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Dehydrogenation of Ethyl Benzene to Styrene Over Cs/Co_3Mo_3N and SnO_2-ZrO_2

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ABSTRACT

The dehydrogenation of Ethyl benzene to styrene has been performed on cesium promoted bimetallic nitride (Cs/Co_3Mo_3N), 50% tin- zirconia (SnO_2-ZrO_2) individually as well as mixing of these catalysts in 1: 1 ratio. The greater catalytic activity shown towards dehydrogenation by mixed catalyst compared to individual catalysts is due to the synergistic effect between these two catalysts. For the first time Cs/Co_3Mo_3N showed activity towards dehydrogenation of ethyl benzene. Freshly prepared catalyst 50% SnO_2-ZrO_2 showed better activity compared to aged catalyst. This is because of transformation of tetragonal phase (freshly prepared) to monoclinic phase (aged catalyst). All of these catalysts are prepared by impregnation, co-precipitation and characterized by XRD, BET surface area and FT-IR.

Key words: Dehydrogenation, Bimetallic nitride, 50% SnO_2-ZrO_2, ethyl benzene, styrene.

INTRODUCTION

Vapor phase dehydrogenation of ethyl benzene is a representative process to produce styrene an important monomer for the synthetic polymers. From the literature dehydrogenation of ethyl benzene has been cited mostly over potassium doped iron oxide catalyst using steam[1]. It is thermodynamically limited and energy consuming process. Oxidative dehydrogenation of ethyl benzene is alternative to above energy consuming process which operates at lower temperature and increases the conversions of ethyl benzene and selectivity to styrene. In this process CO_2 used as a mild oxidant. Literature[2] studies reveal that SnO_2-ZrO_2 catalyst is found to be active towards dehydrogenation of ethyl benzene. Monometallic (Mo_2N, Fe_3N, Co_4N) and bimetallic nitrides (Co_3Mo_3N, Fe_3Mo_3N and Ni_2Mo_3N) have attracted considerable attention due to their properties like electrical, thermal conductivity, hardness, super conductivity, magnetism, catalytical activity[3,4]. Due to this properties these bimetallic nitrides has the potential to replace noble metal catalysts. These catalysts show reactions like hydrazine decomposition, hydrogenation[5], Fisher-Tropsch synthesis, hydrodenitrogenation[6,7], hydrodesulphurisation[8,9] and ammonia synthesis. For the first time we observed considerable amount of dehydrogenation of ethyl benzene by promoted bimetallic nitride (Cs/Co_3Mo_3N). These catalysts Cs/Co_3Mo_3N, 50%SnO_2-ZrO_2 are prepared by impregnation. 50%SnO_2-ZrO_2 is also prepared by co-precipitation method.

EXPERIMENTAL

Catalyst preparation

Cesium promoted Co_3Mo_3N was prepared [10] by dissolving $Co(NO_3)_2.6H_2O$ (31.7379 m.mol), $(NH_4)_6Mo_7O_{24}.4H_2O$ (4.5313 m.mol), Hexamethylenetetramine (HMT) (52.9786 m.mol)and $CsNO_3$ (0.0154 m.mol) in 15% NH_3 solution followed by evaporating the excess of water to dryness at 353-363 K. Obtained solid was calcined at 923 K in the flow of helium for 3h.The product was cooled to room temperature and passivated 6h in the flow of N_2.

50% SnO_2-ZrO_2 prepared by both co-precipitation and impregnation method. In co-precipitation 0.1M mixed aqueous nitrate or chloride precursor salt solution of each component were prepared under vigorous mechanical stirring at room temperature. Stirring continued for 1h for the formation of homogeneous mixed salt solution. Aqueous ammonium hydroxide solution was added drop wise in a controlled manner in a stretch of 1h under vigorous stirring until the attainment of required pH (8-9). The stirring continued for further 2h and allowed it for 12h aging at room temperature. The precipitated mixed gel was separated by filtration and dried at 373 K for 12h and calcined at 873 K for 8h in air. In impregnation, precursor salts dissolved in aqueous media and evaporating to dryness at 373 K. Obtained solid calcined at 873 K for 8h in air. Mixed catalyst prepared by grinding these two catalysts in 1:1 ratio.

Catalyst characterization

XRD

X-ray diffraction analysis for catalysts carried out using Ultima-IV (M/s Rigaku corporation) X-ray diffractometer, Japan using Ni filtered Cu kα radiation (λ=1.5406A^0) with a 2θ scan speed of 4° min^{-1} and a 2θ scan range of 2-80° at 40kV and 20 mA. The mean crystalline diameters of catalysts were estimated by Scherrer's equation from the raw data.

N_2 adsorption at 77K

N_2 adsorption technique was applied using a SMART SORB 92/93 (M/s Smart instruments co. (P) Ltd, India). Prior to the measurements the samples were preheated at 423K for 1hr in order to expel the interlayer water molecules. The BET specific surface area (*S*BET) was calculated by using the standard Brunauer–Emmett–Teller method on the basis of adsorption data.

FT-IR

The FT-IR adsorption spectra were recorded using an Ex caliber (DIGI labs, USA) FT-IR spectrophotometer, by making wafer after mixing the catalyst powder with KBr.

Catalyst activity test

The catalytic activity studies were performed in a fixed bed down flow Quartz reactor at atmospheric pressure. About 1g of catalyst was loaded in the reactor with the help of quartz wool and subjected to pretreatment at 873 K for 0.5h in the flow of N_2 (20ml/min). Reaction was conducted at different temperatures 773, 823, 873 K in the flow of N_2. Ethyl benzene was introduced by feed pump with a feed rate of 8.2mmol/h. Components were analyzed by a Shimadzu GC-17A gas chromatograph using Flame Ionization Detector (FID).

RESULTS AND DISCUSSION

XRD patterns of Cs/Co_3Mo_3N, 50% SnO_2-ZrO_2, Mixed, Spent catalysts were shown in the **Figure 1**. Cs/Co_3Mo_3N contains mainly bimetallic phase (Co_3Mo_3N) and traces of Co. Mo_2N phases are reported in the literature [11]. In the XRD pattern of 50% SnO_2-ZrO_2, ZrO_2 is in tetragonal phase and SnO_2 is in cassiterite phase in the catalyst prepared by co-precipitation method. In the catalyst prepared by impregnation method cassiterite phase of SnO_2 is dominated over ZrO_2 phases. Mixed catalyst contains phases due to individual components.

Table 1:

S. No	Catalyst	Major phase	Particle size of major hase (nm)
1	Cs/Co_3Mo_3N	Co_3Mo_3N	35.3
2	$50\%SnO_2$-ZrO_2(co-ppt*)	tetragonal ZrO_2	34.0
3	$50\%SnO_2$-ZrO_2(imp$^@$)	cassiterite SnO_2	30.3
4	Mixed of 1&2	tetragonal ZrO_2	24.2
5	Mixed of 1&3	tetragonal ZrO_2	17.0

*Co-precipitation (co-ppt), @ impregnation (imp),

Table 2: Summarizes the BET surface areas of Cs/Co_3Mo_3N, 50% SnO_2-ZrO_2, Mixed catalysts. Mixed catalyst surface area was decreased

S.No	Catalyst	Surface area (m^2g^{-1})
1	Cs/Co_3Mo_3N	5.7
2	$50\%SnO_2$-ZrO_2(co-ppt)	21.3
3	Mixed of 1&2	8.6
4	$50\%SnO_2$-ZrO_2(imp)	30.0
5	Mixed of (1&4)	10.2
6	$50\%SnO_2$-ZrO_2 (old)	19.3
6	Mixed of (1&6)	7.6

Table 3: Activity data of Cs/Co_3Mo_3N, 50% SnO_2-ZrO_2 (co-ppt, imp), mixed catalysts

S.	Temperature(K)	773		823		873	
No	Catalyst	EB con^a (%)	ST sel^b (%)	EB con^a (%)	ST sel^b (%)	EB con^a (%)	ST sel^b (%)
1	Cs/Co_3Mo_3N	8.07	100	10.33	100	13.03	100
2	$50\%SnO_2$-ZrO_2(Co-ppt)	3.76	100	4.1	100	20.74	100
3	Mixed (1& 2)	6.22	100	12.99	100	24.23	100
4	$50\%SnO_2$-ZrO_2(imp)	0.73	100	3.61	100	12.19	100
5	Mixed (1& 4)	8.8	100	10.12	100	19.46	100

^{a}Ethyl benzene conversion, ^{b}Styrene selectivity

Table 4: Activity data of freshly prepared and catalysts of Cs/Co_3Mo_3N and 50% SnO_2-ZrO_2

Temperature	50% SnO_2-ZrO_2 (Aged)		50% SnO_2-ZrO_2 (Fresh)	
(K)	EB con (%)	ST sel(%)	EB con (%)	ST sel(%)
773	3.52	100	7.3	100
823	4.0	100	10.78	100
873	16.34	100	23.77	100

It is interesting to observe that before and after the reaction XRD patterns are found to be same. This is a clear indication of robustness of the catalysts during the high temperature reaction. Particle size is calculated from XRD raw data by using Scherrer's equation. Particle sizes of major phases are mentioned in Table 1.

From the FT-IR data, catalyst 50% SnO_2-ZrO_2 prepared by impregnation and co-precipitation shows same pattern where as aged catalyst (co-precipitation) shows different pattern. All the catalysts are absorbed moisture to some extent which is visible from the FT-IR pattern at a wave number of ~3500cm^{-1}.

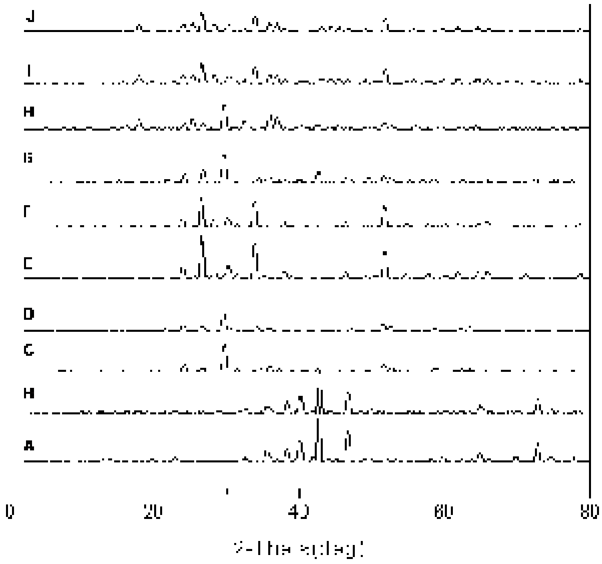

Fig. 1: A) Cs/Co_3Mo_3N, B) Cs/Co_3Mo_3N spent, C) 50% SnO_2-ZrO_2 (co-precipitation), D) Spent of C, E) 50% SnO_2-ZrO_2 (impregnation), F) Spent of E, G) Mixed catalyst of A & C, H) Spent of G, I) Mixed catalyst of A& E, J) Spent of I

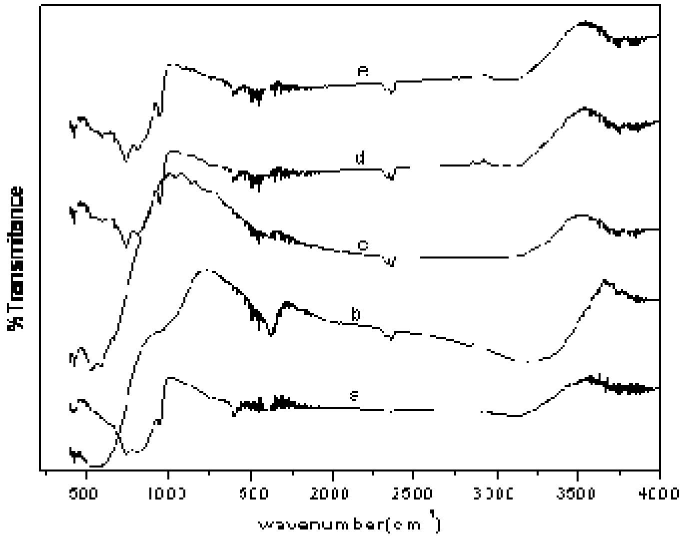

Fig. 2: FT-IR spectra of a) Cs/Co_3Mo_3N b) 50% SnO_2-ZrO_2 (co-ppt), c) 50% SnO_2-ZrO_2 (imp), d) aged catalyst of b d) Mixed of a & b

Activity data of catalysts, Cs/Co_3Mo_3N, 50% SnO_2-ZrO_2 in co-precipitation, impregnation, mixed catalysts are presented in Table 3. Compared to individual catalysts, mixed catalysts show better activity due to synergistic effect between two catalysts. 50% SnO_2-ZrO_2 - prepared in co-precipitation method shows better activity compared to impregnated catalyst. Individual catalysts activity data was obtained on 1gm of the catalyst, mixed catalyst activity data was conducted on 1gm of catalyst which comprises individual catalysts in 1:1 weight ratio. This indicates the synergistic effect between the two components.

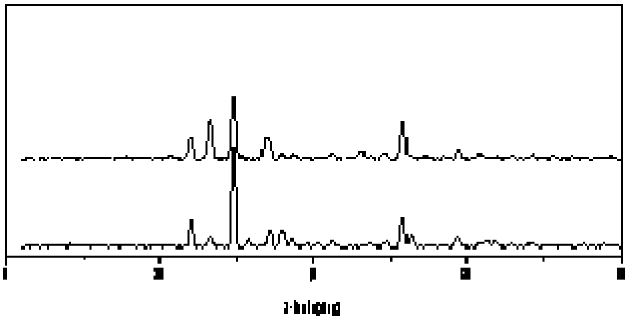

Fig. 4: XRD pattern of freshly prepared 50% SnO_2-ZrO_2 (down), aged 50% SnO_2-ZrO_2 (up) Catalysts

Freshly prepared catalysts shows better activity compared to aged catalyst (50% SnO_2-ZrO_2). This is due to the variation in the crystalline phases as evidenced from XRD patterns (Figure 4). In the case of 50% SnO_2-ZrO_2 which has been prepared by co-precipitation method there is a change in the XRD pattern. In freshly prepared catalyst ZrO_2 is present in metastable tetragonal phase and contaminated with traces of monoclinic phase. But on time (aged for 15 days) monoclinic phase intensity increases which is clearly indicated from figure 4. This is an indication that monoclinic phase of zirconia is less active towards dehydrogenation of ethyl benzene compared to tetragonal phase as stated in the literature [12]. Activity data is given in the Table 4.

CONCLUSIONS

Mixed catalyst shows better activity compared to individual catalysts, which is due to synergistic effect. Freshly prepared (SnO_2-ZrO_2) catalyst show higher activity compared to aged catalysts due to changes in the phases of Zirconia.

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