Short Communication

Dehydrogenation of propane in the presence of N_2O over In_2O_3—Al_2O_3 mixed oxide catalysts

Miao Chen [a,b], Jia-Ling Wu [a], Yong-Mei Liu [a], Yong Cao [a,*], Kang-Nian Fan [a]

[a] Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, PR China
[b] Zhejiang Chemical Industry Research Institute, Hangzhou 310023, PR China

ABSTRACT

Dehydrogenation of propane coupled with N_2O over a series of binary In_2O_3—Al_2O_3 mixed oxides was investigated. In contrast to the poor performance for sole N_2O decomposition, a remarkable synergy was identified between N_2O decomposition and propane dehydrogenation. Among the catalysts tested, the In_2O_3—Al_2O_3 sample containing a 20 mol% In_2O_3 showed the highest activity for propane dehydrogenation in the presence of N_2O. Moreover, stability far superior to those of the conventional iron-based materials was observed, attributable to the moderate surface acidity of the In—Al—O composite. The essential role of N_2O is suggested to generate active oxygen species facilitating propane dehydrogenation.

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1. Introduction

Conversion of lower alkanes to value-added olefins, the building blocks of the petrochemical industry, by *on-purpose* olefin technologies may become a potentially economical viable route for their production in the coming years [1]. In this context, much effort [2–4] has been dedicated to propane dehydrogenation (PDH) given the rapidly growing demand for propylene in the production of propylene oxide, acrylonitrile, and polypropylene. Unfortunately, the high-temperature dehydrogenation (DH) processes are plagued by undesired rapid coke deposition and thermal cracking under reaction conditions [5,6]. To address these issues, oxidative dehydrogenation (ODH) using molecular oxygen is proposed as an attractive alternative that can allow effective transformation of propane at lower temperatures [7,8]. This reaction, however, is often suffered by a poor selectivity, due to the lack of kinetic control [1]. Indeed, propylene is more reactive toward oxidation than propane itself, and substantial formation of deep oxidation by-products (CO, and CO_2) usually occurs.

To suppress the undesired over-oxidation, nitrous oxide (N_2O), a waste by-product generated in many industrial processes such as adipic acid and nitric acid production [9], has attracted considerable attention as a milder oxidizing agent in DH of light alkanes [10–13]. The most frequently employed catalytic system in this field is iron-

based materials [12–16], such as Fe-ZSM-5, bulk $FePO_4$, and FAPO etc., among which steam-activated Fe-ZSM-5 being the most promising candidate [15]. One critical limitation of this material, however, is the rapid deactivation under the operating conditions. Hence, new efficient catalyst systems that can enable stable and efficient PDH under N_2O atmosphere are highly desired. In the present work, we report the development of new efficient In_2O_3—Al_2O_3 mixed oxide system exhibiting significantly enhanced activity and stability for the catalytic PDH in the presence of N_2O. The In—Al—O composite, previously established to be an effective material for PDH in the presence of CO_2 [17], has shown to be particularly active and stable for the N_2O-mediated propane dehydrogenation.

2. Experimental

2.1. Catalyst preparation

A series of mixed In_2O_3—Al_2O_3 oxides with various compositions as well as the simple oxides of Al_2O_3 and In_2O_3 were prepared through a previously developed alcoholic coprecipitation pathway [18]. In a typical synthesis, concentrated NH_4OH and ethanol (50:50 in volume) was added dropwise to the ethanol solution of indium nitrate hydrate ($In(NO_3)_3 \cdot 5H_2O$, Aldrich, 99.99%) and aluminum nitrate hydrate ($Al(NO_3)_3 \cdot 9H_2O$, Fluka, 99.9%) with different In:Al molar ratio until no more precipitation occurred (pH = 8.5). The resulting gel was quickly filtered and washed by ethanol, dried at 373 K overnight, and finally calcined at 873 K for 6 h. The final catalyst is denoted as In—Al-*n* hereinafter where *n* represents the mole percentage of In_2O_3.

* Corresponding author.
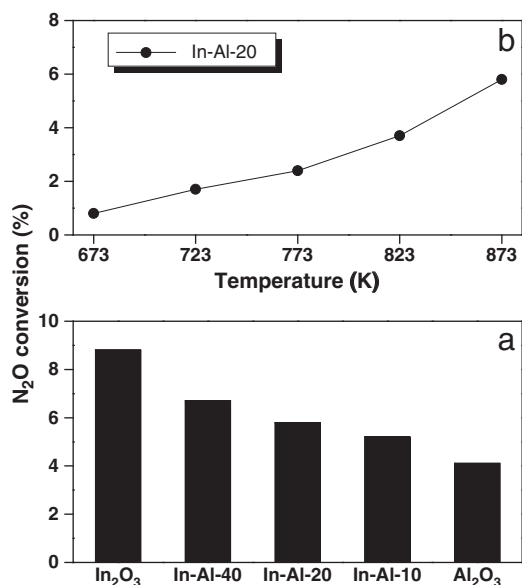 E-mail address: yongcao@fudan.edu.cn (Y. Cao).

Fig. 1. Conversion of N_2O for N_2O decomposition over (a) In_2O_3—Al_2O_3 mixed oxides and their simple oxide analogs at 873 K; (b) In—Al-20 in the temperature range of 673–873 K.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) results were obtained on a homemade apparatus loaded with 50 mg of catalyst. The samples were pretreated in flowing nitrogen at 773 K for 1 h. After cooling to room temperature, the samples were subsequently contacted with an H_2/Ar mixture (H_2/Ar molar ratio of 5/95 and a total flow of 40 mL min^{-1}) and heated at a rate of 5 K min^{-1}, to a final temperature of 1173 K. The H_2 consumption was monitored by an on-line thermal conductivity detector. Since water is produced during reduction, the gas exiting from the reactor was passed through a cold trap before entering the thermal conductivity detector. X-ray photoelectron spectroscopy (XPS) data were recorded on a Perkin Elmer PHI 5000C ESCA system with Mg Kα excitation line ($h\nu = 1253.6$ eV). The carbonaceous C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

2.3. Activity measurement

Catalytic tests were performed in a fixed-bed flow microreactor at atmospheric pressure, and the catalyst amount was 200 mg. The catalysts were pretreated at 873 K for 1 h in 10 mL min^{-1} He flow, and the reaction temperature was 873 K. Reactants, propane and N_2O (BOC gases, propane: 99.5 vol.%, N_2O: 99.995 vol.%), were metered with thermal mass flow controllers. Helium (BOC, 99.99 vol.%) was used as inert diluent. During reaction the gas feed (a total flow of 10.0 mL min^{-1}) contained 2.5 vol.% propane, 10 vol.% N_2O, and a balance of He. The feed and the reaction products were analyzed using an on-line gas chromatograph equipped with a 6-m packed column of Porapak Q and a flame ionization detector. The permanent gas products, including N_2, CO and CO_2, were analyzed on-line by another GC equipped with a TDX-01 column and a TCD detector. All carbon balances closed within 90–95%.

The catalytic activity was also studied for sole N_2O decomposition in the presence of helium. Prior to activity tests, the catalysts were activated at 673 K for 40 min in a He stream (a total flow of 10.0 mL min^{-1}). Then the first GC analysis was firstly performed at 673 K (10 vol.% N_2O, 90 vol.% He, total flow rate: 10.0 mL min^{-1}), and the temperature was increased from 673 K to 873 K in 50 K steps with three analyses of products (at 20 min intervals) at each step.

3. Results and discussion

Characterizations of the In_2O_3—Al_2O_3 mixed oxides in terms of BET surface area, X-ray diffraction (XRD), NH_3-temperature programmed desorption (NH_3-TPD), and TPR measurements were carried out in our previous study [17]. As suggested by XRD, the mixed oxides show far lower crystallinity in contrast to simple In_2O_3, implying higher dispersion of In_2O_3 in mixed oxides. TPR results further confirm the presence of highly dispersed In_2O_3, whose amount shows a linear relationship with corresponding PDH activities. Moreover, both acidic/basic site amount and BET surface areas increased monotonously by increasing the content of Al_2O_3.

We began our study by investigating the N_2O decomposition over the In_2O_3—Al_2O_3. The direct decomposition of N_2O has been extensively investigated over iron-based zeolites in the context of emission control [19]. In the absence of an additional reducing agent, the direct decomposition of N_2O has shown to be very difficult. This is attributed to the fact that the recombination and desorption of active oxygen species (generated via $N_2O \rightarrow N_2 + O^*$), ultimately yielding O_2 ($2 O\bullet \rightarrow O_2$) is the rate determining step [13,14]. In the present study, the N_2O decomposition reaction was performed in the absence of propane. It is observed that both simple oxides and In_2O_3—Al_2O_3 mixed oxides exhibit extremely low N_2O conversions (<10%) at reaction temperature up to 873 K, among which sample In_2O_3 shows the relatively highest result (Fig. 1). With increasing temperature from 673 to 873 K, conversion of N_2O for In—Al-20 increased continuously but is always below 6%.

Subsequent experiments testing the PDH in the presence/absence of N_2O at 873 K showed that all In_2O_3—Al_2O_3 samples underwent an apparent "induction period", which corresponds to the in-situ development of active phase for the DH reaction [17]. It is noted that in both

Table 1
Reaction data in the presence or absence of N_2O at 873 K.

Catalyst	In the presence of N_2O[a]						In the absence of N_2O[a]		
	$X_{propane}^{b}$ (%)	r^c (mmol h^{-1} g^{-1})	TOF[d] (h^{-1})	X_{N2O}^{e} (%)	$S_{propylene}^{f}$ (%)	Yield[g] (%)	$X_{propane}^{b}$ (%)	$S_{propylene}^{f}$ (%)	Yield[g] (%)
In_2O_3	5.2 (0.5)	0.174 (0.0167)	/	16.2 (5.5)	31.8 (41.2)	1.7 (0.2)	5.7 (1.6)	71.2 (68.1)	4.1 (1.1)
In—Al-40	30.8 (24.5)	1.03 (0.820)	1.64 (1.32)	22.6 (17.1)	57.6 (59.3)	17.7 (14.5)	13.5 (11.9)	79.3 (81.0)	10.7 (9.6)
In—Al-20	43.6 (32.7)	1.46 (1.09)	1.36 (0.98)	30.7 (21.5)	63.1 (66.2)	27.5 (21.6)	17.9 (16.1)	82.9 (83.3)	14.8 (13.4)
In—Al-10	35.2 (29.4)	1.18 (0.984)	1.48 (1.13)	24.8 (18.9)	67.4 (70.3)	23.7 (20.7)	15.4 (14.1)	84.1 (87.0)	13.0 (12.3)
Al_2O_3	3.8 (0.5)	0.127 (0.0167)	/	6.9 (2.6)	80.7 (79.9)	3.1 (0.4)	2.6 (0.5)	88.7 (88.2)	2.3 (0.4)

[a] The value outside and inside the bracket are the data obtained at 3 h and 12 h respectively.
[b] Conversion of propane.
[c] Reaction rate of propane per mass of catalyst.
[d] Turn over frequency calculated as follows: $\frac{\text{amount of transformed propane per hour}}{\text{amount of } In^0 \text{ calculated based on XPS data}}$.
[e] Conversion of N_2O.
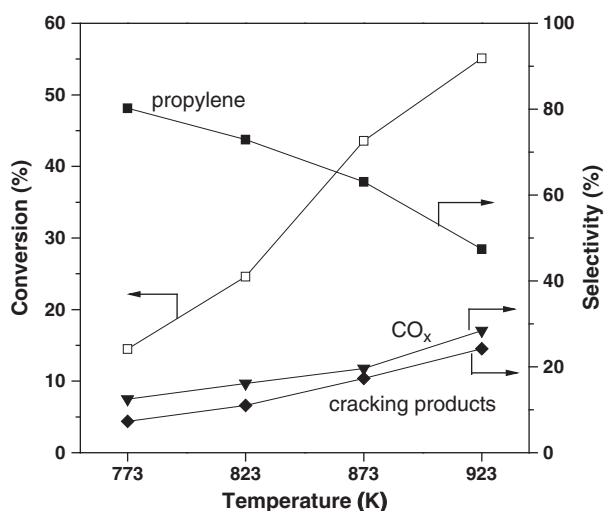[f] Selectivity to propylene.
[g] Yield of propylene.

Fig. 2. Effect of reaction temperature on dehydrogenation of propane over In—Al-20. Conversion of propane (□); selectivity to propylene (■), $CO + CO_2$ (▼) and cracking products (♦). Reaction time: 3 h.

presence/absence of N_2O, the highest "initial" (at 3 h on stream) steady propane conversion has always been obtained over In—Al-20, followed by In—Al-10 and In—Al-40, far superior to those for their simple oxide analogs (Table 1). Since we have previously demonstrated that the DH performance depends closely on the amount of the highly dispersed In_2O_3 species (precursor of metallic In^0), the highest activity for In—Al-20 in the presence of N_2O was ascribed to its highest amount of metallic In^0 available in-situ (evidenced by TPR results) [17]. Particular noteworthy is that the addition of 10 KPa of N_2O in the feed can dramatically boost the "initial" propane conversion, suggesting a remarkable improving effect on propane dehydrogenation by N_2O over In_2O_3—Al_2O_3 samples. It is noted that this was accompanied with a moderate decrease in selectivity to propylene by c.a. 15–25%. Interestingly, the conversions of N_2O in PDH also increase dramatically in contrast to those in the direct N_2O decomposition (from <10% to 20–30%, see Table 1 and Fig. 1). This result, together with the significantly improved propane conversion, suggests that the synergy between
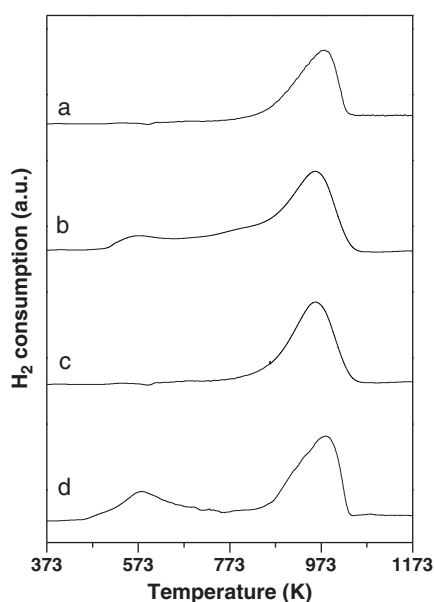
propane dehydrogenation and N_2O transformation is remarkable that allowed high activity in the production of propylene for In_2O_3—Al_2O_3.

The influence of the reaction temperature on the dehydrogenation activity of the In—Al-20 catalyst was further examined. Shown in Fig. 2 is the propane conversion and selectivity at 3 h as a function of reaction temperature. As can be seen, with increasing reaction temperature, propane conversion increased markedly from 14.5% at 773 K to 55.1% at 923 K. On the other hand, the selectivity to propylene kept declining, particularly more obviously at higher temperatures, which corresponds to accelerated over-oxidation as well as homogenous reactions at high temperature that gave rise to the production of carbon oxides (CO, CO_2) and cracking by-products (methane, ethane and ethylene) respectively. Taking both the conversion of propane and the selectivity to propylene into account, reaction at 873 K is the temperature of choice, with a maximum yield of propylene (27.5%) can be achieved.

Comparison of the N_2O-mediated DH activity reveals superior catalytic performance of In_2O_3—Al_2O_3 mixed oxide over conventional iron-based materials especially in terms of long-term stability, which remains a critical issue to be resolved for the conventional Fe-based zeolites. For instance, the steam-activated Fe-ZSM achieved an initial yield of propylene up to c.a. 25% at 798 K, but this is followed by a rapid deactivation during 180 min on-stream [15]. Similar phenomena also occurred with Fe-silicalite with even lower initial activity and de-activates within 400 min [12]. In contrast, with also high "initial" yields of propylene achieved at 873 K (i.e. 27.5% for In—Al-20), far slower deactivation rate for In_2O_3—Al_2O_3 mixed oxide was observed that allows for the maintenance of pronounced yield of propylene at 12 h on stream (i.e. 21.6% for In—Al-20). Meloni et al. has attributed the more serious deactivation of FeZSM-5 catalyst relative to Fe-silicalite to its higher surface acidity leading to rapid coke formation [20]. Therefore, the fact that the In_2O_3—Al_2O_3 mixed oxide is characterized by a moderate surface acidity (the NH_3-TPD results) [17] appears to be the key factor for achieving dramatically higher stability in the titled reaction.

Finally, it should be pointed out that we have previously established that the creation and maintaining of in-situ metallic In^0 species is one of the most important aspects for achieving remarkable activity for catalytic PDH under CO_2 atmosphere [17]. Bearing in mind that N_2O is a stronger oxidant than CO_2 [21], one might consider that the in-situ generated active oxygen species would convert In^0 to In(III), namely the diminishment of the active phase for DH during the reaction. To shed some light on this issue, further TPR tests were carried out over several pretreated In—Al-20 samples. The fresh In—Al-20 exhibits two main reduction domains centered at 580 K and 980 K (Fig. 3d), corresponding to highly dispersed In_2O_3 and bulk In_2O_3 respectively. Whereas a one-hour treatment by propane eliminates the peak signaling highly dispersed In_2O_3 (Fig. 3a), subsequent treatment by N_2O could partially restore the low-temperature peak, inferring that N_2O can oxidize the metallic indium species (Fig. 3b). Further exposure to the mixture feed of N_2O and propane allows the reduction of highly dispersed In_2O_3

Fig. 3. TPR results for various fresh and pre-treated In—Al-20 samples. Sample descriptions refer to Table 2.

Table 2
Summary of XPS studies for fresh and pretreated In—Al-20.

| Sample	Sample description	BE for In $3d_{5/2}$ (eV)		Percentage (%)	
		In^{3+}	In^0	In^{3+}	In^0
a	50 mg In—Al-20 pretreated by a 20 mL min^{-1} mixed gas flow containing 5% propane and 95% He at 873 K for 1 h	444.5	443.5	60.7	39.3
b	Sample (a) subsequently treated by a 20 mL min^{-1} mixed gas flow containing 20% N_2O and 80% He at 873 K for 1 h	444.5	443.5	78.6	21.4
c	Sample (b) subsequently treated by a 20 mL min^{-1} mixed gas flow containing 20% N_2O, 5% propane and 75% He at 873 K for 1 h	444.5	443.5	61.3	38.7
d	Fresh In—Al-20	444.5	/	100	/
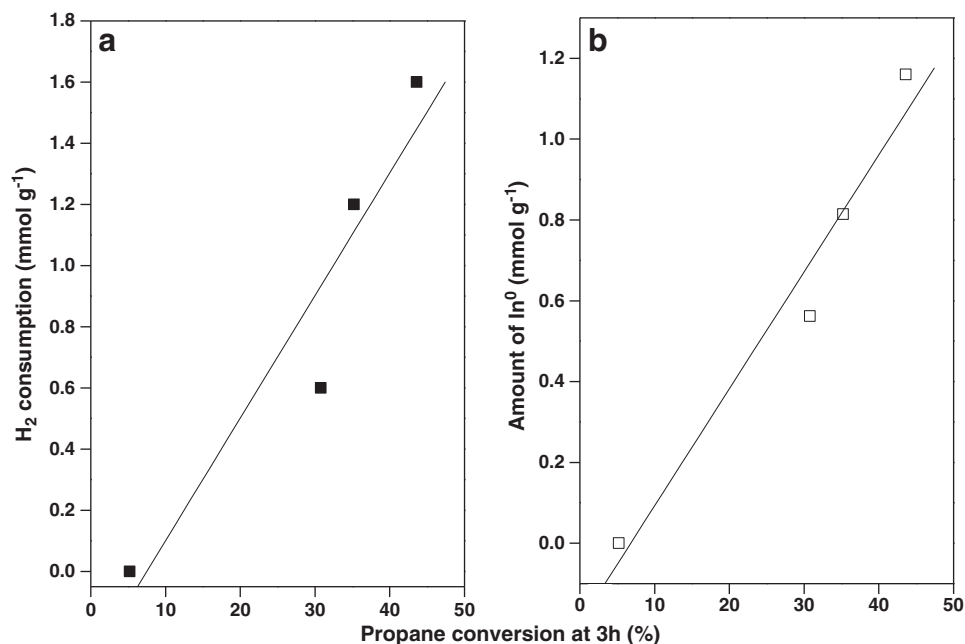
Fig. 4. Correlation of N_2O-mediated propane conversion at 3 h on stream and (a) the corresponding hydrogen consumption for the low-temperature peak in TPR (data see Ref.[17]) or (b) the amount of In^0 (Table 3) for the In—Al—O catalysts.

(Fig. 3c). This implies that the overall atmosphere of N_2O/propane mixture is reductive favoring the surface stabilization of metallic In^0, the assumed active sites for propane dehydrogenation. This conclusion is further supported by the corresponding variation in the chemical state of indium species as followed by XPS (Table 2).

To further clarify the essential role of metallic In^0 species as the key active species for PDH in the presence of N_2O, correlations of the propane conversions and the amount of In^0 for each In—Al—O catalysts were made (Fig. 4). The amount of metallic In^0 was represented either by the hydrogen consumption (Fig. 4a) of low-temperature peak in TPR experiment (data in our previous work [17]) or the value estimated from XPS data (Fig. 4b) for the four samples pre-reduced at 773 K (Table 3). In both cases, a roughly linear dependence of activity on the amount of metallic In^0 was observed, confirming the essential role of In^0 in promoting the propane dehydrogenation reaction. At this juncture, it is also important to note that the turnover frequency (TOF) values do not vary distinctly among different In_2O_3—Al_2O_3 samples (Table 1), thus providing further evidence in support of In^0 as the main active phase.

4. Conclusion

The present work shows the high potential of In—Al—O mixed oxide as effective catalysts for propane dehydrogenation in the presence of N_2O. A particularly attractive advantage for In—Al—O compared to conventional iron-based catalysts is the significantly improved stability. Among all the samples evaluated, In—Al-20 is the optimal that provides a maximum conversion at 43.6% and selectivity to propylene at 63.1% at 3 h on stream. The essential role of N_2O is suggested to serve as a mild oxidant which can generate active oxygen species facilitating propane dehydrogenation.

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Table 3
Summary of XPS studies for In_2O_3—Al_2O_3 catalysts[a].

Sample	BE for In 3d$_{5/2}$ (eV)		Percentage (%)		Amount of In^0 [b] (mmol g^{-1})
	In^{3+}	In^0	In^{3+}	In^0	
In—Al-10	444.5	443.5	51.5	48.5	0.814
In—Al-20	444.5	443.5	60.2	39.8	1.16
In—Al-40	444.4	443.5	87.9	12.1	0.562
In_2O_3	444.4	/	100	/	/

[a] All the samples have been pretreated by H_2/Ar (H_2: 5 vol.%) at 773 K for 1 h.
[b] Amount of In^0 per unit mass of catalyst based on XPS analysis.