Selectivity and Activity of Iron Molybdate Catalysts in Oxidation of Methanol

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انتقائية وفعالية العامل المساعد من موليبيدات الحديد في اكسدة الميثانول

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الخلاصة : تم في هذا البحث دراسة انتقائية و فعالية العوامل المساعدة من موليبيدات الحديد المحضرة بطرق مختلفة ومقارنتها بالعامل المساعد التجاري في اكسدة الميثانول الى الفور ملديهايد وباستخدام المفاعل الانبوبي المحشو عند درجة حرارة تتراوح بين ٤٧٣ الى ٦٢٣ مطلق بثبوت الضغط عند ١٠١٣ كيلو باسكال ونسبة الميثانول الى الاوكسجين ٥.٥٪ حجما. أكدت النتائج التي تم الحصول عليها بان العامل المساعد من موليبيدات الحديد المحضر بطريقِه co-precipitation اعطى اعلى انتقائية للفور مالديهايد (٨٢,٣٪) والتي يمكن الحصول عليها عند درجة حرارة ٥٧٣ مطلق عندما كان التحول (٥٩,٧٪) في اكسدة المثانول بالمقارنة مع العامل المساعد التجاري بينما العوامل المساعدة المحضرة بطريقة العجن والترسيب ثم التبخر اعطت اقل انتقائية واقل فعالية . ثم تمت مناقشة علاقات (الانتقائية – الفعالية) لهذه العوامل المساعدة كدالة لدرجة الحرارة وعلاقتها بطرق التحضير و المساحة السطحية ونسبة التراكيب الكيماوية لهذه العوامل المساعدة. وبربط نتائجنا التي تم الحصول عليها في هذا البحث مع المقالات وبراءات الاختراع المنشورة أظهرنا وبوضوح ترابط كل من الموليبيديوم و الحديد في اكسدة الميثانول الى فور مالديهايد حيث كانت افضل نسبة مئوية من الحديد بحدود ٢,٠– ٣,٠ وان الانتقائية للفور مالديهايد كانت عمليا ثابتة لغاية النسبة المئوية للحديد ٣,٠ ثم تبدا بالانخفاض عند النسبة العالية للحديد كما ان الحديد ممكن اعتباره كمنشط لفعالية العامل المساعد ان فعالية العامل المساعد من موليبيدات الحديد في الاكسدة يمكن ان يعود الى المكونين الاخرين للاساس MoO_3 مثل موليبيدات البزموث والكوبلت. حيث انه في الخطوه المحددة للسرعة يعمل اوكسيد الحديد كقاعدة اكسده لفصل بروتون من المثيل لمجموعة اصرة الميثوكسي للامتزاز الكيماوي للميثانول وقد اقترحنا الصوره الاكيده للعامل المساعد بوجود مجاميع -O-Mo-Fe-O-Mo-O كما وجدت في المكون $Fe(MoO_4)_3$ وان سبب الفقدان في الفعالية للعامل المساعد عند التركيز العالي للحديد هو وجود حبيبات اوكسيد الحديد الذي يساعد في الاكسده الكلية للميثانول وفقدان فعالية صد مواقع الموليبيديوم.

المفردات المفتاحية: انتقائية الاكسدة، موليبيدات الحديد، أكسدة الميثانول.

Abstract: The selectivity and activity of iron molybdate catalysts prepared by different methods are compared with those of a commercial catalyst in the oxidation of methanol to formaldehyde in a continuous tubular bed reactor at 200-350 ºC (473-623 ºK), 10 atm (1013 kPa), with a methanol-oxygen mixture fixed at 5.5% by volume methanol: air ratio. The iron(III) molybdate catalyst prepared by co-precipitation and filtration had a selectivity towards formaldehyde in methanol oxidation comparable with a commercial catalyst; maximum selectivity (82.3%) was obtained at 573ºK when the conversion was 59.7%. Catalysts prepared by reacting iron (III) and molybdate by kneading or precipitation followed by evaporation, omitting a filtration stage, were less active and less selective. The selectivity-activity relationships of these catalysts as a function of temperature were discussed in relation to the method of preparation, surface areas and composition. By combing this catalytic data with data from the patent literature we demonstrate a synergy between iron and molybdenum in regard to methanol oxidation to formaldehyde; the optimum composition corresponded to an iron mole fraction 0.2-0.3. The selectivity to formaldehyde was practically constant up to an iron mole fraction 0.3 and then decreased at higher iron concentrations. The iron component can be regarded as the activity promoter. The iron molybdate catalysts can thus be related to other two-component MoO_3-based selective oxidation catalysts, *e.g.* bismuth and cobalt molybdates. The iron oxide functions as a relatively basic oxide abstracting, in the rate-controlling step, a proton from the methyl of a bound methoxy group of chemisorbed methanol. It was proposed that a crucial feature of the sought after iron(III) molybdate catalyst is the presence of -O-Mo-O-Fe-O-Mo-O- groups as found in the compound $Fe_2(MoO4)_3$ and for Fe^{3+} well dispersed in MoO_3 generally. At the higher iron(III) concentrations the loss of selectivity is due to the presence of iron oxide patches or particles which catalyze the total oxidation of methanol, and the loss of activity to blocking of molybdenum sites.

Keywords: Selective oxidation, Methanol, Formaldehyde, Iron molybdate, Activity

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1. Introduction

Many researches deal with the oxidation of methanol using many different catalysts to produce the formaldehyde which has many important industrial chemical applications in the production of urea, melamine, phenolic resins and ethylene glycol; in the fertilizer and paints industries; and in medicine as a preservative (See, for example, The Formaldehyde Council, Inc. (FCI): Formaldehyde.org).   Formaldehyde is manufactured by the selective oxidation of methanol with oxygen or air over a silver (Jia-Linang Li, *et al*. 2000; Wachs, I.E., 2003) or iron molybdate catalysts (Farrauto, *et al*. 1997; Soares, *et al*. 2001; and Ivanov, *et al*. 2000). Iron molybdate is a typical two-component selective oxidation catalyst. The two components, iron(III) oxide and molybdenum(VI) oxide, interact to produce a catalyst which favours the desired product, formaldehyde, rather than the products of total oxidation of methanol, carbon dioxide and water, or other products like carbon monoxide or dimethyl ether. It is the combination of the two oxides which produces the desired active and selective catalyst. Iron (III) oxide by itself is unselective producing carbon dioxide and water; molybdenum trioxide is selective but with low activity (Bowker, *et al*. 2002 and Wang, *et al*. 2001).

The overall reaction is

$$CH_3OH + 0.5O_2 = CH_2O + H_2O$$
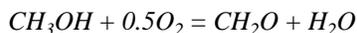
The reaction is exothermic ($\Delta H, = $ -159 kJ mol^{-1}) (Diakov, *et al*. 2002 and Dia Kov, *et al*. 2001). The oxidation proceeds through reaction of methanol with the molybdate surface (McCarron III, *et al*. 1986). At ambient temperature methoxy groups are formed and water is liberated. As the temperature is raised the methoxy groups begin to decompose forming formaldehyde and more water. The rate-limiting step is the abstraction of methoxy hydrogen via breaking of a C-C bond. The products rapidly desorbed leaving the molybdate phase reduced. Re-oxidation is affected by oxygen so completing the catalytic cycle. The active sites are considered to be co-ordinatively unsaturated molybdenum atoms. The overall reaction is in accordance with the Mars-van Krevelen mechanism, i.e. oxygen is supplied to the reactant as lattice oxygen rather than by direct reaction with oxygen. The lattice oxygen is replenished by reactant oxygen.

The technical catalyst composition is 80% MoO_3 and 20 % Fe_2O_3 equivalent to an iron mole fraction 0.31. Iron may be partially replaced by a promoter, *eg*. chromium. The active catalyst is considered to be $Fe_2 (MoO_4)_3$ (Soares, *et al*. 2001). The excess of MoO_3 is said variously to be required to ensure the stability of the catalyst towards loss of MoO_3, to maintain the active species and to enhance the surface area (Soares, *et al*. 2001). We shall see that it may be more profitable to describe the catalyst as Fe^{3+} dispersed in MoO_3.

The chemical composition is the major factor determining the catalytic properties. However the catalytic characteristics depend on catalyst preparation method, reflecting changes in the extent of interaction of the iron and molybdenum oxides, the extent of dispersion, the surface area, the pore structure, and the crystal structure (Boreskov, 1976).   It should be stressed that catalyst structure depends also on other parameter such as metal loading, surface area of the carrier and drying and calcination temperatures (Topsoe, *et al*. 1976). The method of preparation appears to have a significant impact on the activity and selectivity of the catalyst. There have been some studies of different preparation methods, for example sol-gel catalysts by co-precipitated catalysts (Wand, *et al*. 2001; Soares, *et al*. 1997; and Soares, 2003). In the present work iron molybdate catalysts were prepared by three methods-kneading or slurry method, precipitation and evaporation, co-precipitation and filtration. The activities and selectivities in the oxidation of methanol were determined at 473-623°K and compared with the activity and selectivity of a commercial catalyst.

2. Experimental Work

2.1. Catalyst Preparation

Ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$; and iron (III) nitrate nonahydrate, $Fe(NO_3)_3 9H_2O$, analytical grade (>99% purity), were used.

2.1.1. Kneading and Evaporation: Catalyst (1)

To prepare 25 g of catalyst, 24.2 g of ammonium molybdate was added to amount of distilled water which is enough so that when added to 25.31 g of iron nitrate powder gradually with continuous stirring to obtain a homogenous paste. The paste was dried in an oven at 383°K for 2 hours to evaporate water and then calcined at 673-773°K in a current of air for 4 hour. The calcined catalyst was crushed to small pieces, then to powder using a ball mill. The 100 mesh fraction was mixed with a solution of polyvinyl alcohol (3%) in distilled water. The produced paste was then dried, crushed, and sieved. Pellets (or tablets) (7 mm diameter, 4 mm thick) were prepared in a tablet press at 2 atm. The pellets were calcined at 773°K to dissociate the polyvinyl alcohol because it is used as a binder only.

2.1.2. Precipitation and Concentration: Catalyst (2)

Solutions of ammonium molybdate, 24.52 g in 250 ml of distilled water and iron(III) nitrate 25.31 g in 150 ml of distilled water were mixed, the pH was *ca* 2. The precipitate formed was left to settle overnight at room temperature to get rid of excess water and then dried, calcined and formulated as for catalyst 1.

2.1.3. Co-precipitation and Filtration: Catalyst (3)

Solutions of ammonium molybdate and iron(III) nitrate were prepared and mixed as in the preparation of catalyst 2. The precipitate was filtered off and washed several times with distilled water until the pH of the filtrate reached 7. The solid was dried, calcined and formulated
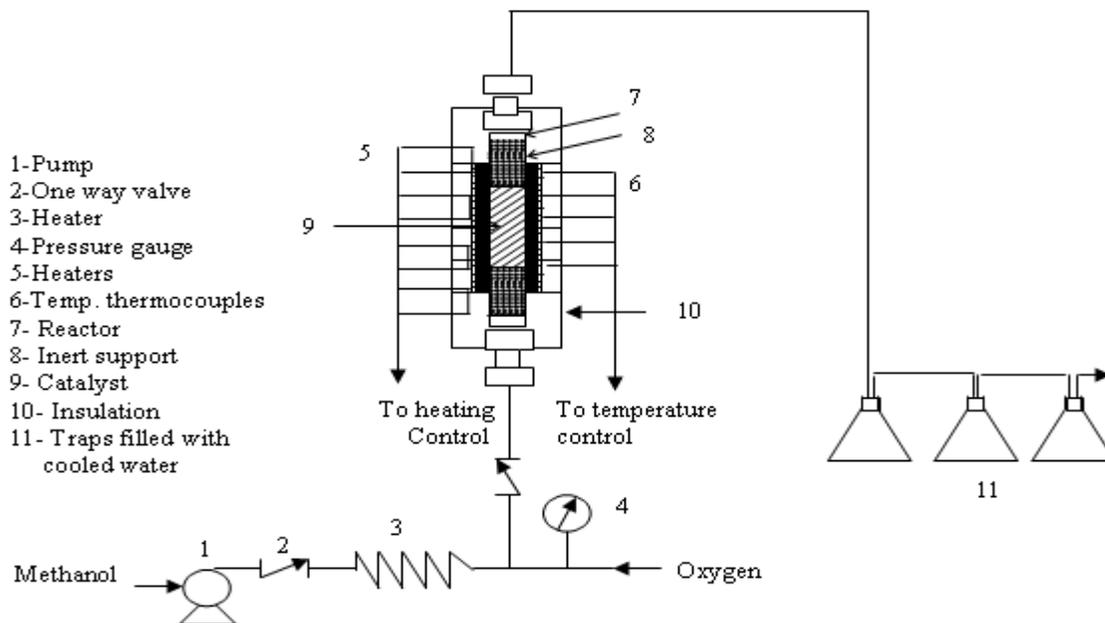
Figure 1. Flow diagram of laboratory oxidation of methanol unit

as before.

2.2. Catalyst Characterization

The analysis of Iron and molybdenum were determined by standard atomic absorption spectrophotometer (PYE UNICAM SP9).

The X-ray diffraction of powder of prepared and commercial catalysts were carried out by using a Phillips X-ray diffractometer with CuK_α radiation (1.542 Å, 40 kV, 20 mA) scanning over the range of angles of 3 to 70 on 2. Peaks were assigned by comparison with the *d* spacing of typical compounds given in the ASTM powder diffraction files (Powder Diffraction File, Swarthmore Pennsylvania, 1978).

Surface areas of the catalysts were determined by the BET method (Le Page, 1987) (carloEraba sorptomic series 1800). Pore volumes and densities were determined by the liquid impregnation method (Satter Filled and Charles, 1980). Hardnesses were determined with the ERWEKA TBH28 hardness meter (Le Page, 1987).

The bulk density is determined by replacing a weight catalyst in a graduated cylinder then shake it by hand on the table or by vibrator and read the volume of it and then calculate the density, it is the packing or load density of the reactor. The solid density is measured by weighting a symmetrical tablet and calculates its volume. It is carried out for several tablets and takes the average.

2.3. Catalyst Testing

Activities and selectivities of the catalysts in the conversion of methanol to formaldehyde were determined in a continuous flow pilot plant (Fig. 1). The reactor was stainless steel (316-heat resistant), length 800 mm, inside diameter, 19 mm. Heaters were in the form of four separately heat-controlled block shells. The reactor was packed with 110 ml of the catalyst between two layers of inert material such as glass, inert alumina or porcelene balls. Test conditions were: reactor temperature 200 to 35°C (473-623°K); pressure, 10 atm (1013 kPa); flow rate, 15.858 cm^3/s; methanol, 5.5% by volume in oxygen.

In a typical run the reactor was purged with N_2 gas and the temperature raised. After establishing steady state conditions, the reaction was started; the methanol-oxygen mixture was pumped upwards into the reactor. The products were passed through three traps in series filled with water cooled to 278°K to absorb formaldehyde, unreacted methanol and side products.

Analysis of the reaction products was carried out periodically after two hours collection of the samples. Formaldehyde analysis was done by treating it with hypodidate solution which was prepared immediately by reacting iodine and NaOH. Then H_2SO_4 was added to liberate iodine again some reacted with HCHO and the excess is backing titrated solution (Monti, *et al*. 1985). Unconverted methanol was determined gas chromatographically with a povpak type T column at 420°K (Monti, *et al*. 1985).

3. Results and Discussion

The results of this work has been tabulated in Table 1. It can be seen that the Catalyst (3) (prepared by co-precipitation) is closest to the commercial catalyst in its composition and physical properties.

They are structurally similar as shown by their X-ray diffraction patterns (Fig. 2). The most obvious difference between the different preparations is the excess MoO3, which is greatest for catalyst (3) Table 1. These preparations along with the commercial catalyst enable us to assess the effect of the molybdenum content on the properties of the catalysts. Excess molybdenum appears to have little effect on the catalyst density. However, the two catalysts with the highest molybdenum (catalyst (3) and the commercial catalyst) have the greatest surface areas,

Table 1. Composition and properties of the catalysts

Composition and Property	Catalyst			
	Catalyst(1) Kneading and evaporation	Catalyst(2) Precipitation and concentration	Catalyst(3) Co-precipitation and filtration	Commercial
Composition/wt %				
Fe	17.2	15.6	13.8	14.0
Mo	50.2	51.7	53.4	53.0
Fe_2O_3	24.6	22.3	19.7	20.0
MoO_3	75.4	77.7	80.2	80.0
MoO_3 excess/wt-%[c]	2.32	4.57	7.12	6.52
Mo/Fe atomic ratio	1.70	1.93	2.25	2.20
Fe/(Fe + Mo) mole fraction	0.371	0.341	0.308	0.312
Colour	Yellow green	Yellow green	Yellow	Yellow
Pellet size/cm	0.9×0.9	0.9×0.9	0.9×0.9	0.45×0.4
Surface area/$m^2 g^{-1}$	283	282	287	290
Pore volume/ $cm^3 g^{-1}$	0.28	0.30	0.40	0.35
Solid density/g $cm^{-3 b}$	0.53	0.50	0.52	0.50
Bulk density/g $cm^{-3 b}$	1.05	1.05	1.05	1.10
Hardness/10^5 dyne	1.70	1.63	2.1	2.3

[a] From small industrial formaeldihyde plant in Ministry of Industry of Iraq

[b] Excess MoO3 over the stoichiometric composition $Fe_2 (MoO_4)_3$ (ie. $Fe_2O_3 + 3MoO_3$)
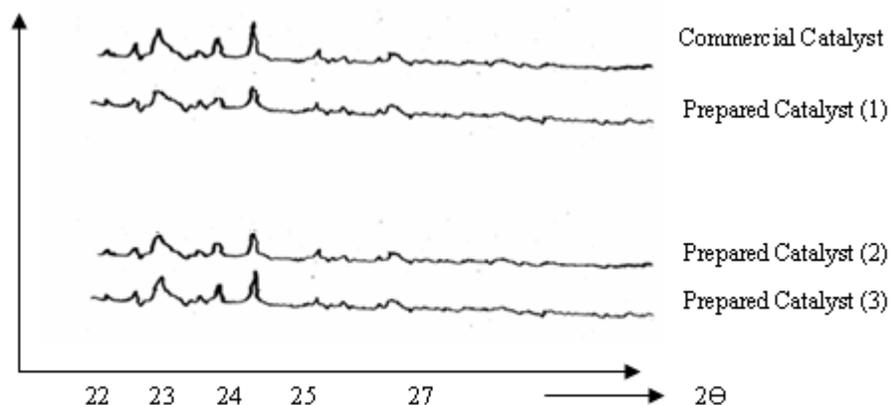
Figure 2. X-Ray powder diffraction patterns of the catalysts

pore volumes and hardness.

The activity and selectivity in the oxidation of methanol to formaldehyde are calculated. The activity is the percentage of methanol converted to all products and the selectivity as the fraction of formaldehyde in the products, *ie*. formaldehyde produced divided by methanol converted. The aim in the catalysis is to maximize both the conversion and the selectivity at the lowest reaction temperature. Activities and selectivities are shown plotted against the reaction temperature in Fig. 3. The behaviors of the catalyst (3) are similar to that of the commercial catalyst. The activities of all catalysts rise with rising temperature and converge to roughly the same conversion at 598ºK. The significant distinction between the catalysts is in the selectivity which passes through a maximum at 573ºK

with the commercial and the co-precipitated catalysts having the highest selectivities. The optimum combination of conversion and selectivity is provided by catalyst (3) and the commercial catalyst. Figure 4 shows that the variation of surface area (which for our catalysts is ±1%) is not significant.

The prepared catalytic results are consistent with the literature, *eg*. (Soares, *et al*. 2001); activities at constant surface area tending to the same value independently on the iron (or molybdenum) content of the catalyst; selectivities passing through a maximum with increasing reaction temperature. The implication of this observation is that during use, the catalyst surface stabilizes to a certain composition during the period of 12 h required to attain the higher tem-
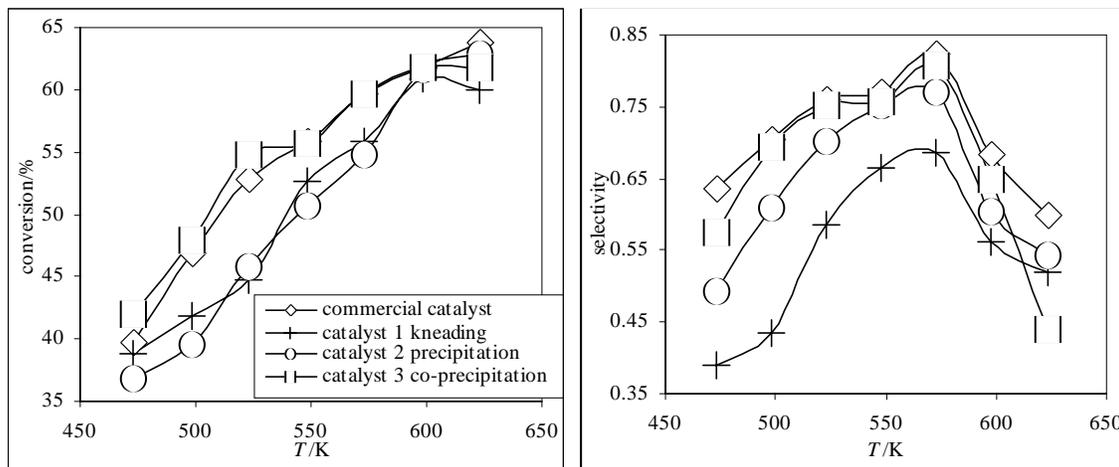
Figure 3. Conversion (left) and selectivity (right) in conversion of methanol to formaldehyde
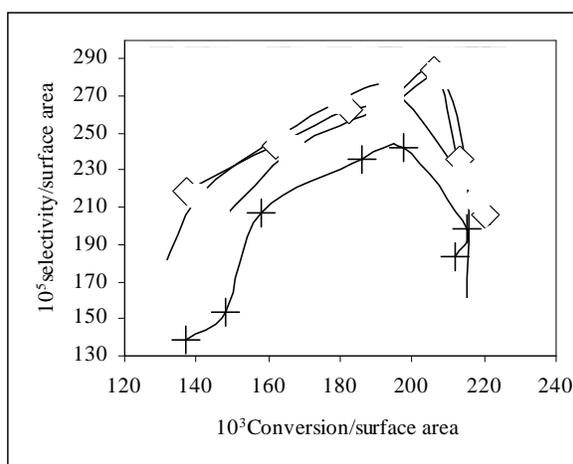
Figure 4. Selectivity towards formaldehyde vs. conversion of methanol for iron molybdate catalysts. Selectivities and activities are normalized to unit surface area. Symbols as in Figure 3

peratures as shown in Fig. 3.

The effect of catalyst composition on the activity and selectivity has been discussed with reference to the investigation results and literature data (Wachs, *et al*. 2000). The above discussion is in terms of excess of MoO_3. However, since MoO_3 is in excess it would seem logical to express the variation of catalyst composition in terms of iron added (or not) to molybdenum, *ie*. the Fe/Mo ratio or the Fe/(Fe+Mo) mole fraction as for other two-component catalysts, for example, the cobalt-promoted molybdenum disulfide based hydrodesulphurization catalyst. It has been observed that in the model of two-component MoO_3-based selective oxidation catalysts; the second component, e.g. bismuth or cobalt as in the selective oxidation of propene, enhances the activity by promoting the slow step, the first C-H bond breaking and the abstraction of H. The first step is catalyzed by the more basic oxide, Bi_2O_3 or CoO. We imagine that the greater basicity (or nucleophilicity) of the oxide of the basic oxide favors interac-

tion of the hydrogen of a methyl group with oxide of the catalyst, and subsequent proton transfer to oxide. When we interpret the data correctly we shall see that the iron molybdate catalyst fits into this pattern. It can be seen also that there was a synergy between iron and molybdenum.

Unfortunately most researchers have not studied a wide range of Fe/Mo compositions. However, it can fit certain patent data (Wachs, *et al*. 2000) to these data and thereby examine a wider range of compositions. Activities and selectivities so obtained are plotted in Fig. 5. Activities and selectivities have been normalized of the commercial catalyst at 573°K to the values for a similar commercial catalyst reported (Wachs, *et al*. 2000).   For the activities it can be seen a typical volcano curve, the activity rising to a maximum value as iron is added to MoO_3 and then dropping off. This behavior demonstrates synergy between iron and molybdenum. Beyond an iron mole fraction of 0.4 the activity begins to increase as Fe_2O_3 takes over. The selectivity to formaldehyde is more or less constant until an iron mole fraction of 0.3 is reached. The selectivity then drops as Fe_2O_3 becomes dominant. This behavior indicates that the selective catalyst is MoO_3. Iron is an activity promoter.

We can now understand more clearly how the iron molybdate catalyst works as also reported in the literature (Bowker, *et al*. 2002).   It can be suggested here that the crucial feature is to have Fe^{3+} well dispersed in MoO_3. The formation of patches or particles of Fe_2O_3 is to be avoided if the selectivity to formaldehyde is to be preserved. The loss of selectivity in Fig. 5 at higher iron levels is evidently associated with formatted of Fe_2O_3. The loss of activity may be attributed to the blocking of MoO_3 sites. The dramatic loss of activity and selectivity seen in Fig. 5 represents a changeover from the preference for formaldehyde on a MoO_3 catalyst to total oxidation on Fe_2O_3. The selective catalysis has often been associated with a definite compound, iron (III) molybdate, $Fe_2(MoO_4)_3$. The formation of iron (III) molybdate seems inevitable in the synthesis of the catalyst. A structural fea-
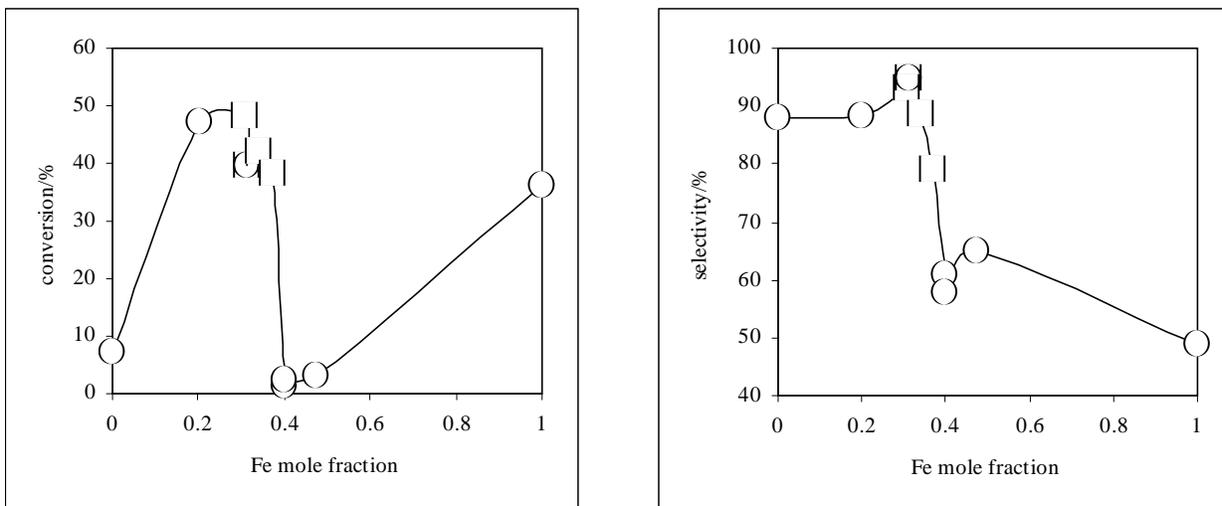
Figure 5. Conversion and selectivity at 573 K for our iron molybdate catalysts (squares) and other reported catalysts (23) (circles) vs. mole fraction of iron

ture of iron (III) molybdate is the presence of -O-Mo-O-Fe-O-Mo-O- groups. Such structures have been regarded as to represent the well dispersed Fe^{3+}. The presence of iron(III) molybdate in our catalysts is indicated from the X-ray diffraction pattern. It had been deducted from the catalytic data that the catalysts with the highest activity and selectivity (commercial catalyst and catalyst 3) have the most favorable Fe^{3+} dispersion. The method of preparation of catalyst (3) (co-precipitation and filtration) is likely lead to a better dispersion of Fe^{3+} and the least likely formation of Fe_2O_3 patches.

4. Conclusions

It was observed that the iron (III) molybdate catalyst prepared in the present work by co-precipitation and filtration method has a higher selectivity towards formaldehyde in methanol oxidation comparable with a commercial catalyst. Catalysts prepared by reacting iron (III) and molybdate by kneading or precipitation followed by evaporation, omitting a filtration stage, are less active and less selective. By combining our catalytic data with data from the patent literature, it can be demonstrated that the synergy between iron and molybdenum in regard to methanol oxidation to formaldehyde with an optimum composition corresponding to an iron mole fraction of 0.2-0.3. The selectivity to formaldehyde is practically constant to an iron mole fraction 0.3 and then decreases at higher iron concentrations. If we think of the iron component as the activity promoter then the iron molybdate catalysts can be related to other two-component MoO_3-based selective oxidation catalysts, *eg*. bismuth and cobalt molybdate. The iron oxide then functions as a relatively basic oxide abstracting, in the rate-controlling step, a proton from the methyl of a bound methoxy group of chemisorbed methanol. The proposed crucial feature of the iron(III) molybdate catalyst is the presence of -O-Mo-O-Fe-O-Mo-

O- groups as found in the compound $Fe_2(MoO_4)_3$ and for Fe^{3+} which is generally the well dispersed in MoO_3. At the higher iron (III) concentrations the loss of selectivity is due to the presence of iron oxide patches or particles which catalyze the total oxidation of methanol and the loss of activity to blocking of molybdenum sites.

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