Catalysis Today 176 (2011) 215–218

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The applications of metal supported chromia-alumina catalysts in C1 reactions

Tomasz P. Maniecki*

Technical University of Lodz. Institute of General and Ecological Chemistry 90–924 Łódź, ul. Żeromskiego 116, Poland

ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form
10 December 2010
Accepted 22 December 2010
Available online 5 February 2011

Keywords:
C1 reactions
CO oxidation
Partial methane oxidation
Methanol synthesis

ABSTRACT

The aim of this work was to determine the catalytic properties of metal (Ni, Cu, Pt) supported catalysts in C1 reactions. Catalytic activity of $Cr_xAl_yO_z$ binary oxides alone and $Me/Cr_xAl_yO_z$ samples were determined in: CO oxidation (by water vapor or oxygen), methanol synthesis (MS) reaction as well as partial oxidation of methane (POM) to synthesis gas.

1. Introduction

In the last years the binary oxides were extensively researched due to their interesting catalytic properties [1–6]. Binary oxides usually have better catalytic as well as mechanical properties in comparison with appropriate monoxides. Introduction of second oxide allows to change such properties as alkalinity, specific surface area, reducibility and others. According to literature data catalysts based on binary oxides contained calcium or magnesium are more resistant to coke deposition [7] due to the increase of support alkalinity [8]. The growth of catalytic activity could be achieved by addition of transitional metals oxides.

The catalysts supported on chromium–aluminum binary oxide show promising catalytic behavior in many reactions: CO oxidation, partial methane oxidation (POM), methanol synthesis (MS) and water gas shift (WGS) reactions.

The copper catalyst with chromium addition demonstrates promising catalytic activity in many industrial applications, such as dehydrogenation reactions. Some researchers [9–14] considered that the chromium addition improves Cu dispersion and prevent the catalyst against sintering. Doca and Segal [15] reported that addition of Cr promoter into copper catalyst could increase the lifetime of catalysts due to the formation of copper oxide junctions. The chromium addition to $CuO\text{-}Al_2O_3$ catalysts can also prevent copper from reacting with alumina, which caused the copper aluminate ($CuAl_2O_4$) formation [10,11].

Platinum is one of the most catalytically active metal. It can be applied in many processes such as CO oxidation, deep oxidation of hydrocarbons, reduction of organic compound and many others. Due to relatively high cost of this metal the researcher efforts are concentrated on the work out the platinum-free catalytic systems. However in many chemical processes the replace of platinum is not possible, especially for such processes as: low temperature CO oxidation, preferential CO oxidation in H_2 stream for fuel cells, selective reduction of organic compounds.

Low temperature CO oxidation:

$$CO + 1/2O_2 \rightarrow CO_2 \qquad \Delta H = -283\,kJ/mol$$

takes place usually on Pt/support or Au/support catalysts. Both of them exhibit good activity in this process. However Pt/support catalysts are used more often due to their better stability in comparison to Au/support catalysts.

The water gas shift (WGS) reaction is one of the main industrial methods for the production of hydrogen. Typically, the carbon monoxide (CO) reactant is derived from the synthesis gas (syngas) obtained from various carbonaceous materials [15].

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.1\,kJ/mol$$

As shown above, WGS is a moderately exothermic and reversible reaction. Thus, the equilibrium constant increases with a decrease of reaction temperatures. The iron oxide-based WGS catalysts were discovered in 1909 by BASF researchers [15]. The active component of the catalyst is magnetite (Fe_3O_4) [15–18]. However, the thermal stability of magnetite is low, this catalysts undergo rapid sintering at the temperature range 300–500 °C. Therefore, a refractory oxide (Cr_2O_3) was added to increase the thermal stability. Among studied

* Corresponding author. Tel.: +48 426313125; fax: +48 426313128.
E-mail address: tmanieck@p.lodz.pl

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.12.053

binary catalysts samples with addition of 14 wt% Cr_2O_3 were more resistant to sintering, on the other hand catalysts contained 8 wt% Cr_2O_3 were more active [18]. In the next step of investigation was found that copper oxide addition increases activity in WGS process. Current industrial WGS catalysts include 2–4 wt% CuO. The role of copper in HT-WGS process is still discussed. Some researchers claim that the effective component is metallic Cu, which acts in the same way as in the $Cu/ZnO/Al_2O_3$ LT-WGS catalyst [15], while others suggest that Cu in the magnetite structure could modify the electronic properties in the standard Fe_3O_4/Cr_2O_3 catalyst [18].

The synthesis of methanol from mixtures of hydrogen and carbon oxide using mixed metals and metal oxides has been under investigation since at least 1914 [19]. Both zinc oxide and chromium oxide, with or without promotion by alkali metal hydroxides, are described as preferred materials for oxygenate synthesis in the BASF patent. In addition, two later patents from BASF issued in 1925 [19] and 1926 [20] concerning of the use of CuO/ZnO and Cr_2O_3/ZnO catalysts. Although $CuO/ZnO/Al_2O_3$ is currently (and has been since ca. 1960) the preferred industrial catalyst for methanol synthesis. Nowdays the academic research efforts are focused on applications of CuO/Cr_2O_3 catalysts in higher alcohol synthesis.

Nickel supported catalysts are commonly used in many different processes. The most important are: reduction of fatty acids, methane steam reforming, partial methane oxidation, methanation of CO and CO_2 and others.

The main method of syngas production is steam reforming of methane (SRM). The major disadvantage of this endothermic process is a large consumption of energy:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0 = 206\,kJ/mol$$

The molar ratio of produced syngas also is not suitable for many applications. For hydrocarbon or oxygenates synthesis more suitable is syngas with CO/H_2 ratio equal 2. Due to this reason another methods of syngas production are extensively studied.

One of the most interesting opportunities is partial oxidation of methane (POM) process. This process is mildly exothermic, which allows to proceed this reaction in isothermal conditions:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0 = -38\,kJ/mol$$

Until now, Ni/Al_2O_3 catalysts were commonly applied in industrial practice in POM reaction. The addition of such components, as chromia or magnesia, to alumina support improves considerably the catalytic properties [21]. The nickel catalysts doped with chromia were studied in work [22]. Danilova and co-workers [22], compared the catalytic behavior of Cr_2O_3-doped and Cr_2O_3-free nickel catalysts in the methane steam reforming process.

This paper is focused on a comparative study of M(Pt, Cu, Ni)/bioxide $Cr_xAl_{2-x}O_3$ ($0 \le x \le 2$) catalysts on their possible application in C1 reactions: Pt catalysts in CO oxidation, Cu catalysts in WGS and MS reactions and Ni catalysts in POM reaction. The main aim of this paper is to elucidate the role of chromium in Cr–Al bioxide support on metal/support catalyst behavior.

2. Experimental

2.1. Catalysts preparation

The chromium and aluminum nitrates were used as a support material precursors. The Cr–Al binary oxides were prepared by ammonia co-precipitation of chromium and aluminum hydroxides with various molar ratios Cr:Al from 3:1 to 1:3. The samples were dried and calcined for 3 h in air at 400 °C.

The supported metal catalysts were prepared by wet impregnation method from appropriate nitrates of Cu, Ni and H_2PtCl_6 solutions. The samples were dried and calcined for 3 h in air at 400 °C. Catalysts tested in methanol synthesis and water gas shift reaction prior to tests were reduced in 5%H_2–95%Ar mixture at 300 °C.

Catalytic activity tests were made in various reactions: CO/CO_2 hydrogenation to methanol (MS), partial oxidation of methane (POM), CO oxidation by oxygen and water gas shift reaction (WGS). Dependently on the reaction type different active metallic phases (Pt, Cu and Ni) supported on chromia-alumina oxides were used.

Platinum supported catalysts were used in CO oxidation by oxygen reaction, the metal loading was 1 wt%. The Cu supported catalysts were applied in CO/CO_2 hydrogenation and WGS processes while Ni catalysts were used in POM reaction.

Activity tests were carried out in fixed bed reactors under atmospheric pressure (for: POM, CO oxidation, WGS) and under pressure 40 atm (for methanol synthesis). The steady-state activity measurements were taken after at least 12 h on the stream. The reaction products were determined by on line a gas chromatographs (Giede 16/18 Chromatron) equipped with FID detector and 10% Carbowax 1500 on Graphpac column for organic compound products. The O_2, CO and CO_2 concentrations were monitored by GC chromatograph (N-504 ELPO) equipped with TCD detector (120 °C, 130 mA) and Carbopshere 60/80 (90 °C) column. An analysis of hydrogen was carried out by CHROM-4 gas chromatograph (Laboratorni Pristroje Praha), molecular sieve 4A, temperature 110 °C with TCD detector (100 mA, temperature 120 °C).

3. Results and discussion

The results of activity tests received for metal (Pt, Cu, Ni) supported on chromia-alumina catalysts are given on the Fig. 1A–D respectively. The catalityc activity of binary Cr–Al oxides (with various Cr/Al ratio) and platinum supported catalysts in CO oxidation by oxygen is presented in Fig. 1A. All measurement tests were carried out in heating–cooling mode. One can notice that the hysteresis of CO conversion are observed for all studied catalytic systems. The higher activity was observed during cooling and the shifts of the temperature were about 50 °C. Results of activity tests show that alumina alone hardly exhibits the activity above 500°. The introduction of chromium leads to the substantial increase of the activity of chromia-alumina binary oxides, in CO oxidation depending on the composition of binary oxides. The most active appeared $Cr_{0.5}Al_{1.5}O_3$ catalyst. The increase of chromium content in binary oxide system leads to the decrease of CO conversion. This fact seems to be caused by decrease of specific surface area of sample with higher chromia loading [23] resulting in decrease of quantity of isolated Cr^{x+} superficial species. One can notice surprising fact that promotion of chromia-alumina oxide by platinum almost does not affect on catalytic activity, moreover platinum doped catalytic system was even slightly less active in comparison to binary oxide alone. This fact could be connected to the poisoning effect caused by chlorine ions, originating from the platinum precursor—H_2PtCl_6.

The influence of support kind (Al_2O_3 and $Cr_{0.5}Al_{1.5}O_3$) and copper loading (5, 10, 20 wt% Cu) on the catalytic activity in CO oxidation by water (WGS) is shown in Fig. 1B. One can notice that alumina alone seems to be inactive in this reaction. Binary oxide $Cr_{0.5}Al_{1.5}O_3$ does not reveal very high activity, CO conversion value achieves only 20%, whereas high selectivity to CO_2 was observed (98%). Copper introduction in all cases leads to the formation of very active and selective suppoeted catalysts. Only one side product–methane was observed independently on catalysts kind. Only in the case of alumina supported copper catalyst both: activity and selectivity were relatively low. The most active was catalyst loading 10% wt Cu. Catalysts with lower and higher copper content (5% and 20%, respectively) were less active, but their

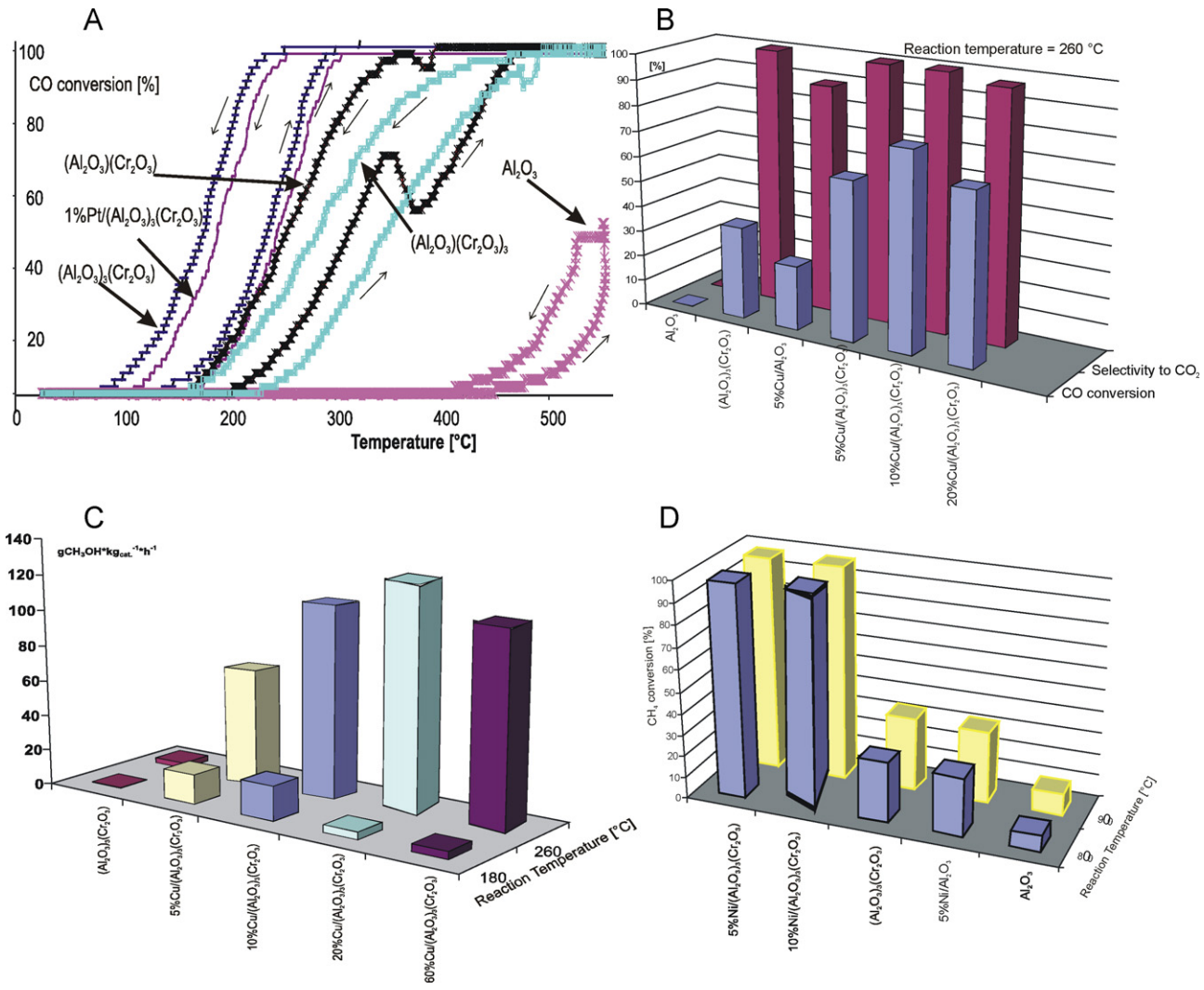

Fig. 1. Results of activity tests for metal supported on chromia-alumina catalysts in: (A) CO oxidation by oxygen (O_2/CO = 10:1, total flow 100 cm^3/min, m_{cat} = 0,1 g, p = 1 atm). (B) CO oxidation by water vapor (H_2O/CO = 2.5:1, total flow 90 100 cm^3/min, m_{cat} = 0,1 g, p = 1 atm). (C) Methanol synthesis ($CO/CO_2/H_2$ = 1:0.5:3, total flow 200 cm^3/min, m_{cat} = 0,1 g, p = 40 atm). (D) Partial methane oxidation (CH_4/O_2 = 2/1, total flow 100 cm^3/min, m_{cat} = 0,1 g, p = 1atm).

selectivity to CO and H_2 was comparable to those charactersistic of 10% wt Cu catalyst. The differences in catalyst activity and selectivity can be connected with the dispersion of copper and quantity of Cu^+ species on catalyst surface. One can expect that dispersion of cooper decreases with the growth of copper content.

The results of activity tests in methanol synthesis reaction from $CO/CO_2/H_2$ = 1:0.5:3 mixture are given in Fig. 1C. The activity tests were taken at two temperatures 180 and 260 °C, under pressure 40 atm. Binary oxide $Cr_{0.5}Al_{1.5}O_3$ alone is practically inactive in this process, but copper introduction increases its activity significantly. The catalytic activity increases with the growth of copper loading from 5 up to 20 wt % Cu. Further increase to 60 wt % Cu leads to drop of catalytic activity. This effect seems to be connected with the decrease of both: total surface area of catalytic system [24] as well as the degree of copper dispersion which plays crucial role in methanol synthesis [25].

The measurements of support (Al_2O_3 and $Cr_{0.5}Al_{1.5}O_3$) and Ni/support activity in partial methane oxidation are given in the Fig. 1D. The results of activity tests taken for supports themselves Al_2O_3 and $Cr_{0.5}Al_{1.5}O_3$ reveal that alumina was inactive in this process, but Cr–Al bioxide appeared moderately active, which can be caused by Cr redox behavior. It can be expected that isolated superficial chromium atoms can change the oxidation state (+3 to +2) and due to partial oxidation of methane takes place according to redox mechanism. The indirect mechanism of partial oxidation of methane can be treated as the sum of three reaction: full oxidation of methane, dry and wet methane reforming. Chromium cations Cr^{2+} and Cr^{3+} can be involved in the reaction of full ocidation of methane [26].

Nickel alumina supported catalyst reveals relatively low activity—only 30% of CH_4 conversion was achieved. Such behavior seems to be connected with the formation of nickel aluminate $NiAl_2O_4$. This compound is very hardly reducible and in the reaction conditions cannot be easily reduced to the metallic Ni which presence is essential to obtain active catalytic system in POM reaction. Catalysts (both 5 and 10% Ni) supported on $Cr_{0.5}Al_{1.5}O_3$ binary oxide were highly active in selective methane oxidation. Methane conversion of both catalysts achieve values 95 and 97% for temperature of reaction 800 and 900 °C, respectively. One can suppose that chromium prevents nickel to the formation of nickel aluminate $NiAl_2O_4$ due to the formation of nickel chromate $NiCr_2O_4$, which can be easily reduced in reaction conditions.

In all studied processes catalytical behavior seems to be connected with the redox properties of binary Cr–Al oxide material used as a support. In all cases chromium containing catalysts were more active in comparison to alumina supported systems.

Chromium addition can prevent against formation hardly reducible aluminates. Also superficial isolated chromium species can be considered as active sites of different reactions. The ability of chromium to change its oxidation degree seems to play a crucial role of supported metal/Cr–Al bioxide catalyst activity.

For low temperature processes which take place in oxidative atmosphere (CO oxidation) one can anticipate that chromium changes its oxidation degree between 3+ to 6+. This hypothesis can be confirmed indirectly by rapid increase of CO oxidation in temperature range 300–400 °C (see Fig 1A). This effect is probably connected to decomposition of chromates (VI) on catalyst surface and rapid increase of oxygen concentration in reaction mixture.

In methanol synthesis reaction as well as partial oxidation of methane only lower oxidation degree of chromia can be considered. In such processes the changes oxidation state 2+ to 3+ can be considered if water will effectively removed from the catalysts surface.

In copper and nickel supported catalysts cases also can be considered the structural effect of chromia, its addition prevents against formation of copper and nickel aluminates, which are inactive in studied processes.

4. Conclusions

1. The binary chromia-alumina oxides can be considered as a promising support material for many catalytic reactions.
2. In all studied reactions (CO oxidation, WGS, methanol synthesis, POM) chromia-alumina oxide alone reveal catalytic activity.
3. Metal (Cu, Ni) catalysts supported on binary oxides were much more active in comparison to catalysts supported on alumina.
4. Platinum promotion does not influence on catalytic activity of chromia-alumina binary system in CO oxidation by oxygen.
5. Introduction of copper significantly increases catalytic activity in WGS reaction, however the most optimal copper loading for WGS and methanol synthesis reaction was 10 wt% Cu.
6. The catalytic activity in methanol synthesis process is determined by the copper quantity, the best activity reveal catalyst contained 20% Cu.
7. Nickel catalysts supported on chromia-alumina were active independently from nickel loading in POM.

References

[1] Y.-H. Chin, D.L. King, H.-S. Roh, J. Catal. 244 (2006) 153.
[2] O. Perales Perez, Y. Umetsu, H. Sasaki, Hydrometallurgy 50 (1998) 223.
[3] T.P. Maniecki, P. Mierczyński, W. Maniukiewicz, D. Gebauer, W.K. Jóźwiak, Kinet. Catal. 50 (2) (2009) 228.
[4] T.P. Maniecki, P. Mierczyński, D. Gebauer, W. Maniukiewicz, W.K. Jozwiak, Pol. J. Chem. 82 (2008) 2367.
[5] T. Kobayashi, A. Nakanishi, K. Fukumura, G. Langouche, J. Appl. Phys. 83 (9) (1998) 4631.
[6] T.P. Maniecki, P. Mierczyński, W. Maniukiewicz, K. Bawolak, D. Gebauer, Pol. J. Chem. 82 (2008) 2389.
[7] T.P. Maniecki, K. Bawolak, D. Gebauer, P. Mierczynski, W.K Jozwiak, Kinet. Catal. 1 (2009).
[8] T.P. Maniecki, P. Mierczynski, K. Bawolak, D. Gebauer, W.K. Jozwiak, Pol. J. Chem. 82 (2008) 2379.
[9] Y.S. Prasad, B.D. Padalia, S.K. Raman, J. Chem. Tech. Biotechnol. 35A (1985) 15.
[10] Y.J. Tu, Y.W. Chen, C.P. Li, J. Mol. Catal. 89 (1994) 179.
[11] J.M. Church, H.K. Joshi, Ind. Eng. Chem. Res. 43 (1951) 1804.
[12] J. Franckaerts, G.F. Froment, CES 19 (1964) 807.
[13] C.-Y. Shiau, T.W. Chen, AIChE J. 22 (1991) 141.
[14] D.A. Hickman, L.D. Schmidt, Science 259 (1993) 343.
[15] N. Doca, E. Segal, React. Kinet. Catal. Lett. 28 (1) (1985) 123.
[16] C. Rhodes, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 2719.
[17] G.C. Chinchen, R.H. Logan, M.S. Spencer, Appl. Catal. 12 (1984) 89.
[18] M.A. Edwards, D.M. Whittle, C. Rhodes, A.M. Ward, D. Rohan, M.D. Shannon, G.J. Hutchings, C.J. Kiely, Phys. Chem. Chem. Phys. 4 (2002) 3902.
[19] A. Mittasch, C. Schneider, US Patent 1,201,850, to Badische Anilin and Soda-Fabrik (BASF) Corporation, 1916.
[20] A. Mittasch, US Patent 1,569,775, to Badische Anilin and Soda-Fabrik (BASF) Corporation, 1926.
[21] S.G. Triantafyllopoulos, Neophytides, J. Catal. 239 (2006) 1871.
[22] M.M. Danilova, Z.A. Sabirova, N.A. Kuzin, V.A. Kirillov, N.A. Rudina, E.M. Moroz, A.I. Boronin, Kinet. Catal. 48 (2007) 116.
[23] T.P. Maniecki, P. Mierczyński, K. Bawolak, D. Gebauer, W.K. Jóźwiak, Pol. J. Environ. Stud. 18 (1B) (2009) 114.
[24] T.P. Maniecki, P. Mierczyński, K. Bawolak, W. Maniukiewicz, W.K. Jóźwiak, Pol. J. Environ. Stud. 18 (1B) (2009) 120.
[25] C.H. Bartholomew, J.F. Farrauto, Fundamentals of Industrial Catalytic Processes, Wiley Interscience, New York, 2006.
[26] K. Bawolak–Olczak, T.P. Maniecki, W.K. Jóźwiak, G.D Mariadassou, Proccedings of of 3th Inernational Annual Meeting 2009: Catalisys for Environment: Depollution, Renevable Energy and Clean Fuels Zakopane2009, Center of Polymer and Carbon Materials, PAN Zabrze, Poland, 2009.