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RESEARCH NOTE

Novel K-Doped Mn–Ce–O Wet Oxidation Catalysts with Enhanced Stability

Syed Tajammul Hussain, Abdelhamid Sayari, and Faïçal Larachi[1]

Department of Chemical Engineering & CERPIC, Laval University, Ste-Foy, Québec, Canada G1K 7P4

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The catalytic wet oxidation of aqueous phenol over Mn–Ce–O mixed oxide catalysts was shown to be accompanied by undesirable formation of heavy polymers on the catalyst surface, leading to severe loss in catalytic activity and in mineralization selectivity. New potassium-doped Mn–Ce–O mixed oxide catalysts were developed and benchmarked for the destruction of concentrated phenolic (10^3 ppm) synthetic wastewater at *very mild* conditions (110°C and 0.5 MPa O_2 pressure). Remarkable improvements in mineralization selectivity were attained. Complete removal of *total* organic pollution was achieved within 10–20 min and mineralization selectivity exceeding 95% was attained over fresh K–Mn–Ce–O catalyst. The leach-proof ability of the catalyst was confirmed from analysis of the treated waters. Detailed characterization of fresh and spent K-doped catalysts revealed drastic reduction in carbonaceous deposits on the catalyst surface, even after successive runs of non-regenerated catalyst samples. The catalyst surface was found to be active after the catalyst was reused thrice, though this time the TPO-detected surface carbonaceous species were far less than those in the nonpromoted Mn–Ce–O catalyst. © 2001 Academic Press

Key Words: **heterogeneous wet oxidation; carbonaceous deposit; deactivation; detoxification.**

INTRODUCTION

Environmental concerns regarding air and water pollution problems have stimulated strong research efforts aimed at the development of cheap and efficient *abiotic* catalytic routes to destroy toxic compounds from gas and liquid streams (1). Catalysts occupy a central place in such processes. Therefore, the design of new catalyst formulations is actively pursued in industry and academia to meet market demands driven by increasingly tight profit margins, especially because no immediate *dollar* profits are expected in cleaning "end-of-pipe" streams.

The increasingly stringent water quality regulations and demand for water reuse after treatment have led to growing interest in catalytic technologies for wastewater detoxification and purification (2). Several successful processes can be applied at various stages of water treatment, and undoubtedly catalytic wet oxidation (CWO) has proven its worth for wastewater treatment, particularly when bio-refractory contaminants at low or moderate organic loads are involved (3, 4).

In CWO, mineralization, that is, the ultimate conversion into CO_2 of CHO-containing organic pollutants, is achieved by reaction with dissolved oxygen in the presence of a *heterogeneous* catalyst. It is suitably dealt with under *lenient* treatment conditions, *i.e.*, moderate temperatures and pressures. Therefore, the vast majority of CWO studies thus far conducted in the literature interrogated the catalyst efficacy, under such low-severity conditions, mostly in terms of the percentage of pollution abatement (3). Lower temperatures promote indeed stronger adsorptive interactions on the catalyst surface but simultaneously facilitate the formation of undesirable heavy polymeric products. The threat of catalyst deactivation by carbonaceous deposits blocking the active sites quickly emerged as a major drawback, shadowing the operational advantages of "low-severity" CWO. Even though the leaching off of catalyst active ingredients can be another frequent cause of deactivation, especially in hot acidic aqueous media (4, 5), the activity loss brought about by strongly chemisorbed carbonaceous deposits on a catalyst surface is a serious matter of concern for the industry, and paradoxically a challenging subject for the scientific community in the field of CWO. Unfortunately, despite its importance this latter cause of catalyst activity loss has thus far been the subject of very few studies (6). It appears that only one single study was released in the literature whose goal was to evaluate the impact of mono- and bimetallic copromotion of transition metal–rare earth composite oxides on the enhancement of mineralization selectivity of phenol CWO. The work hence showed only timid gain in selectivity

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[1] To whom correspondence should be addressed. E-mail: flarachi@gch.ulaval.ca.

whether platinum or silver or both metals are added to the oxide catalyst (7).

Further efforts are being deployed in an attempt to significantly reduce the undesirable phenomenon of carbonaceous deposits accompanying CWO, the ultimate objective being designing “coke-free” CWO catalysts. A common strategy to improve the properties of heterogeneous catalysts is the use of promoters (8). Alkali metals have long been used as promoters for industrial catalysts, the main objective being to enhance one or more of the following properties: activity, selectivity, and stability. This includes Fischer–Tropsch, ethylene epoxidation, and ammonia synthesis catalysts (9, 10). The purpose of this research note is therefore to bring new results by highlighting the potential of potassium doping of Mn–Ce–O mixed oxide catalysts. New K–Mn–Ce–O catalysts were synthesized and tested for phenol CWO at very mild oxidation conditions ($T = 110^\circ$C, $P_{O2} = 0.5$ MPa) with the following objectives: (i) to enhance the mineralization selectivity while preserving high conversions by the doped catalysts; (ii) to improve catalyst stability to leaching and longevity by slowing down the formation of heavy polymeric products.

METHODS

Catalyst Preparation and Characterization

The Mn–Ce–O catalyst (Mn:Ce atom ratio = 1) was synthesized by co-precipitation of manganese(II) chloride (Fischer Scientific Co.) and cerium(III) chloride (Sigma Chemical Co.) using the procedures described in Ref. (11). Following precipitation, the mixture was filtered, washed, and air-dried overnight at 100°C. Potassium was impregnated on Mn–Ce–O according to the incipient wetness method using KNO_3 solution (Aldrich Chemical Co). Then, it was calcined under flowing air at 400°C for 4 h. The final potassium content was 4% by weight. Two sets of samples were prepared, nonpromoted Mn–Ce–O and K–Mn–Ce–O with 4% potassium loading.

The surface area of both catalysts, nonpromoted and K-doped fresh and used Mn–Ce–O was determined using N_2 adsorption at 77 K and the BET model. The adsorption isotherm was measured using an automated volumetric adsorption analyzer, Omnisorp 100 from Coulter.

The carbon content of carbonaceous deposits on the spent CWO catalyst was quantified by CHN elemental analysis (Carlo Erba, Model 1106).

The organic species adsorbed on the catalyst during CWO were also investigated by temperature-programmed oxidation (TPO) using an Altamira AMI1 instrument. In a typical TPO run, 60 to 100 mg of used catalyst was loaded in a U-shaped quartz microreactor, which was then installed in a furnace coupled to a temperature controller programmer. The experimental procedure consisted first of exposing the catalyst to flowing helium (30 mL/min) and, at the same time, starting, at a heating rate of 10°C/min, a linear temperature program from ambient temperature to 120°C. The final temperature was then maintained for 20 min before being cooled down to room temperature. The heating and cooling down treatment was systematically conducted so as to remove the physisorbed water from the catalyst sample without thermally damaging the deposited “coke”. The next step consisted of heating the catalyst up to 650°C at a rate of 8°C/min while a flow of 5% O_2–He passed through the catalyst bed at constant flow rate of 30 mL/min to burn off the eventual carbonaceous deposit. Detection of the gaseous burn-off products at the microreactor outlet was performed using a thermal conductivity (TCD) detector.

Reaction and Analytical Procedures

Phenol (1 g/L) was oxidized in a 300-mL stainless-steel high-pressure Parr agitated autoclave reactor (model 4842, Parr Instrument, Inc.) at 110°C and 5 g/L catalyst load under 0.5 MPa O_2. This oxygen amount corresponded to an O_2/PhOH stoichiometric ratio of ca. 5 (assuming complete conversion of phenol into CO_2 and H_2O). The experimental conditions used in this work are summarized in Table 1. After 10- and 20-min CWO times, aliquots of the solution were withdrawn, filtered, and analyzed:

(i) for total organic carbon (TOC) using a combustion/nondispersive infrared gas analyzer (Shimadzu 5050 analyzer);

(ii) for leached off Mn, Ce, and K measured by means of plasma emission spectrometry on an Optima 3000 spectrometer (Perkin–Elmer) after complete destruction of the water-dissolved organics.

To study the catalyst deactivation, CWO runs were performed on *fresh* catalysts, denoted U_I, then on spent *non-regenerated* catalysts used twice and thrice, denoted U_{II} and U_{III}, respectively. In each case, the following parameters were measured: residual TOC and mineralization selectivity, concentration of the leached-off metal cations (Mn, Ce, and K), amount of carbon built up on the catalyst, BET surface area and average pore size, the burn-off oxygen uptake, and TPO profiles.

TABLE 1

Phenol CWO: Experimental and Operating Conditions

Phenol initial concentration (g/L)	1.0
Catalyst loading (g/L)	5.0
P_{O2} (MPa)	0.5
CWO temperature (°C)	110
Stirrer speed (rpm)	750
CWO reaction time (min)	10 and 20

RESULTS AND DISCUSSION

Catalyst Characterization

Table 2 summarizes the observed physical properties of the catalysts under investigation. The properties of the K-promoted Mn–Ce–O sample differ from those of the nonpromoted one. The surface area and pore size of the K–Mn–Ce–O sample reflect the stability of this catalyst toward CWO, even after it was used thrice (U_{III}) without regeneration.

The TPO was used to characterize the carbonaceous deposits formed on the catalyst surface during CWO. The consumption of oxygen, which is tantamount to the production of carbon dioxide (6, 7), is indicative of the burn-off and the nature of the carbonaceous deposits that deactivate the catalyst. The catalysts were withdrawn from the slurry reactor after 20 min of CWO reaction at 110°C. The oxygen uptake data shown in Table 3 indicates that no burn-off occurs for the K-doped catalysts under U_I and U_{II} conditions, thus supporting the belief that no "coke" lay-down was formed. Furthermore, even after a third consecutive use of the recycled non-regenerated catalyst (U_{III}), the K–Mn–Ce–O catalyst still leads to lower oxygen uptake as compared to the nonpromoted Mn–Ce–O right after its first CWO exposure (U_I). As will be shown later, this finding is consistent with the dramatic improvement in the mineralization selectivity exhibited by the K–Mn–Ce–O catalyst. Consistently, Fig. 1 shows no sign of any burn-off activity, neither obviously for fresh K–Mn–Ce–O (F) nor for K–Mn–Ce–O under U_I and U_{II} conditions, in agreement with the O_2 uptake data. After being used thrice (U_{III}), a broad combustion peak emerged around 340°C.

Furthermore, as can be seen from Table 4, the insignificant buildup of carbonaceous deposits for K–Mn–Ce–O under U_I and U_{II} is confirmed by the CHN elemental analysis. Note that, under U_I utilization, the K–Mn–Ce–O catalyst generates 14 times less carbon than the Mn–Ce–O catalyst (12). In line with the TPO results, the CHN measurements support the fact that K−doping inhibits the formation of carbonaceous deposits and protects the active sites for CWO reaction.

TABLE 2

Physical Properties of the Catalyst under Investigation

	Surface area (m^2/g)				Pore size (nm)			
Catalyst	F	U_I	U_{II}	U_{III}	F	U_I	U_{II}	U_{III}
Mn–Ce–O	120	70	—	—	0.50	—	—	—
K–Mn–Ce–O	132	128	122	97	0.38	0.42	0.47	—

Note. F = fresh; U_I = fresh, first use; U_{II} = spent, used twice; U_{III} = spent, used thrice.

TABLE 3

Oxygen Uptake of Used Catalyst

Catalyst	O_2 uptake (μmol/g)
Mn–Ce–O (F)	0
Mn–Ce–O (U_I)	4635
K–Mn–Ce–O (F)	0
K–Mn–Ce–O (U_I)	0
K–Mn–Ce–O (U_{II})	0
K–Mn–Ce–O (U_{III})	2616

Note. F = fresh; U_I = fresh, first use; U_{II} = spent, used twice; U_{III} = spent, used thrice.

Catalytic Wet Oxidation

The activity tests, expressed in terms of TOC conversion, X_{TOC}, and mineralization selectivity of both nonpromoted and K-promoted catalysts are summarized in Table 5. The mineralization selectivity was defined as

$$\sum\nolimits_{C}^{m} = \frac{\text{Carbon converted to CO}_2}{\text{Carbon vanished from water}} = \frac{\text{TOC}_0 - \text{TOC} - W}{\text{TOC}_0 - \text{TOC}} \times 100, \qquad [1]$$

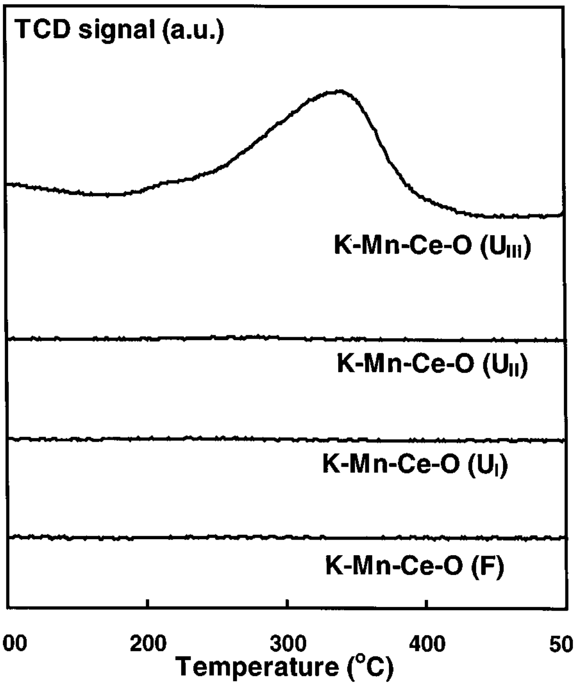

FIG. 1. TPO of catalyst samples withdrawn after 20 min of CWO. From bottom to top: fresh K–Mn–Ce–O (F), K–Mn–Ce–O (U_I) after first utilization without regeneration, K–Mn–Ce–O (U_{II}) after second utilization without regeneration, and K–Mn–Ce–O (U_{III}) after third utilization without regeneration.

TABLE 4

Carbon Elemental Analysis of Used Catalysts

Catalyst	Carbon content (wt% g C/g clean cat.)[a]
Mn–Ce–O (U_I)	9.6[b]
K–Mn–Ce–O (U_I)	0.7
K–Mn–Ce–O (U_{II})	1.2
K–Mn–Ce–O (U_{III})	3.2

Note. U_I = fresh, first use; U_{II} = spent, used twice; U_{III} = spent, used thrice.

[a] Accuracy = ±0.3%.

[b] Taken from Ref. (12).

where TOC_0 is the initial total organic carbon concentration, TOC is the residual total organic carbon concentration, and W is the concentration of "solid" carbon contributed by the deposits per unit volume of the wastewater solution, in ppm. In other words, $\sum_C^m$ measures how many CO_2–carbon entities are yielded per 100 carbon atom converted entities that have left the aqueous solution.

Table 5 shows that complete removal of the *total* organic pollution was achieved within 10 to 20 min using K–Mn–Ce–O. This catalyst suffered less conversion loss after several uses, contrary to its nonpromoted homologue. Most remarkably, K–Mn–Ce–O exhibited high mineralization selectivity, 2.9 times that achieved using Mn–Ce–O in the same CWO conditions. Furthermore, even without catalyst regeneration, this selectivity remained very high, between 80 and 95%, and exceeded by far that attained with the nonpromoted Mn–Ce–O catalyst.

An additional point worth mentioning in the evaluation of the K–Mn–Ce–O mixed oxide catalyst is its "leachproof" ability under CWO reaction conditions. In fact, catalyst degradation during CWO, with the consequence of metal active sites leaching off, represents another major drawback for the implementation of new catalysts at the industrial scale. The stability of K–Mn–Ce–O was checked through plasma emission spectrometry measurements of metal-ion concentration in water subsequent to oxidation and careful filtration of the spent catalysts after consecutive runs U_I, U_{II}, and U_{III}. The results are reported in Table 6 and compared to similar analyses performed earlier in the case of Mn–Ce–O (13). The metal-ion concentration in the effluent is indeed very low, thus securing safe water discharge without any further treatment of the K–Mn–Ce–O mediated CWO.

TABLE 5

TOC Conversion and Mineralization Selectivity

	X_{TOC}(%)						$\sum_C^m$(%)		
	U_I		U_{II}		U_{III}		U_I	U_{II}	U_{III}
Time (min)	10	20	10	20	10	20	10	10	10
Catalyst									
Mn–Ce–O	97.4	97.7	85.6	94.8	—	—	33.2	—	—
K–Mn–Ce–O	98.6	99.3	98.3	99.2	97.8	98.9	95.3	91.9	78.6

Note. U_I = fresh, first use; U_{II} = spent, used twice; U_{III} = spent, used thrice.

TABLE 6

The Extent of Catalyst Leaching Off as Inferred from Metal-Ion Concentration in the Residual Liquor after CWO Reaction

	Metal concentration (ppm)		
Catalyst	Mn	Ce	K
Mn–Ce–O (U_I)[a]	10	<0.1	—
K–Mn–Ce–O (U_I)	0.6	<0.1	0.5
K–Mn–Ce–O (U_{II})	0.6	<0.1	0.7
K–Mn–Ce–O (U_{III})	1.6	<0.1	1.2

Note. F = fresh; U_I = fresh, first use; U_{II} = spent, used twice; U_{III} = spent, used thrice.

[a] From Ref. (13).

The alkali metal involvement in the wet oxidation catalysis as to how it affects the catalyst activity, the coke-induced deactivation, and the prevention of manganese leaching is yet to be delineated. Alkali metals, also referred to as bonding modifiers (14) or chemical promoters (9), are known to influence bonding and reactivity of surface species for several catalytic reactions. For example, CO hydrogenation is promoted through CO dissociation, and the extent of hydrogen chemisorption is reduced, by the addition of potassium to transition metal catalysts (14). In ammonia synthesis, potassium weakens NH_3 bonding to the catalyst active sites, thus lowering the surface product concentration and freeing important sites to further reactions (14). The ability of K_2O to donate electrons to the transition metal is also known to increase the reactivity of the latter to dissociate nitrogen (9). In the present instances, the main function of a wet oxidation catalyst is to interact with the pollutant, either directly or indirectly, to produce active radicals in the first step of the reaction (15). The beneficial role of potassium may be tentatively associated with the effect of the electron-donating ability of K_2O on the activation of oxygen and its subsequent transformation into peroxide O_2^{2-}, (16). Potassium indeed helps the occurrence of an electron-rich environment, which is thought to be propitious for oxygen activation into O_2^{2-}, thus facilitating the electron transfer processes in the radical-producing step (16). Hence, potassium contributes to the production of more peroxides on the catalyst surface; these in turn promote deep oxidation until complete mineralization of the parent pollutant and its intermediates, thus explaining why less carbonaceous deposits are formed on the catalyst upon addition of potassium.

CONCLUSIONS

The K-promoted Mn–Ce–O mixed oxide catalyst holds promise as a highly active and robust system for the catalytic wet oxidation of wastewater. This catalyst has powerfully illustrated its ability to efficiently mineralize the organic matter under nonhostile operating conditions, that is, moderate pressure and near the water normal boiling point. K–Mn–Ce–O yielded the highest mineralization selectivity ever reported in the literature for the Mn–Ce mixed oxide catalysts. Other features exhibited were (i) stability under reaction conditions, and (ii) no catalyst leaching.

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