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NOTE

Synthesis of acetonitrile by dehydration of acetamide on an active ZnO catalyst: A comparison with zeolite catalysts.

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Catalytic activities of three different zinc oxides is evaluated in dehydration of acetamide reaction at 723 K. It is seen that an oxide of zinc, ZnO(u) prepared by decomposition of a mixture of zinc nitrate, urea and oxalic acid method showed much higher activity than other zinc oxides. Also the activity of ZnO(u) was comparable with the reported activities of zeolite catalysts. The activity of the catalysts could be correlated with their acidity.

Organic nitriles are synthesised from a number of reagents[1]. The synthesis of nitriles from esters and amides on various zeolite catalysts has been reported by many investigators[2,3]. Nitriles are important intermediates in the synthesis of several organic compounds; also nitriles like acetonitrile are well known as solvents in chemical industry. In this paper the catalytic activity of various zinc oxides *vis a vis* HY and HZSM-5 zeolite catalysts, towards dehydration of acetamide, has been discussed.

Experimental Procedure

ZnO(u) was prepared by heating at 653 K for 6 h in air, an intimate solid mixture of Zn^{2+}(from nitrate), oxalic acid and urea in the molar ratio 1:1:2 .

ZnO(n) was prepared by heating $Zn(NO_3).6H_2O$ in air at 723 K. ZnO(e) is commercial sample obtained from e-Merck. Catalytic activities were studied in a flow type of reactor system; a known amount of the catalyst was packed in the reactor and was activated in air at 773 K; the temperature was then decreased to the desired value, reactants were then passed through the reactor by means of a syringe feed pump, the products were cooled by circulating ice cold water. The analysis of products was carried out on a Chemito 8610 Gas chromatograph. Acetonitrile was analysed on SE 30 column using FID detector whereas decomposition products from propan-2-ol were analysed on a Carbowax column using TCD detector. TPD of the catalyst was carried out using NH_3 as a probe molecule. Before carrying out adsorption of ammonia, the catalysts were activated at 393 K in a stream of oxygen gas. Dried ammonia gas was then passed over the catalyst for 30 min at a flow rate of 5 mL/min. The amount of ammonia desorped at various temperatures gave measure of catalyst acidity which was expressed in mmol/g of catalyst.

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Results and Discussion

Activity data for zinc oxides and some zeolite catalysts in dehydration reaction of acetamide are presented in Table 1, where as activity of zinc oxides[4] in decomposition of propan-2-ol is presented in Table 2. The zeolites namely HY,

Table 1—Catalytic activity of different catalysts in dehydration of acetamide

Catalyst	%C Acetamide	%S
ZnO(u)	94.32	100
ZnO(n)	20.18	100
ZnO(e)	30.02	100
HY	95.46	100
HZSM-5(Si/Al=40)	95.62	100
HZSM-5(Si/Al=225)	96.16	100
HZSM-5(ref 2)	94	90

Reaction temperature = 723 K, feed = 50% aqueous acetamide solution,

Weight of the catalyst = 2 g , flow rate = 4 mL/h. Total acidity of ZnO(u) = 7.7210 mmol /g, % C and % S refer to percentage conversion of acetamide and percentage selectivity to acetonitrile. % purity of the ZnO samples is close to 99 %.

Table 2—Catalytic activity of zinc oxides in decomposition of propan-2-ol.

Catalyst	% C	%Dehydration	%Dehydrogenation	Acidity (mmol/g)
ZnO(u)	92	63	37	7.0145
ZnO(n)	37	16	84	0.1630
ZnO (e)	92	17	83	0.5642

Reaction temperature = 733 K, weight of the catalyst = 1g Flow rate = 5 mL/h, feed = propan-2-ol.
% dehydration and % dehydrogenation refer to selectivity to propene and acetone, respectively

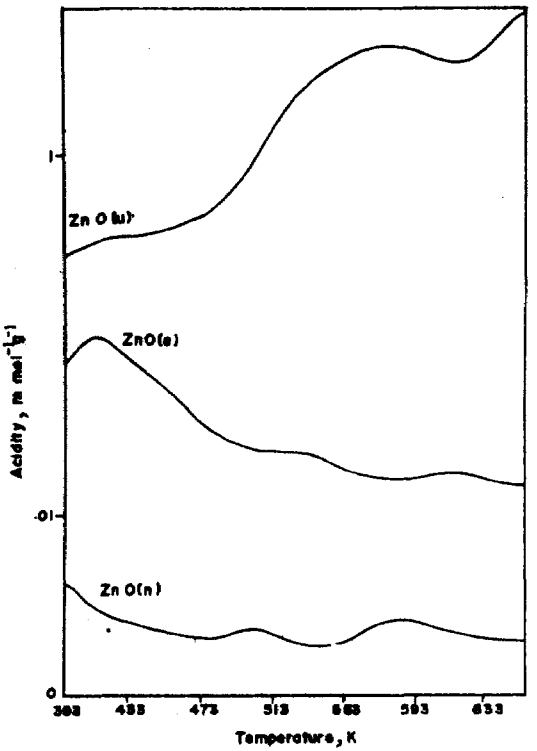

Fig. 1— TPD profiles of zinc oxides

HZSM-5(Si/Al=40) and HZSM-5(Si/Al=225) show % conversion of acetamide as 95.46, 95.62 and 96.16% respectively whereas ZnO(u), ZnO(n) and ZnO(e) showed conversion of 94.32, 20.18 and 30% respectively. It is previously reported[3] that zeolites because of their high acidity are good catalysts in dehydration of acetamide reaction and hence their high activity in this reaction is understandable. However, the high activity of ZnO(u) is little surprising as ZnO catalysts are generally known to be dehydrogenating catalysts. However, the activity of the zinc oxides could be correlated with the total acidity as shown in Tables 2. The exceptionally high catalytic activity of ZnO(u),(conversion>94%) can be attributed to its unusually high acidity (7.7203 mmol g^{-1}); in comparison the other zinc oxides ZnO(n) and ZnO(e) have much lower values of acidities (0.1630 and 0.5642 respectively) and hence lower catalytic activities. It is also clear from Fig. 1. that compared to ZnO(n) and ZnO(e) , ZnO(u) has strong acid sites above 673 K. The acidities of the zinc oxide catalysts are reflected in decomposition reaction of propan-2-ol (Table 2), ZnO(u) shows percentage conversion of 92 with 62% selectivity to dehydration whereas ZnO(n) and ZnO(e) shows percentage conversion of 37 and 92 with selectivity of 16 and 17 to dehydration. It is noteworthy that all the conversions obtained in this work are 100% selective towards production of acetonitrile.

Further it can be seen from Table 1, that almost all the zeolite catalysts are equally active in the dehydration of acetamide. Comparison of results of HZSM-(40) and HZSM-5(225), indicate that the zeolite of high Si/Al ratio (225), which has no significant Bronsted acidity is slightly more active than the more B-acidic HZSM-5(40). Hence it is reasonable to conclude that the L-sites are active in the dehydration of acetamide . Now this argument may be extended to the ZnO catalysts. ZnO(u) catalyst prepared using oxalic acid/ urea decomposition method should be rich both in B and L sites; while ZnO(n), prepared by thermal decomposition of pure zinc nitrate, will obviously have only L-sites, in a small concentration. TPD profile of this zinc oxide (Fig. 1) shows two small but distinct peaks: LT peak at ~ 510 K and HT peak at ~ 590 K. There is no such LT peak maximum for ZnO(u), but has a large HT peak ~ 590 K. Hence, one may tentatively conclude that dehydration of acetamide is catalysed by strong L-acid centers in ZnO(u) and HZSM-5 (Si/Al=225). Infrared spectroscopic investigation is underway for further investigation of these acid centers.

In conclusion the paper describes application of a highly active ZnO catalyst obtained by a simple method for dehydration of acetamide. The activity of this catalyst is found nearly the same as that of zeolite catalysts.

Acknowledgments

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