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Catalytic oxidation of propylene into acetone using a Ti-Mo oxide base catalyst

B.B.Loura^{1*}, M.J.Ketcha², M.Harouna², O.Fioletova³, N.S.Amirgouliane³

¹Department of Chemistry, Faculty of Science, University of Ngaoundere, P.O. Box 454, Ngaoundere, (CAMEROON)

²Thermodynamic and Heat Chemistry Laboratory, Faculty of Science,
University of Yaounde I, P.O. Box 812, Yaounde, (CAMEROON)

³Department of Physical Chemistry, Petroleum and Gas Academy, 20, av. Azadlig, 1010 Bakou, (AZERBAIDJAN)

E-mail : benloura@yahoo.fr; jketcha@yahoo.fr

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ABSTRACT

This study was carried out with the aid of a Ti-Mo oxide base catalyst. The influence of transition elements additives on the Ti-Mo catalyst was studied. The results obtained showed that the activity of the catalyst in the oxidation of propylene depends not only on the concentration of molybdenum but also on the temperature as well as acidic and basic properties that can be regulated by adding specific additives.

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KEYWORDS

Activity;
Catalyst selectivity;
Catalytic oxidation;
Propylene;
Concentration.

INTRODUCTION

The search for more efficient and more economically viable methods for the preparation of acetone by catalytic oxidation of propylene is important for many industries. Most methods used in industries to obtain acetone are multi-step. The single-step method for the oxidation of propylene by an active and selective catalyst to obtain acetone is subject to much research.

This study is focused on the catalytic oxidation of propylene into acetone in one step in the presence of a modified Ti-Mo oxide base catalyst. Oxidation catalysts of ethylene hydrocarbons into acetone were first of all Mg, V, W oxides and complex compounds of B, Al, Si, Ce, Zr, Sn^[1-3]. The output of acetone, at t = 200 °C, was hardly more than 10 % with a selectivity of 75 %. The by-products were aliphatic acid and CO₂. In the oxidation of propylene with the use of complex com-

pound catalysts like HPO₄-H₃BO₃-H₂MoO₄-Ag₂O, propylene conversion rate was 37% and acetone output, 25%^[4-7]. By-products are acetaldehyde, aliphatic acid, acrolein, CO₂ and water.

The system of Ti-Mo oxide base used as oxidation catalyst of propylene into acetone was revealed in 1972^[8,9]. Oxidizing propylene into acetone with the use of a Ti-Mo catalyst composed in the ratio Ti-Mo = 3:1, at t = 130°C and pressure of 0.1 to 2 Mpa, acetone output was 12 % and conversion rate, 15 %. The by-products obtained were acetic aldehyde, acetic acid and CO₂. The low mechanical stability and variable unmodified Ti-Mo catalyst incited us to look for other more efficient catalysts.

For the catalytic oxidation of propylene into acetone, the Ti-Mo system modified with iron and potassium ions is of great interest and characterized by a high stability and good activity in the process. It possesses

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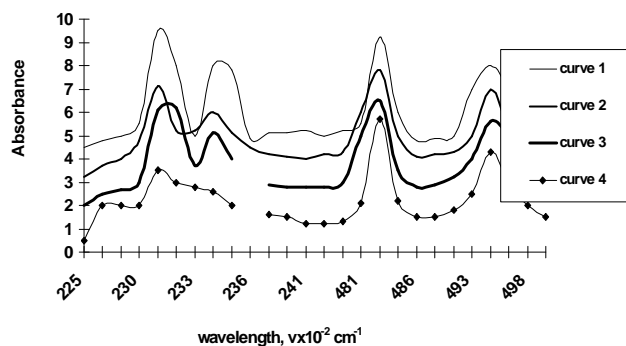


Figure 1 : Infrared spectrum of the Ti-Mo-Fe oxide catalyst without potassium (K) addition (curve 1 and 2) and with potassium (K) addition (curve 3 and 4)

moreover, a high mechanical resistance and is simple at the end of preparation.

MATERIAL AND METHODS

Reactions of the oxidation of propylene into acetone were studied in the laboratory with glass reactors 20mm wide and 180mm long. Analysis of matter and reaction products was done with an LXM-8MD chromatograph equipped with a calorimetric conductivity detector. Two chromatographic columns were used in the analysis. The gas vector was hydrogen and the columns thermostatically fixed at 70°C had each an output of 1.5 litres/hour. The catalytic temperature was 100°C and analysis sensitivity 0.01 mol %. The catalyst synthesis method used was that described by Gasanova et al.^[10] and Adjamov et al.^[11]. The apparatus was equipped with a 1mm thick nickel filter. Spectroscopic infrared analysis of the catalyst was carried out with the aid of a UR-20 spectrophotometer of the 1300-3300 cm^{-1} wavelength range.

RESULTS AND DISCUSSION

Physical and chemical study of the catalyst

The study was carried out with the aid of a modified Ti-Mo oxide base catalyst with the following % composition by mass: $\text{TiO}_2 = 18.0$; $\text{MoO}_3 = 0.25$; $\text{WO}_3 = 0.23$. The result of the infrared spectrum, of absorption as well as kinetics enabled us to reach the conclusion that the Ti:Mo=3:1 oxide base catalyst, calcined at 500°C for 5 hours, is a heterogeneous system containing TiO_2 , MoO_3 and a small solid quantity of Ti and Mo

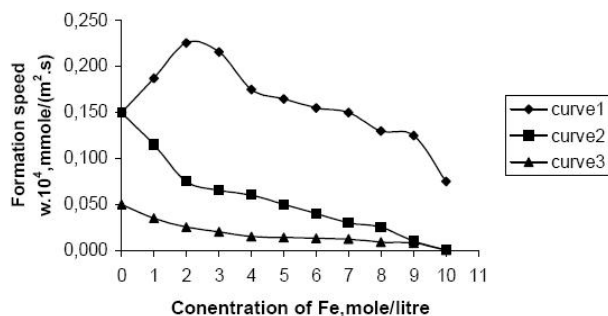


Figure 2 : Rate of formation acetone (curve 1), acetic acid (curve 2) and carbon dioxide formation (curve 3) as a function of the concentration of iron in the oxidation of propylene at 200°C using the Ti-Mo-Fe oxide base catalyst

formed during the substitution of titanium ions by Mo^{4+} and Mo^{5+} in the TiO_2 network. Analysis by infrared spectroscopy (Figure 1) suggested that the catalyst did not change while it was in the reactor.

Influence of temperature

The catalyst used, showed its activity at temperatures varying from 115 to 130°C. Selectivity of the acetone formed was 87 %. With an increase in the temperature to 200°C, output of acetone increased while its selectivity decreased by 75 %. The results obtained are shown in TABLE 1.

The rate of formation of acetone reached a peak when the Ti:Mo ratio was 1:3. Highest acetone output was obtained at a temperature of 200 °C. At temperatures of > 200 °C, acetone output diminished while that of CO_2 and CH_3COOH increased. Increasing the concentration of Mo in the catalyst, the rate of formation of acetone increased and reached a peak when Mo = 15 to 22 % (at.) and then dropped (Figure 2).

Influence of additives

The influence of fourth period transition element additives (V, Cr, Mn, Fe, Ni, Co, Cu, Zn) on the Ti-Mo oxide base catalyst in the oxidation reaction of propylene into acetone was studied (TABLE 2).

TABLE 2 shows the peak output of acetone and acetic acid obtained during the oxidation of propylene using the Ti-Mo catalyst without and with different additives. Contact time was 2 seconds and initial composition of the reaction mixture was as follows, propylene : oxygen : water vapour = 1:11:3. In any case, the atomic ratio of the cations of Mo : Ti : M was maintained at 3 : 1: 0.15.

TABLE 1 : Oxidation of propylene with the use of Ti:Mo = 3:1 metallic oxide base catalyst at different temperatures. Specific speed = 600 h⁻¹; initial concentration in mol % : C₃H₆ = 20; H₂O = 30; O₂ = 20 and N₂ = 20

Temperature, °C	115	130	145	160	172	185	200
Conversion rate, %	1,900	4,100	8,200	12,400	14,300	18,000	20,700
	Selectivity in products, %						
CH ₃ COCH ₃	86,000	87,000	84,900	82,200	86,000	76,700	75,000
CH ₃ CHOHCH ₃	16,000	8,500	4,700	3,500	2,000	1,050	0,650
CH ₃ CHO	0,000	6,700	3,850	3,150	2,080	2,300	2,200
CH ₃ COOH	0,000	0,000	1,400	2,100	2,400	3,000	3,700
CO	0,000	0,000	0,000	1,200	1,100	3,000	3,700
CO ₂	0,000	0,450	5,950	8,900	12,750	14,750	17,950

Apart from cobalt oxide, all additives introduced increased the catalyst selectivity in the acetone formation reaction. Peak yield in acetone for the modified catalyst varied. In introducing Cu, Zn, Mn and V oxides, peak yield in acetone was lower than that of the unmodified Ti-Mo oxide catalyst. The addition of Cr, Ni and especially iron oxides increased acetone yield. Apart from Fe oxide, all other oxide additives reduced output and acetic acid selectivity. It is likely that the addition of iron ions in the composition of the Ti-Mo oxide base catalyst regularized not only the surface acidity of the catalyst but also caused the formation of new active centres for the partial oxidation of propylene.

Influence of water vapour and oxygen

Increasing the partial pressure of the water vapour (P_{H_2O}) in the reaction mixture to 50 kilo-Pascal (KPa) caused an increase in the conversion rate of propylene. However, further increase in the partial pressure of water vapour (P_{H_2O}) caused a decrease in the propylene conversion rate. This is due probably to the competition of H₂O molecules with C₃H₆ absorbed on the same active centre of the catalyst. The use of water vapour is positive since it participates directly in the formation of acetone. Using the mixture (propylene and water vapour) without oxygen through the catalyst layer, the oxidation of propylene into acetone was observed for only 30 mn, then the output of acetone dropped to zero. The phenomenon is also noticed when the quantity of oxygen used in the mixture is smaller than is required by the stoichiometry of the oxidation of propylene into acetone.

Variation of the partial pressure of oxygen (P_{O_2}) in

TABLE 2 : Influence of additives on the activity of Ti-Mo catalyst and on the selectivity of the oxidation of propylene. Volumic speed= 600 h⁻¹; initial concentration in mol % : C₃H₆ = 20 : H₂O = 30 : O₂ = 20 and N₂ = 20

Additives (masse, %)	Output in CH ₃ COCH ₃ , %	Selectivity in CH ₃ COCH ₃ , %	Selectivity in CH ₃ COOH, %	Selectivity in CH ₃ COOH, %
V	9,500	58,200	6,400	24,000
Cr	11,020	55,400	16,200	37,800
Mn	5,900	52,100	6,600	23,000
Fe	19,400	82,100	39,000	59,000
Co	10,000	42,600	6,400	22,600
Ni	11,000	57,000	12,700	21,000
Cu	8,000	56,100	12,700	21,000
Zn	6,200	47,000	10,500	21,000
-	10,250	42,000	20,500	42,000

the 5 to 30 KPa interval did not have any influence on the output of acetone. With an increase in the partial pressure of oxygen (P_{O_2}) a constant increase in the output of CO₂ and CH₃COOH was noticed. Consequently the selectivity in acetone dropped.

Comparing the speeds of oxidation of propylene, of acetone, of isopropyl alcohol and of acetic acid by the Ti-Mo oxide base catalyst, it could be said that the addition of iron positively influenced the formation speed of isopropyl alcohol and of acetone resulting from propylene oxidation.

By introducing first group elements into the Ti-Mo-Fe catalyst composition, its activity and especially its selectivity increased. Peak activity was obtained with the catalyst that contained 0.70 % of potassium.

Adding alkaline metals into the composition of the Ti-Mo-Fe oxide base catalyst reduced its acidity. The more the base addition was increased the more the acidity decreased.

CONCLUSION

With an increase in acidity, rate of formation of acetone increased and then decreased. On the other hand, the rate of formation of acetic acid and CO₂ continued to increase. Increasing the concentration of the base in the catalyst increased the rate of formation of acetone and reduced the oxidation rate of propylene.

According to the results of the infrared spectrum (Figure 1) the surface of the Ti-Mo-Fe and Ti-Mo-Fe-K catalysts contained of titanium, molybdenum and oxy-

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gen ions while those of iron and potassium were absent. This suggests that their presence in the MoO_3 structure is more advantageous.

Deoxidising the modified catalyst, the degree of oxidation of molybdenum ions varied while that of the titanium ions did not change. On the infrared spectrum of the deoxidised Ti-Mo-Fe catalyst were found weak signals related to Mo^{5+} . The stability of the Mo^{5+} -O link is lower than that of the MO^{6+} -O as the presence of the potassium (K) ion increased the stability of the Mo-O link. From every evidence, the alkaline metals that are linked to the variation of the degree of molybdenum oxidation were responsible for the appearance of new active centres. These active centres facilitated the partial oxidation of propylene into acetone.

Thus, the Ti-Mo oxide catalyst, modified with oxides of iron and other alkaline metals at a temperature of 200 °C, can realise the oxidation of propylene into acetone, with a sufficiently high selectivity. The Ti-Mo catalyst used in this study is a poly-phased element and its activity, excluding its duration, depends on acidic as well as basic properties that can be regulated by adding specific additives.

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