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Cyclohexane oxidation and carbon deposition over metal oxide catalysts

C. Hettige, K.R.R. Mahanama, D.P. Dissanayake *

Department of Chemistry, University of Colombo, Colombo 3, Sri Lanka

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Abstract

Catalytic activity of V, Mn, Ni, Cu, Zn, Mo, Zr and Ce oxides over an α-alumina support was evaluated for cyclohexane oxidation under oxygen deficient conditions in order to understand the relation between carbon deposition and catalytic activity/selectivity. Carbon formation over the catalysts during the oxidation reaction was measured by means of Fourier transformed infrared spectroscopy (FTIR). Catalysts Mn/Al_2O_3 and Ce/Al_2O_3, which are selective for deep oxidation of cyclohexane, possessed relatively carbon free surfaces. The catalysts with relatively high carbon deposition (V, Ni, Cu, Zn, Mo and Zr) produced CO in addition to CO_2. Traces of formaldehyde were produced over the catalysts Mo and V. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon formation; VOC; Oxidation catalysts; Cyclohexane oxidation; Combustion

1. Introduction

Exhaust emissions of internal combustion engines and many industrial processes contain volatile organic compounds (VOCs). Ceramic supported solid catalysts containing precious metals has been the method of choice to control pollutants emitted from such processes (Koltsakis and Stamatelos, 1997). The use of precious metals has made their application expensive and practically unwelcome in many cases as a method of pollution control. Therefore, in the recent times attention has been drawn on research to develop catalyst systems that are efficient, low cost and easily replaceable (Syczewska and Musialik-Piotrowska, 1995; Cordi et al., 1997; Tahir and Koh, 1997; Baldi et al., 1998; Ferri and Forni, 1998; Hamoudi et al., 1998; Lahousse et al., 1998; Trawczynski, 1998; Tsyrulnikov et al., 1998).

A catalyst to be employed for VOC oxidation must be highly active, resistant to carbon deposition, selective for deep oxidation and structurally strong. In addition to those properties, the catalyst itself must be non-toxic, non-volatile and non-corrosive. Many of the studies on oxide catalysts have been conducted under conditions where ample oxygen is available for oxidation. However, such conditions might not reveal the propensity of a catalyst for carbon deposition because oxygen in the gas phase can also participate in the oxidation of carbon deposits. Secondly, many metal oxides produce partially oxygenated compounds when hydrocarbons are oxidized under low oxygen partial pressures. These partially oxygenated compounds include carbonmonoxide, alcohols, aldehydes, ketones, acids and aromatic compounds and a catalyst selective to such products may not be desirable as a VOC oxidation catalyst. Therefore, one should pay attention to the above aspects in designing catalysts for VOC oxidation.

In the present study, we investigated the catalysts containing oxides of V, Mn, Ni, Cu Zn, Mo, Zr and Ce over an α-alumina support for oxidation of cyclohexane

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* Corresponding author. Tel.: +94-1-503367; fax: +94-1-503148.

E-mail address: dpd@chem.cmb.ac.lk (D.P. Dissanayake).

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under oxygen deficient conditions. Carbon deposition over oxide catalysts was measured using Fourier transformed infrared spectroscopy (FTIR) and correlated with their selectivity to deep oxidation.

2. Experimental

Catalysts were prepared using metal carbonates or nitrates (general purpose grade) from BDH. All the gases were obtained from Ceylon Oxygen company and the purity was 99.99% or better. Cyclohexane used was from Fluka Chemie AG. and was of general purpose grade.

Catalysts were prepared by impregnating the support (α-Alumina) with an aqueous solution of the active metal to give a metal loading of 25% by weight. For this, the required weight of the metal (in the form of nitrate or the carbonate) was dissolved in a minimum amount of distilled water. This was then added to the slurry of the support made by mixing the support with distilled water. The resultant metal salt and alumina slurry was stirred well and evaporated to dryness. The solid was dried in an oven at 120°C and then calcined at 700°C for two hours, which was sufficient to yield a stable metal oxide catalyst.

Catalytic activity for oxidation of cyclohexane was measured by passing a mixture of helium (100 ml min^{-1}), oxygen (10 ml min^{-1}) and vapor of cyclohexane (10 ml min^{-1} at standard temperature and pressure) over 300 mg of the catalyst in a quartz tubular reactor. All the catalytic experiments were performed using this composition of the reactants.

The gas flows were controlled using needle valves and the flow rates were measured using bubble flow meters calibrated for respective gases. Cyclohexane was added to the gas stream containing He and O_2 by bubbling the gas stream through cyclohexane in a container. The temperature of the container was controlled to maintain the desired composition of cyclohexane in the reactant gas stream. The amount of cyclohexane in the reactant gas stream was analyzed by gas chromatography and this was equivalent to a gas phase volume of 10 ml min^{-1} at standard temperature and pressure. All the tubing prior to and after the reactor was heated and maintained above 120°C in order to prevent condensation of water and cyclohexane. The reactor was maintained at the desired temperature and 1 ml gas samples of the product stream were injected to the gas chromatograph (GC) for analysis using an online gas sampling valve. Under the testing conditions, the amount of oxygen in the reactant gas stream was sufficient to convert only ~10% of cyclohexane completely into carbondioxide and water. The catalyst evaluation system was coupled to a GL science, model GC-380 equipped with a thermal conductivity detector. Conversion of cyclohexane into carbondioxide was calculated using GC analysis of the product stream. Temperature of the catalyst bed was controlled to ±2°C using a tubular furnace and a temperature controller (Cole–Palmer). Control experiments were carried out by passing the same reactant mixture over a bed of quartz chips at each temperature.

Carbon deposition over catalysts was measured by FTIR using a Jasco, model-5300 FTIR spectrometer. Catalyst samples for FTIR measurements were pressed into thin pellets transparent to the IR beam. These pellets were then heated to 600°C in a flow of oxygen to oxidize any hydrocarbon residues. IR spectra of the catalysts after the oxygen treatment showed no carbon deposits on them. The same pellet was then treated in the reactant gas stream at the desired temperature for 15 min. After the treatment, the catalyst sample was transferred to the IR instrument and the spectrum was recorded. The amount of carbon formed was estimated from a previously prepared plot of percentage weight gain, calculated by weighing the catalyst pellet Vs the area under the absorption band in the region 1400–1700 cm^{-1}. The values calculated from the plot were randomly checked by weighing the catalyst before and after the treatment in cyclohexane.

3. Results and discussion

The activities of metal/α-alumina catalysts are displayed in Figs. 1 and 2. All the experiments were carried out under oxygen deficient conditions as described in the experimental section.

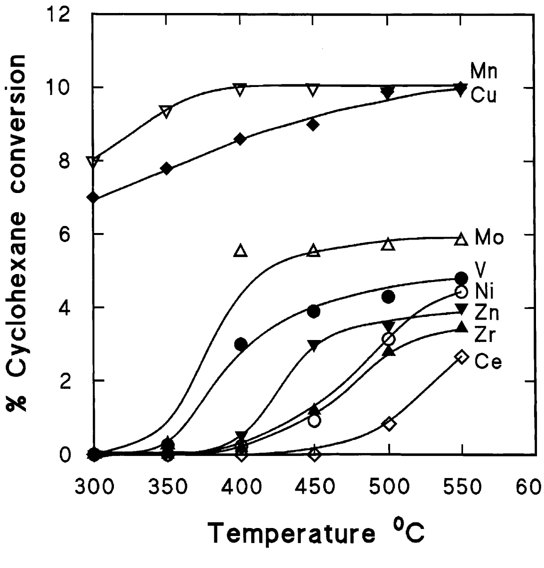

Fig. 1. Percent conversion of cyclohexane over metal oxide catalysts.

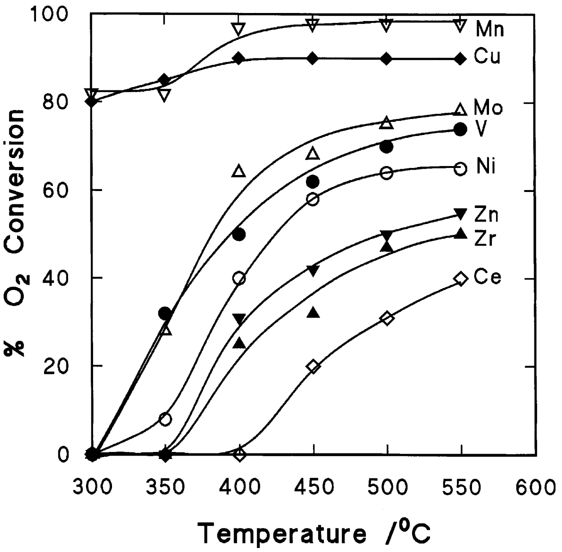

Fig. 2. Percent conversion of oxygen over metal oxide catalysts.

As can be seen from the Figs. 1 and 2, the catalysts Cu/Al_2O_3 and Mn/Al_2O_3 displayed the highest activity. The activity over these catalysts reached the maximum limit (10%) at 500°C and at this temperature almost 99% oxygen conversion was observed (Fig. 2). The catalyst Mn/Al_2O_3 displayed 100% selectivity to carbondioxide and water (Fig. 3). However, the selectivity of Cu/Al_2O_3 catalyst for deep oxidation of cyclohexane was less than 90% at all the temperatures tested (Fig. 3). This shows that the apparent high conversion of cyclohexane over Cu/Al_2O_3 is mainly due to the formation of carbonmonoxide (Table 1). Had cyclohexane been converted completely and only into carbondioxide and water over Cu/Al_2O_3 catalyst, the conversion would have been low. The catalysts Mo/Al_2O_3 Zn/Al_2O_3, Ni/Al_2O_3, V/Al_2O_3 and Zr/Al_2O_3 displayed moderate activities (Figs. 1 and 2). These catalysts recorded less than 100% selectivity for deep oxidation of cyclohexane and produced carbonmonoxide in small quantities (Table 1). Although, Ce/Al_2O_3 displayed a low activity, this catalyst recorded 100% selectivity to carbondioxide (Figs. 1–3).

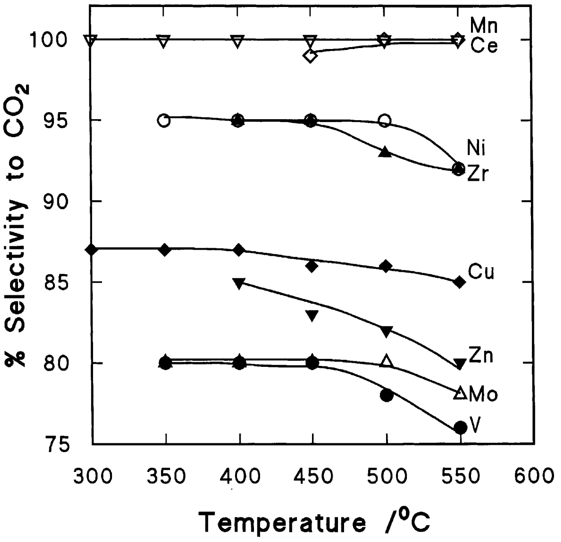

Fig. 3. Percent selectivity to carbondioxide over metal oxide catalysts.

Table 1
Product distribution at 500°C

Catalyst	% Selectivity to products		
	CO_2	CO	H_2CO
V/Al_2O_3	77	21	2
Mn/Al_2O_3	100	–	–
Ni/Al_2O_3	95	5	–
Cu/Al_2O_3	86	14	–
Zn/Al_2O_3	83	17	–
Mo/Al_2O_3	80	18	2
Zr/Al_2O_3	93	7	–
Ce/Al_2O_3	100	–	–

FTIR measurements of catalysts were carried out in the wave number region of 800–2400 cm^{-1}. Catalyst pellets were not transparent to the IR beam at the wave numbers below 1000 cm^{-1}. When the used catalysts were analyzed by FTIR, growth of a broad band in the region 1400–1700 cm^{-1} was observed. This region covers aromatics and unsaturated hydrocarbons. A growth of this band was observed as carbon was deposited over the catalyst when exposed to the reacting gases at high temperatures. Further, the catalysts V/Al_2O_3, Ni/Al_2O_3, Zn/Al_2O_3, Mo/Al_2O_3 and Zr/Al_2O_3 became opaque to the IR beam when heated in the reactant stream to 500°C or to higher temperatures due to carbon formation (indicated by '–' in Table 2). The amount of carbon formed was estimated by measuring the area under the absorption band. Carbon deposition results of the catalysts are shown in the Table 2. An interesting observation made here was that the catalysts, which are selective for deep oxidation, possess relatively carbon free surfaces.

As can be seen from Table 2, carbon formation over Mn/Al_2O_3 is very low and this is in accordance with its high activity (Figs. 1 and 2) and selectivity (Fig. 3) for deep oxidation. Mn has been reported as one of the most effective catalysts for deep oxidation of hydrocarbons (Syczewska and Musialik-Piotrowska, 1995; Tahir and Koh, 1997; Baldi et al., 1998; Lahousse et al., 1998). This may be due to oxygen storage ability of manganese oxide. It has been reported that MnO_x supported on $LaAlO_3$ has the ability to store oxygen (Chang and McCarty, 1996). Stored oxygen may be efficiently utilized in the deep oxidation of surface carbon species

Table 2
Carbon deposition over metal oxide catalysts

Catalyst/ temperature	% Weight gain due to carbon deposition			
	300°C	400°C	500°C	600°C
Al_2O_3	3	12	12	15
V/Al_2O_3	3	19	25	–[a]
Mn/Al_2O_3	3	13	14	17
Ni/Al_2O_3	8	18	30	–
Cu/Al_2O_3	4	18	25	30
Zn/Al_2O_3	4	18	20	–
Mo/Al_2O_3	3	16	–	–
Zr/Al_2O_3	4	17	20	–
Ce/Al_2O_3	4	15	16	17

[a] – Indicates heavy carbon deposition, the pellet was not transparent to the IR beam.

resulting a surface free of carbon deposits. Therefore, it may be possible that all the hydrocarbon molecules that are adsorbed over the surface of the catalyst be oxidized completely into carbondioxide, without forming carbon deposits. When carbon deposits are formed, inefficient oxidation yields carbonmonoxide (Table 1).

The catalysts Ni/Al_2O_3, Mo/Al_2O_3 and Zr/Al_2O_3 have shown heavy carbon deposition (Table 2). The metals Ni, Mo and Zr are known to adsorb hydrocarbons very strongly (Bond, 1997). Strong adsorption of hydrocarbons over these catalysts could have made the catalyst depleted of oxygen facilitating continuous growth of carbon. Formation of carbon over Ni/Al_2O_3, Mo/Al_2O_3 and Zr/Al_2O_3 catalysts caused the fragmentation of the catalysts into a fine powder. Compared to Ni, Mo and Zr containing catalysts, the carbon formation over V/Al_2O_3 and Zn/Al_2O_3 was low. These catalysts did not fragment due to carbon deposition.

The catalyst Cu/Al_2O_3 displayed fairly high activity for cyclohexane oxidation. Carbon deposition over this catalyst is high compared to Mn/Al_2O_3 and Ce/Al_2O_3 but low compared to the other catalysts investigated. Further, this catalyst produced comparatively high amounts of partially oxidized products (Table 1). It has been reported that lattice oxygen of CuO is utilized for deep oxidation and the rate of the oxidation is limited by diffusion of lattice oxygen to the surface (Cordi et al., 1997). Therefore, under oxygen deficient conditions, it is possible that incomplete oxidation could take place forming carbon deposits on the surface of Cu/Al_2O_3. The catalyst Ce/Al_2O_3 displayed low carbon deposition together with high selectivity for carbondioxide. It has been reported that Ce containing catalysts are also capable of oxygen storage but inferior compared to manganese oxide (Chang and McCarty, 1996; Ferri and Forni, 1998).

Therefore, in summary it can be said that a catalyst suitable for oxidation of VOCs must be highly resistant to carbon deposition. Such a catalyst should be able to oxidize VOCs selectively to carbondioxide and water. Among the catalysts tested, over the Mn/Al_2O_3 catalyst, the oxidation of cyclohexane produced only carbondioxide and water. Further, this catalyst recorded a very low carbon deposition. The catalysts Ni/Al_2O_3, Mo/Al_2O_3 and Zr/Al_2O_3 recorded heavy carbon deposition, which resulted in the fragmentation of the catalyst into a fine powder. In comparison, carbon deposition was moderate over the catalysts V/Al_2O_3, Cu/Al_2O_3, and Zn/Al_2O_3, which produced partially oxidized products. It can be suggested that deep oxidation is facilitated by oxygen storage capacity of the catalyst. Strong adsorption of hydrocarbon leads to heavy carbon deposition. Catalysts selective for deep oxidation of VOCs retain relatively carbon free surfaces during reaction.

Acknowledgements

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