



Catalytic Combustion of Diesel Soot Particles and Total Oxidation of Propene in Presence of Molybdenum Doped Ceria. Study of the Sulphur Poisoning Effect

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Abstract--The influence of molybdenum on ceria activity, CO₂ selectivity and resistance to sulphur poisoning was investigated. Different molybdenum-ceria catalysts, with various atomic ratios (Mo/Ce= 0.001, 0.01, 0.1, 0.2, 0.3), have been prepared and tested with respect to the black carbon (BC) combustion and the oxidation of propene before and after treatment under SO₂. Based on their catalytic behaviour and according to molybdenum loadings, the catalysts have been classified into two groups. The first is that of ceria and the catalysts with low molybdenum loading (1Mo1000Ce, 1Mo100Ce) which presents a good activity, an excellent CO₂ selectivity and a bad resistance to sulphur poisoning. However, the second group of catalysts containing higher molybdenum loadings (1Mo10Ce, 2Mo10Ce, 3Mo10Ce) shows lower activity and CO₂ selectivity but a better resistance to sulphur poisoning. The role of molybdenum against ceria sulphur poisoning has been evidenced.

Keywords: Diesel soot combustion, Molybdenum-ceria catalyst, Propene oxidation, Sulphur poisoning.

I. INTRODUCTION

The incomplete combustion that occurs in gasoline or diesel engines, leads to enormous ejects of atmospheric pollutants as soot particles and toxic gases (CO, CO₂, SO₂, NO_x, Volatile Organic Compounds (VOC)...). Reducing these emissions is very important on preventing their bad effects on environment and health. In this case, catalytic oxidations at low temperatures about 400°C (maximum value reached in the exhaust steam), have been performed and extensively investigated. Cerium oxide has been considered and widely used as support in many catalytic oxidation reactions [1], for its ability to act as an oxygen buffer by storing and releasing O₂ due to the Ce⁴⁺/Ce³⁺ redox couple [2]. Upon heating CeO₂ at elevated temperatures under vacuum, or reducing it by either

H₂ or CO at moderate temperatures, non-stoichiometric oxides CeO_{2-x} (0<x<0.5) are easily obtained [2], [3]. Oxygen vacancies are the predominant atomic point defects more easily formed on ceria surface than in the bulk [4]. They are responsible for non-stoichiometric and oxygen mobility on ceria surface, which is favourable for the oxidation reactions [5]. However, the emission of sulphur oxide from fuel combustions causes a real poison for ceria, which occupies the active vacant sites [6]. In fact, ceria is well known to react with SO₂ over a wide range of temperatures. Several types of sulphur species can be formed according to the oxidation state, the surface basicity and the sulphatation conditions of ceria [7]-[10].

A lot of studies have shown that catalysts based on pure or supported molybdenum MoO₃ are frequently used for a great number of different reactions, of the redox type, particularly, for partial oxidation of propene [11], [12]. Moreover, it is well known that catalysts containing molybdenum are largely used in desulphuration reactions [13], [14]. Thus, the combination of molybdenum with ceria can yield to catalytic systems with an attractive activity, and resistance to sulphur poisoning.

Catalysts containing various amounts of molybdenum were prepared. Catalytic activity and CO₂ selectivity towards the combustion of black carbon and the oxidation of propene have been investigated in the presence of molybdenum-ceria catalysts before and after treatment under SO₂, in order to evidence the role of molybdenum against ceria sulphur poisoning.

II. EXPERIMENTAL SECTION

A. Solids preparation

Ceria hydroxide Ce(OH)₃ was prepared by precipitation from cerium (III) nitrate hexahydrated solution Ce(NO₃)₃·6H₂O 1M with an alkali solution NaOH 2M.

The resulting hydroxide Ce(OH)₃ was filtered, washed and dried for about 20h in a drying oven at 100°C. Different solutions of ammonium heptamolybdate Mo₇O₂₄(NH₄)₆·4H₂O have been impregnated on the drying hydroxide in order to obtain solids with different atomic ratios (Mo/Ce= 0.001, 0.01,

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0.1, 0.2, 0.3). These solids have been called respectively 1Mo1000Ce, 1Mo100Ce, 1Mo10Ce, 2Mo10Ce, 3Mo10Ce. After drying at 100°C for about 20h, solids were stabilized by calcination under dried air ($35\text{mL}\cdot\text{min}^{-1}$) at 500°C for 4h. The temperature was raised at a rate of $0.5^\circ\text{C}\cdot\text{min}^{-1}$.

Sulphated catalysts have been prepared by treating the calcined solids under a flow of pure SO_2 gas ($15\text{mL}\cdot\text{min}^{-1}$) for 40min.

A. Experimental conditions

The catalytic test towards the combustion of black carbon N330 (DEGUSSA) was studied by simultaneous TG-DTA analysis with NETZSCH STA 409 apparatus. Before test, 20wt% of black carbon and 80wt% of catalyst (before and after sulphation) were mixed in a ball miller RETSCH S 1000 for 40 min. 50 mg of this mixture were loaded in an alumina crucible and heated from room temperature up to 800°C ($5^\circ\text{C}\cdot\text{min}^{-1}$) under air flow of $75\text{mL}\cdot\text{min}^{-1}$.

The propene (C_3H_6) oxidation was realised in a catalytic micro reactor coupled to a Varian 3600 gas chromatography using a double detection FID and TCD. The catalysts were reactivated at 500°C for 1h under a flow of dried air $35\text{mL}\cdot\text{min}^{-1}$. 100 mg of the catalyst were tested in the presence of propene ($2.3\text{mL}\cdot\text{min}^{-1}$) and air ($97.7\text{mL}\cdot\text{min}^{-1}$).

Propene conversion (%) at 400°C was calculated through the following relation:

$$\frac{[(\text{CO}+\text{CO}_2)_{400^\circ\text{C}}/(\text{CO}+\text{CO}_2+3\text{C}_3\text{H}_6)_{400^\circ\text{C}}] \times 100}{\text{CO}_2 \text{ selectivity of the catalysts can be deduced from the ratio:}}$$

$[\text{CO}_2/(\text{CO}+\text{CO}_2)]$.

III. RESULTS AND DISCUSSION

A. Black carbon (BC) combustion

1) before treatment of molybdenum-ceria catalysts under SO_2

Fig.1 shows the DTA curves for the BC combustion both in the absence and in the presence of molybdenum-ceria catalysts.

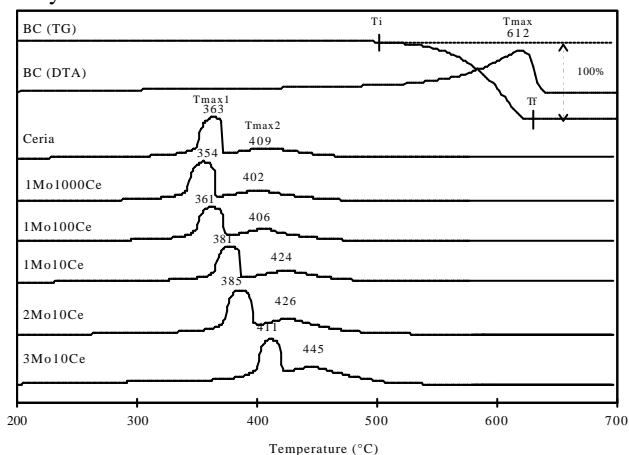


Fig. 1. DTA curves of BC combustion in the absence and in the presence of molybdenum-ceria catalysts

Tmax1 and Tmax2 represent respectively the maximum temperature for the first and the second DTA peak of BC combustion. Ti and Tf corresponding respectively to the initial and final combustion temperatures are deduced from the TG curves. As shown in Fig.1, Ti is the temperature of the starting

weight loss, whereas, Tf is deduced at the end of weight loss. The total combustion of BC without any catalyst exhibits only one exothermic peak with a maximum of combustion temperature at about 612°C (Fig.1). In the presence of molybdenum-ceria catalysts, two exothermic peaks were observed after the total combustion of BC (20%). According to literature [15]-[18], these latter revealed that two BC combustion phenomena occurred. The first peak corresponds to a fast phenomenon leading to BC oxidation at low temperatures, whereas the second peak corresponds to a slower one. These phenomena have been related to BC-catalyst contact, and to thermal and oxygen transport limitations.

When the combustion was performed in the presence of molybdenum-ceria catalysts, a decrease about 250°C and 150°C of the temperature values was respectively observed at the maximum of the first and the second peaks (Fig.1). Thus, the BC combustion is favoured by the presence of molybdenum-ceria catalysts, which enable the soot particles combustion to occur at low temperatures ($\sim 400^\circ\text{C}$). Nevertheless, the catalytic reactivity decreases progressively with the increase of molybdenum loading. The 1Mo10Ce, 2Mo10Ce and 3Mo10Ce catalysts are less reactive than pure ceria with respect to soot particles combustion. Thus, the content, the structure and the dispersion of molybdenum oxide on ceria surface play an important role in the catalytic behaviour of the system during the oxidation reaction of BC. Different authors [19]-[21], have shown that the dispersion capacity and the structure of molybdenum oxide MoO_3 on ceria depend on the loading of molybdenum on ceria. At low loadings, only surface species were formed, resulting from the incorporation of Mo^{6+} into the surface vacant sites of CeO_2 , which play a crucial role in the activity and CO_2 selectivity of ceria during oxidation reactions [5]. The higher the quantity of molybdenum, the lower the number of active vacant sites of ceria and the activity and selectivity in CO_2 of the catalytic system. Otherwise, the difference between the final (Tf) and the initial (Ti) BC combustion temperatures ($\Delta T = \text{Tf} - \text{Ti}$) decreases in the presence of molybdenum. The value of ΔT is more important after the combustion of BC alone and in the presence of ceria, 1Mo1000Ce and 1Mo100Ce ($\Delta T \sim 150^\circ\text{C}$), whereas, it is about ($\Delta T \sim 130^\circ\text{C}$) in the presence of 1Mo10Ce, 2Mo10Ce and 3Mo10Ce. This, can be related to the temperature range of BC combustion, it is lower for ceria, 1Mo1000Ce and 1Mo100Ce ($300\text{--}460^\circ\text{C}$) than for the catalysts with higher molybdenum loadings ($355\text{--}490^\circ\text{C}$). In fact, the diffusion of oxygen is difficult at low temperatures and the oxidation reaction occurred slower than at higher temperatures. However, compared to the non catalytic combustion of BC for which ΔT is about 120°C , the temperature range of BC combustion in the presence of 2Mo10Ce and 3Mo10Ce is lower with a comparable value of ΔT ($\sim 125^\circ\text{C}$). Thus, it seems that the presence of high molybdenum loadings is favourable for an easier diffusion of oxygen at low temperatures ($400\text{--}450^\circ\text{C}$).

From these results, it is evident that molybdenum-ceria oxides are outstanding catalysts, which allowed the total combustion of BC to occur at low temperatures around 450°C .

The decrease of catalytic activity with respect to BC combustion, in the presence of molybdenum, indicates that molybdenum is added on ceria for its capacity to enhance ceria resistance to sulphur. In order to investigate the role of molybdenum against ceria sulphur poisoning, catalytic combustion of BC has been performed after catalysts treatment under SO₂.

2) After catalysts treatment under SO₂

Fig. 2 shows the TG-DTA curves of BC combustion realized in the presence of molybdenum-ceria catalysts treated under SO₂.

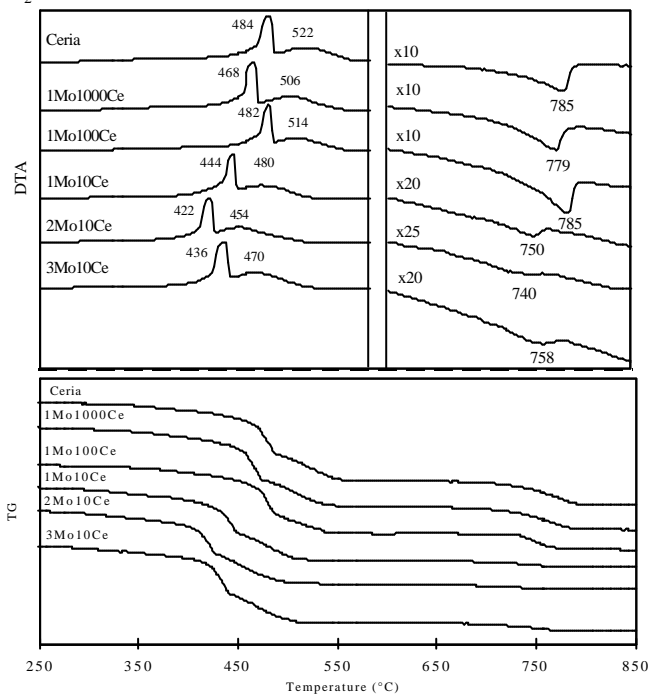


Fig. 2. DTA-TG curves obtained during the catalytic combustion of BC in the presence of molybdenum-ceria catalysts treated under SO₂

The values of Tmax1 and Tmax2 for the catalysts are largely elevated after treatment of the catalysts under SO₂. For pure ceria, 1Mo1000Ce and 1Mo100Ce, Tmax1 and Tmax2 increases about 120°C, whereas, the delay of the BC combustion in the presence of 1Mo10Ce, 2Mo10Ce and 3Mo10Ce is not more than 50°C. It can be deduced then, that the SO₂ acts as a real poison for the catalysts lowering their activity with respect to the BC combustion. However, the presence of molybdenum enhances ceria resistance to sulphur poisoning. Moreover, as shown in Fig. 1 and Fig. 2, the values of ΔT increase after treatment of the catalysts under SO₂. In fact, ΔT is about 155°C for pure ceria, whereas, it is about 188°C for ceria treated under SO₂. Thus, the presence of SO₂ seems to delay the oxygen diffusion through the catalytic system, making difficult the combustion of BC and lowering then the catalytic activity.

Otherwise, in addition to the presence of the double exothermic peak related to rapid and slow BC combustion phenomenon, a weak endothermic peak can be detected for the catalysts treated under SO₂ at higher temperature (>740°C) (Fig.2). This endothermic peak is due to SO₂ catalysts treatment, since it was not observed for the catalysts before

treatment under SO₂ (Fig.1). In addition, the same endothermic peak was observed after thermal decomposition of the catalysts treated under SO₂. The intensity of this peak decreased considerably with the increase of molybdenum content in the catalyst. 6.3% of experimental weight loss was observed after thermal decomposition of sulphated ceria, whereas, 1.4% of weight loss is obtained for sulphated 3Mo10Ce catalyst. The results are shown in Table I.

TABLE I.

Experimental weight loss obtained after thermal decomposition of sulphated catalysts with the theoretical and experimental weight losses of sulphated catalysts obtained after BC combustion

Catalyst	CeO ₂ (%)	Weight loss (%)*	Theoretic al weight loss (%)	Experiment al weight loss (%)	% of sulphation
Ceria	100	6.3	39.43	7.7	19.5
1Mo1000Ce	99.9	5.6	39.39	7.4	18.7
1Mo100Ce	99.1	5.2	39.10	5.1	13.1
1Mo10Ce	92.2	2.3	36.38	2.4	6.6
2Mo10Ce	85.6	1.5	33.77	1.6	4.7
3Mo10Ce	79.9	1.4	31.51	1.5	4.7

*(TG results of sulphated catalysts)

In order to attribute this endothermic peak, sulphated solids have been investigated by thermal analysis, Raman and EPR spectroscopies showing the presence of Ce(III) sulphate phase on ceria surface after SO₂ treatment [22]. In addition, the TG curves shown in Fig.2, exhibit a weight loss (%) at temperatures higher than 740°C due to the decomposition of cerous sulphate phase [Ce₂(SO₄)₃]. It is important to note that the observed weight loss decreases with the increase of molybdenum loading, as it was observed after thermal decomposition of sulphated catalyst (Table I).

The values of experimental and theoretical weight loss (%) observed at 785°C after BC combustion in the presence of sulphated catalysts (80%) are presented in Table I, in comparison with the results obtained after thermal decomposition of sulphated catalysts.

The experimental weight losses observed for sulphated ceria and 1Mo1000Ce catalyst after BC combustion are higher than those obtained after thermal decomposition. However, in the presence of higher molybdenum loadings the values are similar. This can be explained by the fact, that ceria and 1Mo1000Ce are contaminated by sulphur present as impurities

in BC (0.45%). However, in the presence of molybdenum, the catalytic system is less contaminated. Thus, the presence of molybdenum enhances ceria resistance to sulphur poisoning.

The theoretical weight loss was determined according to the following decomposition reaction of $Ce_2(SO_4)_3$ phase :



The percentage of ceria sulphation can be deduced from the ratio of experimental and theoretical weight losses. The resulted values are presented in Table 1. It is evident that the weight loss of cerous sulphate and the percentage of ceria sulphation decreases in the presence of molybdenum. 19.5% of ceria is sulphated, whereas, the percentage of ceria sulphation for 3Mo10Ce catalyst is about 4.7%. These results can be related to the dispersion of molybdenum oxide on ceria surface through the incorporation model [19]-[21] : Mo^{6+} ions occupied the active vacant sites of ceria surface. The more the quantity of molybdenum is important, the less is the number of active sites available for the adsorption of SO_2 and the lower is the formation of cerous sulphate phase. Thus, the presence of molybdenum weakens ceria interaction with SO_2 lowering then the quantity of resulted cerous sulphate phase. Moreover, it should be noted that the decomposition of cerous sulphate occurred at lower temperatures in the presence of molybdenum. It is about $785^\circ C$ for pure ceria, 1Mo1000Ce and 1Mo100Ce catalysts, it decreases to $\sim 750^\circ C$ in the presence of the catalysts with higher molybdenum loadings (Fig.2). Indeed, the presence of molybdenum enhances ceria resistance to sulphur poisoning and should play an important role against the deactivation of the catalytic system after several combustion cycles of black carbon, by reducing the affinity of ceria towards sulphur oxide and decreasing the temperature of cerous sulphate decomposition.

Analyses of CO and CO_2 gas released after the combustion of BC particles before and after ceria sulphation have shown that the presence of SO_2 affects the selectivity of the catalytic system towards the formation of CO_2 . The variation of CO_2 selectivity of molybdenum-ceria catalysts towards BC combustion, before and after sulphation is shown in Fig.3.

100% of CO_2 selectivity is obtained for ceria and the catalysts containing low molybdenum loadings (1Mo1000Ce, 1Mo100Ce, 1Mo10Ce).

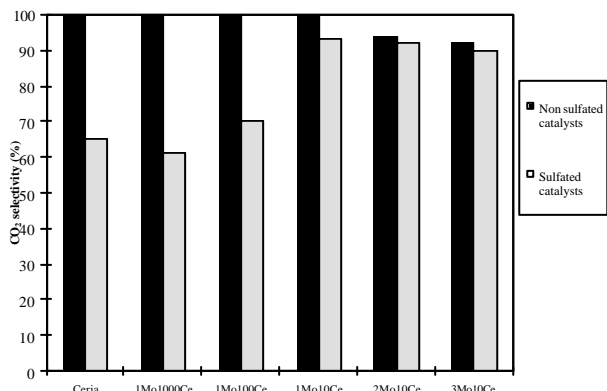


Fig. 3. Variation of CO_2 selectivity before and after sulphation of

molybdenum-ceria catalysts towards BC combustion

After sulphation a large decrease of CO_2 selectivity can be observed for these catalysts. 65% of CO_2 is formed after the combustion of BC in the presence of sulphated ceria. Whereas, for the catalysts with higher molybdenum loadings, CO_2 selectivity slightly decreases after sulphation (Fig.3). CO_2 selectivity of 3Mo10Ce catalyst is respectively equal to 92% and 90% before and after sulphation. Thus, the presence of SO_2 is not favourable for the activity and CO_2 selectivity of pure ceria, 1Mo1000Ce and 1Mo100Ce catalysts with respect to BC combustion. However, in the presence of higher molybdenum loadings, the effect of SO_2 is considerably reduced.

B. Propene oxidation

Fig. 4 shows the catalytic activity and the selectivity in CO_2 with respect to the oxidation reaction of propene at $400^\circ C$ in the presence of molybdenum-ceria catalysts before and after treatment under SO_2 .

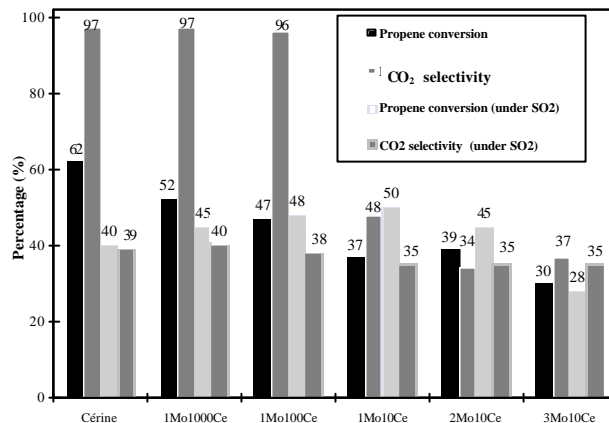


Fig. 4. Propene conversion and CO_2 selectivity obtained after propene oxidation at $400^\circ C$ in the presence of molybdenum-ceria catalysts before and after SO_2 treatment.

The propene conversion ratio is about 62% for pure ceria catalyst, with a high selectivity in CO_2 (97%). Lower activity but similar selectivity in CO_2 were obtained when the reaction is performed in the presence of catalysts with low amounts of molybdenum (1Mo1000Ce, 1Mo100Ce). Whereas, for catalysts with higher molybdenum loadings a lower activity is obtained with the formation of a large quantity of CO during the propene oxidation. Only, 30% of propene is oxidized in the presence of 3Mo10Ce with the formation of 63% of CO ($CO_2/(CO+CO_2) = 37\%$). Thus, the presence of molybdenum decreases the catalytic activity and lowers its selectivity in CO_2 with respect either to propene oxidation reaction or to BC combustion. These results can be explained also by the dispersion of molybdenum oxide on ceria which decreases the number of active vacant sites favourable for oxidation reactions. Furthermore, according to a previous work based on propene oxidation at $400^\circ C$ in the presence of molybdenum-ceria catalysts [23], the decrease of catalytic activity in the presence of molybdenum can be explained by the strong interaction of

molybdenum oxide with propene. It has been shown that propene is physisorbed and completely oxidized on pure ceria. However, it is partially oxidized at room temperature to carbonated species on molybdenum oxide (MoO_3) with the formation of intermediate allylic species [23]. Thus, the low activity of 1Mo10Ce, 2Mo10Ce and 3Mo10Ce is due to the fact that, at the beginning of the catalytic test and at low temperatures ($<100^\circ\text{C}$), a partial oxidation of propene occurred on molybdenum oxide MoO_3 leading to the formation of carbonated species (ethene or coke) deposited on the surface. In fact, this process can induce a modification of catalyst surface structure and a modification of oxygen arrangement in the solid that can affect the activity and CO_2 selectivity of the catalytic system in the presence of molybdenum. Moreover, the oxidation reaction of propene is in competition with that of coke or ethene deposit on the catalyst surface, which can explain the decrease of the catalyst activity and selectivity in the presence of high molybdenum loadings.

Furthermore, as shown in Fig.4, a large decrease of propene conversion ratio is observed after sulphation of ceria, 1Mo1000Ce and 1Mo100Ce catalysts. However, SO_2 has no effect on catalysts activity with higher molybdenum loadings. In fact, 62% of propene is converted in the presence of pure ceria, whereas 40% is converted after ceria sulphation. In the presence of 3Mo10Ce catalysts, 30% and 28% of propene conversions are obtained respectively before and after treatment of the catalyst under SO_2 .

Although molybdenum-cerium catalysts with high molybdenum loadings show better resistance to sulphur poisoning, the catalytic behaviour of the catalysts with no or low molybdenum loadings (ceria, 1Mo1000Ce, 1Mo100Ce) remains better after sulphation than the catalysts with higher molybdenum loadings for either BC combustion or propene oxidation. The addition of molybdenum should be important then, to improve the catalytic resistance to sulphur poisoning after several combustion cycles.

IV. CONCLUSION

The catalytic results have shown the performance of molybdenum-cerium catalysts for the combustion of BC particles and for propene total oxidation. In fact, these reactions can occur in the presence of molybdenum-cerium catalysts at low temperatures around 400 and 450°C , instead of 612°C for BC combustion without catalyst. Based on these results, molybdenum-cerium catalysts can be classified into two groups according to molybdenum loading. The first group is that of pure ceria and the catalysts containing low molybdenum loadings (1Mo1000Ce, 1Mo100Ce) presenting a high activity and excellent CO_2 selectivity with respect to the oxidation reaction of BC particles and propene. Whereas, the second is the group of catalysts with higher molybdenum loadings (1Mo10Ce, 2Mo10Ce, 3Mo10Ce) for which the catalytic activity is less important with the formation of CO.

The catalytic study of molybdenum cerium oxides towards BC combustion and propene oxidation after sulphation has evidenced the poisoning effect of SO_2 on the catalysts behaviour and the role of molybdenum for a better catalytic

resistance against SO_2 . A large decrease of the activity and CO_2 selectivity has been observed for the first group of catalysts, whereas, for the second, the effect of SO_2 is negligible as for the combustion of BC or the oxidation of propene.

After sulphation, the catalytic behaviour of the first group remains better than the second for one cycle of either BC or propene combustion, mainly that of 1Mo100Ce. Thus, a small quantity of molybdenum seems necessary to be added on ceria in order to obtain a catalytic system with an attractive activity, a good CO_2 selectivity and a high resistance to sulphur poisoning.

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