ti-containing) alumino-silicate filter) decreases drastically once the filter is pre-sulphated but that this decrease is ameliorated somewhat by the addition of NO to the gas phase. In this work we analyse the effects of SO<sub>4</sub><sup>2-</sup> on the activity of Al<sub>2</sub>O<sub>3</sub>-supported catalysts for soot combustion.

## 2. Experimental

### 2.1. Sample Preparation.

1% Na/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using conventional incipient wetness impregnation of commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (crushed and sieved between particle sizes of 212-600  $\mu$ m) using solutions of NaNO<sub>3</sub>. Sulphate was dosed on to the support either alone (by impregnating with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) or with Na (by impregnating with Na<sub>2</sub>SO<sub>4</sub>). "Blank" support samples were prepared by impregnation with NH<sub>4</sub>NO<sub>3</sub>. The samples were dried in an oven at 110 °C and calcined at 500 °C for 2 h. Previous experiments over Al<sub>2</sub>O<sub>3</sub> supported catalysts have shown that SO<sub>4</sub><sup>2-</sup> remains on the catalyst surface following the calcination of SO<sub>4</sub><sup>2-</sup> salts while NH<sub>4</sub><sup>+</sup> cations and NO<sub>3</sub><sup>-</sup> anions are removed (as NO<sub>2</sub>) during calcination<sup>10</sup>.

### 2.2. Activity Measurements.

The catalysts were physically mixed with samples of a model soot (Degussa Printex L) in a ratio of 1 part catalyst:2 parts soot). The mixture was then compressed at a pressure of 5 tonnes in a Grazeby Specac press. The resultant pellets were crushed and sieved to particle sizes of between 212-600  $\mu$ m. 50 mg of these mixtures were held, using plugs of quartz wool, in a glass reactor tube. Mixtures of Air and N<sub>2</sub> (4.7% O<sub>2</sub> in a total flow of 114ml min<sup>-1</sup>) or Air, N<sub>2</sub> and NO/He (3.9% O<sub>2</sub> and 1387 ppm NO with a total flow of 137 ml min<sup>-1</sup>) were flowed over the samples at various temperatures and samples of the exit gas were periodically removed and analysed using on-line GC-FID detection (Shimadzu fitted with a methanator). Peaks relating to CO and CO<sub>2</sub> were monitored and converted into  $\mu$ mol for presentation. Gases were from BOC or BOC Special Gases and were used without further purification.

Typically steady state production of CO and CO<sub>2</sub> were obtained after ~ 15 minutes in a stream of either O<sub>2</sub> or NO/ O<sub>2</sub> at a particular temperature and then the temperature was raised by either 50 or 100 °C (between 300 and 550 °C) and the measurements repeated. Each catalyst/soot mixture was subjected to exactly the same regime and the catalyst/soot mixture was replaced between experiments.

### *Temperature Programmed Desorption Measurements*

A quartz tubular reactor was loaded with 50 mg of the samples of interest and dosed with a mixture of NO + O<sub>2</sub> (1250 ppm NO + 22% O<sub>2</sub>) at 100 °C until saturated. The outlet of the reactor was connected to a mass spectrometer (Prolab), which continuously analysed signals due to NO and O<sub>2</sub>. Once the catalyst was saturated the NO<sub>x</sub> and O<sub>2</sub> were then removed from the gas phase and the sample cooled to 50 °C in a flow of He. The Temperature was then ramped at a rate of 20 °C / min between 50 and 650 °C while the NO signal was continuously monitored.

## **3. Results and discussion**

### *3.1 Activity Measurements.*

Figure 1 compares the combustion activities of two 1% Na/Al<sub>2</sub>O<sub>3</sub> catalysts (made from NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> precursors) for the production of CO<sub>x</sub> using O<sub>2</sub> and NO/O<sub>2</sub> mixtures respectively as oxidants. The ex-SO<sub>4</sub><sup>2-</sup> catalyst is as active (indeed slightly more active) than the ex-NO<sub>3</sub><sup>-</sup> material when air is used as an oxidant so it is clear that the presence of SO<sub>4</sub><sup>2-</sup> in no way hinders the reaction that takes place between the O<sub>2</sub> and C<sub>(s)</sub>. Activity is related to temperature and also to Na loading with a 5% and 10 % Na catalysts being substantially more active than the 1% (results not shown).

Figure 2 shows the activity of the same catalysts when soot is oxidised using mixtures of NO and O<sub>2</sub>. Over the ex-NO<sub>3</sub><sup>-</sup> catalyst these activities are higher than in the case where O<sub>2</sub> was the oxidant. It is known that this increased activity is due to the formation of NO<sub>2(g)</sub>, which subsequently reacts with the soot to form CO (or CO<sub>2</sub> or CO<sub>ads</sub>) and regenerate NO<sup>5</sup>. There is no reduction of NO<sub>2</sub> (as measured using a chemiluminescent NO<sub>x</sub> analyser) to any species other than NO (total NO<sub>x</sub> remains constant throughout the reaction).

The promoting effect seen in the case of the ex-NO<sub>3</sub><sup>-</sup> catalysts is not seen over the ex-SO<sub>4</sub><sup>2-</sup> materials. The conversion of soot to CO<sub>x</sub> is *decreased* in the presence of NO at all the temperatures studied. Thus it seems that the presence of SO<sub>4</sub><sup>2-</sup> on the surface has no effect on the Na/Al<sub>2</sub>O<sub>3</sub> activity for the C + O<sub>2</sub> reaction, but the improved activity of the catalyst seen in the presence of NO is not seen when SO<sub>4</sub><sup>2-</sup> is present. Temperature programmed desorption of NO<sub>x</sub> was used as a probe to attempt to explain these observations in terms of the proposed NO / NO<sub>2</sub> redox cycle.

### 3.2 Temperature Programmed Desorption Measurements.

Figure 3 shows Temperature Programmed Desorption profiles relating to the Desorption of NO<sub>x</sub> from Al<sub>2</sub>O<sub>3</sub>, 1% Na/Al<sub>2</sub>O<sub>3</sub>, 1% Na/Al<sub>2</sub>O<sub>3</sub> (ex SO<sub>4</sub><sup>2-</sup>) and Al<sub>2</sub>O<sub>3</sub> (treated with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and calcined). As has been previously seen in TPDs of NO<sub>x</sub> from Al<sub>2</sub>O<sub>3</sub>-based catalysts there are two areas of desorption, i.e. 150-250 °C and 450 – 600 °C. The latter peak is accompanied by desorption of O<sub>2</sub> and relates to the decomposition of surface nitrates and the former peak relates to the decomposition of surface nitrites<sup>11</sup>.

Previous results showing the effect of sulphation<sup>11</sup> (via SO<sub>2</sub> adsorption and oxidation) on the NO<sub>x</sub> adsorption capacity of Al<sub>2</sub>O<sub>3</sub>-based catalysts have shown that

the concentration of nitrate-type surface sites decreased following sulphation. This has been explained in terms of  $\text{SO}_4^{2-}$  species irreversibly adsorbing on these site. Similar results are seen here for these 1%Na-containing catalysts.

The effect of doping the catalysts with 1%Na can be analysed by comparing the profiles relating to the Na/ $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  catalysts. There are slightly higher concentrations of surface sites available for the formation of both nitrite and nitrate species in the presence of Na. The stability of the nitrite type species (as measured by the temperature of maximum desorption) is unchanged by the presence of Na while the nitrate type species are more stable in the presence of Na (compare a temperature of maximum desorption of 520 °C in the presence of Na and 496 °C in the absence of Na).

The presence of surface  $\text{SO}_4^{2-}$  removes (presumably through the surface poisoning mechanism discussed above) almost all of the adsorption sites that lead to the formation of surface nitrates. Sulphate increases the concentration of sites available for nitrite formation (see table 1). This is possibly due to a conversion of some of the sites that were available for nitrate formation into those suitable for nitrite formation through the blocking of a surface oxygen site. However this is a relatively small effect and in the presence of both Na and  $\text{SO}_4^{2-}$  it is not noticeable.

These sulphated catalysts are as active as the un-sulphated materials in the soot oxidation with  $\text{O}_2$  but are less active than the un-sulphated analogues when the NO promoter is included in the reaction stream. It is certain that the presence of  $\text{SO}_4^{2-}$  decreases the positive effect of  $\text{NO}_x$  on the reaction and TPD studies show that this decrease is probably related to the blocking of the NO oxidation pathway, which is intimately involved in the  $\text{NO}_x$  promotion mechanism.



It seems that in the absence of  $\text{SO}_4^{2-}$  the  $\text{Al}_2\text{O}_3$  surface is a sufficiently good catalyst to oxidise NO to  $\text{NO}_2$  (as has been reported over  $\text{BaO}/\text{Al}_2\text{O}_3$   $\text{NO}_x$  trapping materials<sup>15</sup> where the oxidation of NO to  $\text{O}_2$  is also a required first step in the formation of  $\text{Ba}(\text{NO}_3)_2$ ) but in the presence of  $\text{SO}_4^{2-}$  this activity is lost since adsorption sites required for the first step in the oxidation are lost.

#### 4. Conclusions

The activity of 1%Na/ $\text{Al}_2\text{O}_3$  catalysts for the combustion of soot is related to the presence of NO as a gas phase promoter and the presence of  $\text{SO}_4^{2-}$  remaining on the catalyst surface.

NO in the gas phase increases the activity of Na/ $\text{Al}_2\text{O}_3$  catalysts for the soot combustion reaction. This promotional effect is considered to operate through the formation and utilisation of  $\text{NO}_2^5$  and is lost when  $\text{SO}_4^{2-}$  is present with Na on the  $\text{Al}_2\text{O}_3$  surface. Surface  $\text{SO}_4^{2-}$  also decreases the concentration of NO adsorption sites. These sites are important in the overall mechanism of NO promotion of the combustion reaction since NO adsorbs onto the catalyst before it is oxidised to  $\text{NO}_2$ .  $\text{NO}_{(\text{g})}$  forms adsorbed nitrites which are subsequently oxidised to adsorbed nitrates. The latter desorb as  $\text{NO}_2$  and go on to oxidise the soot. Thus a decrease in the concentration of  $\text{NO}_{\text{ads}}$  sites directly changes the activity of the system for the production of CO and  $\text{CO}_2$ .

This disruptive effect of oxidised sulphur species on the  $\text{NO}_x$  oxidation reaction (and thus on overall soot combustion) should be taken into account when studying the activity of various catalysts in model soot oxidation studies since  $\text{SO}_2$  is generally present in exhaust gases (leading to catalyst adsorbed sulphate under

oxidising conditions) and also when it is considered that the particulates themselves are considered to form around sulphate cores.

### Acknowledgements

We would like to gratefully acknowledge the Irish Research Council for Science, Engineering and Technology for partly funding this work under grant number SC/02/227. The Faculty of Science UCD is also gratefully acknowledged for the provision of a start-up grant.

### References

- 1 Dobbins, R. A., Fletcher, R. A. and Chang, H.-C. *Combustion and Flame*, **115**, (1998), 285.
- 2 Hansen, J. and Nazarenko, L., *Proc. Natl. Acad. Sci.*, 101, (2004), 423-428.
- 3 Seagrave, J.C., Knall, C., McDonald, J.D, Mauderly ,J.L., *Inhalation Toxicology*, **16**, (2004), 93, Suppl 1.
- 4 Yu, Fangqun. Abs. Paps., 224th ACS National Meeting, Boston, MA, United States, August 18-22, (2002).
- 5 Shangguan, W.F., Teraoka, Y., Kagawa, S., *Appl. Catal. B: Env.*, **12**, (1997), 237.
- 6 Carrascull, A., Lick, I.D., Ponzi, E.N. and Ponzi , M.I., *Catal. Comm.*, **4**, (2003), 124.
- 7 *Catalyst Handbook*, 2nd Ed., Ed. M.V. Twigg, Manson Publishing, 1996.
- 8 Burch, R., Halpin, E., Hayes, M.J., Ruth, K. and Sullivan, J.A. *Appl. Catal B: Env.*, 19, (1998), 199.

- 9 Sullivan, J.A. and Doherty, J.A., Accepted for publication in *Appl. Catal., B: Env.*, (2005).
- 10 Sullivan, J.A., **79**, *Catal. Letts.* (2002), 59.
- 11 Burch, R., Halpin, E. and Sullivan, J.A., *Appl Catal B-Environ*, **17**, (1998), 115.
- 12 Burch, R., Sullivan, J.A. and Watling, T.C., *Catal. Today*, **42**, (1998), 13.
- 13 Sullivan, J.A., at the 3<sup>rd</sup> International Taylor conference, Belfast, September (2004).
- 14 Ciambelli, P., Palma, V., Russo, P. and Vaccaro, S., *Catal.Today.* (2000), **60**, 43.
- 15 Maciejewski, M., Piacentini, M. and BaikerA., *EuropacatVI*, Innsbruck, Sept. 2003.

	T <sub>max</sub> Nitrite	NO desorbed μmol g <sup>-1</sup>	T <sub>max</sub> Nitrate	NO desorbed μmol g <sup>-1</sup>
Al <sub>2</sub> O <sub>3</sub>	164	13	496	286
Na/Al <sub>2</sub> O <sub>3</sub>	193	48	530	304
Al <sub>2</sub> O <sub>3</sub> / SO <sub>4</sub> <sup>2-</sup>	234	38	496	9
Na/Al <sub>2</sub> O <sub>3</sub> /SO <sub>4</sub> <sup>2-</sup>	185	51	510	5

Table 1 showing the amounts and maximum temperature of NO desorbed in each NO<sub>x</sub>-TPD experiment.

### Figures

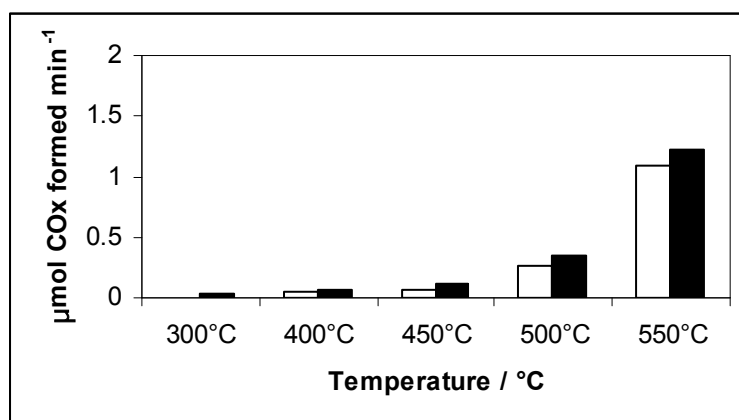


Figure 1, Histogram showing  $\mu\text{mol CO}_x \text{ formed min}^{-1}$  over 1% Na/Al<sub>2</sub>O<sub>3</sub> catalyst (white) and a 1% Na/Al<sub>2</sub>O<sub>3</sub> catalyst containing SO<sub>4</sub><sup>2-</sup> (black) using O<sub>2</sub> as an oxidising agent.

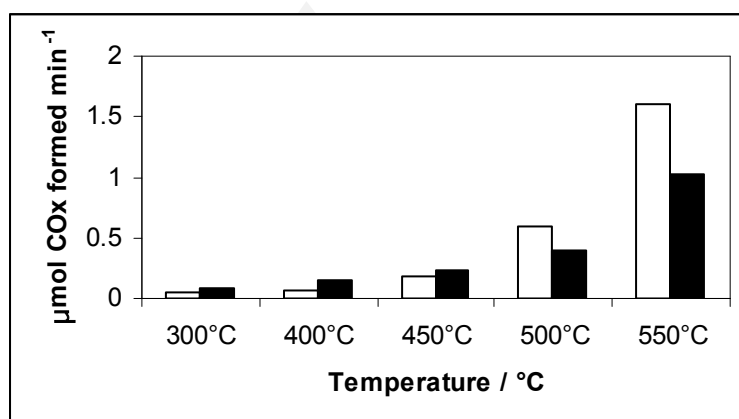


Figure 2, Histogram showing  $\mu\text{mol CO}_x \text{ formed min}^{-1}$  over 1% Na/Al<sub>2</sub>O<sub>3</sub> catalyst (white) and a 1% Na/Al<sub>2</sub>O<sub>3</sub> catalyst containing SO<sub>4</sub><sup>2-</sup> (black) using mixtures of NO and O<sub>2</sub> as an oxidising agent.

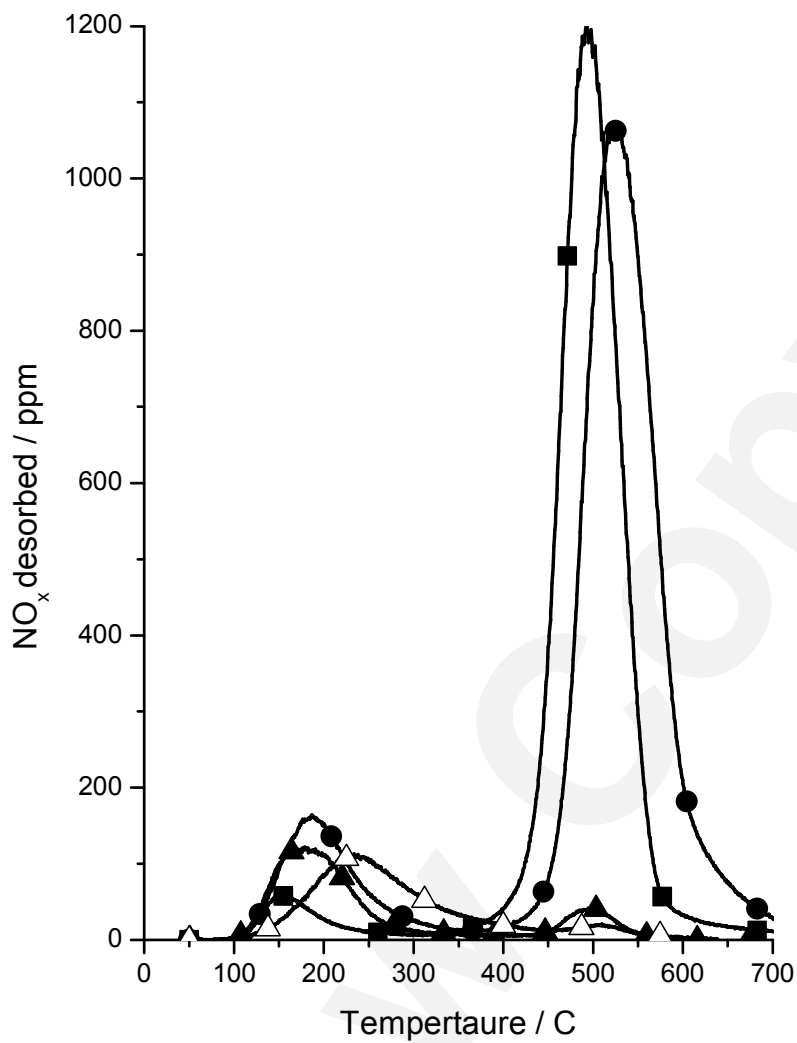


Figure 3. Temperature Programmed Desorption of NO<sub>x</sub> from various Al<sub>2</sub>O<sub>3</sub>-supported catalysts. (■) Al<sub>2</sub>O<sub>3</sub>, (●), Na/Al<sub>2</sub>O<sub>3</sub>, (▲) Al<sub>2</sub>O<sub>3</sub>/S, (△)Na/Al<sub>2</sub>O<sub>3</sub>/S.