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Oxidation of dibenzothiophene by a metal–oxygen–aldehyde system

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Abstract

The oxidation of dibenzothiophene by an oxygen/aldehyde system, using heterogeneous (unsupported and alumina-supported oxides) and homogeneous (acetate salts) catalytic systems based on Mn, Co and Ni, was examined. In all instances, Co- and Mn-based systems were the most active catalysts. In contrast, a markedly lower activity was measured for Ni(II) acetate whereas NiO and the alumina-supported NiO were inactive. The study indicates that involvement of homogeneous catalysis cannot be excluded when using the supported catalysts.

Keywords: Liquid phase oxidation; Heterogeneous catalysis; Radical mechanism; Leaching

1. Introduction

Combustion of organosulfur compound produces SO_2 gas which contributes to air pollution and acid rain. Thus, in Europe, a specification of 15 ppmw of sulfur in diesel has been established in 2005 (Auto-oil 2). Due to an increasing environmental concern, lower sulfur content is expected to be mandated in the near future. Hydrodesulfurisation is the conventional process for removal of organosulfur compounds in fuels. Following this treatment, the sulfur content is about 400 ppmw. Thus, more stringent conditions of temperature and pressure are needed to obtain an ultra low sulfur diesel. These conditions result in increasing the operating costs due to the large amount of hydrogen required and a shorter catalyst life-cycle [1]. A complementary method of desulfurisation is the oxidative desulfurisation process (ODS). ODS consists in oxidizing the organosulfur compounds to their corresponding sulfone and sulfoxide which can be easily separated from the fuel. Recent research aims to develop heterogeneous catalytic system for this process. The oxidants usually used in heterogeneous ODS studies are hydrogen peroxide (H_2O_2) and *tert*-butyl hydro peroxide (TBHP) [2–8]. However, large-scale storage and use of such peroxides carry a potential risk and thus alternative oxidants that are more environmentally friendly are desirable.

Oxygen is potentially a more interesting oxidant. However, only a few studies dealt with this oxidant [9,10]. In a previous work, Murata et al. [10] have shown that an homogeneous catalytic system based on metal salt, aldehyde and oxygen was active in ODS reaction of model and commercial diesel fuels. The objective of the present study is to develop a transition metal heterogeneous catalyst–oxygen–aldehyde system. For the purpose of comparison, heterogeneous (unsupported and supported catalysts) and homogeneous catalytic systems have been studied for ODS of dibenzothiophene, a model molecule for organosulfur compounds in diesel fuel.

2. Experimental

Homogeneous tests were carried out using the following metal salts: $Co(II)(C_2H_3O_2)_2 \cdot 4H_2O$ (97%, Acros Organics), $Mn(II)(C_2H_3O_2)_2 \cdot 4H_2O$ (>99%, Sigma–Aldrich), $Ni(II)(C_2H_3O_2)_2 \cdot 4H_2O$ (98%, Sigma–Aldrich).

The unsupported catalysts were prepared from their nitrate salts ($Co(NO_3)_2 \cdot 6H_2O$ (Labosi), $Ni(NO_3)_2 \cdot 6H_2O$ (99.999%, Aldrich)). The manganese salt was obtained by drying of an aqueous solution of $Mn(NO_3)_2$ (50% w/w, Sigma–Aldrich) at 453 K for 24h. The salts were calcined at 773 K for 3 h with a ramp of 3 °C min^{-1} in flowing air (100 mL min^{-1}).

Supported oxides Me/Al_2O_3 with Me: Co, Mn, Ni were prepared by pore volume impregnation of the alumina support with aqueous solution of the metal nitrate salts. The metal loading was chosen in order to have the same number of metal atoms per square nanometer of support (1 atom nm^{-2}) for the

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three supported catalysts. The corresponding amount of nitrate salt was dissolved in purified water at ambient temperature. Before impregnation, γ-alumina pellet (AX-350, 97%, from Criterion, $S_{BET} = 308\ m^2\ g^{-1}$, pore volume $0.61\ mL\ g^{-1}$) was ground, sieved between 0.2 and 0.5 mm, and then calcined at 773 K for 3 h with a ramp of $3\ K\ min^{-1}$ under $100\ mL\ min^{-1}$ air flow. The calcined support was then impregnated with metal nitrate solution for 8 h at ambient temperature. The mixture was placed in an oven at 393 K for 24 h and then calcined at 773 K for 3 h with a ramp of $3\ K\ min^{-1}$ under air flow ($100\ mL\ min^{-1}$).

XRD analysis was performed on X'pert PRO MPD (Philips). The Raman spectra were recorded under ambient conditions at room temperature with a Labram 300 instrument (Jobin Yvon) equipped with confocal microscope and a CCD detector.

The oxidation reaction was carried out in a refluxed round bottom flask at 323 K under N_2/O_2 gas mixture ($P_{O_2} = 0.2$ bar; $25\ mL\ min^{-1}$) while stirring at $1250\ round\ min^{-1}$. In the standard reaction test, 1 mmol of dibenzotiophene (DBT) from Acros Organics (99%) was dissolved in 10 mL of a (9/1) mixture of dodecane (99%, Sigma–Aldrich)/tetradecane (99%, Sigma–Aldrich). Four millimole of octanal (Alfa Aesar) and an amount of catalyst corresponding to 0.05 mmol of metal were added. Aliquots of the reaction mixture were periodically withdrawn and analyzed by GC (Varian 3400 CX; BPX5). DBT is quantitatively converted to the corresponding sulfone. Only traces of sulfoxide were detected. For the homogeneous tests 1.6 mmol of octanoic acid (99%, Sigma–Aldrich) was added in order to dissolve the salts. Metal content of the final solution was analyzed by atomic absorption (Spectra AA 220, Varian).

3. Results and discussion

A standard reaction test has been carried out in the absence of the catalyst. Under these conditions and following 90 min of reaction time, conversion of aldehyde and oxidation of DBT were typically lower than 3%. Scheme 1 gives the partial mechanism of peroxy acid formation and DBT oxidation as proposed by Murata et al. [10].

In the absence of metal to catalyze the formation of the first radical molecules, the initiation can be thermal, aliphatic aldehyde being the reactive molecule. With Co(II) acetate but without aldehyde or without oxygen, no DBT conversion is observed after 18 h. These experiments confirm that, under standard conditions, DBT oxidation requires the presence of both oxygen and aldehyde, in accordance with the proposed oxidation mechanism (Scheme 1).

$$RCO^{\cdot} + O_2 \rightarrow RCO_3^{\cdot} \quad (1)$$
$$RCO_3^{\cdot} + RCHO \rightarrow RCO_3H + RCO^{\cdot} \quad (2)$$
$$RCO_3H + R'SR' \rightarrow RCO_2H + R'SOR' \quad (3)$$
$$RCO_3H + R'SOR' \rightarrow RCO_2H + R'SO_2R' \quad (4)$$

Scheme 1. Mechanism of peroxy acid formation and DBT oxidation as proposed by Murata et al. [10]. In this scheme R stands for alkyl or aryl group of the aldehyde. $R'SR'$, $R'SOR'$ and $R'SO_2R'$ represent, respectively sulfides, sulfoxides and sulfones. (1) and (2) correspond to the propagation steps. (3) and (4) are the oxidation steps. Initiation and termination steps are omitted.

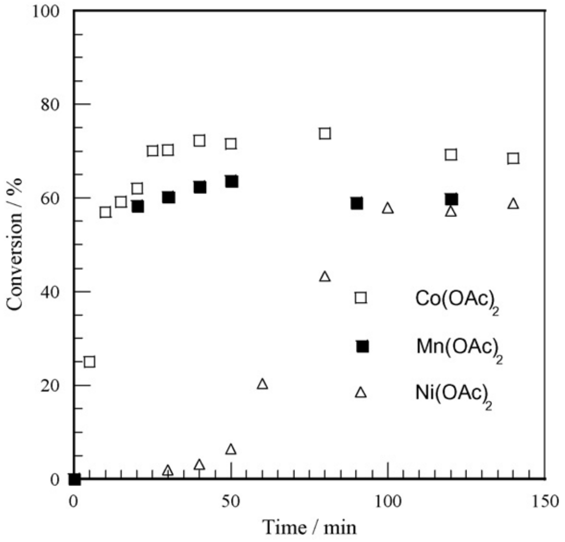

Fig. 1. Dibenzothiophene oxidation using Co, Mn and Ni acetates.

Fig. 1 reports the DBT conversion versus time with different metal acetate salts. Co(II) and Mn(II) acetates were the most active for DBT oxidation. Higher DBT conversion rates were reported by Murata et al. [10] at lower temperature for the same metal salts (90%, in 15 min). However, the comparison is not straightforward since a less polar solvent was used in the present study (alkane mixture versus benzene in [10]).

Ni(II) acetate was also active for the DBT oxidation following an induction period of 40 min. Once the reaction has started, the oxidation rate with Ni(II) acetate ($0.011\ mmol\ DBT\ min^{-1}$) was significantly lower than that observed with Co(II) and Mn(II) acetates (respectively 0.058 and $0.052\ mmol\ DBT\ min^{-1}$).

For the three salts, DBT conversion reaches a plateau ascribed to the total conversion of octanal. Indeed, in an independent experiment, it was verified that addition of aldehyde once the plateau is reached brings about an increase in DBT conversion. Since the initial ratio of aldehyde/DBT consumed corresponds to ca. twice the stoichiometry (Scheme 1), it appears that part of the converted aldehyde does not lead to DBT conversion. One possible explanation is that the peroxy acid formed undergoes parallel reactions:

$$RCO_3H + RCHO \rightarrow 2RCO_2H \quad (5)$$

$$2RCO_3H \rightarrow 2RCO_2H + O_2 \quad (6)$$

Comparison of DBT conversion after the aldehyde has been totally consumed shows that the addition of the same amount of aldehyde in two steps (2× 2 mmol) leads to a higher conversion than one step addition of 4 mmol (Fig. 2). This can be attributed to an inhibition of the parallel reactions (5) and (6) at lower aldehyde concentration.

XRD results for the unsupported oxides indicate the formation of crystalline Co_3O_4, MnO_2, and NiO phases. For the Mn system, Raman spectra confirmed the absence of intermediates oxides (Mn_2O_3, Mn_3O_4). The surface areas of the

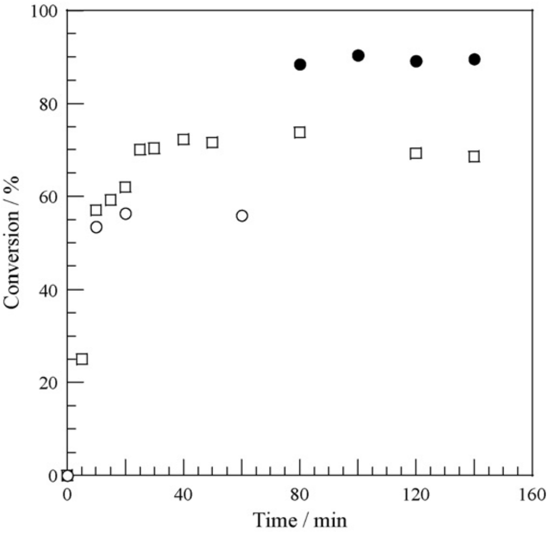

Fig. 2. Dibenzothiophene oxidation using cobalt (II) acetate. Influence of the stepwise addition of octanal (4 mmol in two steps) ((○) first step; (●) second step) as compared to one step addition of 4 mmol (□).

prepared oxides, obtained by N_2 adsorption–desorption, are reported in Table 1.

Peaks characteristic of bulk oxides were not detected in the XRD patterns of the supported systems. However, Raman results for the Co system indicate the presence of Co_3O_4. The Raman spectra for the Mn system exhibit a weak band which could be attributed to Mn_3O_4. Under similar synthesis conditions the supported phases reportedly consist of Co_3O_4 and Co aluminate-like species [11], a mixture of microcrystalline MnO_2, Mn_2O_3 and Mn_3O_4 [12], and surface Ni-aluminate-like phase [13]. The surface area of the alumina support was little affected by the deposition of the metal phase.

The unsupported Co_3O_4 and MnO_2 oxides were active in DBT oxidation (Fig. 3). At the plateau, conversions around 90% are obtained for these oxides. Based on the time required to reach 30% conversion, MnO_2 is more active than Co_3O_4. NiO was not active after 7 h of reaction time.

Fig. 4 shows the DBT conversion versus time for the three supported oxides Me/Al_2O_3, with Me=Co, Mn or Ni. As observed in the case of the homogeneous and the unsupported systems, supported cobalt and manganese oxides are active for DBT oxidation. The conversion values at the plateau are similar for Co and Mn-supported catalysts. However, the time necessary to reach 30% of DBT conversion (respectively 37 and 11 min) indicates a higher activity of the Mn-based system. Nickel-supported oxide was inactive for the DBT oxidation. This is consistent with the results for the unsupported oxides.

Table 1
BET surface area of unsupported Co, Mn and Ni oxides

Oxide	Surface area ($m^2 g^{-1}$)
Co_3O_4	8.5
MnO_2	18.2
NiO	10.1

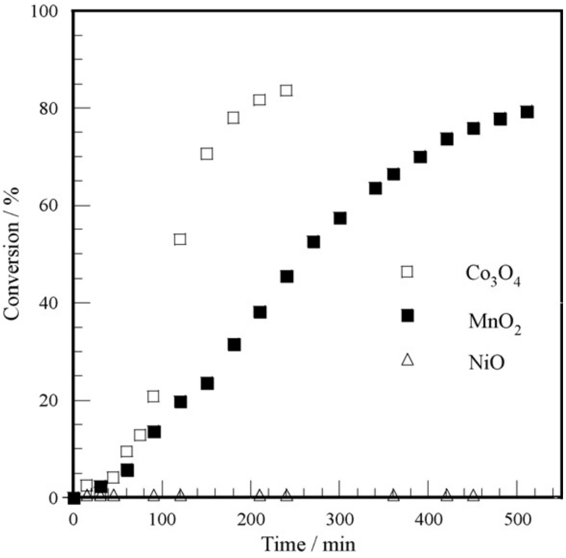

Fig. 3. Dibenzothiophene oxidation using unsupported Co, Mn and Ni oxide catalysts.

As noted in the case of the homogeneous system, the DBT conversion plateau observed for the heterogeneous catalysts is attributed to the total consumption of the aldehyde. Subsequent addition of aldehyde leads to an increase in DBT conversion.

In order to verify the heterogeneous aspect of the Co/Al_2O_3–oxygen–octanal system; a hot filtration test has been carried out. This test, developed by Arends and Sheldon [14], consists in filtering off the catalyst at the reaction temperature, during the course of the reaction (step I), and allowing the filtrate to react further (step II). The hot filtration test was carried out with the 3% Co/Al_2O_3 catalyst under the standard conditions of ODS test. The two steps lasted 30 min. At the end of step I, the conversion of DBT was 15%. After filtration, oxidation of DBT does proceed; the conversion reaches 62%, i.e. a value close to that observed without filtration of the catalyst after 60 min of

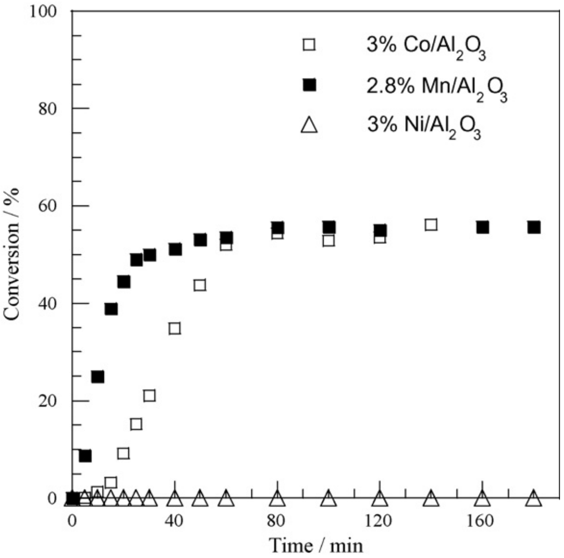

Fig. 4. Dibenzothiophene oxidation using supported Co, Mn and Ni oxide catalysts.

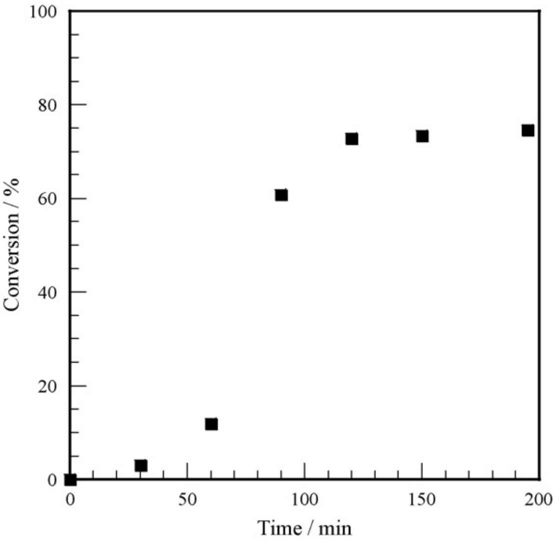

Fig. 5. Dibenzothiophene oxidation using the cobalt phase leached from Co_3O_4.

reaction. Atomic absorption spectroscopy analysis of the solution after 30 min of reaction indicates that ca. 6% of the supported cobalt (25 ppm) have leached into the solution. These results are consistent with the participation of homogeneous catalysis. However, according to the ODS mechanism proposed by Murata et al., the catalyst plays a role mainly in the initiation step to create the first $RCO^{\bullet}$ radicals. Thus, it is not clear whether the leached cobalt or the heterogeneous phase is responsible for the initiation process. A test has been carried out to check if the leached cobalt phase is able to initiate the reaction. Cobalt oxide was left in the solvent for 30 min in the presence of octanoic acid. Thereafter, the solid was filtered and the amounts of DBT and octanal used in the standard ODS test were added. As shown in Fig. 5, after an induction period, the oxidation of DBT takes off. This clearly indicates that the leached cobalt oxide phase is active for the oxidation of DBT.

4. Conclusions

Homogeneous Co and Mn salts and heterogeneous unsupported and supported Co and Mn oxides are active for the oxidation of DBT by the oxygen/aldehyde system. In contrast, a markedly lower activity was measured for Ni(II) acetate whereas NiO and the alumina-supported NiO were inactive.

The heterogeneous nature of the supported systems was evaluated in the case of the Co/Al_2O_3–oxygen–octanal system. The results of the hot filtration test and the detection of leached cobalt in solution indicate that participation of homogeneous catalysis cannot be excluded.

References

[1] J.L. Garcia-Gutierrez, G.A. Fuentes, M.E. Hernandez-Teran, F. Murrieta, J. Navarrete, F. Jimenez-Cruz, Appl. Catal. A: Gen. 305 (2006) 15.
[2] L. Cedeno Caero, J. Forge, A. Navarro, A. Gutierrez-Alejandre, Catal. Today 116 (2006) 562.
[3] V. Hulea, F. Fajula, J. Bousquet, J. Catal. 198 (2001) 179.
[4] L.F. Ramírez-Verduzco, E. Torres-García, R. Gómez-Quintana, V. González-Peña, F. Murrieta-Guevara, Catal. Today 98 (2004) 289.
[5] E. Dumitriu, C. Guimon, A. Cordoneanu, S. Casenave, T. Hulea, C. Chelaru, H. Martinez, V. Hulea, Catal. Today 66 (2001) 529.
[6] F. Figueras, J. Palomeque, S. Loridant, C. Fèche, N. Essayem, G. Gelbard, J. Catal. 226 (2004) 25.
[7] E. Torres-García, G. Canizal, L.F. Ramírez-Verduzco, F. Murrieta-Guevara, J.A. Ascencio, Appl. Phys. A 79 (2004) 2037.
[8] D. Wang, E.W. Qian, H. Amano, K. Okata, A. Ishihara, T. Kabe, Appl. Catal. A: Gen. 253 (2003) 91.
[9] H.Y. Lü, J. Gao, Z.X. Jiang, Y.X. Yang, B. Song, C. Li, Chem. Commun. (2007) 150.
[10] S. Murata, K. Murata, K. Kidena, M. Nomura, Energy Fuels 18 (2004) 116.
[11] W.-J. Wang, Y.-W. Chen, Appl. Catal. 77 (1991) 223.
[12] F. Kapteijn, A.D. Vanlangeveld, J.A. Moulijn, A. Andreini, M.A. Vuurman, A.M. Turek, J.M. Jehng, I.E. Wachs, J. Catal. 150 (1994) 94.
[13] J. Wang, L. Dong, Y. Hu, G. Zheng, Z. Hu, Y. Chen, J. Solid State Chem. 157 (2001) 274.
[14] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A: Gen. 212 (2001) 175.