A Kinetic Study of Methyl-Isobutyl Ketone Catalytic Combustion on LDH-Derived Cobalt Containing Mixed Oxides

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A Co-MgAlO mixed oxide with 20 at % Co obtained from a layered double hydroxide (LDH) precursor was synthesized and its activity has been studied in the catalytic combustion of the methyl isobutyl ketone (MIBK). The characterization of the catalyst was performed by XRD, EDX and nitrogen adsorption. Its catalytic activity was evaluated in a fixed-bed continuous flow reactor in operating conditions typical for depollution applications, in the temperature range 100 - 400 °C and compared with MgAlO free of Co support and Co_3O_4. A reasonable good activity for the synthesized material at relatively low temperature was found. The catalyst was further subjected to a kinetic study in order to identify the temperature and composition dependencies of the combustion rate.

1. Introduction

Volatile organic compounds (VOC) represent an important category of atmospheric pollutants, with direct impact to human health or environmental negative influence due to their intrinsic toxicity to life beings or by their contribution to the formation of photochemical smog and destruction of ozone layer (Monod et al., 2001). Different technologies have been proposed for VOC removal from industrial gaseous effluents, one of the most efficient being the catalytic combustion, due to its low energetic requirements, especially when VOC concentrations are lower than 10,000 ppm (Tseng et al., 2005). Methyl isobutyl ketone is one of the VOCs released in significant amounts into the atmosphere. This compound is mainly used as a solvent in vinyl, epoxy and acrylic resins industry, dies and ink manufacture, extraction agent for removal of paraffins from mineral oils, or as an intermediary in several chemical processes (Ullmann, 2005).

There are two categories of catalysts used in the catalytic combustion processes: mixed metal oxides and supported noble metals. Considering their high catalytic activity and in spite of their relatively high price, the supported noble metals are widely used catalysts for commercial combustion processes. In order to counteract the continuous increase in the price of noble metals, different oxide-based materials have been proposed in the literature as effective catalysts for combustion processes. Spinel chrome-containing Mg and Co oxides have been tested by Hu et al. (2014) in the catalytic combustion of methane within the temperature range 300 – 800 °C. The Mg spinel showed a promising activity among the tested materials. The mesoporous manganese oxides were tested by Zhou et al. (2014) for the combustion of toluene, total conversion being achieved at temperatures close to 280 °C using MnO_x catalyst prepared by hard-template method. Other type of Mn catalysts, exhibiting honeycomb structure and consisting in $LaMnO_3$ have been used in catalytic combustion of methane at relatively high pressures 12 bar (Barbato et al., 2013).

To our knowledge, there are only few studies in the literature regarding the MIBK combustion. Low concentration MIBK-air mixtures were subjected to combustion on Pt/alumina (Tseng et al., 2005) as well as Pt/zeolites catalysts (Tsou et al., 2003). The results reported by Tseng et al. (2005) showed that, among other intermediary compounds, carbon monoxide is predominant. Total MIBK conversion at temperatures around 250 °C has been reported by Tseng et al. (2005). The MIBK combustion results on a Pt/alumina catalyst

published by Boşomoiu et al. (2008) evidenced that, depending on the gas flow rate, the complete combustion to carbon dioxide occurs at temperatures higher than 350 °C.

Co-containing LDH-derived mixed oxides have been shown to be effective catalysts for methane combustion in the temperature range 400 - 800 °C (Jiang et al., 2010), the best catalytic activity being observed for an optimum Co/Mg/Al atomic ratio of 1.5/1.5/1. Similar catalysts were studied in propane oxidative dehydrogenation reaction in the temperature range 450 - 600 °C (Mitran et al., 2012) and it has been shown that at high Co-loadings the combustion of propane prevails. Therefore, it was of interest to study the catalytic properties of CoMgAlO with high Co content in the combustion of methyl isobutyl ketone within a lower temperature range. As from our knowledge, no kinetic studies has been published previously regarding the MIBK combustion on Co-containing LDH-derived mixed oxides, the CoMgAlO catalyst will be further subjected to an extended activity study.

2. Experimental

2.1 Catalysts preparation and characterization

The LDH precursor of the CoMgAlO mixed oxide was prepared by coprecipitation as described elsewhere (Mitran et al., 2012). Thus, an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Mg/Al = 3) was added dropwise at room temperature into a well-stirred beaker containing 200 mL of suitable amount of cobalt nitrate solution ($Co(NO_3)_2 \cdot 6H_2O$). The cobalt content, as atomic percent with respect to cations, was for the present material 20 % (Co/(Co+Mg+Al)). Simultaneously, appropriate volume of NaOH (2 M) was added at a controlled rate to maintain the pH close to 10 using a pH-STAT Titrino (Metrohm) apparatus. The precipitate formed was aged in its mother liquor overnight at 80 °C under stirring, separated by centrifugation, washed with deionized water until a pH of 7 was reached and dried at 80 °C overnight. The dried LDH sample was hereafter noted CoMgAl-LDH. The Co-containing mixed oxide catalyst was obtained by calcination of the previously dried sample in air at 750 °C for 8 h. It was labeled as CoMgAlO. The Co-free Mg-Al mixed oxide and the corresponding precursor were obtained following the same protocol and were noted MgAlO and MgAl-LDH, respectively. The same method was used for preparing cobalt oxide.

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D5000 Diffractometer and the Cu-Kα1 radiation with 0.02° (2θ) steps over the 3 – 70° 2θ angular range with 1 s counting time per step.

The chemical composition of the mixed oxide samples was determined by EDX microprobe on a Cambridge Stereoscan 260 apparatus.

The textural characterization was achieved using conventional nitrogen adsorption/desorption method, with a Micromeritics ASAP 2010 automatic analyzer. Specific surface areas were calculated using the BET method. Prior to nitrogen adsorption, the samples were outgassed for 8 h at 250 °C.

2.2 Catalyst testing

Commercial methyl isobutyl ketone (Sigma-Aldrich, 99.5 wt % purity) was used in our experimental study. The combustion process was performed in a quartz tube reactor at atmospheric pressure, operated in isothermal regime. When the CoMgAlO was used for the kinetic study, 0.06 g of catalyst was loaded to the reactor, between two layers of quartz beads in order to achieve an uniform gas flow across the catalytic bed. The reactor temperature was recorded by a Pt/Rh thermocouple with an accuracy of 0.1 °C, placed in the centre of the bed in a 1 mm external diameter thermowell. The temperature level was ensured by placing the reactor inside a furnace provided with temperature control. The carbonyl compound concentration was achieved by bubbling a stream of air through a vessel containing the liquid, placed in a thermoregulated bath. The stream of air saturated in MIBK was further diluted with another stream of air in order to achieve the desired concentration at the reactor inlet. The gas flow rates were controlled by using electronic mass flow controllers. Further details concerning the experimental setup are given in a previous published work (Boşomoiu, 2008). The reaction products were analyzed online by using a Varian CP-3800 gas chromatograph, equipped with methanizer, FID and TCD detectors. A CP-Sil 5CB capillary column for organic compounds, a molecular sieve 5 Å column for N_2, O_2, CO and organic compounds separation and a Hayesep Q column for CO_2 analysis have been used. In order to check the consistency of our experimental results, the carbon balance has been evaluated from inlet and outlet flows, as well as from the concentrations of carbon containing compounds. A maximum error of 8 % for all the experiments was found.

3. Results and discussion

3.1 Catalysts characterization

The XRD patterns of the LDH precursors and of the corresponding mixed oxides are presented in Figure 1. The LDH precursors exhibited the XRD pattern characteristic of the LDH structure (JCPDS 37-0630). Notable, no Co-containing phase was detected in CoMgAl-LDH sample suggesting that multicationicbrucite-like layers containing Co, Mg and Al cations were formed in the precursor. The materials calcined at 750 °C exhibited the characteristic pattern of the well-known Mg(Al)O mixed oxide phase with the periclase-like structure (JCPDS-ICDD 4-0829). Diffraction peaks ascribed to $CoAl_2O_4$ (PDF 70-0753) and/or Co_3O_4 (PDF 09-0418) spinel phases were also observed for CoMgAlO. The XRD pattern of cobalt oxide corresponded to highly crystallized pure Co_3O_4.

The chemical compositions of the samples, estimated by EDX analysis, and their BET surface areas are reported in Table 1. It can be observed that the cobalt content was higher than the nominal value for the CoMgAlO sample while the Mg/Al atomic ratio varied around a value of 3 in solution. The specific surface area of the MgAlO mixed oxide decreased significantly for the CoMgAlO catalyst. Pure cobalt oxide has the lowest surface area.
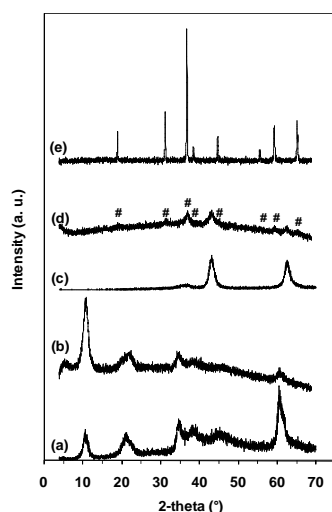

Figure 1: XRD patterns of the precursors and mixed oxides: (a) MgAl-LDH, (b) CoMgAl-LDH, (c) MgAlO, (d) CoMgAlO, (e) Co_3O_4 (# - $CoAl_2O_4$ and/or Co_3O_4).

Table 1: Specific surface areas and chemical compositions of the mixed oxide catalysts.

Catalyst	Specific surface area (m^2 g^{-1})	Co/(Co+Mg+Al) (at. %)	Mg/Al atomic ratio
MgAlO	188	-	3.3
CoMgAlO	114	22.4	2.4
Co_3O_4	11	-	-

3.2 Kinetic study

Preliminary results obtained from blank test combustion evidenced that the reactor internals have no catalytic effect. The experimental results are presented as conversion-temperature diagrams (light-off curves) on the whole range of temperatures considered for MIBK combustion. The selectivity of transformation into carbon dioxide was also calculated from ketone and carbon dioxide measurements. Conversion measurements were repeated periodically in identical operating conditions and did not evidence a significant catalyst deactivation during the experimental run. No other byproducts apart of carbon monoxide have been identified.

In order to evidence the catalytic activity of different constitutive metal oxides in the CoMgAlO catalyst, the pure phases MgAlO and Co_3O_4 have been tested individually in similar operating conditions. The results obtained are presented in Figure 2. Even if the pure Co oxide presents a good catalytic activity in terms of MIBK conversion, its selectivity is relatively poor (Figure 2B). Among the tested materials, the Co-containing

LDH-derived catalyst presented the best catalytic activity in terms of MIBK conversion as well as CO_2 selectivity.
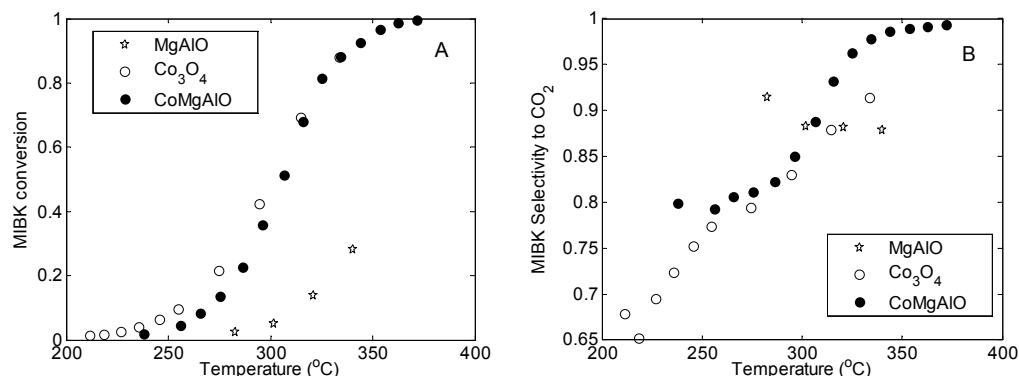

Figure 2: Conversion (A) and selectivity (B) of MIBK transformation into CO_2 for MgAlO, Co_3O_4 and CoMgAlO catalysts.

The kinetic experiments have been performed for MIBK concentration in the range 500 – 1,200 ppm and gas flow rates of 100 – 200 mL min^{-1}. The conversion-temperature light-off curves are presented in Figure 3A and the selectivity in CO in Figure 3B. As expected, an increase in the gas flow rate has as an effect the decrease of the MIBK conversion, especially at intermediate temperatures (Figure 3). The MIBK concentration influence is evidenced in Figure 3, the increase of which inducing a decrease of conversion (negative reaction order). This effect could be explained by the strong MIBK adsorption and presumably, the competition of oxygen and MIBK adsorption on the same active sites.
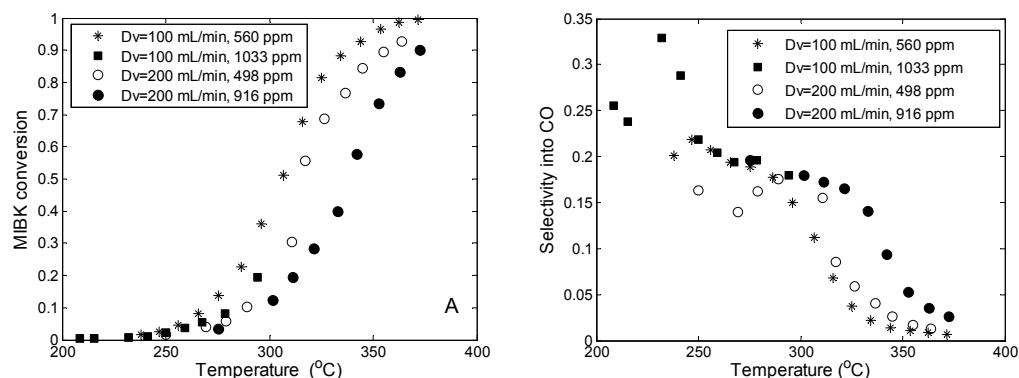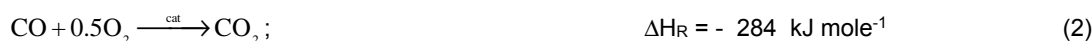

Figure 3: Conversion (A) and selectivity into CO (B) data for CoMgAlO catalyst.

Due to the formation of significant amounts of CO in the process, the MIBK combustion was considered to take place following the reactions:

$$CH_3\text{-}CO\text{-}C_4H_9 + 5.5O_2 \xrightarrow{\text{cat}} 6CO + 6H_2O \; ; \qquad \Delta H_R = -1824 \text{ kJ mole}^{-1} \qquad (1)$$

$$CO + 0.5O_2 \xrightarrow{\text{cat}} CO_2 \; ; \qquad \Delta H_R = -284 \text{ kJ mole}^{-1} \qquad (2)$$

In order to develop a kinetic model, one can consider the most simple power-law reaction rate expression. This approach is useful for preliminary kinetic investigations and conceptual design purposes. The combustion rate dependence on the composition and temperature can be expressed by Eq(3).

$$r_i = k_i(T)\, p_{j,i}^n \; ; j = \text{MIBK, CO}; \; i = 1, 2 \qquad (3)$$

Given the high correlation between the prexponential factor and activation energy parameters in the kinetic constant Arrhenius expression, it is advised to reparametrize around the mean temperature ($\overline{T}$) of the experimental runs (Puaux et al., 2007):

$$k_i = k(\overline{T}) \exp\left(\frac{E_i}{R} z\right); \qquad z = \frac{1}{\overline{T}} - \frac{1}{T} \tag{4}$$

A heterogeneous reactor model that takes into account the concentration and temperature interfacial gradients and assumes the plug flow of gas phase and isothermal catalyst bed was considered. The mass balance equation in terms of molar extent of the reactions was used in the form:

$$\frac{d\xi_i}{dm_c} = k_i p_{j,s} \tag{5}$$

The balance equations for MIBK and CO in the solid phase can be written:

$$S_{ext} k_g \left(C_{MIBK,g} - C_{MIBK,s}\right) = V_p \rho_p r_{MIBK}; \; r_{MIBK} = k_1 p_{MIBK,s}$$
$$S_{ext} k_g \left(C_{CO,s} - C_{CO,g}\right) = V_p \rho_p r_{CO}; \; r_{CO} = 6 k_1 p_{MIBK,s} - k_2 p_{CO,s} \tag{6}$$

The temperature gradient is evaluated from a balance equation around a catalyst particle:

$$S_{ext} \alpha \left(T_s - T_g\right) = V_p \rho_p k_1 p_{MIBK,s} \left(-\Delta H_{R,1}\right) + V_p \rho_p k_2 p_{CO,s} \left(-\Delta H_{R,2}\right) \tag{7}$$

The physical properties involved in the calculations were evaluated using data and correlations published by Reid et al. (1987) and the gas-solid mass (k_g) and heat transfer (α) coefficients evaluated by relations reported by Froment and Bischoff (1990).
The kinetic parameters were estimated by using the classical least-square approach, using the "lsqcurvefit" function implemented in Matlab programming environment. The estimated values of the parameters along with their 95 % confidence intervals are given in Table 2.
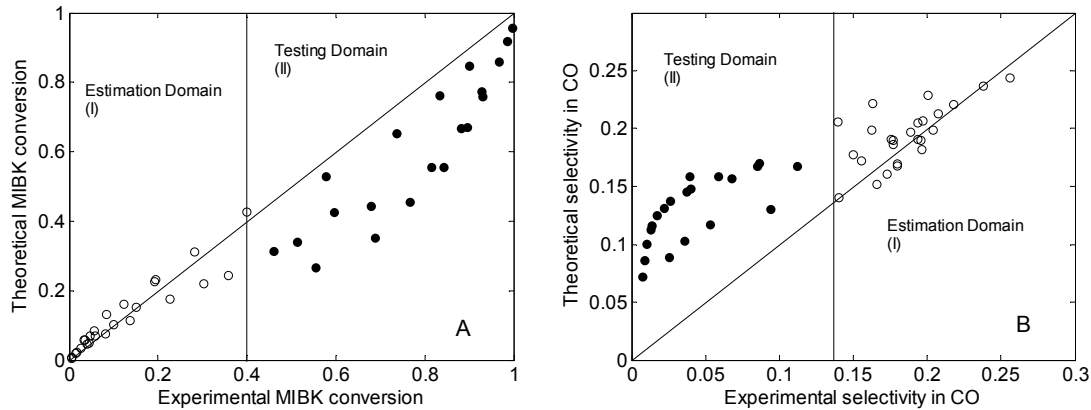

Figure 4: Theoretical vs experimental values for MIBK conversion (A) and selectivity into CO (B).

In order to avoid the diffusion influences, in the estimation procedure it was used experimental data for MIBK conversions below 40 %. Figure 4 shows the calculated conversion (A) and CO selectivity (B) values versus the corresponding experimental ones, for the estimation region as well as for the whole conversion range. As it resulting from Figure 4A, a good agreement between the calculated and experimental values for MIBK conversion in the estimation domain (I) can be observed. However, the CO selectivity on the region (I) is reasonable good. This is suggesting the necessity to develop more complex kinetic models based on a higher volume of experimental data, in order to take into account the competitive adsorption of different species on the catalyst active sites.
Arguments proving the adequacy of the proposed kinetic model are the relatively close 95 % confidence intervals of parameters and the correlation coefficient with a reasonably close to unity value (R^2 = 0.88). The parity diagrams can be divided into two regions, the first one representing the values used in the estimation, whereas the second, the data not used in the estimation. On the testing domain (II), the conversion calculated values are systematically below the experimental ones. This could be explained by slightly higher temperatures in the bed, as a result of temperature gradients developed inside the catalyst bed.

Table 2: Kinetic parameters for MIBK combustion over CoMgAlO catalyst.

Parameter	k_0 (kmol kg^{-1} s^{-1} bar^{-1})	E/R (K)	n
Reaction 1	$2.5961\cdot10^{-4}$ (1 ± $5.8747\cdot10^{-3}$)	12818 (1 ± $5.8745\cdot10^{-3}$)	1
Reaction 2	6.7958 (1 ± 1.6885)	2516 (1 ± 0.4074)	0.923 (1 ± $8.7193\cdot10^{-3}$)

4. Conclusions

The paper presents an experimental investigation of LDH-derived Co-containing catalyst activity in MIBK combustion in lean gaseous mixture with air. Significant amounts of CO are produced at lower temperature but it is practically disappearing at temperatures higher than 370 ºC, corresponding to total conversion level. Consequently, this catalyst demonstrated a promising activity in the MIBK catalytic combustion. A power law expression kinetic model fitted reasonably the experimental data. The experimental results evidenced that kinetic limitations of the physical steps of the process become significant at temperatures higher than 220 ºC.

Acknowledgements

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